

CHAPTER 1

THE SCHMIDT REACTION

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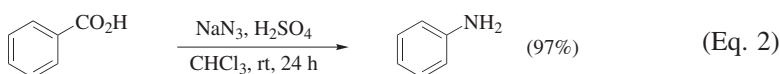
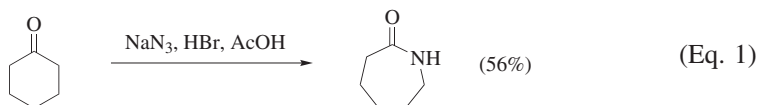
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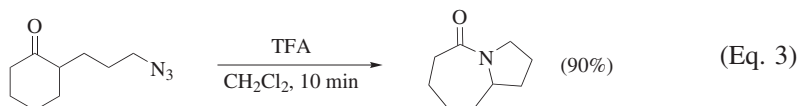
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INTRODUCTION

The term “Schmidt reaction” describes a family of related reactions that use hydrazoic acid or an alkyl azide to react with an electrophile. A few representative examples are depicted in Eqs. 1–3.^{1–3} Depending on the reactants employed, the product of the reaction can contain an amide or a number of related functional groups (Fig. 1). Despite this diversity, all Schmidt reactions have the characteristic of incorporating nitrogen into the product and it is this feature that has placed this chemistry among the most useful means for the synthesis of nitrogenous compounds.





The Schmidt reaction was first reported in 1924 by K. F. Schmidt,⁴ but came into its own in the 1940's and 1950's, largely through the efforts of P. A. S. Smith^{1,5-8} and L. H. Briggs.^{9,10} The classical Schmidt reactions, defined as those that specifically employ hydrazoic acid as the azide component, are the subject of an earlier *Organic Reactions* chapter.¹¹ In addition, extensive review literature exists on the subject.¹²⁻²⁰

The most commonly used variant of the Schmidt reaction is the reaction of a ketone or aldehyde with hydrazoic acid to afford an amide. These reactions usually employ a stronger protic acid to enhance the reactivity of the carbonyl group. Cyclic ketones afford lactams that contain one additional ring atom relative to the starting material. The utility of this reaction is heightened by the availability

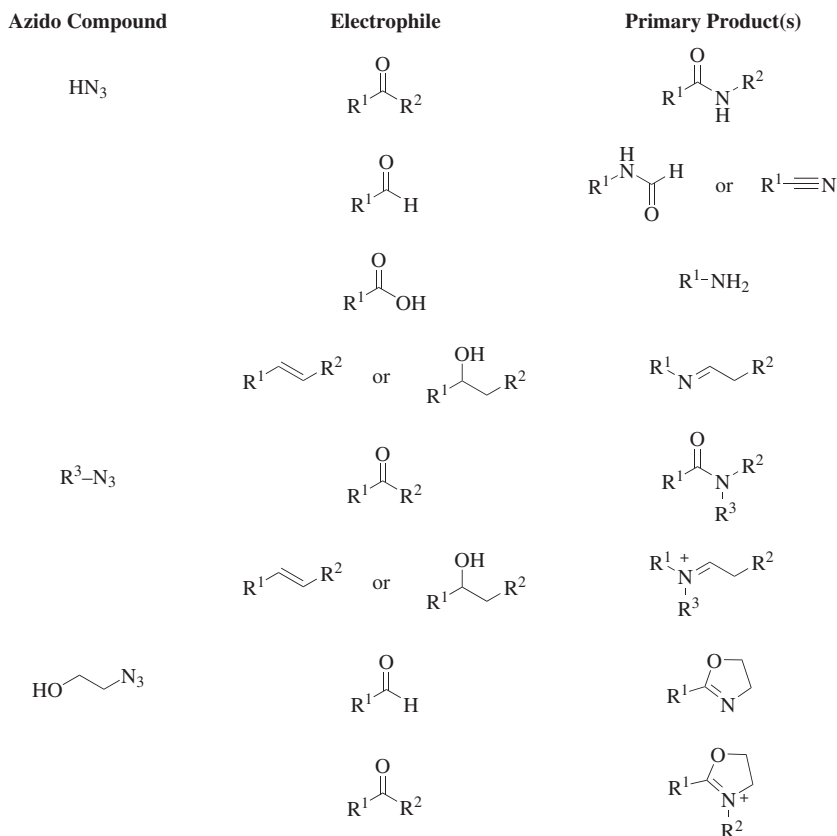


Figure 1. The family of Schmidt reactions.

of an essentially limitless number of ketones and by the ready reduction of the amide carbonyl group to afford the corresponding amino compound. In addition, most Schmidt reactions of this type occur with predictable (if not fully selective) site selectivity and stereoselectivity.

Hydrazoic acid also reacts with related species such as carboxylic acids and carbocations derived from alcohols or alkenes. The identification of all of these processes as variants of the Schmidt reaction is due to their common mechanistic features, involving first, the nucleophilic addition of hydrazoic acid to the reactive electrophile and, second, the rearrangement of this unstable adduct to afford the product. The loss of molecular nitrogen during the second stage of these reactions provides a powerful driving force for conversion into product. The mechanistic variations among classes are discussed in the appropriate sections.

The superficial similarity of alkyl azides to hydrazoic acid, entailing only the replacement of the proton in HN_3 with an alkyl group, immediately suggests that azides should undergo their own Schmidt reactions when encountering an electrophilic species. In the 1950's, Boyer reported a limited series of successful reactions of alkyl azides with aromatic aldehydes to afford amides.²¹ In the 1990's, it was reported that Lewis acids could effect the addition of azides to ketones and also that azides were facile partners in Schmidt reactions of carbocations, thus opening the door to the direct synthesis of *N*-alkylated amides from ketones^{3,22} or tertiary amines from cations derived from alcohols or alkenes.^{23,24} Simultaneously, it was recognized that intramolecular variants of these reactions can provide routes to multicyclic nitrogen heterocycles.^{3,23}

This chapter will discuss progress in all of the above classes of reactions, with the main restriction that only examples not included in the 1946 edition of *Organic Reactions*¹¹ will appear in the tables, ending with references published through the end of 2009.

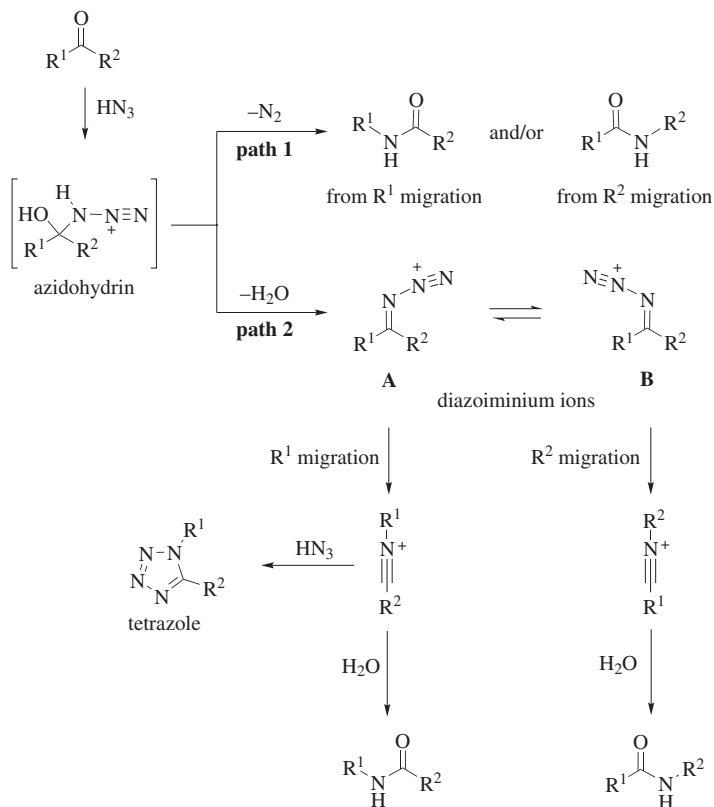
MECHANISM AND STEREOCHEMISTRY

All Schmidt reactions involve the initial nucleophilic attack of hydrazoic acid or a related azide species onto an electrophile. Although the latter is most commonly a carbonyl group activated by a protic or Lewis acid, the electrophile can also be either a stabilized or unstabilized carbocation. The greatest mechanistic diversity through the class arises from the ultimate fate of the intermediate formed in this initial step. Every one of these reactions is driven by the loss of molecular nitrogen en route to its nitrogen-containing product. Each of the different classes of Schmidt reactions will be considered separately.

Reactions of Hydrazoic Acid with Ketones

The most heavily studied variant of the Schmidt reaction is that of a ketone with hydrazoic acid (Scheme 1). This reaction begins with the addition of HN_3 to the protonated carbonyl group to afford an azidohydrin intermediate. At this stage, the reaction can proceed via one of two principal routes. In path 1, rearrangement of the azidohydrin intermediate directly affords an amide via a mechanism related

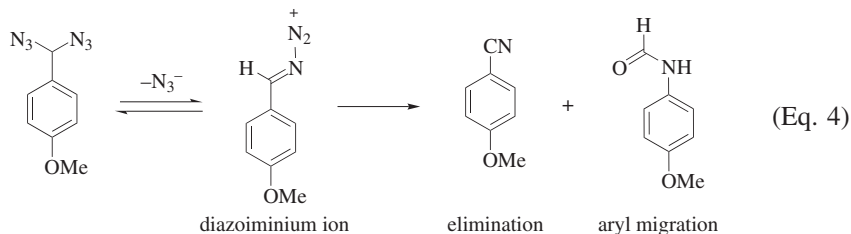
to that of the Baeyer–Villiger reaction.²⁵ Alternatively, path 2 involves elimination of water to afford a diazoiminium species, which can subsequently rearrange to form an iminium ion that must be hydrated to give the final product (analogous to the commonly accepted mechanism of the Beckmann rearrangement).



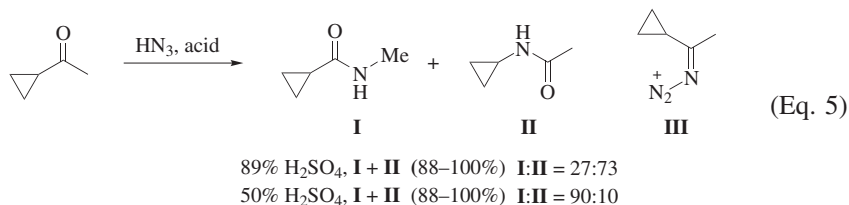
Scheme 1

The Beckmann mechanism was originally proposed by Smith¹ and, although the subject of considerable spirited discussion over the years, this mechanism is still favored by most authors. The main reasons are (1) the correlation of the migrating group with size, which is consistent with formation of the least sterically encumbered diazoiminium ion and antiperiplanar migration (also seen in the Beckmann rearrangement); and (2) the fact that tetrazoles are common byproducts of the Schmidt reaction, and form in increasing amounts when high concentrations of hydrazoic acid are present. The diazoiminium ion generated in the absence of water from the diazidoalkyl species shown in Eq. 4 gives the Schmidt reaction product; in this case, both elimination to nitrile (typical of Schmidt reactions of aldehydes) and aryl migration are noted.^{26,27} Parenthetically, a protonated gem-diazide has been suggested as a possible intermediate

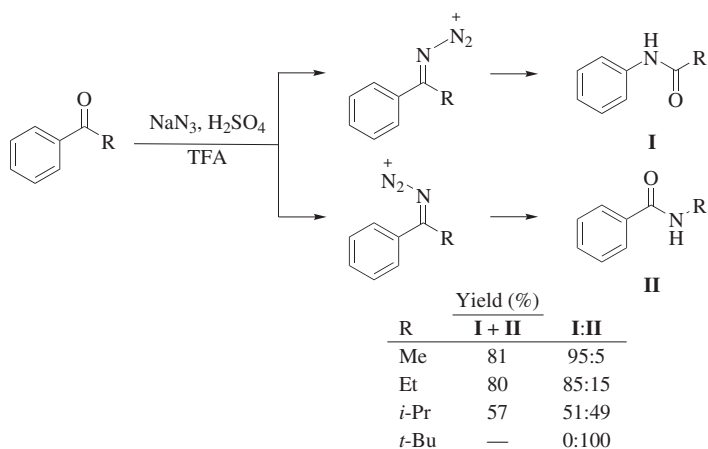
in some Schmidt reactions.²⁸ Although this work proves that diazoiminium ions are possible intermediates in the reaction, it is difficult to establish the *required* involvement of such species.



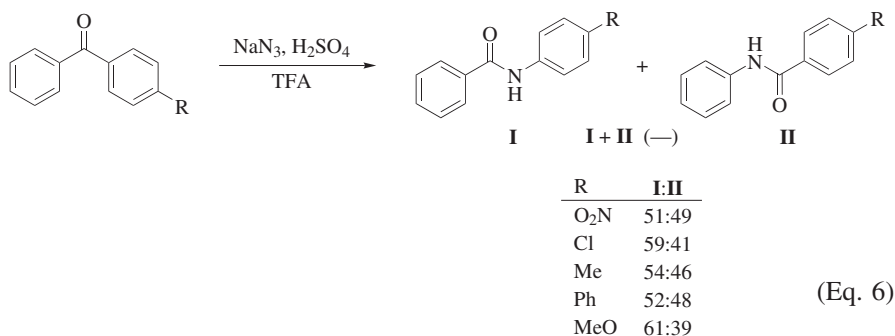
The demonstration of successful Schmidt reactions of alkyl azides clearly removes any objection to a mechanism involving direct azidohydrin rearrangement.^{3,22,29} Thus, despite the general acceptance of the Beckmann mechanism, it has been suggested that the Baeyer–Villiger mechanism can operate under certain conditions. For example, Shechter has suggested that the mechanism of the Schmidt reaction of cyclopropyl ketones depends in part on the acid strength of the reaction medium (Eq. 5).^{30,31} However, alternative explanations, such as the preferential formation of stereoisomeric intermediate **III** in 50% sulfuric acid, cannot be totally ruled out.



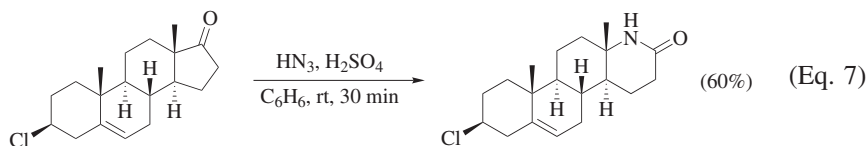
Under the Beckmann mechanism, stereoelectronic effects determine which group undergoes migration. In a systematic examination of a series of phenyl ketones containing increasingly larger alkyl substituents, the product ratio correspondingly favors alkyl group migration (Scheme 2).⁶ These results are consistent with the hypothesis that the ratio of the intermediate diazoiminium ions, coupled with the synchronous and antiperiplanar migration of the carbon to the electron-deficient nitrogen, determines the site selectivity. An important proviso is that theoretical calculations suggest a high barrier for direct interconversion of the diazoiminium ions.³² However, intermediates leading to **A** or **B** (Scheme 1) can interconvert via reversible addition of water under the reaction conditions (i.e., by reversion to the azidohydrin and subsequent dehydration); it is also possible that their ratio is kinetically controlled. An analogous study of substituted benzophenones does not belie any clear dependence of migrating group selectivity on the electronic nature of the aromatic rings, suggesting that “migratory aptitude” does not play a strong role in determining the site selectivity in these particular reactions (Eq. 6).⁷



Scheme 2

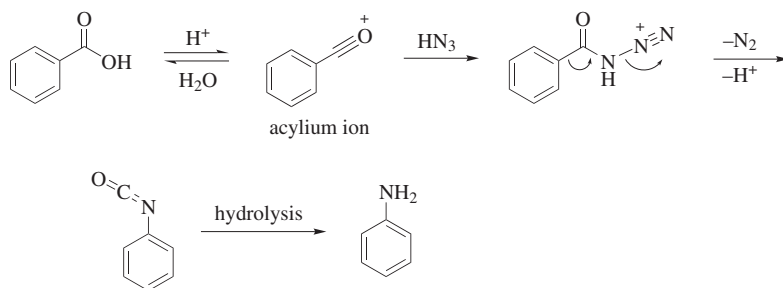


An important feature of the Schmidt reaction is that a stereogenic carbon migrates with retention of configuration. This behavior is consistent with related processes such as the Beckmann³³ and Baeyer–Villiger²⁵ reactions and extends throughout the entire family of Schmidt reactions. The reaction of the steroidal ketone shown in Eq. 7 is typical; for an acyclic example, see Eq. 60 in the “Applications to Synthesis” section.³⁴



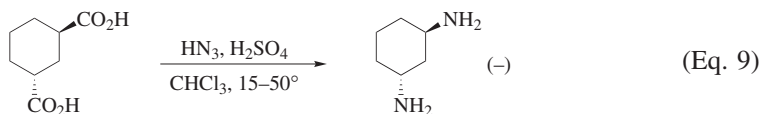
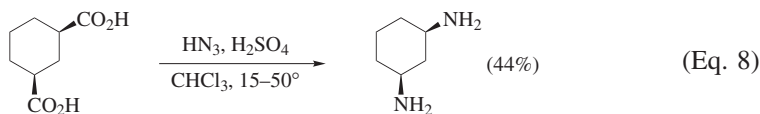
Reactions of Hydrazoic Acid with Carboxylic Acids and Aldehydes

These variants of the Schmidt reaction are mechanistically less ambiguous. The reactions of carboxylic acids with hydrazoic acid uniformly afford amines as there is only the possibility of migration of a single group in an acyl azide intermediate. In these cases, the primary product formed following alkyl or aryl group migration is an isocyanate. Addition of water followed by loss of carbon dioxide leads to the final product, an amine (Scheme 3).



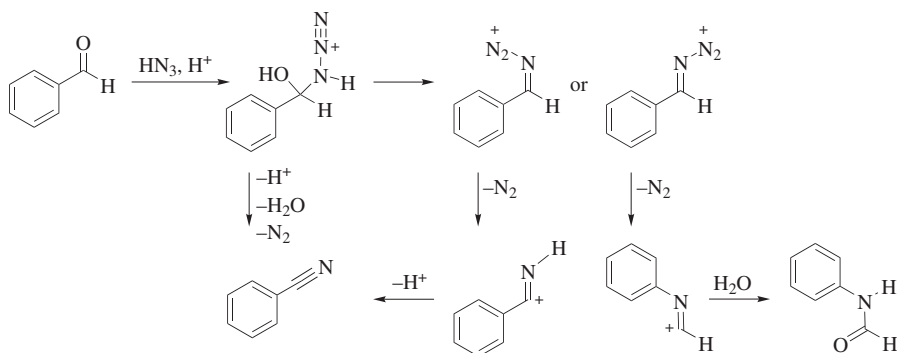
Scheme 3

The reactions of carboxylic acids with hydrazoic acid permit the stereospecific synthesis of amines via migration of a stereogenic carbon with retention of configuration (Eqs. 8 and 9).³⁵



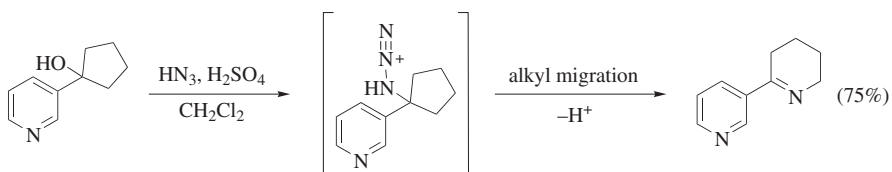
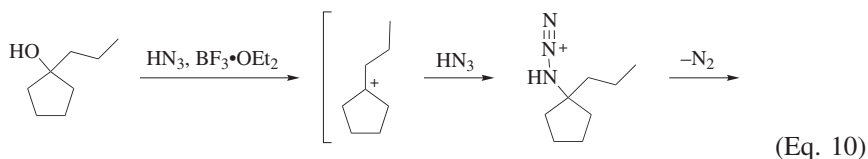
The mechanism of the reaction of hydrazoic acid with an aldehyde has not been fully established, partly because this variant of the Schmidt reaction is not as useful as others and therefore little work has been devoted to understanding it. These reactions are believed to occur via the Beckmann mechanism, affording first a diazoiminium ion that can rearrange via migration of an aryl or alkyl group to ultimately afford a formamide derivative upon hydration and tautomerization. However, the predominant product of this reaction is usually a nitrile (Scheme 4). One mechanism for the formation of a nitrile requires the intermediacy of the sterically unfavorable diazoiminium ion; however, this isomer may be kinetically favored.³⁶ Formation of the nitrile from this intermediate occurs by either hydride migration followed by proton elimination or concerted elimination. An alternative proposed mechanism is that the unprotonated version of the azidohydrin intermediate is converted into the nitrile (by an unspecified series

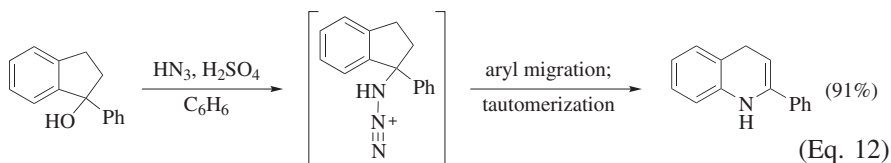
of steps), whereas the formamide product arises from the diazoiminium ion as shown (Scheme 4).^{37,38} This proposed mechanism is based in part on the observation of overall second-order kinetics and on the dependence of product ratio on acid strength.^{37,38}



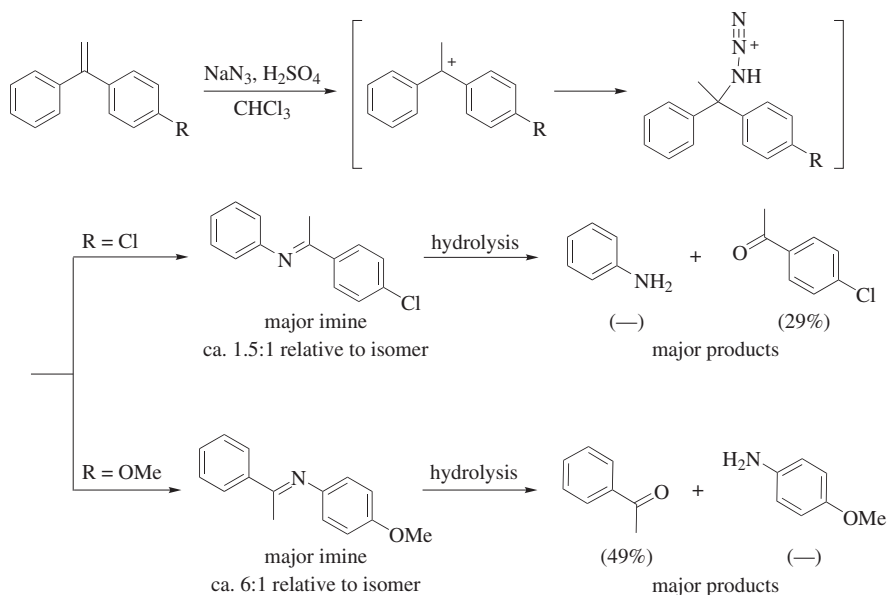
Reactions of Hydrazoic Acid with Carbocations Derived from Alkenes or Alcohols

The reactions of hydrazoic acid with carbocationic species generated from alcohols or alkenes afford imines that result from nucleophilic addition of hydrazoic acid to the cation followed by alkyl or aryl group migration (Eqs. 10³⁹ and 11⁴⁰). For cyclic compounds, imines are the usual reaction products, but tautomerization to the corresponding enamine is possible (Eq. 12).⁴¹





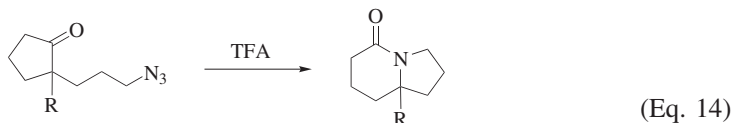
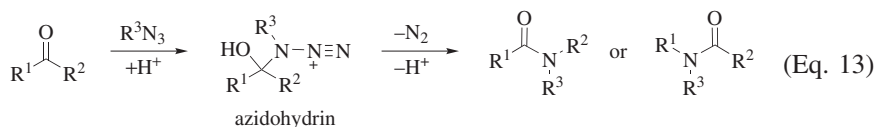
Also possible, and often observed in acyclic substrates, is hydrolysis of the imine to an amine and a carbonyl compound. Migratory aptitude likely plays a role in determining the site selectivity of the migration step due to the lack of a stereochemically defined diazoiminium intermediate in the reaction (Scheme 5).⁴²



Scheme 5

Reactions of Alkyl Azides and Hydroxyalkyl Azides with Electrophiles

The discovery that alkyl azides react with various electrophiles^{3,21,23} expands the scope of the Schmidt reaction and adds to the understanding of its mechanism. Specifically, because the adduct of an alkyl azide and a ketone is very unlikely to undergo loss of water to afford a diazoiminium ion containing adjacent positive charges, the competency of the initially formed azidohydrin species to directly afford an amide is generally viewed as unambiguously established. This reaction proceeds in both the intermolecular sense (Eq. 13)²² and also when the azide is covalently attached to the ketone (Eq. 14).³

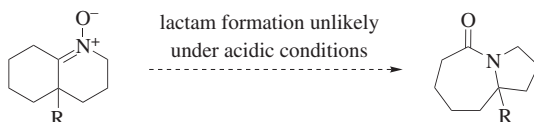
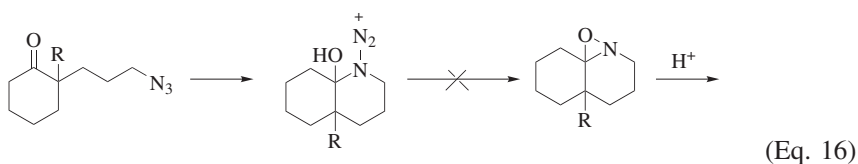
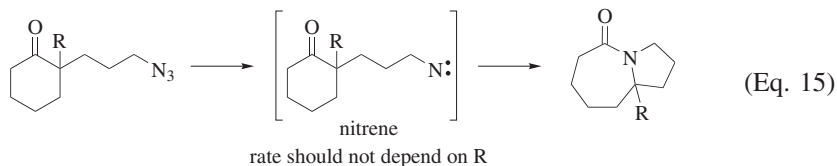


R = H, 10 min (83%)

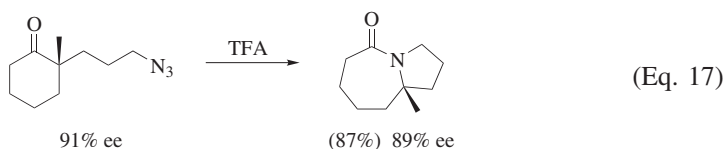
R = CO₂Me, 10 min, >90% recovered starting material

R = CO₂Me, 16 h (66%)

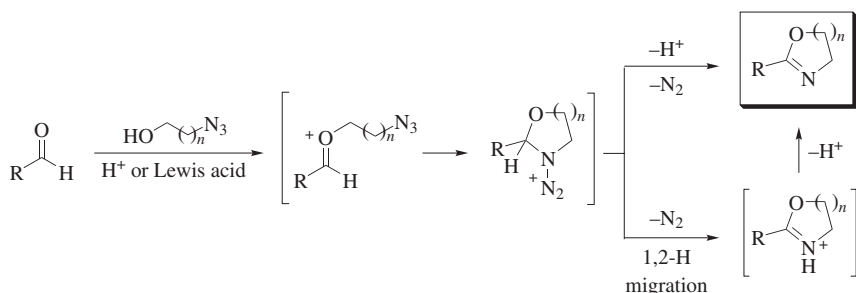
The possible involvement of nitrene intermediates is ruled out by comparing the rates of reactions of electronically disparate ketones. Whereas 2-(3-azidopropyl)cyclopentanone undergoes complete reaction in trifluoroacetic acid within 10 minutes at room temperature, similar treatment of an analog containing a 2-carbomethoxy group does not give significant conversion (Eq. 14).³ However, it is possible to achieve a 66% yield of the lactam upon extended exposure to trifluoroacetic acid. It would be extremely unlikely that the rate of decomposition to a nitrene would be affected by the presence of a distant ester group (Eq. 15). In addition, the recovery of intact ester-substituted azide under conditions sufficient for the complete reaction of the unsubstituted version rules out nitrene intervention in at least the intramolecular reaction. Another unlikely mechanism is conversion of an azido hydrin to an oxaziridine via O–N bond formation (Eq. 16). Although oxaziridines can undergo thermal rearrangements to lactams,⁴³ they rearrange under acidic conditions to afford nitrones rather than amides.⁴⁴ Neither oxaziridines nor nitrones have ever been reported as products from the reactions of azides and carbonyl compounds.



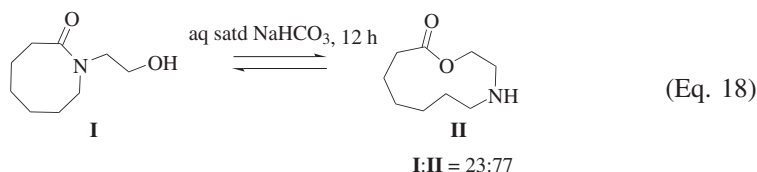
The intramolecular Schmidt reaction of alkyl azides and ketones proceeds with retention of configuration of the migrating carbon atom (Eq. 17).²⁹

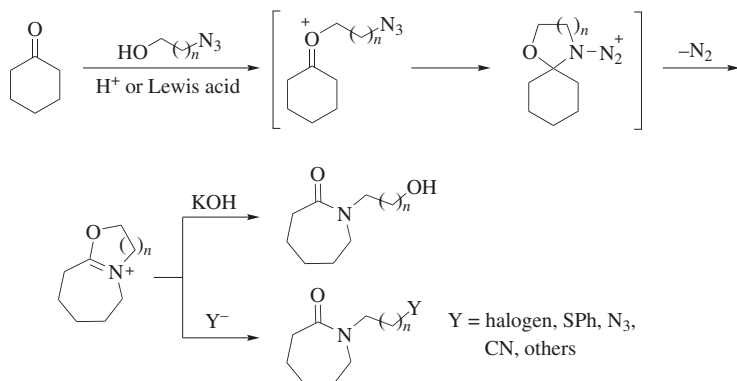


Hydroxyalkyl azides react with aldehydes or ketones under acidic conditions to afford oxocarbenium ions. Once formed, the cation is intercepted by the nucleophilic azido group to afford an azidohydrin-like intermediate that rearranges with loss of nitrogen to afford an iminium ether as the primary product. In the case of aldehydes, where the initial product is a protonated imino ether, loss of both a proton and nitrogen ensue to provide oxazolines or dihydrooxazines when $n = 1$ or 2, respectively (Scheme 6).⁴⁵ It is not known whether the proton is lost in concerted elimination reaction or if a 1,2-hydride migration precedes deprotonation.



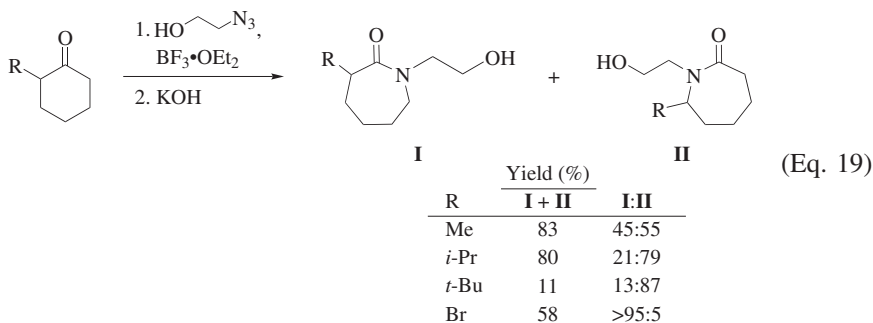
For ketones, the reaction results in an iminium ether as the initial product (Scheme 7). Most often, the iminium ether is converted into an amide by the addition of hydroxide ion. In addition, it may be combined with a variety of other nucleophiles to afford terminally substituted *N*-alkyl lactams.⁴⁶ *N*-(Hydroxyalkyl)amides or lactams derived from acyclic or medium-ring ketones are subject to reorganizations to afford amine-substituted esters or lactones, respectively (Eq. 18).^{47,48} These reactions are highly structure- and condition-dependent.





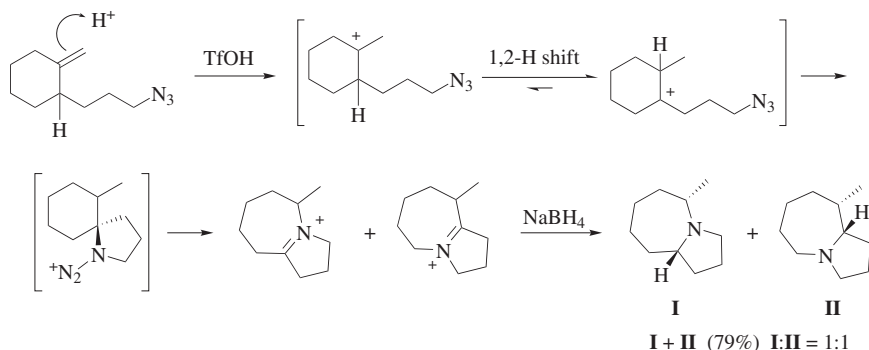
Scheme 7

The constitutional outcome of the reactions of unsymmetrical cyclohexanones has been briefly studied (Eq. 19).⁴⁹ The extent of migration of the substituted carbon increases with the size of the ketone α -substituent. Interestingly, several ketones bearing an electron-withdrawing group afford a high proportion of the product resulting from migration of the unsubstituted methylene group. These observations have been analyzed by consideration of competing conformational and electronic factors in the azide adducts.⁴⁹



Alkyl azides also react with carbocations derived from precursors such as alkenes or alcohols. The mechanism of this reaction is analogous to the related reactions of hydrazoic acid, with a key difference being that an intramolecular version is possible for azides. In the reaction shown (Scheme 8),^{50,51} the initially generated intermediate is in equilibrium with an isomeric carbocation via a 1,2-hydride migration. Because both are of roughly equal stability, it is likely that the length of the chain between each cation and the azide determines which one will lead to product. In this example, two different carbon-to-nitrogen migration reactions occur to afford a pair of iminium ions as the primary products of the reaction. Because of the small energetic difference between the two possible iminium intermediates in this reaction, a roughly 1:1 mixture of isomers

is observed. The addition of an exogenous reducing agent ultimately affords the reduced heterocyclic products via the least sterically hindered direction of hydride attack. The use of other cation precursors will be described in the “Scope and Limitations” section.



Scheme 8

SCOPE AND LIMITATIONS

The reaction scope varies greatly with each version of the Schmidt reaction. In general, the reactions of hydrazoic acid with various electrophiles accommodate a broad range of substrates whereas the various Schmidt reactions involving alkyl azides are often more limited.

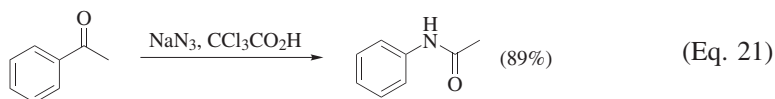
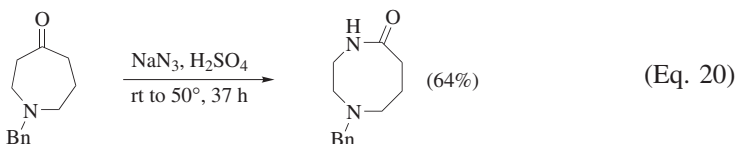
Schmidt Reactions of Hydrazoic Acid

Reactions with Ketones and Aldehydes. The most commonly used Schmidt reaction is the conversion of a ketone into an amide or lactam with hydrazoic acid. The corresponding reactions of aldehydes are less important because they bifurcate into nitriles or insertion products depending on substrates and conditions. Also less useful from a preparative perspective is the use of Schmidt conditions for the conversion of carboxylic acids to provide amines bearing one fewer carbon. In this case, the reaction suffers in comparison with the Curtius rearrangement,^{18,52} which carries out the same transformation under milder conditions.

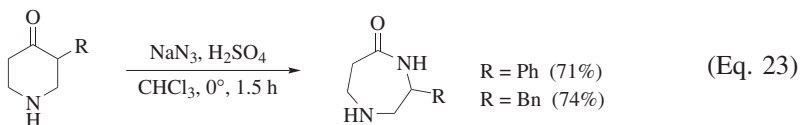
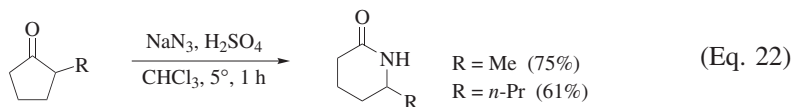
The main practical issues pertinent to ketone/hydrazoic acid reactions are (1) site selectivity, and (2) the formation of tetrazole side products (which can often be minimized by changing the reaction conditions). Many more ketones undergo Schmidt reactions than do not; the most problematic examples are ketones that provide serious steric obstacles to nucleophilic addition to the carbonyl group.

The fact that structurally diverse ketones are so readily available also contributes to the popularity of the Schmidt reaction in synthesis. A noteworthy application is the synthesis of medium-size rings that are hard to make by direct

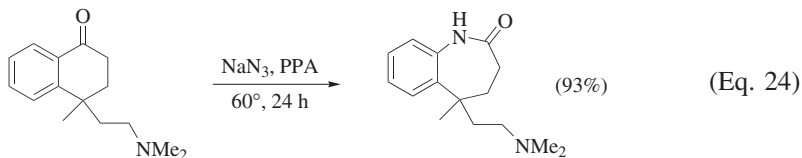
cyclization. Thus, readily available 6- and 7-membered ring ketones are attractive precursors to the corresponding 7- and 8-membered lactams (Eq. 20).⁵³⁻⁵⁶ In contrast, application of the Schmidt reaction to acyclic ketones is less common because acyclic amides are effectively made by a passel of coupling methods. The useful application of the Schmidt reaction on an acyclic substrate is the synthesis of aromatic amides from ketone precursors (Eq. 21).¹

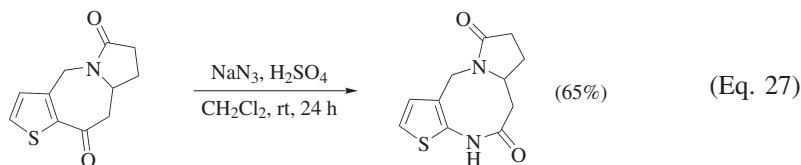
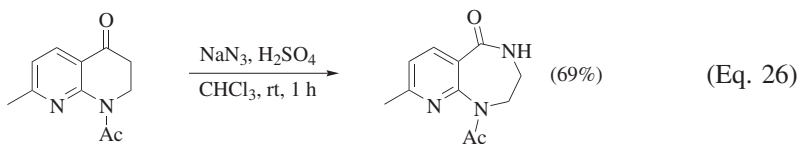
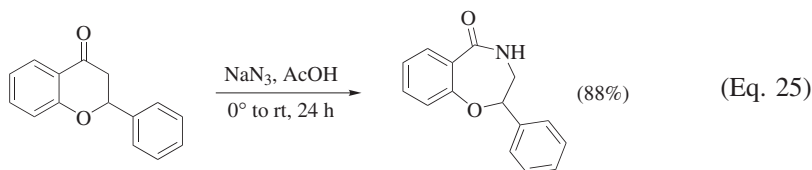


A significant remaining limitation of the Schmidt reaction is that no variant reliably inserts into an α -monosubstituted ketone with migration of the less substituted carbon. For reasons discussed in the previous section, the most substituted α -carbon generally migrates in the reactions of unsymmetrical ketones. Two illustrative examples are shown in Eq. 22^{16,53} and Eq. 23.⁵⁷

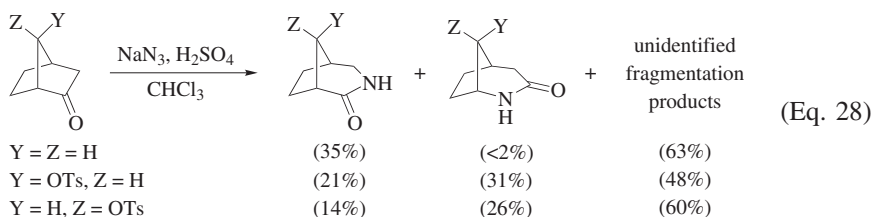


Aromatic ketones often react via migration of the aromatic group (Eq. 24),⁵⁸ but exceptions are known. In some cases, these reactions are readily understandable mechanistically; for example, electron-rich aromatic rings should migrate more readily than an alkyl group.^{59,60} As discussed in the previous section, the steric demands of the alkyl group also play a role.⁷ Other examples are harder to explain; for example, compare Eqs. 24 and 25.⁶¹⁻⁶⁴ The migratory preferences in reactions involving heteroaromatic ketones are particularly difficult to predict (Eqs. 26⁶⁵ and 27⁶⁶).

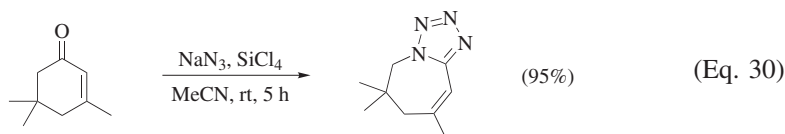
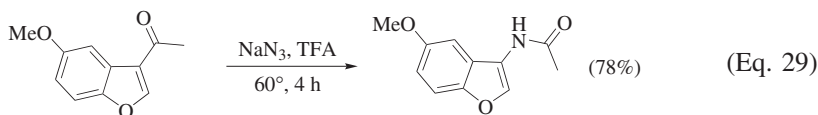


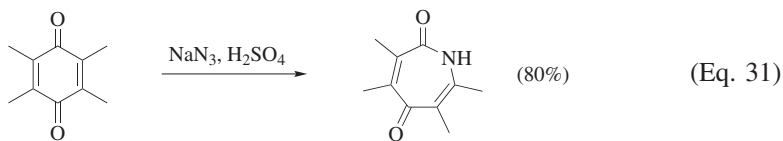


The Schmidt reactions of bicyclic ketones tend to proceed with poor site selectivity and are often accompanied by fragmentation byproducts.^{16,67} A few systems, such as norcamphor, react with high selectivity for a particular isomer but the reactions are not necessarily high yielding (Eq. 28).⁶⁸

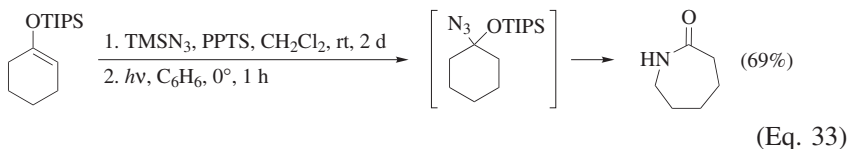
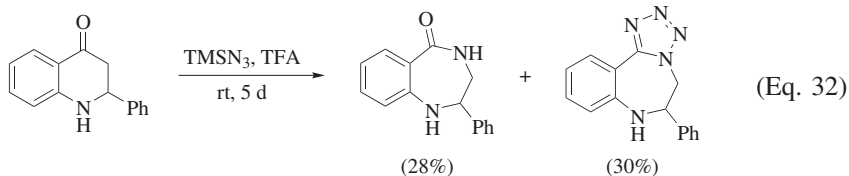


The reaction is also tolerant of α,β -unsaturation with many cases of enones reacting under standard Schmidt conditions. Often a simple enone containing a single adjacent double bond affords a product resulting from migration of the sp^2 -hybridized α -carbon (Eq. 29),⁶⁹ but exceptions do exist (Eq. 30).⁷⁰ Quinones and other compounds containing only adjacent sp^2 -hybridized carbons are perfectly competent Schmidt reaction substrates (Eq. 31).⁷¹

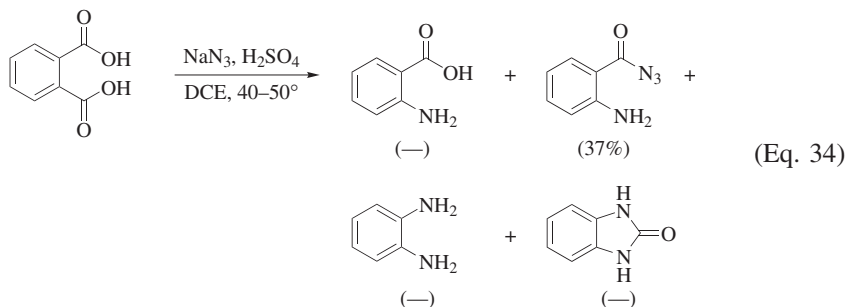




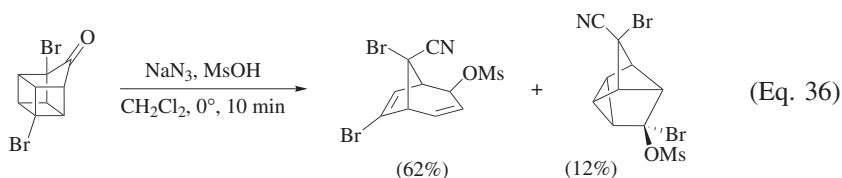
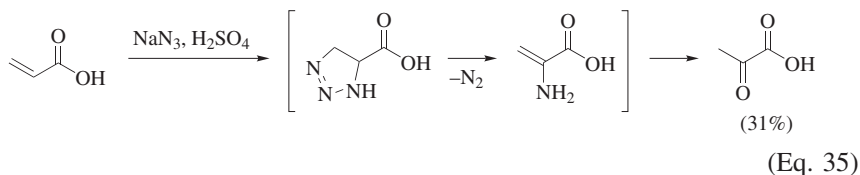
Besides the use of sodium azide and hydrazoic acid in the Schmidt reaction, trimethylsilyl azide provides an alternative source with diminished explosive properties.⁷² This reagent reacts with ketones and their enol ethers under acidic conditions (Eq. 32)⁷³ or irradiation (Eq. 33)⁷⁴ to yield lactams. As with the reactions of hydrazoic acid, tetrazoles are often isolated as byproducts in the acid-promoted reactions.



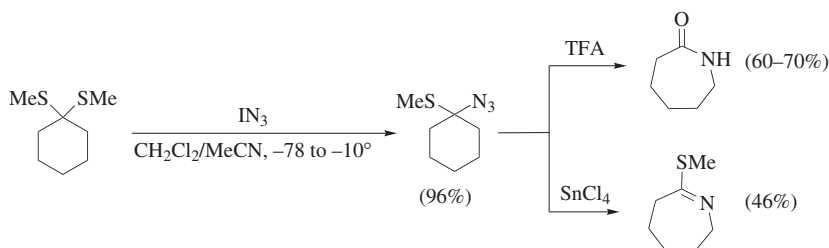
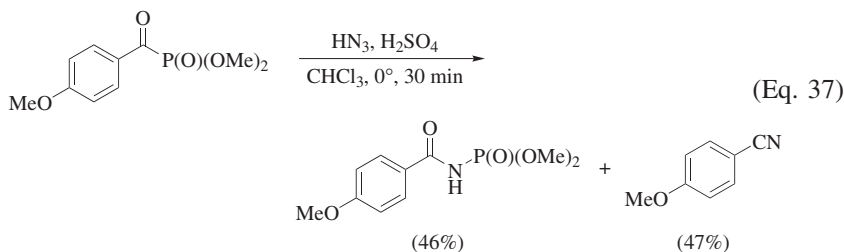
Unusual Reactions and Alternative Electrophiles. A variety of interesting pathways have been reported in the nearly 100 years since the Schmidt reaction was first described.⁷⁵⁻⁷⁷ This diversity is not surprising given the involvement of high-energy reactive intermediates and does not really detract from the overall utility of the reaction. For example, reaction of phthalic acid affords aniline products from one and two standard Schmidt reactions, respectively, along with a presumed acyl azide intermediate and a urea resulting from intramolecular trapping of an isocyanate (Eq. 34).^{78,79} Instead of a Schmidt reaction, acrylic

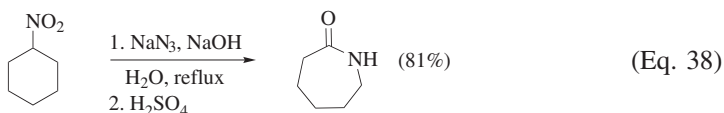


acid undergoes a formal dipolar addition of azide to the double bond followed by acid-promoted decomposition to pyruvic acid (Eq. 35).⁸⁰ Similar cycloaddition reactions of alkyl azides are used to effect conversions of α,β -unsaturated ketones into aziridines (see “Schmidt Reactions of Alkyl Azides with Ketones and Aldehydes” section). Highly strained compounds often undergo skeletal rearrangements when exposed to HN_3 (Eq. 36).⁸¹



Schmidt reactions also can be carried out with *O,O*-dialkyl acylphosphonates (Eq. 37).^{28,82} In addition, a version of the Schmidt reaction is known in which a dithioketal is activated by treatment with iodine azide to afford an α -azido sulfide (Scheme 9). This intermediate is converted into the corresponding ring-expanded lactam or thioimino ether upon treatment with trifluoroacetic acid or stannic chloride, respectively.⁸³ Finally, a little-used variation employs nitroalkanes as a carbonyl equivalent. Treatment of nitroalkanes with basic sodium azide affords amides in moderate to good yields (Eq. 38).⁸⁴

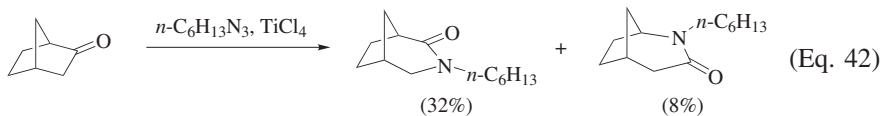
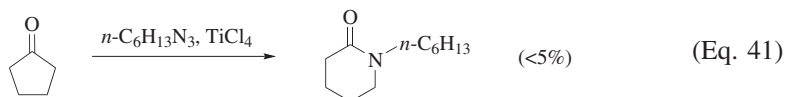
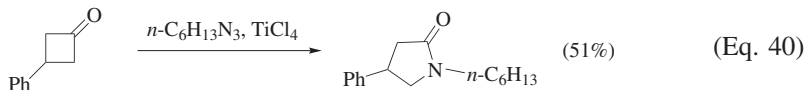
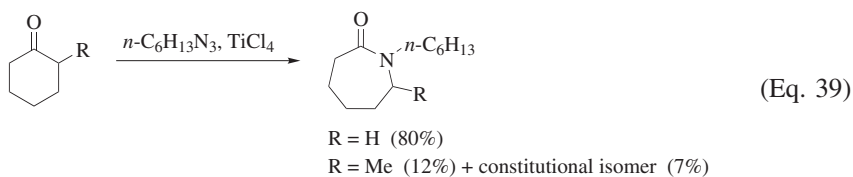




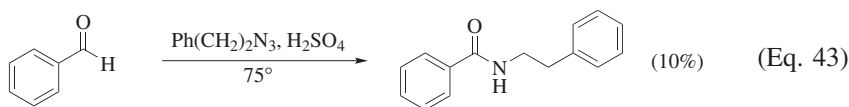
Schmidt Reactions of Alkyl Azides

The reactions of electrophiles with alkyl azides are considerably less general than those with hydrazoic acid. This section is organized according to the electrophile, beginning with a discussion of the reactions of azides with carbonyl groups and their equivalents and moving onto the reactions of alkyl azides with carbocations generated from double bonds or other precursors.

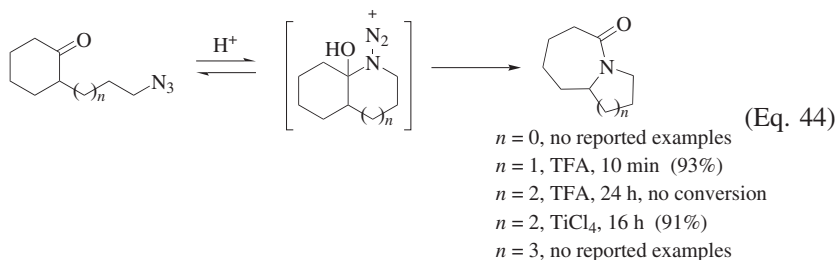
Reactions with Ketones and Aldehydes. The transformation of largest scope in this category involves intramolecular reactions of azidoalkyl-substituted ketones. Intermolecular reactions of azides and ketones have been only sparingly examined to date.^{22,85} The known examples of this variation are poorly site selective, often poorly efficient, and limited by even moderate steric hindrance or the size of the ketone ring. The different yields obtained from reactions of *n*-hexyl azide either with cyclohexanone or with 2-methylcyclohexanone (Eq. 39)²² exemplify the sensitivity of the reaction to additional steric bulk near the reacting carbonyl. Good yields are obtained in a few cases using a strong Lewis acid such as TiCl_4 .^{22,85} Even under these conditions, the reactions are severely limited (Eqs. 40–42). The reaction of alkyl azides with acyclic ketones is of similarly narrow utility.⁸⁵



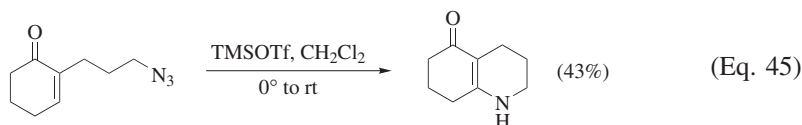
Azides and aldehydes afford amides under protic acid conditions, but only from a few substrates, and in poor yields (Eq. 43).²¹

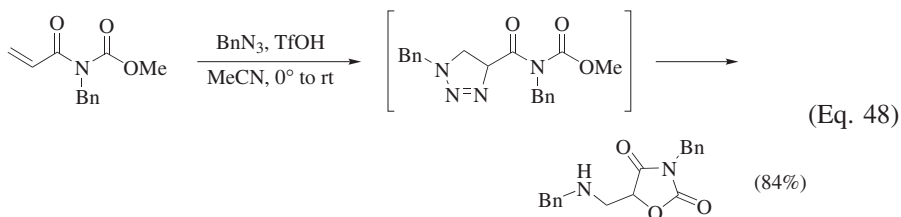
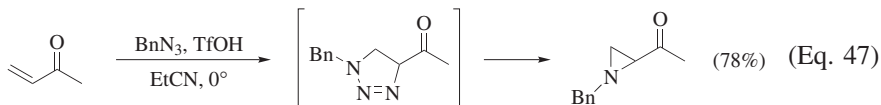
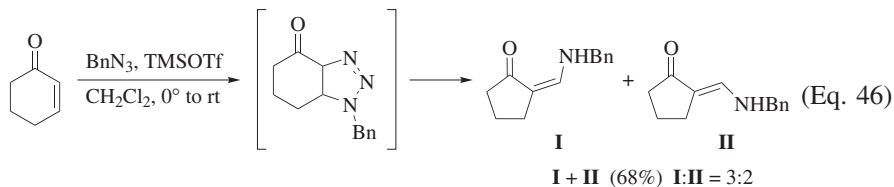


The intramolecular reactions are substantially superior in terms of scope, yields, allowable conditions, and selectivity—nearly every characteristic that one typically associates with synthetic utility. The prime restriction is that the distance between the carbonyl and azide groups must usually be 4 or 5 atoms for high yields. The former is preferred, presumably because it involves the formation of a six-membered cyclic intermediate. Examples involving five carbons typically require stronger Lewis acids (Eq. 44).³

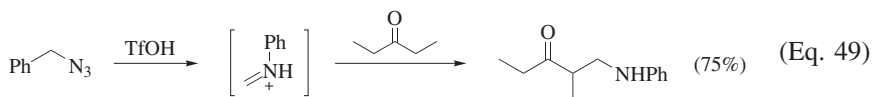


The intramolecular process accommodates a great deal of variation in the ketone component such that successful reactions can be achieved with various ring sizes (reactions of cyclic 4–12 membered ketones have been reported²⁹) and with acyclic versions. Apart from alkyl substituents, little work has been done to determine which functional groups are tolerated when adjacent to the ketone or the azide group. Electron-withdrawing substituents adjacent to the ketone slow down the reaction but are tolerated.³ α,β -Unsaturated ketones containing appropriately tethered azides do not provide lactam products but instead afford products of apparent conjugate addition reactions (Eq. 45).⁸⁶ In a few cases, lactams have been prepared from α,β -unsaturated ketones upon irradiation (see “Comparison with Other Methods” section). The intermolecular version of this reaction also leads to non-amide products (Eqs. 46⁸⁷ and 47^{88,89}). Similarly, unsaturated imides react to afford aminohydroxylation products (Eq. 48).⁸⁸ Presumably, the Lewis acid activates the enone so that it is more susceptible to 1,3-dipolar cycloaddition rather than 1,2-addition of azide to the ketone.⁸⁷

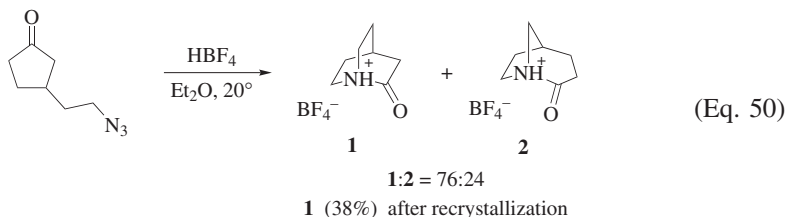




Benzylic azides are unreliable partners with saturated ketones in both intermolecular⁸⁵ and intramolecular⁹⁰ versions of the Schmidt reaction. Thus, in cases where the Schmidt reaction is retarded due to steric crowding or the use of non-optimal tether lengths, the benzylic azides may undergo conversion into iminium ions under the reaction conditions. In such cases, products of Mannich-like processes have been reported (Eq. 49).⁸⁵

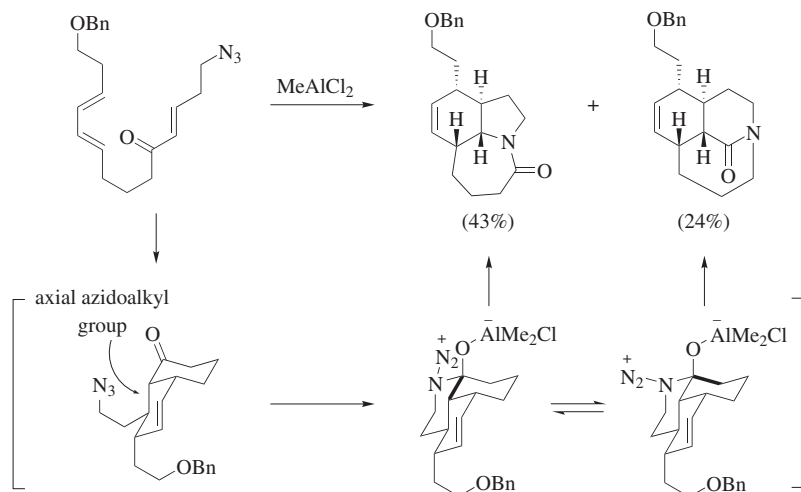


Although possible, reactions affording bridged lactams are rare. One important example entails the reaction of a ketone that bears an azidoalkyl side chain non-adjacent to the carbonyl group, a situation that necessitates bridged lactam formation. One of the two lactams formed is the long-sought “twisted” amide 2-quinuclidone (**1**) (Eq. 50).⁹¹



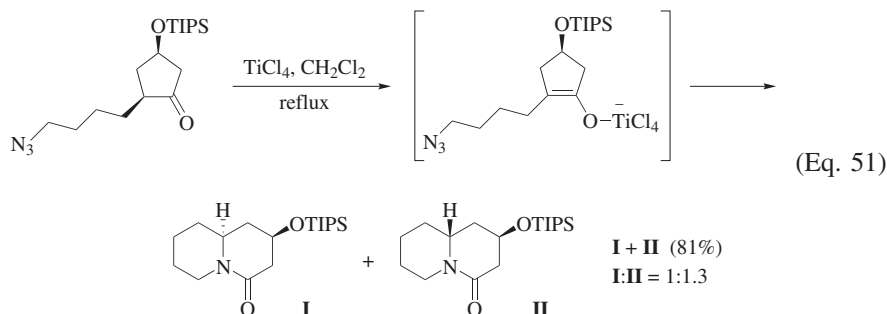
In another example, intramolecular Schmidt reaction of a complex ketone containing an azidoalkyl group in an axial orientation gives a bridged lactam as

a minor product (Scheme 10).⁹² The Schmidt substrate is formed by an *endo*-selective intramolecular Diels–Alder reaction (an *exo* Diels–Alder pathway that affords another lactam product in 12% yield is omitted from the scheme). Presumably, two stereoisomeric azidohydrins can form from the intermediate shown, each of which leads to a lactam by antiperiplanar carbon–carbon bond migration with synchronous loss of nitrogen. In this system, one of these intermediates affords the usual fused lactam product whereas the other affords the bridged product.



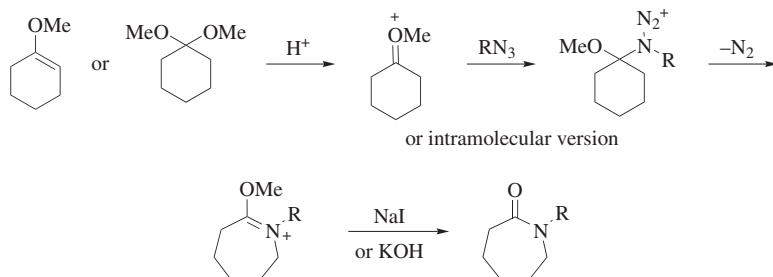
Scheme 10

As noted in the previous section, the intramolecular Schmidt reaction of alkyl azides generally occurs with retention of configuration. However, non-stereoselective reactions are observed in examples in which the carbon α to the carbonyl group undergoes reversible enolization under the reaction conditions (Eq. 51).⁹³



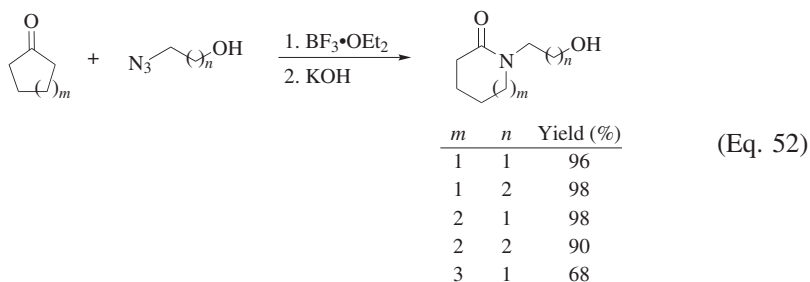
Reactions of Enol Ethers, Ketals, or Hydroxyalkyl Azides. Ketals or enol ethers undergo a closely related reaction with alkyl azides to afford iminium ethers (Scheme 11).⁹⁴ In many cases, these intermediates can be isolated and

characterized, but are more frequently converted into lactams by treatment of the iminium ether with aqueous base or sodium iodide. The former reaction proceeds via addition of hydroxide to the C=N bond and breakdown of the tetrahedral intermediate, while the latter involves direct S_N2 attack on the *O*-alkyl group. As with the reactions of alkyl azides and carbonyl groups, these reactions are most efficiently carried out intramolecularly.



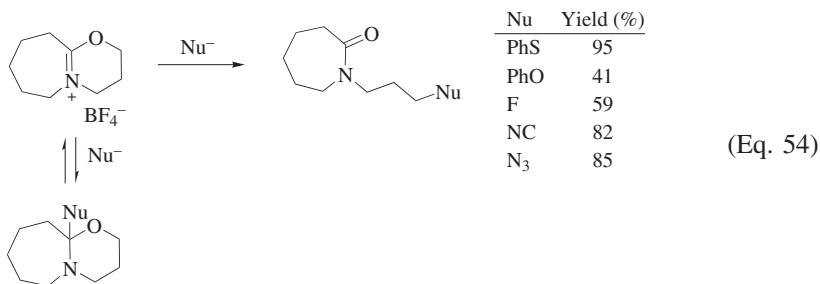
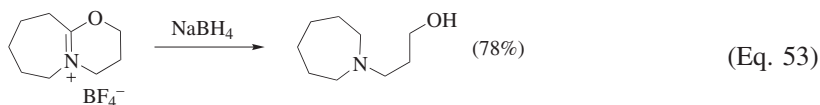
Scheme 11

In a related process, 1,2- or 1,3-hydroxyalkyl azides react with cyclic ketones to afford lactams after hydrolysis of the primary iminium ether products (Eq. 52).^{95,96} These reactions provide practical synthetic equivalents to the direct reactions of alkyl azides with ketones, despite the mechanistic differences (see previous section). This reaction works well for 5- to 7-membered cyclic ketones and is generally tolerant of substitution. Other products resulting from transamidation/transacylation processes may be obtained in reactions of ketones having 7 or more ring atoms (Eq. 18).^{47,48}

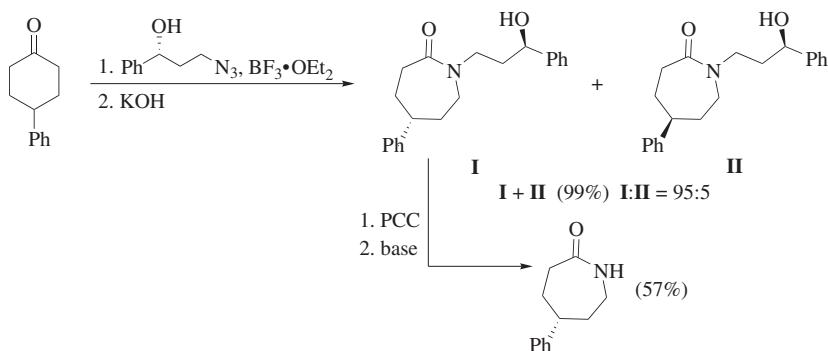


The iminium ether intermediates in these reactions can react with nucleophilic species other than hydroxide. Depending on the nucleophile, reactions at two positions are possible.⁴⁶ The site selectivity is rationalized on the basis of reversibility of the initial addition reaction.⁹⁷ Thus, kinetic attack occurs at the formal cationic center as exemplified by the irreversible addition of hydride (Eq. 53).⁴⁶ However, most nucleophiles react reversibly at this center until they carry out an irreversible S_N2 displacement to afford an ω -functionalized *N*-substituted lactam

(Eq. 54).⁴⁶ In the examples shown, the iminium ether intermediate is isolated prior to treatment with the nucleophile (yields are from the iminium ether).



The site selectivity of the Schmidt reaction in 2-substituted cycloalkanones is complex and depends on the substituent (see Eq. 22). However, an interesting mode of selectivity becomes possible in the reactions of symmetrically substituted ketones, such as 4-phenylcyclohexanone, with chiral hydroxyalkyl azides (Scheme 12).^{95,98,99} In these cases, the methylene groups adjacent to the ketone are enantiotopic, so that stereoisomeric lactams result depending on which methylene group migrates. These reactions afford up to 95:5 ratios of diastereoisomers in favorable cases. Following separation of the diastereomeric lactams, removal of the nitrogen substituent affords the enantiomerically pure lactam.

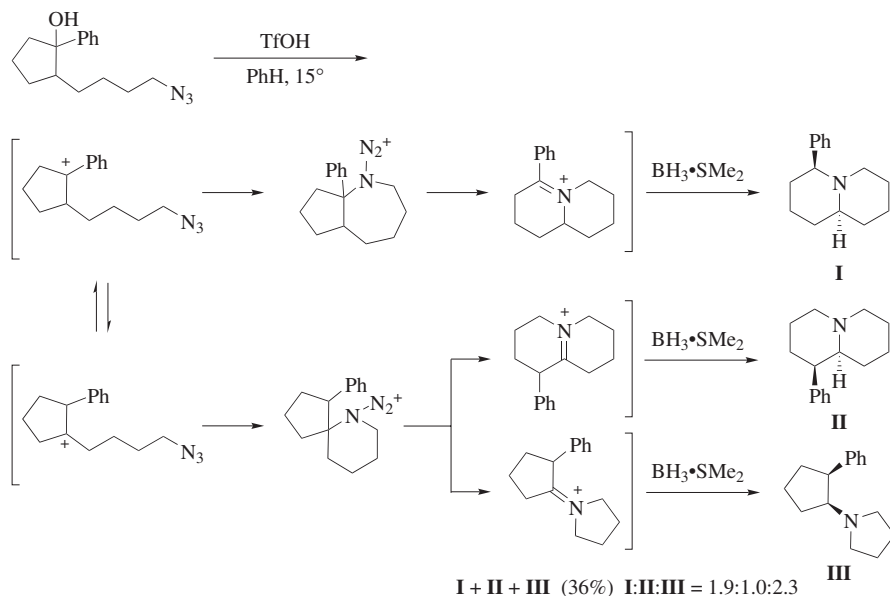


Scheme 12

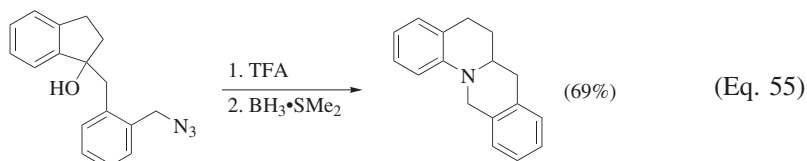
Reactions with Alkenes, Alcohols, and Other Carbocation Precursors.

The reactions of alkyl azides with carbocations, followed by a hydride reduction step, provide amines rather than lactams.^{17,23,24,51,100–103} The reaction scope appears to be quite broad for intramolecular reactions. Most of the substrates have four carbons between the azide and the initial site of attack, with examples

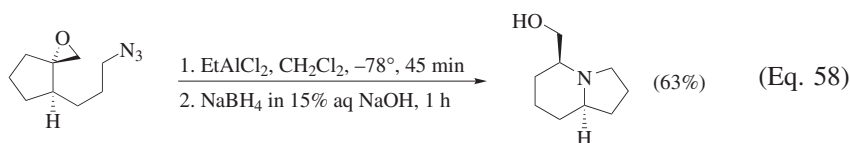
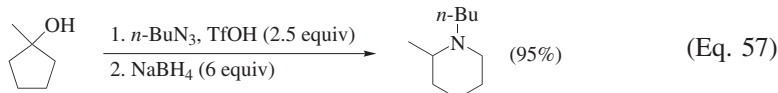
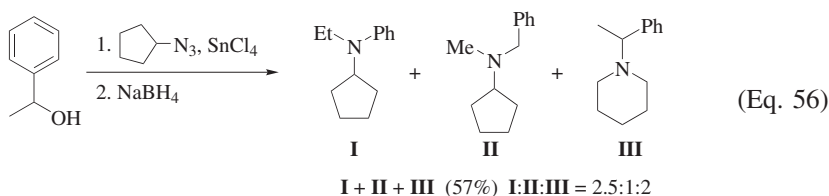
of both fused and bridged intermediates being reported. In some cases, multiple products are observed due to the intervention of carbocationic rearrangements prior to azide attack (Scheme 13).¹⁰¹ In addition, each azide adduct is in principle subject to up to six possible alkyl, aryl, or hydride migrations in the ensuing step. In practice, however, only a few of the possible products are generally observed and in many cases careful synthetic planning can steer the reaction toward a single product in high yield (Eq. 55).¹⁰²



Scheme 13



The reactions of benzylic or tertiary carbocations with alkyl azides are also feasible in an intermolecular sense. As in the preceding cases, multiple products resulting from the migration of various groups are often observed (Eq. 56),¹⁷ but in favorable cases the reactions can result in a single product (Eq. 57).^{17,24} Epoxides are also effective cation precursors (Eq. 58).¹⁰⁴ As above, the primary product in each of these reactions is an iminium ion that is reduced to afford a tertiary amine.

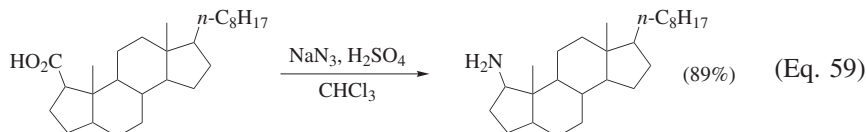


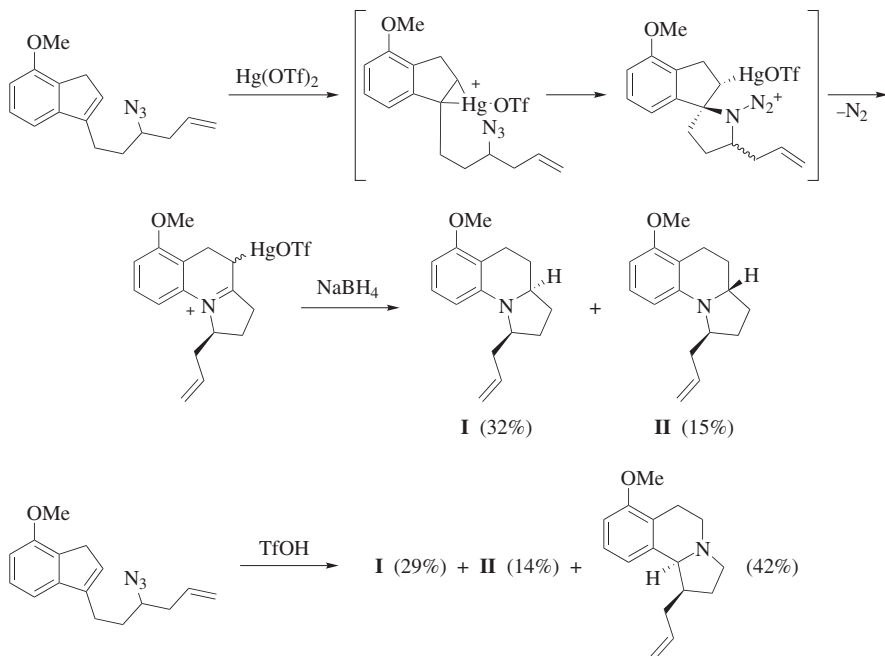
Double bonds are also converted into cation equivalents through the addition of an electrophilic mercury salt (Scheme 14).⁵⁰ Attack of azide upon the mercuronium species affords an intermediate that loses nitrogen and undergoes a carbon-to-nitrogen migration. Subsequent addition of reducing agents affords products similar to those obtained when the reaction is promoted by proton sources. In some cases, useful differences in site selectivity are obtained using Hg(II) promotion in comparison to the acid-mediated conversions. Thus, with Hg(II), only products resulting from aryl migration are observed. In contrast, reaction of the same azide under protic conditions affords an approximately equal quantity of products from aryl and alkyl migrations (Scheme 14).⁵⁰

Metal activation of a triple bond provides another electrophilic species that is subject to azide attack (Scheme 15).¹⁰⁵ Thus, treatment of tethered azide-containing alkynes with a gold salt leads to pyrroles via attack of azide. A mechanistic hypothesis involving gold(I)-induced activation of the alkyne toward addition by the proximal nitrogen of the azide is shown. Subsequent loss of dinitrogen produces a cationic intermediate that is stabilized by electron donation from gold. A formal 1,2-shift regenerates the cationic gold(I) catalyst and produces a 2*H*-pyrrole that tautomerizes to the observed product.

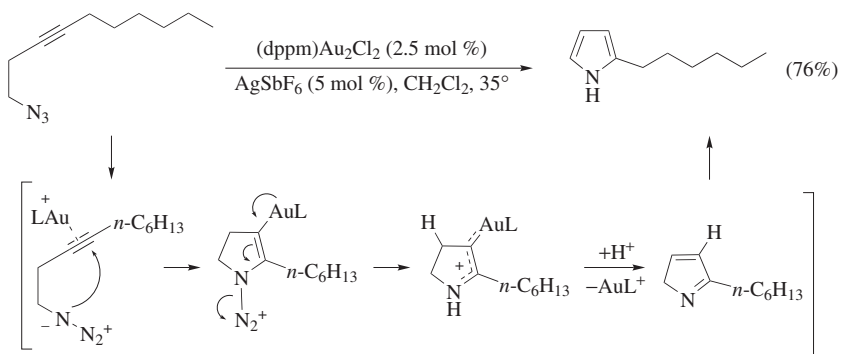
APPLICATIONS TO SYNTHESIS

Both inter- and intramolecular Schmidt reactions are encountered as key steps in syntheses of alkaloids and other biologically interesting molecules. Simple examples are found in a route toward bisnorsteroids (Eq. 59)¹⁰⁶ and as a key, albeit poorly selective, step in a total synthesis of lycoramine (Scheme 16).¹⁰⁷



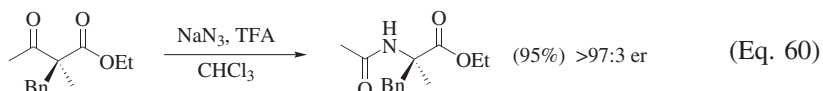


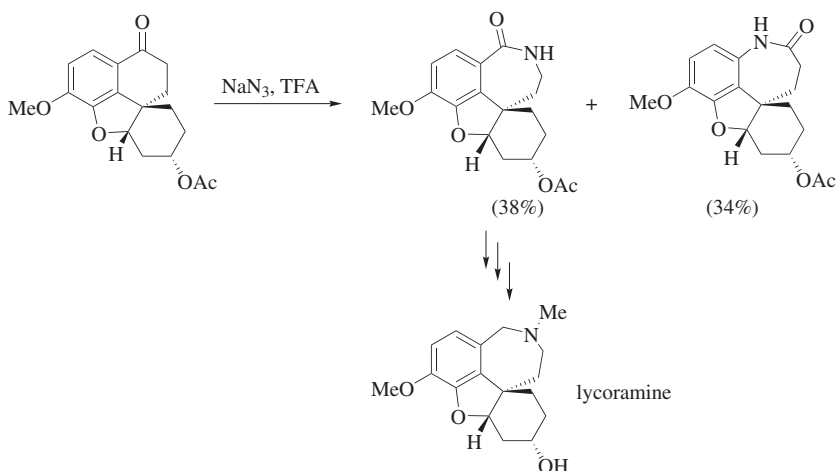
Scheme 14



Scheme 15

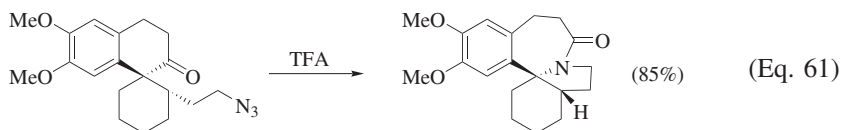
Several groups have taken advantage of the stereospecificity of the Schmidt reaction en route to non-natural, quaternary amino acid derivatives.^{108,109} In this approach, an α,α -disubstituted β -keto ester, prepared by asymmetric alkylation, is subjected to hydrazoic acid to afford the *N*-acetylamino ester with high enantiomeric purity (Eq. 60).^{108,109}





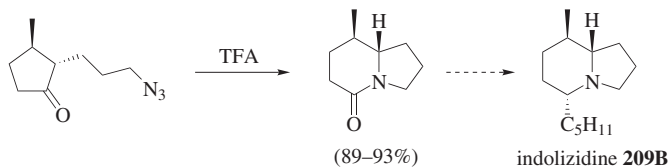
Scheme 16

More recent work has used intramolecular Schmidt reactions in routes to multicyclic alkaloid skeletons. An early example was directed toward the homorythrina spirocyclic ring system (Eq. 61).¹¹⁰ Instructively, neither Beckmann nor HN_3 -mediated Schmidt reaction conditions succeed in converting the corresponding keto mesylate into the lactam. Presumably, the location of the ketone adjacent to a quaternary center limits the facility of intermolecular azido hydrin formation in the latter case.

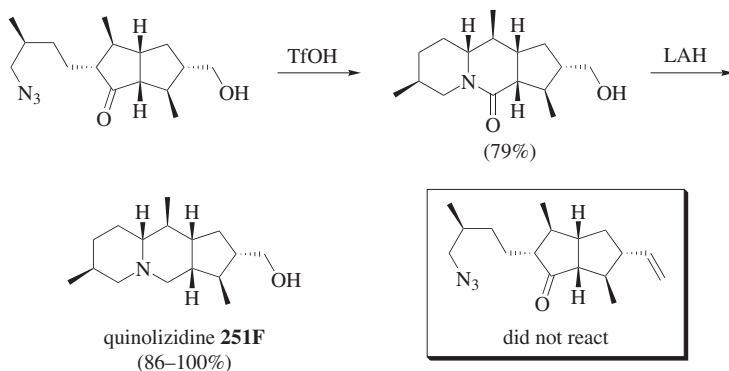


Several applications of the Schmidt reaction have been directed toward alkaloids isolated from South American frogs. The first example, used to synthesize indolizidine **209B**, contains the ideal arrangement of four carbons between the azide and carbonyl groups (Scheme 17).¹¹¹ Accordingly, simple dissolution of the azide in trifluoroacetic acid initiates a smooth ring expansion process. On the other hand, the formation of a quinolizidine ring system requires harsher conditions; in the example shown in Scheme 18, triflic acid is needed.¹¹² Subsequent treatment of the lactam with LAH affords the quinolizidine **251F** (Scheme 18). Notably, the analog with an alkene in place of the terminal alcohol (box) could not be made to react with the azide in this system.

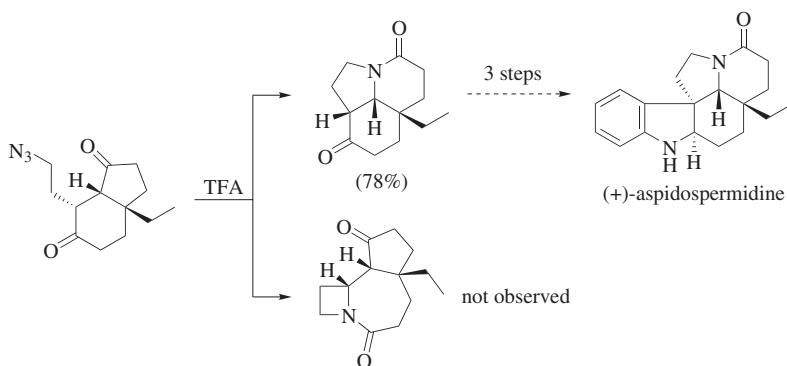
An interesting competition was examined in a route to aspidospermidine (Scheme 19).^{113,114} Two lactams can be formed depending on which carbonyl group is attacked by the azide, but only the ketone bearing a 1,6-relationship with the azide reacts. The alternative pathway, which would lead to a product containing a four-membered ring, is not observed.



Scheme 17



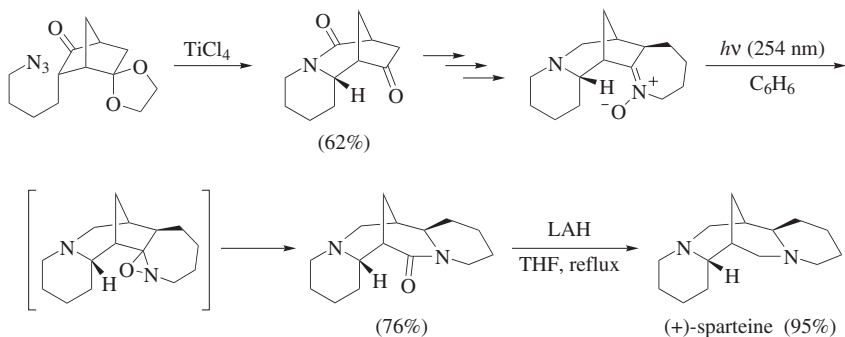
Scheme 18



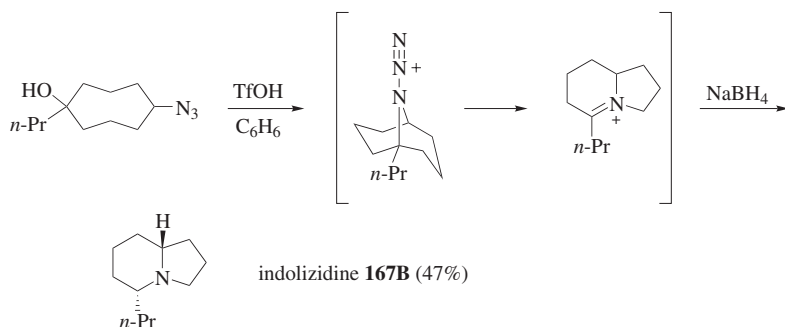
Scheme 19

An intramolecular Schmidt reaction in a bridged ring system is used in the context of a total synthesis of (+)-sparteine (Scheme 20).¹¹⁵ In this synthesis, the initial Schmidt reaction proceeds smoothly, but it is not possible to use an analogous Schmidt reaction to create the rest of the ring system. A photochemical nitrene rearrangement is ultimately used to complete the synthesis.

An elegant example of a cation-mediated Schmidt reaction is used in a route to another South American frog toxin (Scheme 21).^{51,104} In this case, carbocation formation is followed by transannular attack of azide. Only one iminium



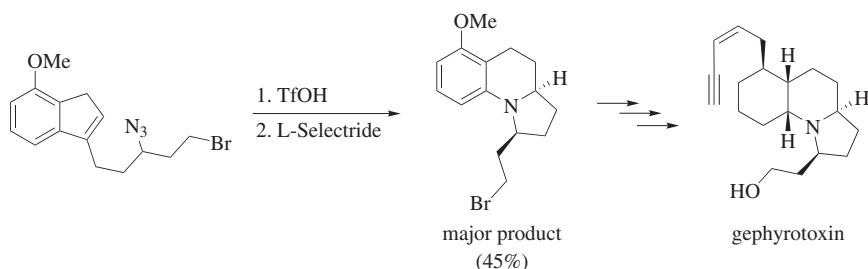
Scheme 20



Scheme 21

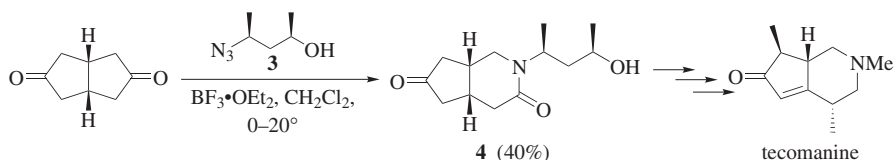
ion can be formed following carbon-to-nitrogen migration because of symmetry. Reduction of this ion occurs stereoselectively to afford indolizidine **167B**.

An additional application of the cation-initiated Schmidt reaction is directed toward a formal synthesis of gephyrotoxin as shown in Scheme 22.¹⁰² The major product involves migration of the phenyl group (a small amount of the alternative alkyl migration product, not shown, is also obtained).



Scheme 22

An asymmetric, hydroxyalkyl-azide-mediated Schmidt reaction is employed in the synthesis of tecomanine.¹¹⁶ In the key step, the *meso* [3.3.0] bicyclic dione reacts with chiral azide **3** (Scheme 23). Two lactams are formed in a ca. 2:1 ratio; the major isomer **4** is isolated in 40% yield. Removal of the nitrogen substituent and additional modification leads to the natural product.

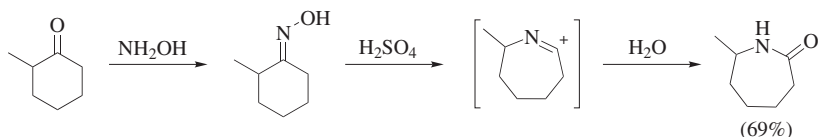


Scheme 23

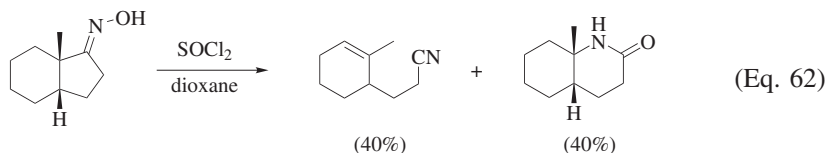
COMPARISON WITH OTHER METHODS

The Schmidt reaction of hydrazoic acid with ketones and the Beckmann reaction are often compared due to the similarity of the electrophiles employed and the products (Scheme 24).^{33,117} Unlike the Schmidt reaction, the Beckmann reaction involves two steps: the preparation of an oxime from the starting carbonyl compound followed by either acid treatment or conversion of the hydroxyl group to a leaving group, e.g., by treatment with POCl_3 . Like the Schmidt reaction using hydrazoic acid, the Beckmann rearrangement is limited to the synthesis of *N*-unsubstituted lactams.

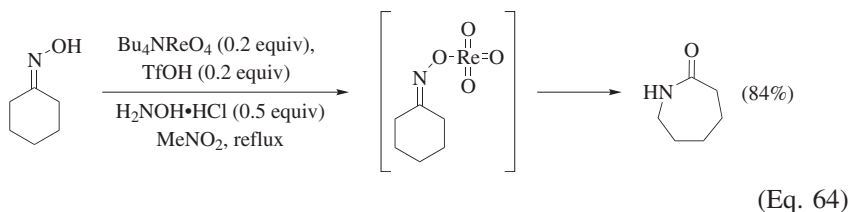
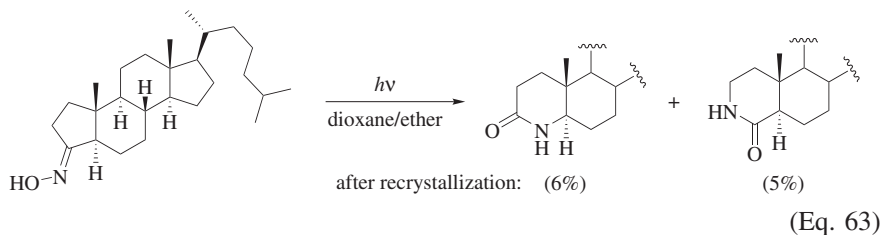
The two reactions are comparable in scope, site selectivity, and synthetic utility. Very often, both Schmidt and Beckmann conditions are investigated when a nitrogen insertion is needed. Although it could be argued that the need for two steps to execute a Beckmann rearrangement is a drawback, in practical terms oxime formation is usually easy and sufficiently high yielding that it does not appreciably detract from using the process. Both sets of procedures have broad scope. Like the Schmidt reaction, the Beckmann rearrangement is also subject to competing nitrile formation from aldehydes. In addition, ketones bearing a cation-stabilizing group in the β position undergo Beckmann fragmentation reactions. Although these reactions have themselves been used to considerable advantage in synthesis, fragmentation when ring expansion is desired is clearly a drawback (Eq. 62).^{118,119}



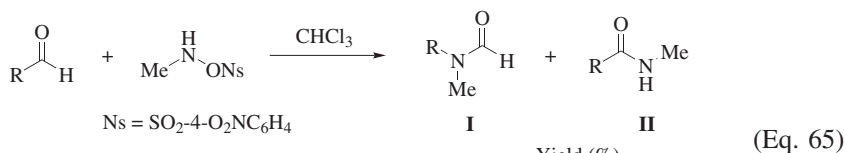
Scheme 24



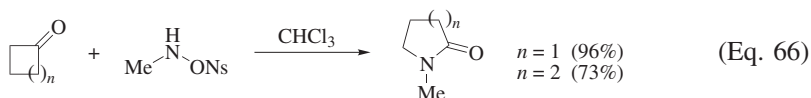
Although exceptions exist, the Schmidt and Beckmann reactions generally afford the same constitutional isomer, i.e., that resulting from migration of the more highly substituted carbon. For the Beckmann reaction, this outcome is due to the preferential formation of the more stable oxime (OH group *anti* to the more bulky group) coupled with stereospecific migration of the antiperiplanar group in the rearrangement step. The similarity of product profiles for a given substrate in the Schmidt and Beckmann reactions has been often used to imply the intermediacy of diazoiminium ethers in the former reaction. Oximes can also be rearranged to provide lactams under photochemical conditions that obviate the need for highly acidic reaction conditions (the photo-Beckmann rearrangement, Eq. 63).¹²⁰ Another modification of the Beckmann reaction is promoted by a combination of tetrabutylammonium perruthenate and triflic acid (Eq. 64).^{121,122}



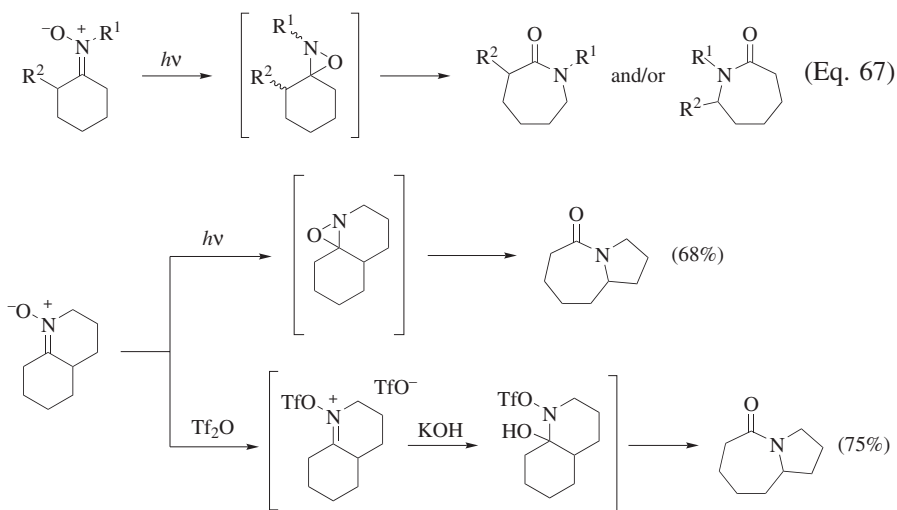
Relatively few alternatives exist to the Schmidt reactions of alkyl azides. One way of directly converting an aldehyde or ketone into an *N*-alkylated amide is to treat the substrate with a reagent of the type RNHOSO_2Ar . The initial carbonyl addition step leads to a species that is pre-activated for loss of sulfonate and rearrangement (Eqs. 65¹²³ and 66^{124–127}). Like the intermolecular Schmidt reaction of alkyl azides promoted by TiCl_4 , this protocol does not have a particularly broad scope but has been usefully employed in particular contexts.



R	Yield (%)	
	I + II	I:II
Ph	96	23:1
4-BrC ₆ H ₄	82	2:1
Et	64	1:7



The photochemical rearrangement of nitrones to amides (Eq. 67),¹²⁸⁻¹³¹ which also provides *N*-substituted lactams, probably proceeds via the initial rearrangement of the nitron to the corresponding oxaziridine. This heterocycle then undergoes photochemically mediated *in situ* rearrangement to the lactam. This reaction has also been explored in the intramolecular context to provide a variety of ring systems.^{130,132-136} The reaction can also be promoted by converting the nitrones into their *O*-trifluoromethanesulfonyl derivatives followed by base-mediated rearrangement (Scheme 25).¹³⁶ Like the photo-Beckmann reaction, this reaction is useful for cases in which strongly acidic conditions are not desirable.^{93,115}

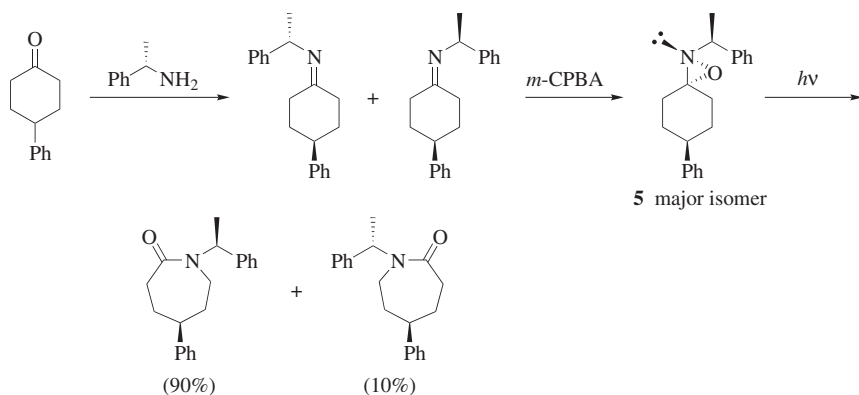


Scheme 25

Oxaziridines can also be prepared from ketones or aldehydes via the corresponding imine derivatives, which are oxidized using *m*-CPBA or other common

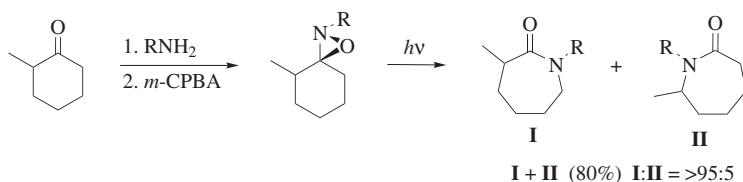
oxidants.^{43,137–140} In addition to their likely involvement in photo-Beckmann reactions, oxaziridines are useful precursors to lactams in their own right, via photolytic rearrangement.^{78,141–143} Rearrangements can also be induced by treatment with certain low-valent metal salts (iron(II) or copper(I)).^{131,144–146}

The photochemical oxaziridine rearrangement is subject to a stereoelectronic effect that has an important synthetic ramification. Chiral oxaziridine **5** (Scheme 26) undergoes stereoselective rearrangement to afford the lactam with 9:1 stereoselectivity. In general, the predominant product from such photochemical rearrangements results from migration of the bond antiperiplanar to the lone pair on the oxaziridine nitrogen atom (which is non-invertible under the reaction conditions).^{147,148}



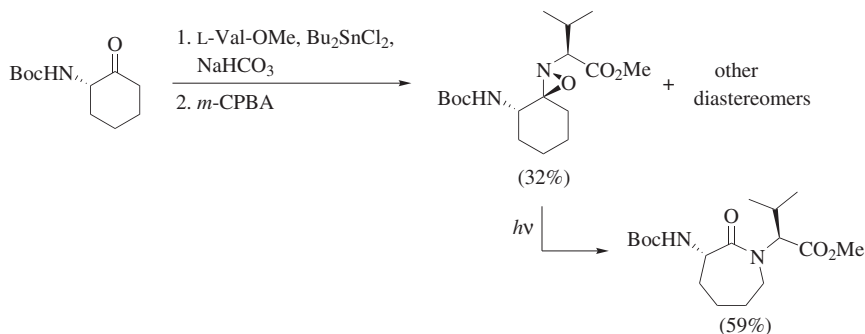
Scheme 26

Because of this effect, the oxaziridine rearrangement reaction is the only nitrogen insertion reaction known that provides a reliable route to lactams resulting from migration of the less substituted carbon in unsymmetrical cycloalkanones (Scheme 27).^{149–151} Thus, the oxaziridine intermediate that is generally formed places the *N*-alkyl group away from the more highly substituted carbon on the ketone.¹⁴² An example using this strategy to prepare a series of peptide analogs is shown in Scheme 28.¹⁵²



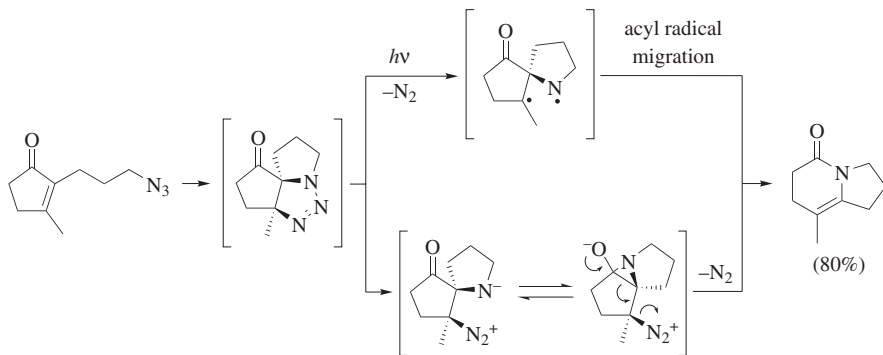
Scheme 27

A significant limitation of the intramolecular Schmidt reaction of alkyl azides is its inapplicability to unsaturated ketones (Eq. 45). In contrast, insertion products



Scheme 28

of azides appended to such partners are observed under irradiation.^{153–156} These reactions are proposed to involve a thermally allowed [3+2] cycloaddition onto the enone, photochemical generation of a diradical with loss of dinitrogen, and finally molecular reorganization to afford the final products (Scheme 29).⁸⁶ An ionic mechanism may also be operative in this case.

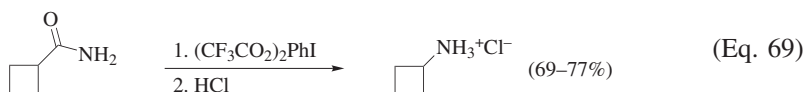
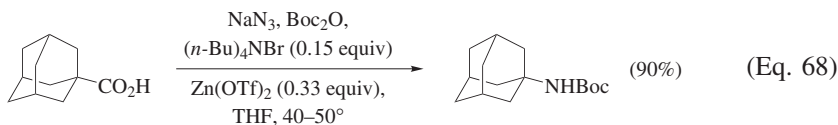


Scheme 29

As noted earlier, the Schmidt reactions of hydrazoic acid with carboxylic acids or with aldehydes are rarely used by synthetic chemists. In the former case, the Curtius reaction of carboxylic acids, which involves the conversion of the carboxylic acid into an acyl azide that is then subjected to thermal rearrangement, is the most common reaction for the synthesis of amines from acids. The acyl azide can be prepared via the acyl chloride (typically readily made from the acid), other kinds of activated acids,¹⁵⁷ or directly from the acid via in situ activation, e.g., by reaction with diphenyl phosphoryl azide.¹⁵⁸

The Curtius reaction has been widely adopted because its conditions are relatively mild and do not require the use of the toxic and explosive hydrazoic acid as a reagent. In addition, the thermal acyl azide rearrangement provides as its initial product an isocyanate; hydrolysis of this species with water affords the

amine. Even better, the isocyanate can be combined with alcohols or amines to afford carbamates or ureas, respectively. A one-pot version of the Curtius reaction that provides *N*-Boc amines in 50–94% yields has also been reported (Eq. 68).¹⁵⁹ Another widely used reaction that does not involve the formation of N_3 -containing species is the Hofman rearrangement of amides to afford amines (Eq. 69).¹⁶⁰



EXPERIMENTAL CONDITIONS

Schmidt reactions using hydrazoic acid are generally accomplished by generating HN_3 in situ from NaN_3 , i.e., by adding it to sulfuric acid, HCl , or polyphosphoric acid.¹⁶¹ Cosolvents such as chloroform or DME may be used. In some cases, an additional protic or Lewis acid such as SnCl_4 , trichloroacetic acid, or $\text{BF}_3 \cdot \text{OEt}_2$ is added. Heating is often required. Some older procedures involve preparation of stock solutions of HN_3 in chloroform or other solvents, although these are rarely used nowadays.¹¹

The use of hydrazoic acid is hazardous, as it is both explosive and toxic. Proper precautions that include safety shields and an efficient hood are essential. Typically, the workup of the reaction involves a basic extraction step that makes it possible to remove hydrazoic acid in the aqueous layer (as NaN_3 for example). For reasons discussed below, it is best not to use methylene chloride as the organic solvent in such extractions.

Intermolecular Schmidt reactions in which alkyl azides react with carbonyl compounds are generally carried out in methylene chloride using commercial solutions of TiCl_4 . Intramolecular reactions can be carried out under similar conditions, although a wider range of Lewis acids are usable for these more reactive substrates. Alternatively, protic acid conditions can be used, with neat trifluoroacetic acid or triflic acid/methylene chloride being most common in this context. Similar conditions can be employed for the reactions of azides with cations derived from olefins or alcohols.

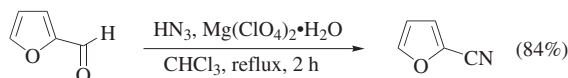
Either protic or Lewis acids can be used to facilitate the intermolecular reactions of hydroxyalkyl azides with ketones; a comparative study suggests that $\text{BF}_3 \cdot \text{OEt}_2$ is the most effective promoter for this reaction.⁹⁶ The key difference between these reactions and those noted above is that the initial product is not a lactam or amide but rather an iminium ether. These salts can be isolated using

standard workup conditions and in some cases have been chromatographed. Treatment with an aqueous base like KOH or NaHCO₃ is commonly used to convert these initial products into lactams.

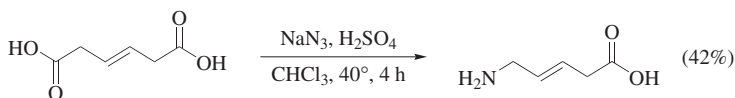
Two safety considerations come into play for the reactions with alkyl azides. The first is the nature of the azide itself. *The authors advise readers to assume that any alkyl azide is a possible explosion hazard and to treat azides having low formula weights with particular caution.* Specific manipulations to be avoided include heating (especially in the absence of solvent), vacuum distillation, preparing on large scale, or allowing exposure to metals.

A second consideration should be heeded when preparing azides from sodium azide. *NaN₃ is believed to pose a particular hazard when heated or evaporated in methylene chloride solutions; the formation of diazidomethane is possible under these conditions and explosions have been documented.*¹⁶² One can also prepare alkyl azides via halogen displacement or epoxide opening by azidotrimethylsilane activated by fluoride or a Lewis acid.^{163,164} However, *azidotrimethylsilane has been associated with toxic reactions, possibly by environmental hydrolysis to form hydrazoic acid.*¹⁶⁵ Finally, a variation of the Mitsunobu reaction using Zn(N₃)₂ can be used to prepare azides directly from alcohols.¹⁶⁶

EXPERIMENTAL PROCEDURES

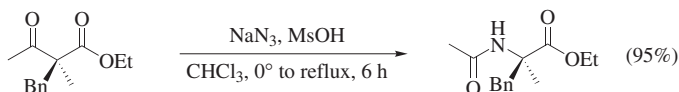


Furan-2-carbonitrile [Schmidt Reaction of an Aldehyde with Hydrazoic Acid to Afford a Nitrile].¹⁶⁷ To a three-necked flask with a mechanical stirrer and a reflux condenser were added 2-furaldehyde (9.61 g, 0.1 mol), a solution of HN₃ in CHCl₃ (15 mL, 0.11 mol), and Mg(ClO₄)₂ (25.0 g, 0.1 mol). The release of gaseous nitrogen began after 5 min. The flow of nitrogen became strongest after 10 to 15 min. When the release of nitrogen had stopped, the reaction mixture was brought to its boiling point and kept there for 2 h. The contents of the flask were cooled to rt, water was added, and the mixture was filtered. The organic layer was washed twice with water, dried (Na₂SO₄), and evaporated. The residue was distilled under vacuum to give the desired product (7.82 g, 84%): bp 147°; ¹H NMR (300 MHz, CDCl₃) δ 6.63 (dd, *J* = 1.8, 3.7 Hz, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.82 (d, *J* = 0.75 Hz, 1H); IR (neat) 3110, 2200, 1575 cm⁻¹. Anal. Calcd for C₅H₃NO: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.44; H, 3.61; N, 14.91.

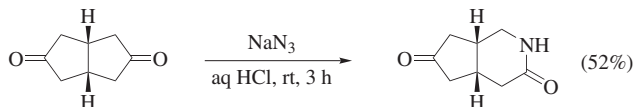


(*E*)-5-Aminopent-3-enoic Acid [Schmidt Reaction of a Carboxylic Acid with Hydrazoic Acid to Afford an Amine].¹⁶⁸ (*E*)-2-Butene-1,4-dicarboxylic

acid (1.4 g, 9.71 mmol) was suspended in CHCl_3 (40 mL), and concentrated sulfuric acid (4.0 mL) was added. NaN_3 (0.65 g, 10 mmol) was added in small amounts over 30 min while the mixture was stirred rapidly. After a further 4 h at 40° the CHCl_3 layer was decanted from the viscous residue which was washed again with CHCl_3 (30 mL). The residue was dissolved in water (150 mL), filtered, and added to a column of Dowex 50 W (H^+) ion-exchange resin (50 mL). The column was washed with water to neutral pH and then the amino acid was eluted with aqueous pyridine (300 mL, 1 M). Evaporation of the solvent afforded an oil (600 mg) that slowly solidified. Recrystallization from water/ethanol gave the desired product as white needles (0.437 g, 42%): mp $165\text{--}167^\circ$; IR (nujol) $3500\text{--}2400$, 2180, 1625 cm^{-1} ; ^1H NMR (89.6 MHz, $\text{D}_2\text{O}/\text{DCI}$) δ 3.64 (d, $J = 6.1$ Hz, 2H), 4.03 (d, $J = 5.7$ Hz, 2H), 6.28 (m, 2H); MS (EI) m/z : $[\text{M} + \text{H}]^+$ 116 (100), 99 (86), 98 (11), 85 (10), 70 (13). Anal. Calcd for $\text{C}_5\text{H}_9\text{NO}_2$: C, 52.2; H, 7.9; N, 12.2. Found: C, 52.0, H, 7.9; N, 12.4.

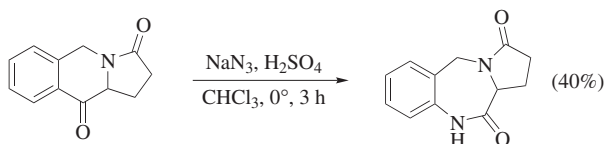


(*R*)-Ethyl 2-Acetamido-2-methyl-3-phenylpropanoate [Schmidt Reaction of an Acyclic Ketone with Hydrazoic Acid to Afford an Amide].¹⁰⁹ Methanesulfonic acid (0.73 mL, 10.0 mmol) was added dropwise to the stirred solution of ethyl (*S*)-2-benzyl-2-methylacetoacetate (234 mg, 1.00 mmol) in CHCl_3 (5 mL) at 0° , and then NaN_3 (325 mg, 5.0 mmol) was added. After being refluxed for 6 h, the reaction mixture was cooled to rt, diluted with H_2O , neutralized with diluted aqueous NH_3 , extracted with Et_2O , and dried over MgSO_4 . Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (hexane/ EtOAc 9:1) to give the desired product as a colorless oil (237 mg, 95%): $[\alpha]_{\text{D}}^{25} - 63.8$ (c 1.10, CHCl_3), lit. $[\alpha]_{\text{D}} - 47.8$ ($>97.5:2.5$ er); ^1H NMR (CDCl_3) δ 1.35 (t, $J = 3.0$ Hz, 3H), 1.66 (s, 3H), 1.96 (s, 3H), 3.21 (d, $J = 13.5$ Hz, 1H), 3.60 (d, $J = 13.5$ Hz, 1H), 4.29 (m, 2H), 6.09 (br s, 1H), 7.02–7.08 (m, 2H), 7.18–7.30 (m, 3H); ^{13}C NMR (CDCl_3) δ 14.1, 23.4, 24.0, 41.0, 61.2, 61.8, 126.8, 128.2, 129.8, 136.6, 169.5, 173.9; IR (neat) 3300 (br), 1720, 1660 cm^{-1} . FABMS m/z : $[\text{M} + \text{H}]^+$ 250.

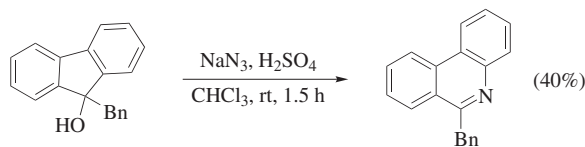


(*1R^,*6S^**)-3-Azabicyclo[4.3.0]nona-4,8-dione [Schmidt Reaction of a Cyclic Ketone with Hydrazoic Acid to Afford a Lactam].¹¹⁶** Sodium azide (0.60 g, 9.1 mmol) was added portionwise over 20 min to a solution of *cis*-bicyclo[3.3.0]octane-3,7-dione (1.0 g, 7.2 mmol) in 36% aqueous HCl (20 mL), while keeping the temperature below 35° . The mixture was stirred for 3 h at rt and then brought to pH 10 with 20% aqueous NaOH at 0° . Precipitated NaCl

was filtered off and the aqueous layer was extracted continuously with CHCl_3 for 48 h. Drying the organic phase over MgSO_4 , followed by removal of solvent, furnished a residue that was separated on a silica gel column (30 g). Elution with $\text{CH}_2\text{Cl}_2/\text{acetone}$ (85:15) gave unreacted diketone (240 mg) and the desired product (576 mg, 52%): mp 120–122°; $^1\text{H NMR}$ (CDCl_3) δ 2.10–2.30 (m, 3H), 2.40–2.90 (m, 5H), 3.21 (ddd, $J = 3.0, 6.8, 13.0$ Hz, 1H), 3.52 (ddd, $J = 3.5, 5.8, 13.0$ Hz, 1H), 6.3 (br s, 1H); $^{13}\text{C NMR}$ (D_2O) δ 30.7 (d), 31.3 (d), 31.9 (t), 40.9 (t), 41.9 (t), 43.6 (t), 175.4 (s), 223.7 (s); IR (neat) 3246, 2935, 1735, 1667, 1638 cm^{-1} ; MS m/z : M^+ 153 (100), 125 (10), 112 (33), 96 (35), 82 (53), 68 (33), 54, (82), 41 (78). Anal. Calcd for $\text{C}_8\text{H}_{11}\text{NO}_2$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.76; H, 7.21; N, 9.11.

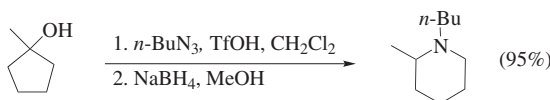


10,11a-Dihydro-1*H*-benzo[*e*]pyrrolo[1,2-*a*][1,4]diazepine-3,11(2*H*,5*H*)-dione [Schmidt Reaction of a Heterocyclic Ketone with Hydrazoic Acid to Afford a Lactam].¹⁶⁹ To a solution of 1,2-dihydropyrrolo[1,2-*b*]isoquinoline-3,10(5*H*,10*aH*)-dione (1.5 mmol) in CHCl_3 (30 mL) at 0°, was added concentrated sulfuric acid (24.3 mL). NaN_3 (214 mg, 3.3 mmol) was added portionwise and the mixture was stirred for 3 h at this temperature. Ice (250 g) was then added. The mixture was extracted with CH_2Cl_2 (3×50 mL), and the organic extracts were washed with water (2×25 mL) and dried over MgSO_4 . After evaporation under vacuum, the crude product was purified by chromatography on a silica gel column (240–400 mesh) using $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (99:1, v/v) as eluent to give the desired product (40%): mp 202–204°; $^1\text{H NMR}$ (CDCl_3) δ 2.00–2.10 (m, 2H), 2.40–2.70 (m, 2H), 4.18 (q, $J = 7.1$ Hz, 1H), 4.28 (d, $J = 14$ Hz, 1H), 4.77 (d, $J = 14$ Hz, 1H), 7.09 (d, $J = 8$ Hz, 1H), 7.22 (d, $J = 8$ Hz, 1H), 7.35 (d, $J = 8$ Hz, 1H), 7.37 (d, $J = 8$ Hz, 1H), 8.06 (s, 1H); $^{13}\text{C NMR}$ (CDCl_3) δ 18.75, 29.9, 44.6, 57.8, 122.1, 126.4, 127.3, 129.6, 130.4, 136.8, 169.3, 173.4; IR (neat) 3160, 1670 cm^{-1} ; MS m/z : M^+ 216. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$: C, 66.65; H, 5.59; N, 12.95. Found: C, 66.39; H, 5.47; N, 13.18.

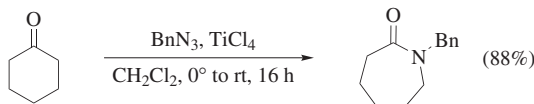


9-Benzylphenanthridine [Schmidt Reaction of an Alcohol and Hydrazoic Acid to Afford an Imine].¹⁷⁰ To a suspension of NaN_3 (7.3 g, 11.0 mmol) in CHCl_3 (15 mL), cooled in ice, was added dropwise sulfuric acid (98%, 29 mL) with stirring that was continued for 10 min at 0°. The ice bath was replaced

by a water bath maintained at rt, and a solution of 9-benzylfluoren-9-ol (2.0 g, 7.3 mmol) in CHCl_3 (20 mL) was added during 1 h to the vigorously stirred mixture. Stirring was continued for a further hour; the mixture was then poured on ice (1.2 kg) and shaken. From the aqueous acidic solution, and from the sulfate (which frequently separated), the base was liberated by addition of 2 N NaOH. The product was filtered off, washed, and dried. The desired product was obtained after crystallization from ethanol and short-path distillation at $130^\circ/0.4$ mm as yellow needles (0.8 g, 40%): mp 112° . Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{N}$: C, 89.2; H, 5.6; N, 5.2. Found: C, 88.7; H, 5.7; N, 5.15.

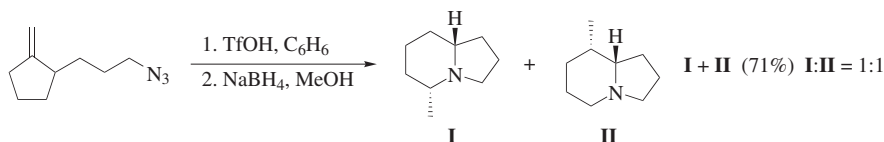


1-(*n*-Butyl)-2-methylpiperidine [Schmidt Reaction of an Alcohol with an Alkyl Azide to Afford an Amine].²⁴ Triflic acid (0.959 g, 6.33 mmol) was added to a solution of 1-methylcyclopentan-1-ol (0.250 g, 2.49 mmol) and *n*-butyl azide (1.48 g, 15.0 mmol) in CH_2Cl_2 at 0° over 10 min. Sodium borohydride (1.25 g, 38.0 mmol) in MeOH (10 mL) was added at 0° . After stirring at rt overnight, 2 N HCl (10 mL) was added and the mixture was washed with ether (2×20 mL), then basified with aqueous 15% NaOH (30 mL) and extracted with ether (2×20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na_2SO_4 , and concentrated to afford the desired product as a clear oil (0.369 g, 95%): ^1H NMR (300 MHz, CDCl_3) δ 0.92 (t, $J = 7.3$ Hz, 3H), 1.06 (d, $J = 6.3$ Hz, 3H), 1.20–1.33 (m, 4H), 1.35–1.50 (m, 2H), 1.52–1.68 (m, 4H), 2.12 (dt, $J = 3.0, 10.6$ Hz, 1H), 2.21–2.30 (m, 1H), 2.31–2.38 (m, 1H), 2.58–2.72 (m, 1H), 2.80–2.90 (m, 1H); ^{13}C NMR (90 MHz, CDCl_3 , JMOD) δ 14.0, 19.1, 20.9, 24.1, 26.2, 27.2, 34.6, 52.1, 53.8, 55.70; IR (neat) 2859 (s), 2786 (s), 2592 (w), 1455 (m), 1372 (m), 1330 (w), 1277 (w), 1132 (w), 1076 (w), 900 (w) cm^{-1} ; MS (EI) m/z : M^+ 155 (12.6), 140 (59.4), 126 (5.3), 112 (100), 98 (9.7), 84 (20.1), 70 (6.1), 55 (18.1), 44 (18.5). HRMS m/z : calcd for $\text{C}_{10}\text{H}_{21}\text{N}$, 155.1674; found, 155.1669.

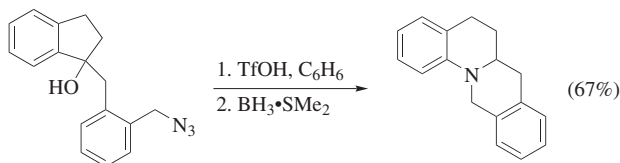


1-Benzyl-2H-hexahydroazepin-2-one [Intermolecular Schmidt Reaction of a Ketone with an Alkyl Azide to Afford an Amide].⁸⁵ To a solution of cyclohexanone (0.100 g, 1.02 mmol) and benzyl azide (0.271 g, 2.04 mmol) in CH_2Cl_2 (2.5 mL), in an ice bath, was added dropwise TiCl_4 (0.484 g, 2.55 mmol). The reaction mixture was allowed to warm to rt (with gas evolution). A precipitate formed after 15 min, and the suspension was stirred for a total of 16 h, at which time it was diluted with EtOAc (20 mL) and partitioned between EtOAc (200 mL) and saturated NaHCO_3 solution (30 mL). The organic layer

was washed with brine (30 mL) and dried over anhydrous Na_2SO_4 . Evaporation of the solvent followed by silica gel chromatography (hexanes/EtOAc 4:1) gave the desired product as a clear oil (0.365 g, 88%): ^1H NMR (300 MHz, CDCl_3) δ 1.46–1.53 (m, 2H), 1.70–1.75 (m, 4H), 2.64–2.66 (m, 2H), 3.26–3.33 (m, 2H), 4.60 (s, 2H), 7.26–7.32 (m, 5H); ^{13}C NMR (75.6 MHz, CDCl_3) δ 23.4, 28.0, 29.9, 37.1, 48.8, 51.0, 127.2, 128.1, 128.4, 137.8, 175.9; IR (neat) 2923, 1637 cm^{-1} ; MS (EI) m/z : M^+ 203, 106, 91, 55. HRMS m/z : calcd for $\text{C}_{13}\text{H}_{17}\text{NO}$, 203.1310; found, 203.1313.

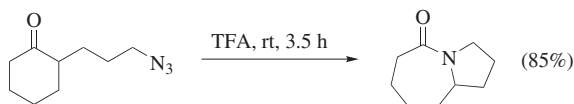


(5*R,8*aR**)-5-Methylindolizidine and (8*S**,8*aS**)-8-Methylindolizidine [Intramolecular Schmidt Reaction of an Azidoalkyl Alkene to Afford an Amine].⁵¹** Triflic acid (1.250 g, 8.34 mmol) was added to a cooled (5°) solution of 1-(3-azidopropyl)-2-methylenecyclopentane (0.920 g, 5.56 mmol) in benzene (55 mL). After 45 min, NaBH_4 (0.631 g, 16.7 mmol) was added via a pressure equalizing solid addition funnel. Methanol (10 mL) was immediately added, and the resulting mixture was stirred for 10 h. Aqueous NaOH (25 mL, 15% w/v) was added, and the resulting mixture was extracted with ether (3×15 mL). The combined organic extracts were washed with brine (2×25 mL) and water (2×25 mL), then dried (MgSO_4) and concentrated. Silica gel was deactivated by the addition of 20% by weight of hexamethyldisilazane to a suspension of SiO_2 in hexane. Chromatography on the deactivated silica gel (hexane/acetone 88:12) afforded a 1:1 mixture of the title compounds (0.546 g, 71%) as an inseparable mixture as determined by GC analysis: ^1H NMR (on mixture, 360 MHz, CDCl_3) δ 0.84 (s, 1H), 0.86 (s, 1H), 0.95 (dd, 1H), 1.07 (s, 1H), 1.09 (s, 1H), 1.1–2.1 (m, 18H), 2.95–3.1 (m, 2H), 3.15–3.25 (m, 1 H); ^{13}C NMR (90 MHz, CDCl_3) δ 18.9, 20.5, 21.1, 23.3, 24.7, 25.8, 29.1, 30.6, 31.1, 33.5, 34.3, 36.9, 51.8, 52.9, 54.6, 58.9, 64.8, 70.9; IR (on mixture, neat) 2928 (s), 2779 (s), 2370 (m), 2274 (m), 1457 (m), 1328 cm^{-1} . Data for (5*R**,8*aR**)-5-methylindolizidine: MS (EI) m/z : M^+ 139, 138, 124 (100), 110, 97, 96, 70, 69, 68, 57, 56, 55, 54, 42, 41, 39. GCMS data for (8*S**,8*aS**)-8-methylindolizidine: MS (EI) m/z : M^+ 139, 138, 124, 111, 110, 97, 96 (100), 84, 83, 82, 70, 69, 68, 67, 56, 55, 54, 53, 43, 42, 41, 40, 39.



6,6*a*,7,12-Tetrahydro-5*H*-12*a*-azabenz[*a*]anthracene [Intramolecular Schmidt Reaction of an Azidoalkyl Alcohol to Afford an Amine].¹⁰² Triflic

acid (0.339 g, 2.26 mmol) was added to a solution of 1-[2'-(azidomethyl)benzyl]-2,3-dihydro-1*H*-inden-1-ol (0.544 g, 1.95 mmol) in benzene (30 mL) at rt. After 10 min, the solution was cooled to 0° and treated with borane dimethyl sulfide complex (3.0 mL of a 2.0 M solution in THF, 6.0 mmol). After the mixture was warmed to rt with stirring for 14 h, 15% aqueous NaOH (15 mL) was added, and the resulting mixture was extracted with ether (3 × 15 mL). The combined organic extracts were washed with brine, then dried (MgSO₄) and concentrated. Chromatography (hexane/ether 7:1) afforded the desired compound (0.307 g, 67%): ¹H NMR (300 MHz, CDCl₃) δ 1.87–1.96 (m, 1H), 2.01–2.11 (m, 1H), 2.65–2.96 (m, 4H), 3.30–3.38 (m, 1H), 4.22 (d, *J* = 15.8 Hz, 1H), 4.76 (d, *J* = 15.8 Hz, 1H), 6.66–6.71 (m, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 7.12–7.21 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 26.7, 29.7, 37.5, 50.3, 53.1, 112.1, 117.2, 125.2, 126.0, 126.1, 126.3, 127.1, 128.2, 128.3, 134.2, 134.8, 146.1; IR (neat) 1603 cm⁻¹; MS (EI) *m/z*: M⁺ 235 (100), 220, 84; HRMS *m/z*: calcd for C₁₇H₇N, 235.1361; found, 235.1352.



Hexahydro-1*H*-pyrrolo[1,2-*a*]azepin-5(6*H*)-one [Intramolecular Schmidt Reaction of an Azidoalkyl Ketone to Afford a Lactam].²⁹ 2-(3-Azidopropyl)cyclohexanone (0.099 g, 0.55 mmol) was dissolved in TFA (5 mL) at rt, and the solution was stirred. After 3.5 h, the solution was concentrated under vacuum. Ether (100 mL) was added, and the solution was washed with NaHCO₃ (1 × 25 mL) and brine (1 × 25 mL). The organic layer was dried over Na₂SO₄ and concentrated to give an oil. The crude product was purified by silica gel chromatography (Et₂O, then EtOAc) to give the desired product (0.071 g, 85%) as an oil: ¹H NMR (300 MHz, CDCl₃) δ 1.30–1.46 (m, 1H), 1.46–1.56 (m, 2H), 1.56–1.76 (m, 2H), 1.77–1.90 (m, 3H), 1.90–2.02 (m, 1H), 2.15–2.29 (m, 1H), 2.36–2.47 (m, 1H), 2.56 (dd, *J* = 6.9, 15.0 Hz, 1H), 3.37 (dt, *J* = 7.2, 11.8 Hz, 1H), 3.62–3.76 (m, 2H); ¹³C NMR (75.6 MHz, CDCl₃) δ 23.2, 29.6, 34.8, 35.6, 38.0, 46.7, 58.7, 173.9; IR (neat) 2922, 1635 cm⁻¹. MS (EI) *m/z*: M⁺ 153, 124, 96, 84, 70 (100), 55. HRMS *m/z*: calcd for C₉H₁₅NO, 153.1154; found, 153.1154.

TABULAR SURVEY


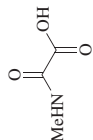

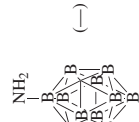


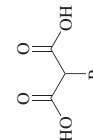
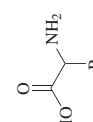
The tables contain literature references for each of the Schmidt reaction variants discussed in this chapter. The coverage is from 1946 (when the previous *Organic Reactions* chapter on the Schmidt reaction was published)¹¹ to the end of 2009. In the tables, all carbon counts include protecting groups. The substrates are divided among the tables based on the reacting center, grouped by mechanism and oxidation state. For example, Table 1, “Schmidt Reactions of Carboxylic Acids with HN₃”, also includes esters and anhydrides. Compounds

that contain both a reacting carboxylic acid and an acyclic ketone are placed in Table 3, "Schmidt Reactions of Acyclic Ketones with HN_3 ". Compounds that contain both a reacting cyclic and acyclic ketone are placed in Table 4, "Schmidt Reactions of Carbocyclic Ketones with HN_3 ". Table 5, "Schmidt Reactions of Heterocyclic Ketones with HN_3 ", only contains substrates in which the heterocyclic ketone is the reacting center, not just present in the molecule. Ketones that react via initial carbocation formation are placed in Tables 8 and 10, along with alcohols, alkenes, alkynes, and epoxides that react with a similar mechanism.

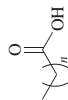
The following abbreviations are used in the tables:

BINOL	1,1'-bi(2-naphthol)
dppm	bis(diphenylphosphino)methane
eq	equivalent(s)
g	gas
MW	microwave irradiation
PNB	4-nitrobenzyl
<i>s</i>	secondary
<i>t</i>	tertiary

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN₃

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ 	NaN ₃ , H ₂ SO ₄ or AcOH	MeNH ₂ (89)	171
C ₃ 	NaN ₃ , H ₂ SO ₄ , PhH, 80°, 4 h	MeHN-C(=O)-NH ₂ (—)	172
	HN ₃ , H ₂ SO ₄	 (—)	173
C ₃₋₅ 	NaN ₃ , H ₂ SO ₄ , 40°, 17 h		80
C ₃₋₉ 	1. HN ₃ , H ₂ SO ₄ , CHCl ₃ , 50°, 8 h 2. Amberlite IR-4B		R H (49) Me (83) Et (89) <i>n</i> -Pr (61) <i>i</i> -Pr (68) <i>n</i> -Bu (50) <i>s</i> -Bu (66) <i>t</i> -Bu (67) <i>n</i> -C ₃ H ₁₁ (54) <i>i</i> -C ₃ H ₁₁ (59) <i>n</i> -C ₆ H ₁₃ (38)

C₃₋₁₈



n		n
1		(-)
2		(-)
3		(-)
4		(72)
5		(-)
6		(-)
7		(-)
8		(70)
10		(81)
12		(80)
14		(85)
16		(90)

NaN₃, H₂SO₄, PhH, 50-60°

175-181
177, 181,
177a, 179

182

183

177

182

182

184

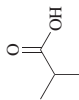
184, 182

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184, 185

184, 183

C₄

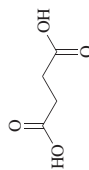


NaN₃, H₂SO₄, 40°

(96)



171



NaN₃, H₂SO₄

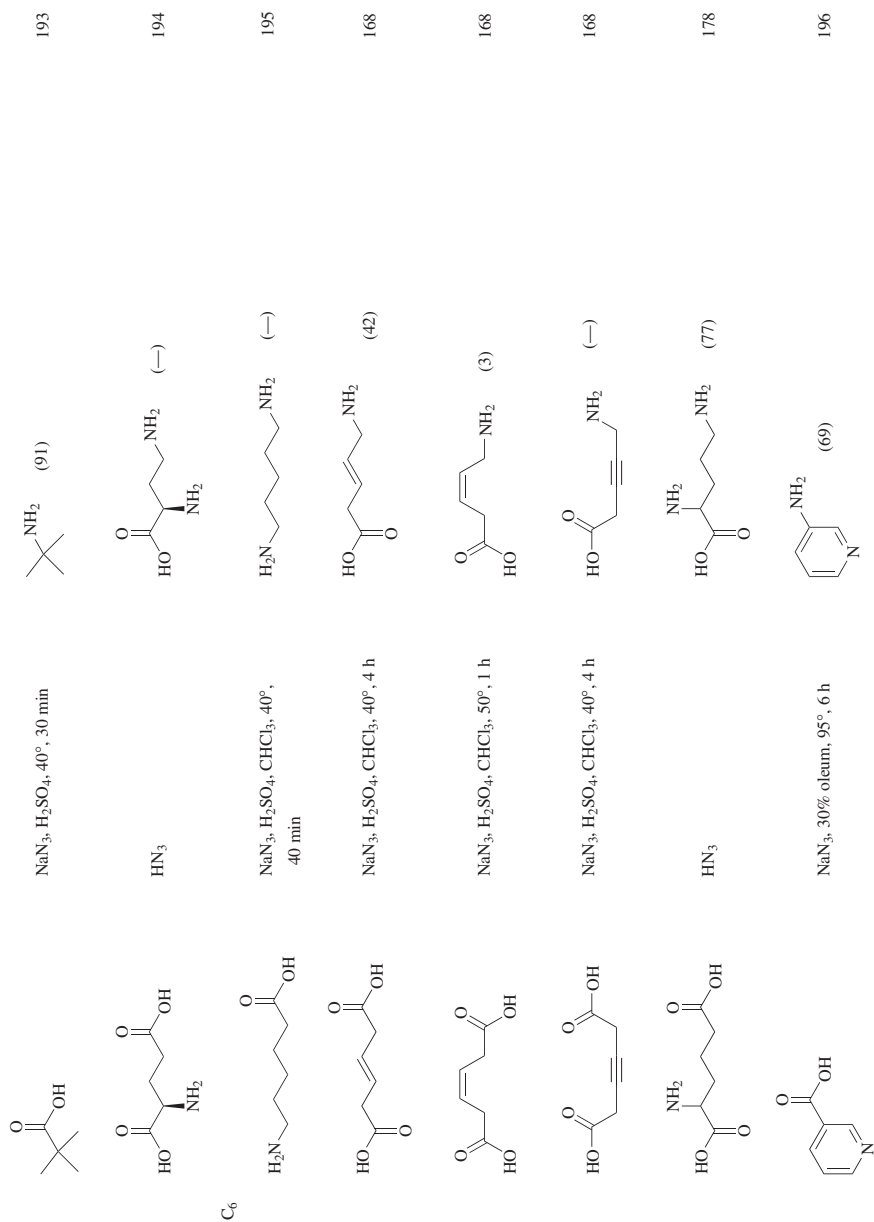
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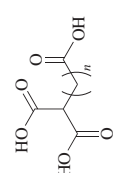
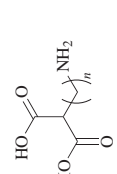
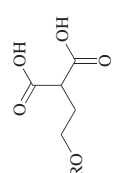
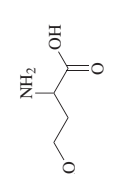
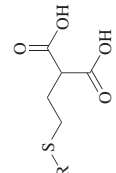
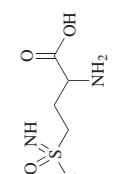
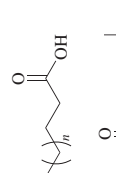
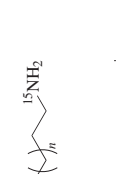
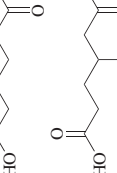
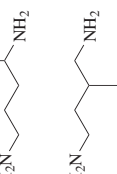
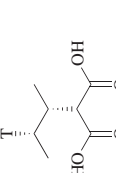
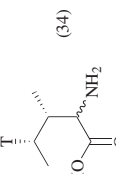


TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{O}_2\text{N}-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{OH} \\ \quad \\ \text{O}_2\text{N} \quad \text{NO}_2 \end{array} $	1. NaN ₃ , TFA 2. NaNO ₂	$ \begin{array}{c} \text{O}_2\text{N}-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{OH} \\ \quad \\ \text{O}_2\text{N} \quad \text{NO}_2 \end{array} $ (88)	187	
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \\ \parallel \\ \text{O} \end{array} $	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 60°	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{N}_3-\text{C}-\text{NHR} \\ \text{I} \end{array} + \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NHR} \\ \text{II} \end{array} $	$ \begin{array}{c} \text{R} \\ \hline \text{Me} \\ n\text{-Pr} \\ n\text{-Bu} \end{array} $	188
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{MeO}-\text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{C} \quad \text{C} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array} $	1. HN ₃ , H ₂ SO ₄ , CHCl ₃ , 60° 2. H ₂ O, reflux	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{C}-\text{C}-\text{C}-\text{NH}_2 \\ \quad \\ \text{C} \quad \text{C} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array} $	$ \begin{array}{c} n \\ \hline 1 \quad (58) \\ 2 \quad (79) \\ 4 \quad (74) \\ 6 \quad (-) \\ 7 \quad (81) \\ 8 \quad (83) \end{array} $	189 189 189 190 189 189
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{C} \quad \text{C} \end{array} $	NaN ₃ , H ₂ SO ₄ , PhH, 50–60°	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{C} \quad \text{C} \end{array} $	(—)	175
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{T}-\text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{C} \quad \text{C} \end{array} $	HN ₃ , H ₂ SO ₄ , CHCl ₃	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{T}-\text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{C} \quad \text{C} \end{array} $	(—)	191
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{C} \quad \text{C} \end{array} $	NaN ₃ , H ₂ SO ₄	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{C} \quad \text{C} \end{array} $	(—)	192



C₆

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₆₋₉	HN ₃ , H ₂ SO ₄ , CHCl ₃ , 60°, 2 h	 n 2 (39) 3 (42) 4 (44) 5 (—) R	197 197 197 190
	HN ₃ , H ₂ SO ₄ , PhH, 50°, 3 h	 Me (23) Et (29) <i>n</i> -Pr (13) <i>n</i> -Bu (15) R	198
	HN ₃ , H ₂ SO ₄ , PhH, 50°, 3 h	 Me (25) Et (29) <i>n</i> -Pr (25) <i>n</i> -Bu (30) R	199
 C ₆₋₁₈	Na ¹⁵ N ₃ , PPA, 50°, 8 h	 n 2 (72) 14 (98)	183
 C ₇	HN ₃	 (—)	200
	HN ₃	 (83)	200
	HN ₃ , H ₂ SO ₄ , CHCl ₃ , rt to 55°, 4 h	 (34)	191

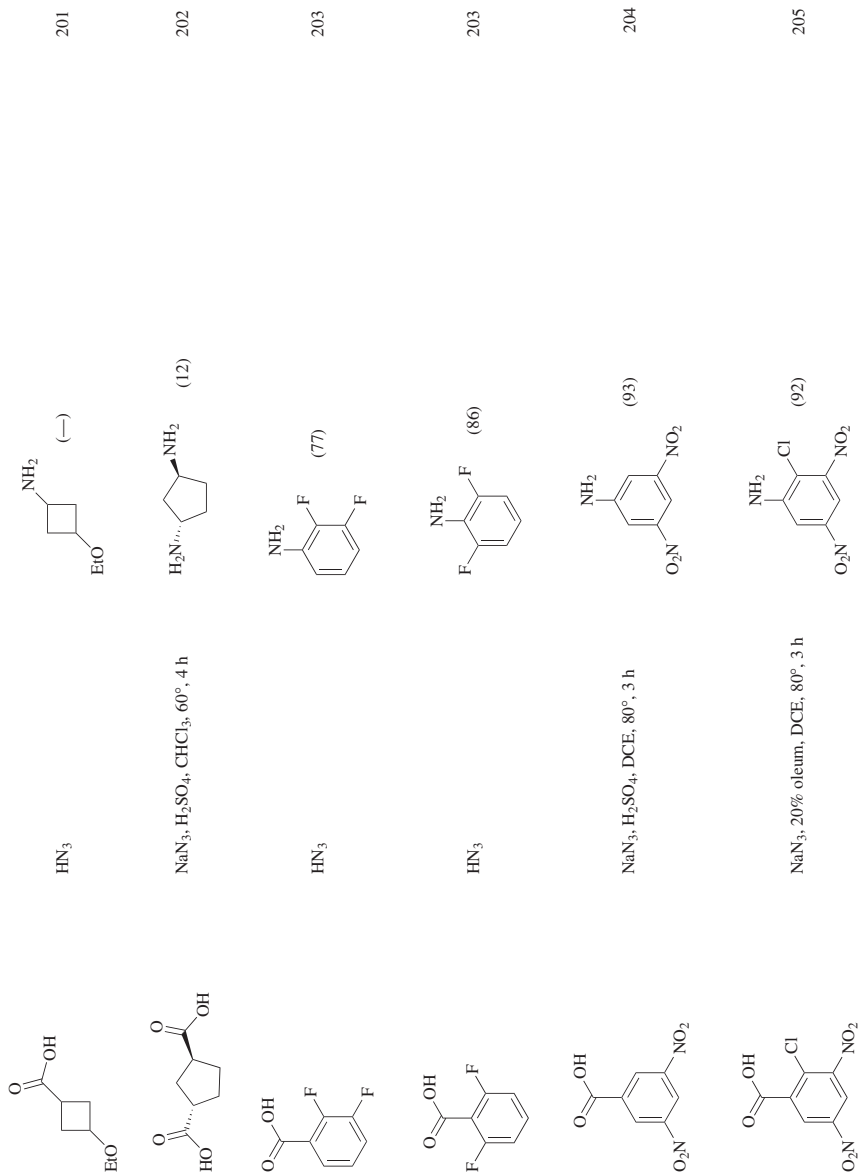
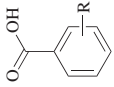
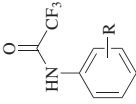
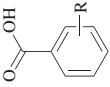



TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₇₋₈	<p>NaN₃, TFA, TFAA, 48 h</p> 	<p>H (72) 2-Br (95) 3-Br (0) 4-Br (0) 2-O₂N (62) 3-O₂N (0) 4-O₂N (0) 2-Me (87) 3-Me (79) 4-Me (71)</p>	206
 C ₇₋₁₁	<p>A: NaN₃, H₂SO₄, 40–50°, 2–12 h B: NaN₃, PPA, rt C: NaN₃, H₂SO₄, CHCl₃, rt, 2–24 h</p> 	<p>R H (97) 2-F (59) 2-Cl (80) 2-Br (73) 2-I (81) 2-O₂N (98) 3-Cl (71) 3-Br (70) 3-O₂N (100) 4-F (92) 4-Cl (99) 4-Br (96)</p>	<p>2 207 2 2 2 2 2 2 208 208 208 208</p>

4-O₂N (99) A 208
 2-Me (86) C 2
 3-Me (84) C 2
 4-Me (50) C 2
 4-NC (73) A 208
 4-CF₃ (41) A 208
 4-MeO (80) B 161
 2-Et (83) C 2
 2-*t*-Pr (87) C 2
 2-*t*-Bu (82) C 2
 2,4,6-Me₃ (91) B 161

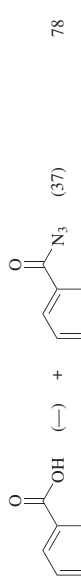
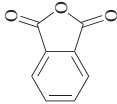
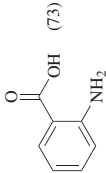
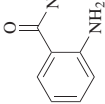
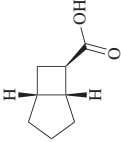
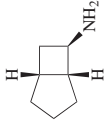
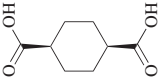

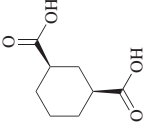
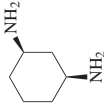


TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₈	NaN_3 , H_2SO_4 , 110° , 30 min	 (73)	210
	NaN_3 , AcOH , 50° , 3 h	 (12)	78
	HN_3	 (21)	211
	NaN_3 , H_2SO_4 , CHCl_3 , $15-50^\circ$, 8 h	 (22)	212
	HN_3 , H_2SO_4 , CHCl_3 , $15-50^\circ$, 8 h	 (44)	35, 213

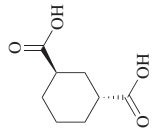
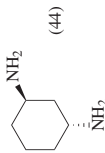
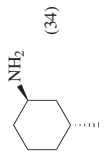
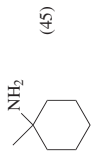
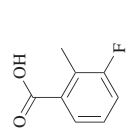
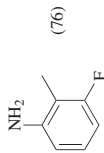
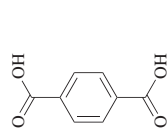
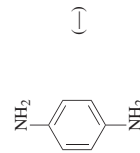
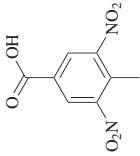
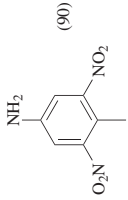
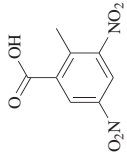
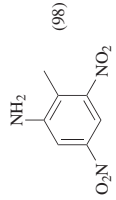
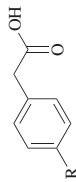
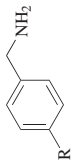
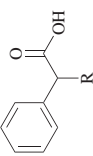
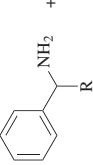
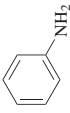
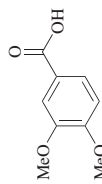
	$\text{HN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 15-50^\circ,$ 8 h		35
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 15-50^\circ,$ 8 h		214
	$\text{NaN}_3, \text{H}_2\text{SO}_4, 55^\circ, \text{overnight}$		209
	HN_3		215
	$\text{NaN}_3, \text{H}_2\text{SO}_4$		216

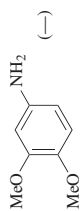
TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
<p>C₈</p> 	NaN ₃ , H ₂ SO ₄ , 0–60°, 4 h	 <p>(90)</p>	217												
	NaN ₃ , H ₂ SO ₄ , 0–60°, 4 h	 <p>(98)</p>	217												
<p>C₈₋₉</p> 	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 80°, 3 h	 <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R</td> <td>O₂N</td> <td>(70)</td> </tr> <tr> <td></td> <td>Cl</td> <td>(51)</td> </tr> <tr> <td></td> <td>H</td> <td>(77)</td> </tr> <tr> <td></td> <td>Me</td> <td>(5)</td> </tr> </table>	R	O ₂ N	(70)		Cl	(51)		H	(77)		Me	(5)	218
R	O ₂ N	(70)													
	Cl	(51)													
	H	(77)													
	Me	(5)													
<p>C₈₋₁₂</p> 	NaN ₃ , PPA, 50°, 8 h	 <p>I</p> <p>+</p>  <p>II</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R</td> <td>I</td> <td>II</td> </tr> <tr> <td>H</td> <td>(68)</td> <td>(0)</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>(49)</td> <td>(46)</td> </tr> </table>	R	I	II	H	(68)	(0)	<i>n</i> -Bu	(49)	(46)	219			
R	I	II													
H	(68)	(0)													
<i>n</i> -Bu	(49)	(46)													

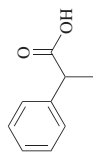
C₉



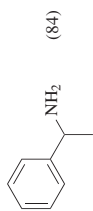
HN₃



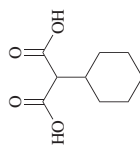
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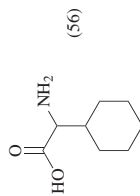
NaN₃, H₂SO₄, CHCl₃, rt to 45°,
1 h



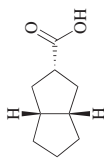
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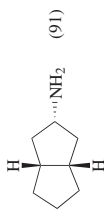
NaN₃, H₂SO₄, PhH, 50°, 5 h



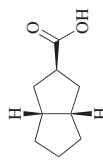
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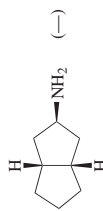
NaN₃, H₂SO₄, CHCl₃, 50°



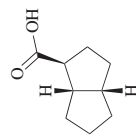
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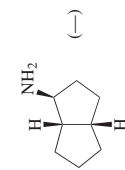
NaN₃, H₂SO₄, CHCl₃, 50°



224

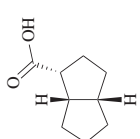
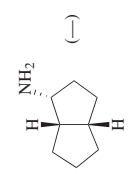
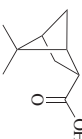

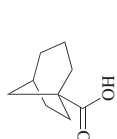
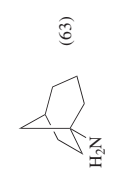
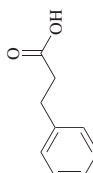
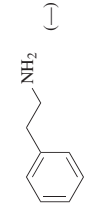
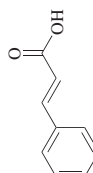
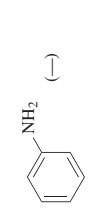
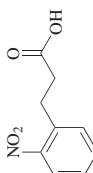
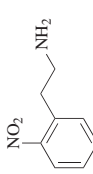
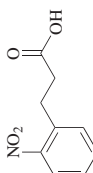
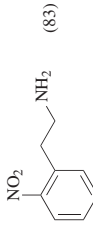


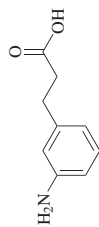
NaN₃, H₂SO₄, CHCl₃, 50°



225

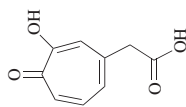
TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 50^\circ$	 (—)	226
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 50^\circ, 2 \text{ h}$	 (61)	227
	HN_3	 (63)	228
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3,$ rt to $45^\circ, 2 \text{ h}$	 (—)	229
	$\text{Na}^{15}\text{N}_3, \text{PPA}, 50^\circ$	 (71)	183
	$\text{NaN}_3, \text{H}_2\text{SO}_4$	 (—)	230
	$\text{HN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 45^\circ$	 (83)	231



$\text{HN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 45^\circ$

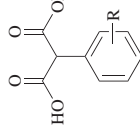
231



$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 40^\circ$

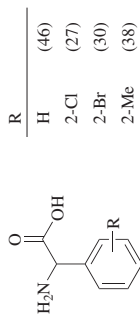
232

C_{9-10}



$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH}, 50^\circ, 5 \text{ h}$

222

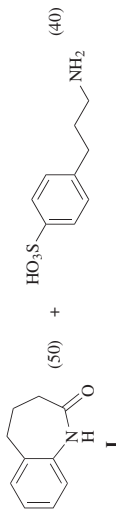


C_{10}



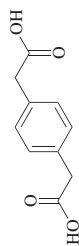
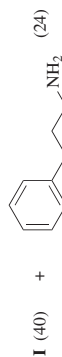
$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 40^\circ, 1 \text{ h}$

75



$\text{NaN}_3, \text{PPA}, 85^\circ, 2 \text{ h}$

75



$\text{NaN}_3, \text{H}_2\text{SO}_4$

216

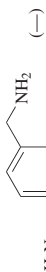
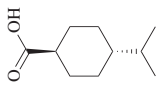

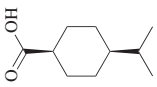
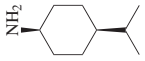
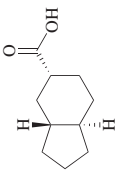
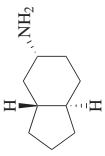
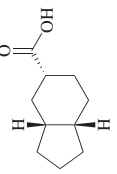
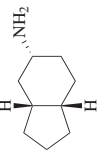
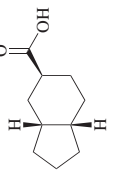
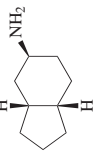


TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{10}	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 55^\circ,$ 30 min	 (85)	233
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 55^\circ,$ 30 min	 (81)	233
	HN_3	 (—)	234
	HN_3	 (—)	234
	HN_3	 (—)	234

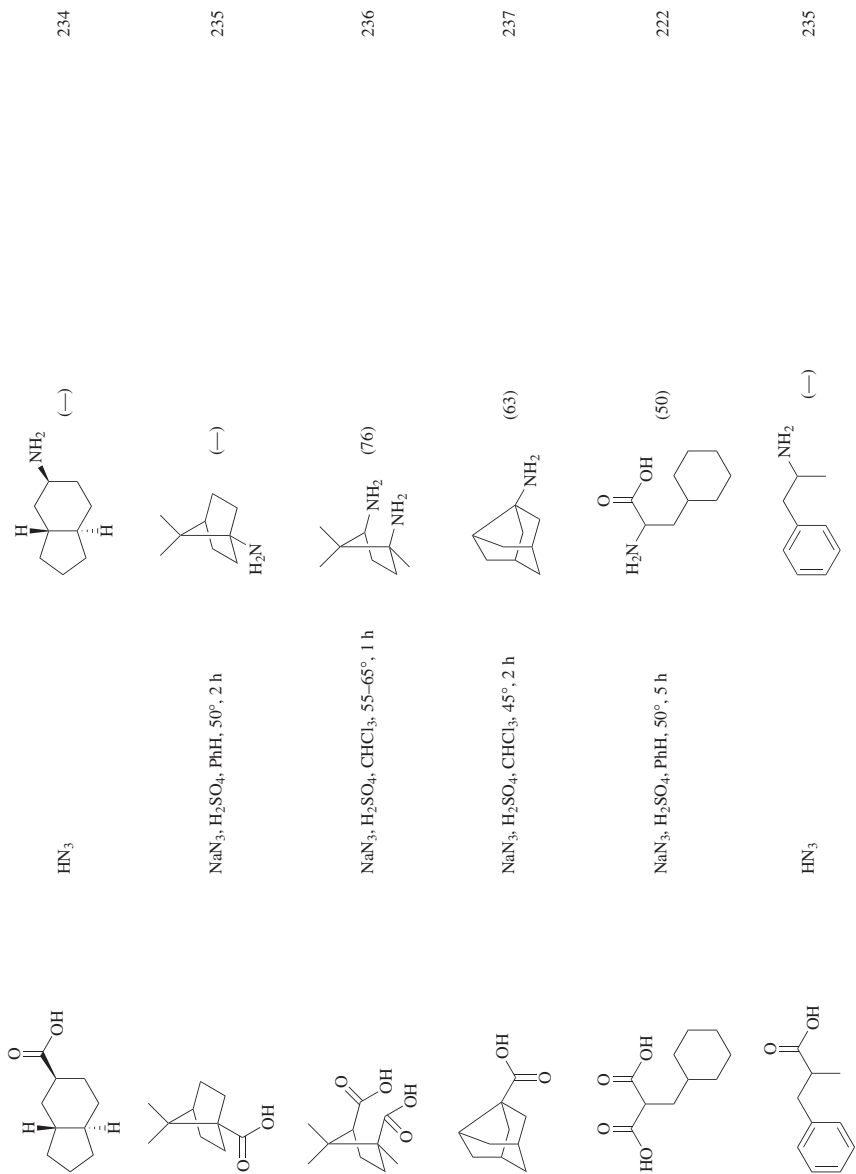
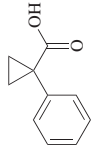

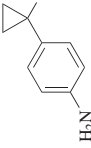
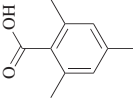
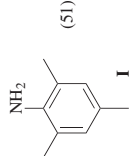
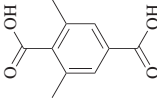
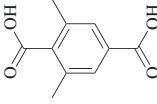
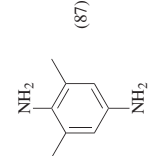
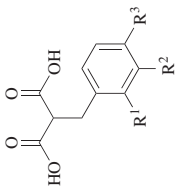
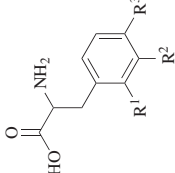
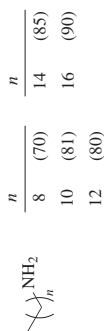


TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																														
 C_{10}	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 80^\circ, 3 \text{ h}$	 (16) +  (5)	218																														
	$\text{NaN}_3, \text{H}_2\text{SO}_4, 0^\circ$	 (51)	238																														
	$\text{NaN}_3, \text{PPA}, \text{rt}$	I (91)	161																														
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, \text{rt}$	 (87)	238																														
 C_{10-11}	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH}, 50^\circ, 5 \text{ h}$	 <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>R^1</th> <th>R^2</th> <th>R^3</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>Cl</td> <td>H</td> <td>H</td> </tr> <tr> <td>Br</td> <td>H</td> <td>H</td> </tr> <tr> <td>I</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>H</td> </tr> <tr> <td>H</td> <td>Br</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>Cl</td> </tr> <tr> <td>H</td> <td>H</td> <td>Br</td> </tr> <tr> <td>H</td> <td>H</td> <td>I</td> </tr> </tbody> </table> (19) (37) (30) (0) (19) (20) (36) (25) (0)	R^1	R^2	R^3	H	H	H	Cl	H	H	Br	H	H	I	H	H	H	Cl	H	H	Br	H	H	H	Cl	H	H	Br	H	H	I	222
R^1	R^2	R^3																															
H	H	H																															
Cl	H	H																															
Br	H	H																															
I	H	H																															
H	Cl	H																															
H	Br	H																															
H	H	Cl																															
H	H	Br																															
H	H	I																															

H H O₂N (32)
 Cl H Cl (22)
 H Cl Cl (21)
 Me H H (0)
 MeO H H (0)
 H H Me (0)

184

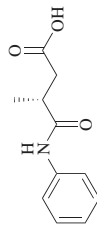


NaN₃, H₂SO₄, PhH, 50–60°

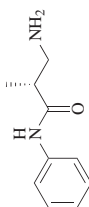
C_{10–18}



C₁₁

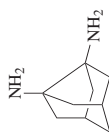


NaN₃, H₂SO₄, CHCl₃, 50°, 3 h

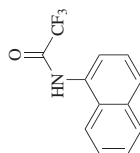


239

NaN₃, H₂SO₄, CHCl₃, 45°, 2 h



240



NaN₃, TFA/TFAA, 48 h

TFA/TFAA	TFA/TFAA
10:0 (0)	4:6 (92)
9:1 (76)	3:7 (57)
8:2 (85)	2:8 (28)
7:3 (98)	1:9 (12)
6:4 (97)	0:10 (0)
5:5 (97)	

206

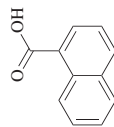
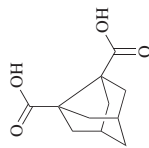
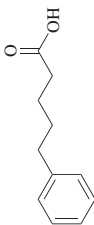
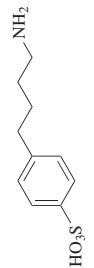
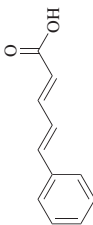


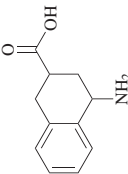
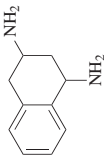
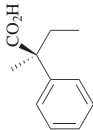
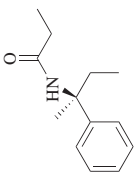
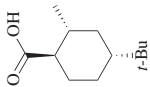
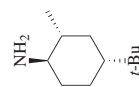
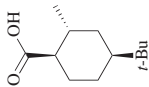
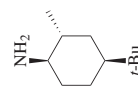
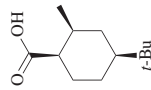


TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (Continued)

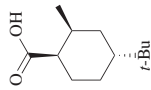
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{11}	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 40^\circ, 1 \text{ h}$	 (80)	75
	$\text{HN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 50^\circ, 1 \text{ h}$	 (6) +  (13)	241
	$\text{NaN}_3, \text{CHCl}_3, 45^\circ, 20 \text{ h}$	 (55)	242
	1. $\text{NaN}_3, \text{MsOH}, 0^\circ$ to reflux 2. EtCOCl	 (64)	243
 C_{12}	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 55^\circ, 30 \text{ min}$	 (88)	233
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 55^\circ, 30 \text{ min}$	 (78)	244



$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 55^\circ,$
30 min

(66)

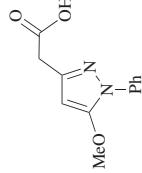
233



$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 55^\circ,$
30 min

(78)

233



$\text{HN}_3, \text{CHCl}_3, 45^\circ, 10 \text{ h}$

(35)

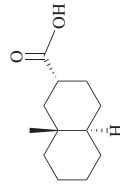
245



$\text{HN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 45^\circ$

(60)

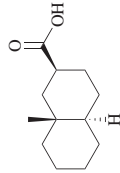
231



$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 55^\circ,$
30 min

(51)

233

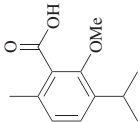
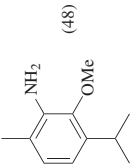
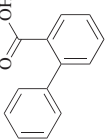
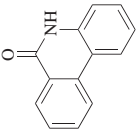
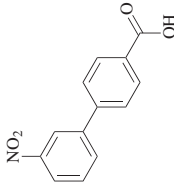
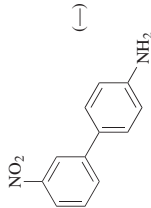
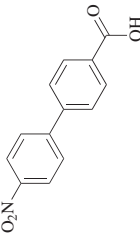
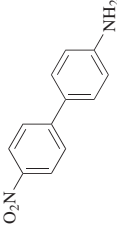
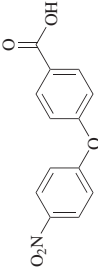
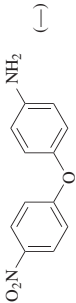


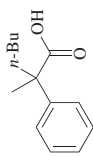
$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 55^\circ,$
30 min

(57)

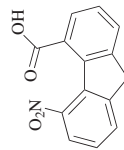
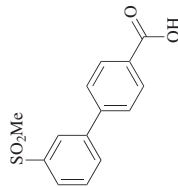
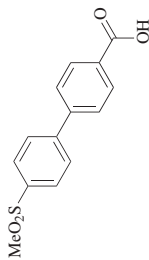
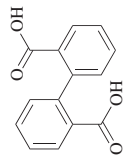
233

TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (Continued)

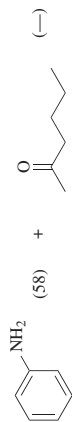
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₂</p> 	<p>HN_3, PhH, 40°, 1 h</p>	 <p>(48)</p>	246
<p>C₁₃</p> 	<p>NaN_3, H_2SO_4, CHCl_3</p>	 <p>(84)</p>	218
	<p>HN_3, 50°, 30 min</p>	<p>(—)</p>  <p>(—)</p>	247
	<p>HN_3, 50°, 30 min</p>	<p>(—)</p>  <p>(—)</p>	247
	<p>HN_3</p>	<p>(—)</p>  <p>(—)</p>	248



C₁₄



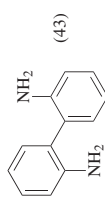
NaN₃, PPA, 50°, 8 h



(58)

(-)

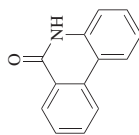
219



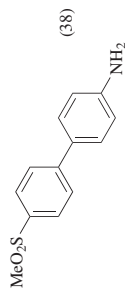
(43)

(6)

NaN₃, H₂SO₄, DCE, 40°, 2.5 h



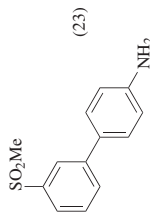
78



(38)

HN₃, 50°, 30 min

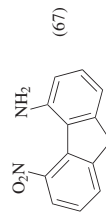
247



(23)

HN₃, 50°, 30 min

247

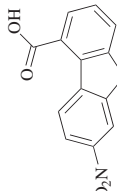
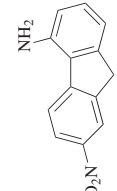
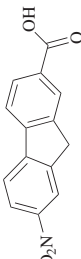
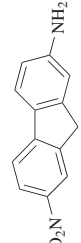
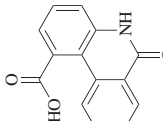
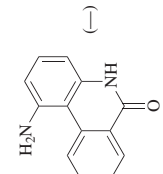
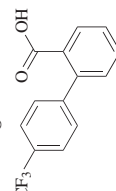
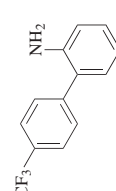
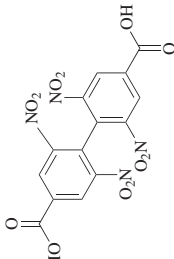
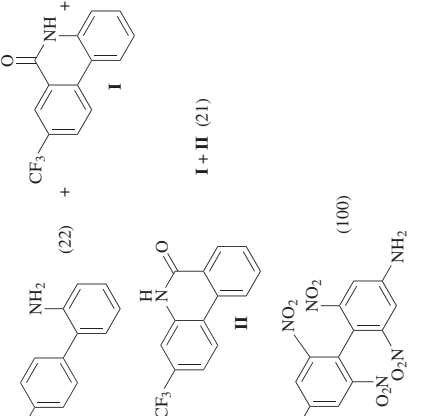


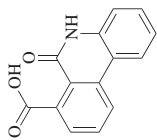
(67)

NaN₃, H₂SO₄, CHCl₃, 40°, 2 h

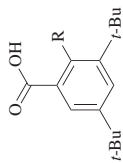
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TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN₃ (Continued)

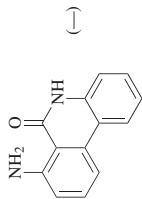
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <chem>O=C(O)c1ccc2c(c1)c3ccccc3c2[N+](=O)[O-]</chem>	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 40°, 2 h	 <chem>NC(=O)c1ccc2c(c1)c3ccccc3c2[N+](=O)[O-]</chem> (70)	250
 <chem>O=C(O)c1ccc2c(c1)c3ccccc3c2[N+](=O)[O-]</chem>	NaN ₃ , H ₂ SO ₄ , CHCl ₃	 <chem>NC(=O)c1ccc2c(c1)c3ccccc3c2[N+](=O)[O-]</chem> (—)	251
 <chem>O=C(O)c1ccc2c(c1)c3ccccc3c2N</chem>	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 40°, 2 h	 <chem>NC(=O)c1ccc2c(c1)c3ccccc3c2N</chem> (—)	252
 <chem>O=C(O)c1ccc(cc1)C2=CC=C(C=C2)C(F)(F)F</chem>	NaN ₃ , H ₂ SO ₄ , CHCl ₃	 <chem>NC(=O)c1ccc(cc1)C2=CC=C(C=C2)C(F)(F)F</chem> (22)	218
 <chem>O=C(O)c1ccc(cc1)C2=CC=C(C=C2)C(F)(F)F</chem>	NaN ₃ , DCE, reflux, 5 h	 I + II (21)	253



C₁₅



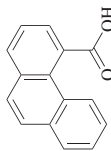
NaN₃, H₂SO₄, CHCl₃



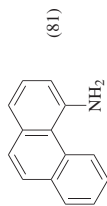
254

NaN₃, H₂SO₄, CHCl₃, rt

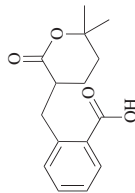
R	
H	(86)
O ₂ N	(79)
Cl	(87)
Br	(90)
I	(96)



1. NaN₃, TFA, TFAA
2. KOH

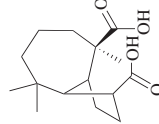


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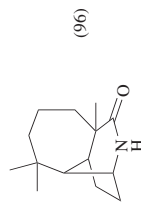


(-) + CO₂

257

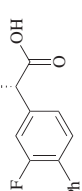
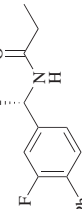
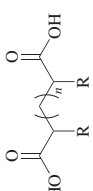
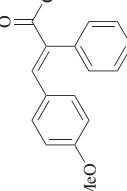

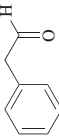


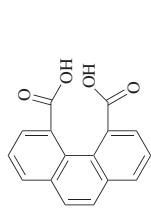
HN₃, H₂SO₄, CHCl₃, rt, 1 h



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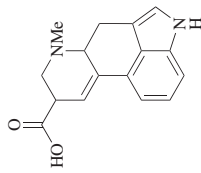
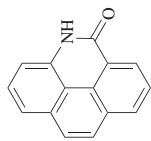
TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																													
<p>C_{15}</p> 	<p>1. NaN_3, MeOH 2. EtOCl</p>	 <p>(—)</p>	243																																													
<p>C_{15-24}</p> 	<p>NaN_3, H_2SO_4, PhH, rt</p>	<table border="1" data-bbox="390 416 815 868"> <thead> <tr> <th>n</th> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>3</td> <td><i>n</i>-Bu</td> <td>(60)</td> </tr> <tr> <td>3</td> <td><i>i</i>-Bu</td> <td>(75)</td> </tr> <tr> <td>3</td> <td><i>n</i>-C_3H_7</td> <td>(78)</td> </tr> <tr> <td>3</td> <td><i>i</i>-C_3H_7</td> <td>(80)</td> </tr> <tr> <td>3</td> <td><i>n</i>-C_6H_{13}</td> <td>(75)</td> </tr> <tr> <td>3</td> <td>2-ethyl-1-hexyl</td> <td>(35)</td> </tr> <tr> <td>4</td> <td><i>n</i>-Bu</td> <td>(60)</td> </tr> <tr> <td>4</td> <td><i>n</i>-C_3H_7</td> <td>(60)</td> </tr> <tr> <td>4</td> <td><i>i</i>-C_3H_7</td> <td>(76)</td> </tr> <tr> <td>4</td> <td><i>n</i>-C_6H_{13}</td> <td>(80)</td> </tr> <tr> <td>4</td> <td>2-ethyl-1-hexyl</td> <td>(87)</td> </tr> <tr> <td>5</td> <td><i>n</i>-Bu</td> <td>(79)</td> </tr> <tr> <td>5</td> <td><i>i</i>-Bu</td> <td>(55)</td> </tr> <tr> <td>5</td> <td><i>n</i>-C_6H_{13}</td> <td>(80)</td> </tr> </tbody> </table>	n	R	Yield (%)	3	<i>n</i> -Bu	(60)	3	<i>i</i> -Bu	(75)	3	<i>n</i> - C_3H_7	(78)	3	<i>i</i> - C_3H_7	(80)	3	<i>n</i> - C_6H_{13}	(75)	3	2-ethyl-1-hexyl	(35)	4	<i>n</i> -Bu	(60)	4	<i>n</i> - C_3H_7	(60)	4	<i>i</i> - C_3H_7	(76)	4	<i>n</i> - C_6H_{13}	(80)	4	2-ethyl-1-hexyl	(87)	5	<i>n</i> -Bu	(79)	5	<i>i</i> -Bu	(55)	5	<i>n</i> - C_6H_{13}	(80)	259
n	R	Yield (%)																																														
3	<i>n</i> -Bu	(60)																																														
3	<i>i</i> -Bu	(75)																																														
3	<i>n</i> - C_3H_7	(78)																																														
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5	<i>i</i> -Bu	(55)																																														
5	<i>n</i> - C_6H_{13}	(80)																																														
<p>C_{16}</p> 	<p>HN_3, H_2SO_4, CHCl_3, 55°, 1 h</p>	 <p>(34) + </p> <p>(35)</p>	241																																													



NaN₃, H₂SO₄, DCE, 40°, 2.5 h

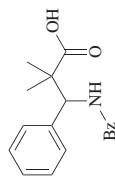
(67)



HN₃

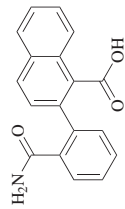
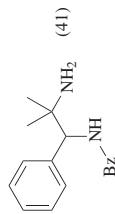
(-)

C₁₈



NaN₃, H₂SO₄, CHCl₃, 55°, 1.5 h

(41)



NaN₃, H₂SO₄, 60°, 1 h

(-)

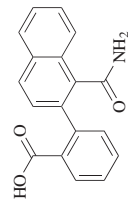
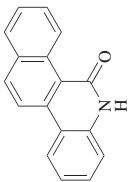
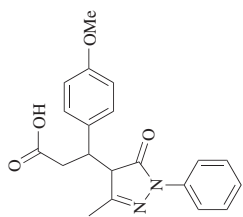
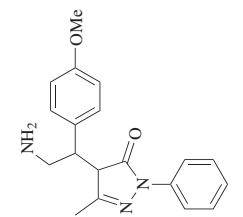
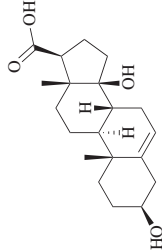
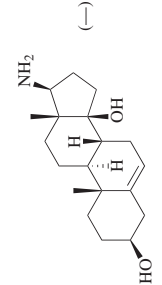
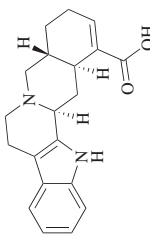
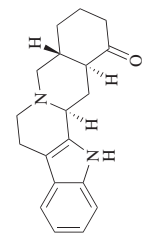
78

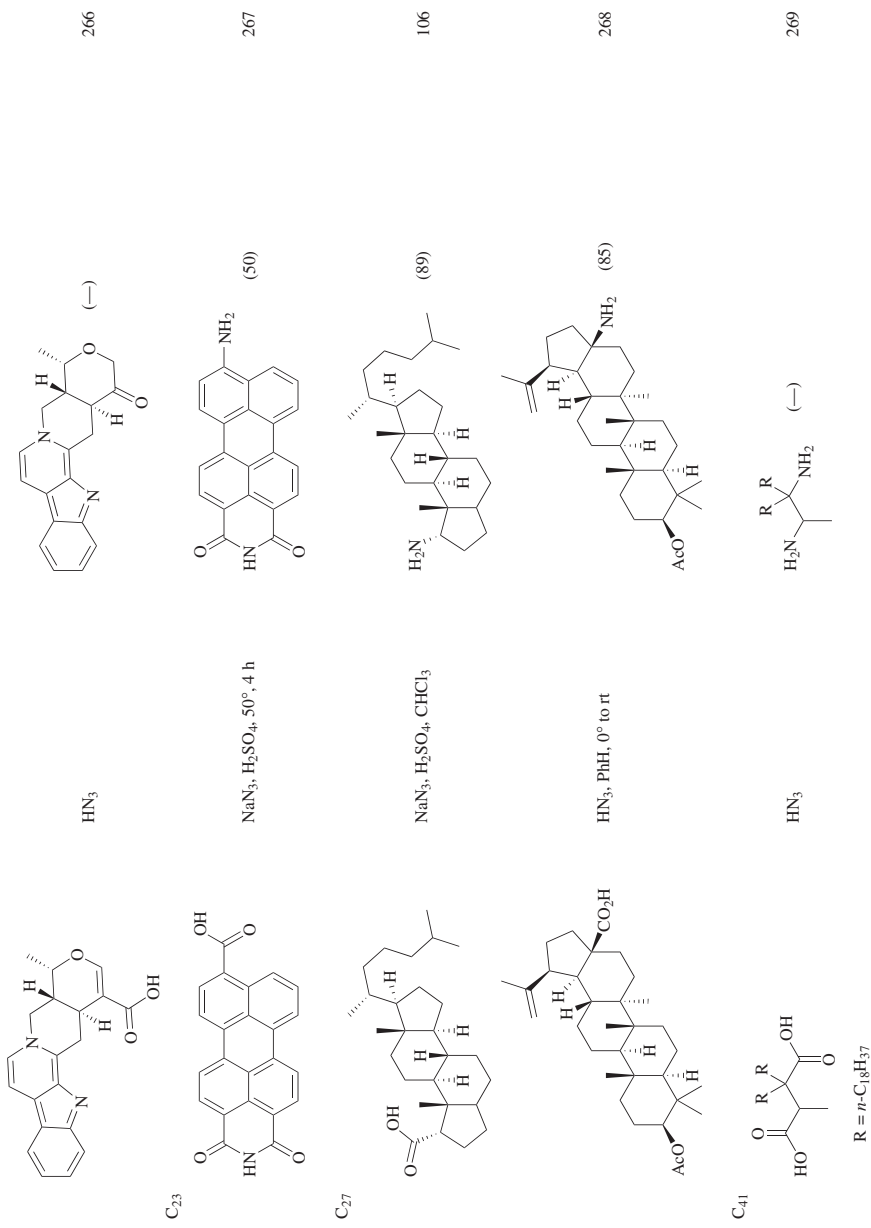
260

261

262



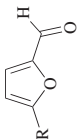

TABLE I. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN₃ (Continued)

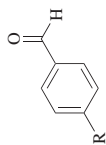
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₈</p> 	<p>NaN₃, H₂SO₄, 60°, 1 h</p>	<p>(95)</p> 	262
<p>C₂₀</p> 	<p>NaN₃, H₂SO₄, CHCl₃, 0–50°, 5 h</p>	<p>(64)</p> 	263
	<p>HN₃</p>	<p>(—)</p> 	264
	<p>HN₃, H₂SO₄, CHCl₃</p>	<p>(20)</p> 	265



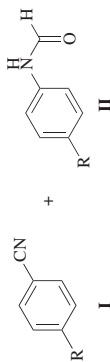
R = *n*-C₁₈H₃₇

TABLE 2. SCHMIDT REACTIONS OF ALDEHYDES WITH HN₃

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃ 	NaN ₃ , HCl, rt	 (37)	270
C ₅₋₁₃ 	HN ₃ , Mg(ClO ₄) ₂ •H ₂ O, CHCl ₃ , reflux, 2 h	R H (84) Br (88) I (85) O ₂ N (96) Me (91) MeS (79) ClCH ₂ (96) 2-C ₄ H ₉ S (90) EtO ₂ CCH ₂ S (78)  (89) 5-NC-2-C ₄ H ₉ S (92) Ph (90) PhO ₂ S (98) 4-O ₂ NC ₆ H ₄ (85) 4-ClC ₆ H ₄ O (81) 2,4-(O ₂ N) ₂ C ₆ H ₃ S (93) 4-MeC ₆ H ₄ O (79) PhCOS (90) 3-BrC ₆ H ₄ COS (91) 4-MeC ₆ H ₄ O ₂ S (98) Ph-≡- $\left\{ \begin{array}{l} \text{---} \\ \text{---} \\ \text{---} \end{array} \right\}$ - (94)	167

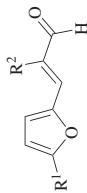
C₇₋₈

NaCN, H₂SO₄ (x eq), PhH, 0° to rt



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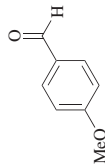
R	x	I	II
H	2	(32)	(14)
H	6.6	(10)	(59)
Cl	2	(55)	(12)
Cl	6.6	(15)	(48)
O ₂ N	2	(72)	(2)
O ₂ N	6.6	(46)	(23)
Me	2	(50)	(6)
Me	6.6	(13)	(43)
MeO	2	(86)	(0)
MeO	6.6	(64)	(0)

C₇₋₁₄

HN₃, Mg(ClO₄)₂•H₂O,
CHCl₃, rt to reflux, 2 h

R ¹	R ²	R ¹	R ²
H	H	H	H
H	Me	H	Me
O ₂ N	H	O ₂ N	H
Me	H	Me	H
Me	Me	Me	Me
Ph	H	Ph	H
Ph	Me	Ph	Me
2,4,6-Cl ₃ C ₆ H ₂	H	2,4,6-Cl ₃ C ₆ H ₂	H

271

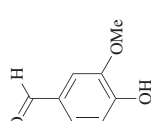
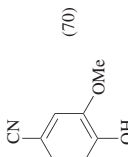
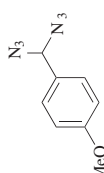
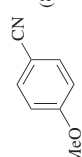
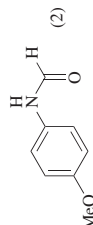
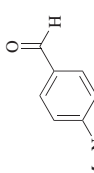
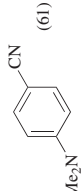
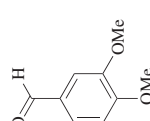
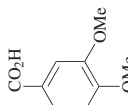
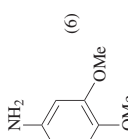
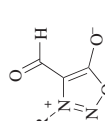
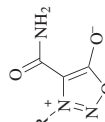
C₈

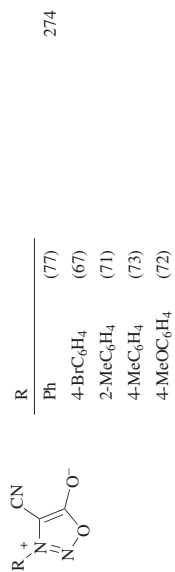
NaCN, H₂SO₄, CHCl₃, 0-45°, 3 h



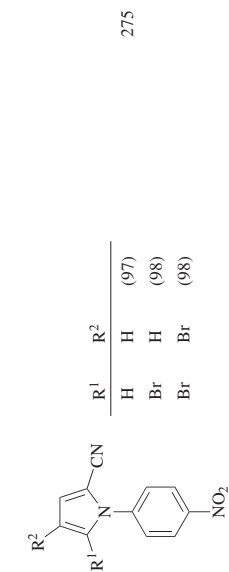
63

TABLE 2. SCHMIDT REACTIONS OF ALDEHYDES WITH HN₃ (Continued)

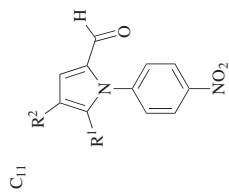
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
<p>C₈</p> 	NaN ₃ , H ₂ SO ₄ , 0°, 2 h	 (70)	272												
<p>C₉</p> 	H ₂ SO ₄ , MeCN	 (86) +  (2)	27												
<p>C₉</p> 	NaN ₃ , H ₂ SO ₄ , 10°	 (61)	273												
<p>C₉₋₁₀</p> 	NaN ₃ , H ₂ SO ₄ , 0°, 2 h	 (84) +  (6)	272												
<p>C₉₋₁₀</p> 	NaN ₃ , H ₂ SO ₄ , rt, 10 h	 R + <table border="1" data-bbox="860 520 1010 694"> <thead> <tr> <th>R</th> <th>Ref.</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>(74)</td> </tr> <tr> <td>4-BrC₆H₄</td> <td>(63)</td> </tr> <tr> <td>2-MeC₆H₄</td> <td>(60)</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>(68)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>(47)</td> </tr> </tbody> </table>	R	Ref.	Ph	(74)	4-BrC ₆ H ₄	(63)	2-MeC ₆ H ₄	(60)	4-MeC ₆ H ₄	(68)	4-MeOC ₆ H ₄	(47)	274
R	Ref.														
Ph	(74)														
4-BrC ₆ H ₄	(63)														
2-MeC ₆ H ₄	(60)														
4-MeC ₆ H ₄	(68)														
4-MeOC ₆ H ₄	(47)														



NaN₃, aq H₂SO₄, rt, 10 h



HN₃, Mg(ClO₄)₂•H₂O,
CHCl₃, rt to reflux, 3 h



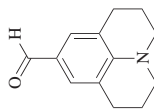
C₁₁



NaN₃, H₂SO₄, 10°

(77)

C₁₃



HN₃

(-)

C₁₆

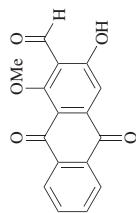
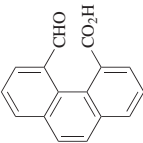
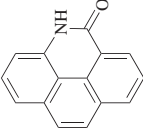


TABLE 2. SCHMIDT REACTIONS OF ALDEHYDES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.	
 <p><chem>O=Cc1ccc2c(c1)ccc(C(=O)O)c2</chem></p>	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{DCE}, 40^\circ, 2.5 \text{ h}$</p>	 <p><chem>O=C(N)c1ccc2c(c1)ccc(C(=O)O)c2</chem></p>	<p>(-)</p>	<p>(-)</p>	<p>78</p>

C₁₆

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃




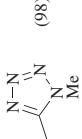

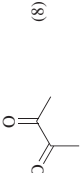
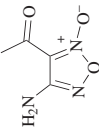
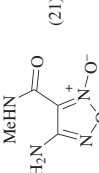
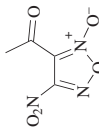
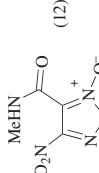
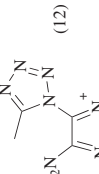

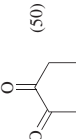

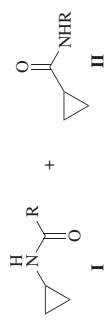


Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃ 	NaN ₃ , H ₂ SO ₄ , PhH	 (—) + MeNH ₂ (—)	277
	SiCl ₄ , NaN ₃ , MeCN, rt, 12 h	 (98)	70
C ₄ 	NaN ₃ , HCl, rt	 (8)	270
	NaN ₃ , PPA, rt, 48 h	 (21)	278
	NaN ₃ , PPA, rt, 48 h	 (12) +  (12)	278
C ₅ 	NaN ₃ , HCl, rt	 (50)	270

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.				
<p>C₃₋₁₀</p> 	<p>A: NaN₃, 89% H₂SO₄, CHCl₃ B: NaN₃, 83% H₂SO₄, CHCl₃ C: NaN₃, 69% H₂SO₄, CHCl₃ D: NaN₃, 50% H₂SO₄, CHCl₃ E: NaN₃, CCl₃CO₂H, 63°</p>		30				
				R	Conditions	I + II	I:II
				Me	A	(88-100)	73:27
				Me	B	(88-100)	74:26
				Me	C	(88-100)	44:56
				Me	D	(—)	10:90
				Me	E	(88-100)	27:73
				Et	B	(88-100)	82:18
				Et	C	(88-100)	82:18
				Et	D	(—)	26:74
Et	E	(88-100)	26:74				
<i>i</i> -Pr	B	(88-100)	92:8				
<i>i</i> -Pr	C	(88-100)	96:4				
<i>i</i> -Pr	D	(—)	82:18				
<i>i</i> -Pr	E	(88-100)	48:52				
Ph	A-C, E	(88-100)	7:93				
<p>C₅₋₁₂</p> 	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , rt		279				
				R	I + II	I:II	
				Me	(75)	1:3:3	
				Ph	(86)	1:19	
				2-MeC ₆ H ₄ 4-MeC ₆ H ₄ (<i>E</i>)-PhCH=CH	(85) (61) (35)	1:19 1:19 1:10	

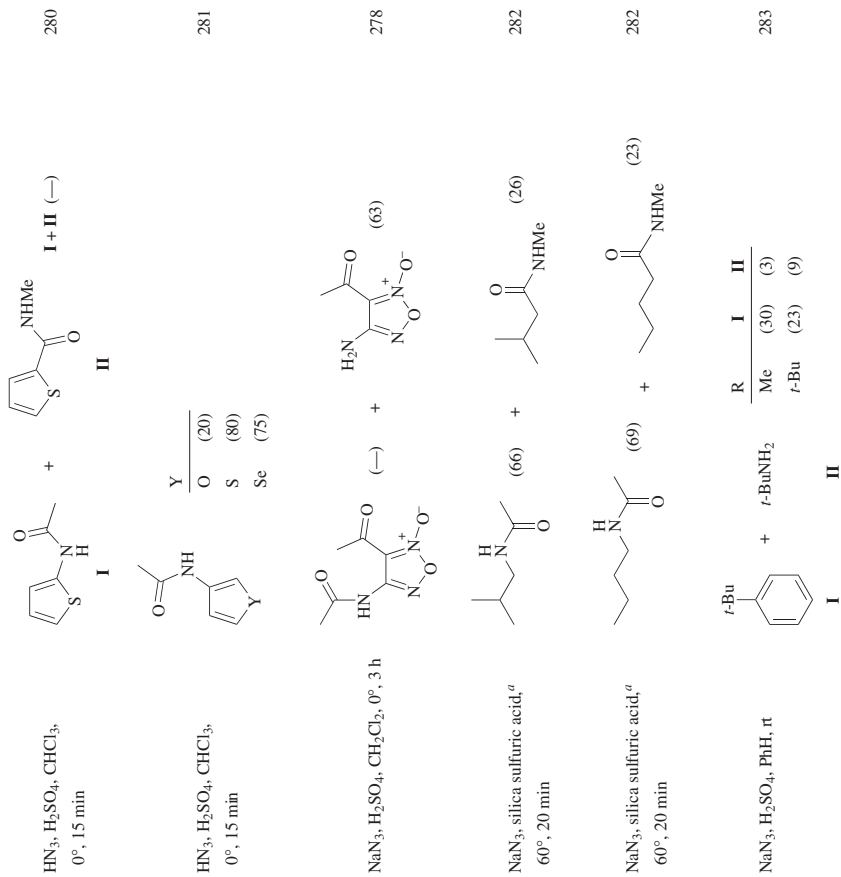
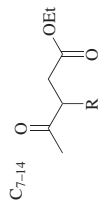
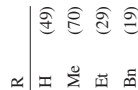
C₆C₆₋₉

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

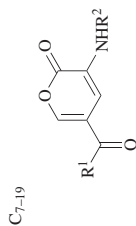
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																									
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1\text{C}-\text{C}-\text{P}(\text{OR}^2)_2 \\ \parallel \\ \text{O} \end{array} $	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1\text{HN}-\text{C}-\text{P}(\text{OR}^2)_2 \\ \parallel \\ \text{O} \end{array} + \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1\text{C}-\text{C}-\text{N}(\text{H})\text{P}(\text{OR}^2)_2 \\ \parallel \\ \text{O} \end{array} + \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1\text{HN}-\text{C}-\text{H} \\ \parallel \\ \text{O} \end{array} + \text{R}^1\text{NH}_2 + \text{R}^1\text{CN} $	28																																																																																																										
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1\text{HN}-\text{C}-\text{C}-\text{R} \\ \parallel \\ \text{O} \end{array} $	$ \text{HN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, \\ 0^\circ, 30 \text{ min} $	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> <th>III</th> <th>IV</th> <th>V</th> </tr> </thead> <tbody> <tr> <td><i>i</i>-Pr</td> <td>Me</td> <td>(0)</td> <td>(0)</td> <td>(57)</td> <td>(0)</td> <td>(0)</td> </tr> <tr> <td>3-C₆H₄</td> <td>Me</td> <td>(0)</td> <td>(1)</td> <td>(39)</td> <td>(7)</td> <td>(0)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>Me</td> <td>(0)</td> <td>(46)</td> <td>(0)</td> <td>(0)</td> <td>(47)</td> </tr> <tr> <td>4-MeOC₆H₄^b</td> <td>Me</td> <td>(0)</td> <td>(45)</td> <td>(0)</td> <td>(0)</td> <td>(51)</td> </tr> <tr> <td>Ph</td> <td>Et</td> <td>(9)</td> <td>(3)</td> <td>(53)</td> <td>(14)</td> <td>(0)</td> </tr> <tr> <td>4-ClC₆H₄</td> <td>Et</td> <td>(19)</td> <td>(2)</td> <td>(65)</td> <td>(4)</td> <td>(0)</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>Et</td> <td>(11)</td> <td>(3)</td> <td>(70)</td> <td>(7)</td> <td>(7)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>Et</td> <td>(0)</td> <td>(30)</td> <td>(0)</td> <td>(0)</td> <td>(62)</td> </tr> <tr> <td>4-MeOC₆H₄^c</td> <td>Et</td> <td>(0)</td> <td>(31)</td> <td>(0)</td> <td>(0)</td> <td>(54)</td> </tr> <tr> <td>3-MeOC₆H₄</td> <td>Et</td> <td>(0)</td> <td>(2)</td> <td>(59)</td> <td>(9)</td> <td>(6)</td> </tr> <tr> <td>3,4-(OCH₂)C₆H₃</td> <td>Et</td> <td>(0)</td> <td>(28)</td> <td>(0)</td> <td>(0)</td> <td>(51)</td> </tr> <tr> <td>2,6-(MeO)₂C₆H₃</td> <td>Et</td> <td>(0)</td> <td>(0)</td> <td>(0)</td> <td>(0)</td> <td>(62)</td> </tr> <tr> <td>2,4,6-Me₃C₆H₂</td> <td>Et</td> <td>(0)</td> <td>(0)</td> <td>(0)</td> <td>(43)</td> <td>(0)</td> </tr> <tr> <td>2,6-Me₂-4-MeOC₆H₂</td> <td>Et</td> <td>(0)</td> <td>(0)</td> <td>(0)</td> <td>(50)</td> <td>(0)</td> </tr> </tbody> </table>	R ¹	R ²	I	II	III	IV	V	<i>i</i> -Pr	Me	(0)	(0)	(57)	(0)	(0)	3-C ₆ H ₄	Me	(0)	(1)	(39)	(7)	(0)	4-MeOC ₆ H ₄	Me	(0)	(46)	(0)	(0)	(47)	4-MeOC ₆ H ₄ ^b	Me	(0)	(45)	(0)	(0)	(51)	Ph	Et	(9)	(3)	(53)	(14)	(0)	4-ClC ₆ H ₄	Et	(19)	(2)	(65)	(4)	(0)	4-MeC ₆ H ₄	Et	(11)	(3)	(70)	(7)	(7)	4-MeOC ₆ H ₄	Et	(0)	(30)	(0)	(0)	(62)	4-MeOC ₆ H ₄ ^c	Et	(0)	(31)	(0)	(0)	(54)	3-MeOC ₆ H ₄	Et	(0)	(2)	(59)	(9)	(6)	3,4-(OCH ₂)C ₆ H ₃	Et	(0)	(28)	(0)	(0)	(51)	2,6-(MeO) ₂ C ₆ H ₃	Et	(0)	(0)	(0)	(0)	(62)	2,4,6-Me ₃ C ₆ H ₂	Et	(0)	(0)	(0)	(43)	(0)	2,6-Me ₂ -4-MeOC ₆ H ₂	Et	(0)	(0)	(0)	(50)	(0)	
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2,6-Me ₂ -4-MeOC ₆ H ₂	Et	(0)	(0)	(0)	(50)	(0)																																																																																																						
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1\text{C}-\text{C}-\text{C}-\text{R} \\ \parallel \\ \text{O} \end{array} $	$ \text{NaN}_3, \text{MsOH}, \text{DME}, \\ -30^\circ \text{ to rt, 3 h} $	<table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(47)</td> </tr> <tr> <td>Bn</td> <td>(26)</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>(100)</td> </tr> <tr> <td>(<i>E</i>)-PhCH=CHCH₂</td> <td>(79)</td> </tr> </tbody> </table>	R	Yield (%)	Me	(47)	Bn	(26)	Ph(CH ₂) ₂	(100)	(<i>E</i>)-PhCH=CHCH ₂	(79)	56																																																																																															
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NaN₃, H₂SO₄, CHCl₃, 5°

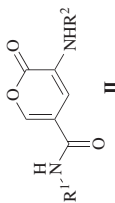


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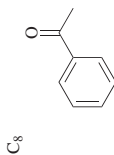
A: NaN₃, H₂SO₄, -10 to 0°, 3 h;
then rt, 2 h

B: NaN₃, H₂SO₄, 32-35°, 2 h

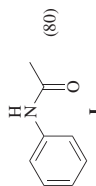


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R ¹	R ²	Conditions	I + II	I:II
Me	H	A	(96)	1:0
Me	H	B	(86)	1:0
Me	MeCO	A	(86)	1:0
Me	PhCO	A	(98)	1:0
Ph	H	A	(87)	3.9:1
Ph	H	B	(92)	3.6:1
Ph	MeCO	A	(72)	3.7:1
Ph	PhCO	A	(99)	3.5:1



NaN₃, MsOH, DME,
-30° to rt, 3 h



56

NaN₃, AcOH, HBr, 55-65°

I

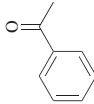
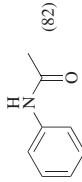
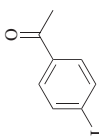
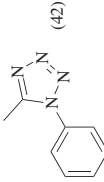
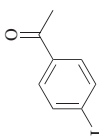
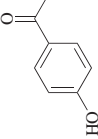
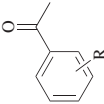
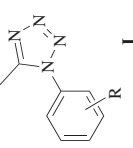
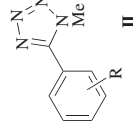
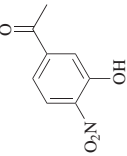
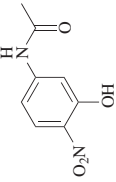
NaN₃, CCl₃CO₂H, 55-65°

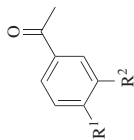
I

Azide	Time
I	TMSN ₃ 30 min (85)
I	NaN ₃ 2 h (76)

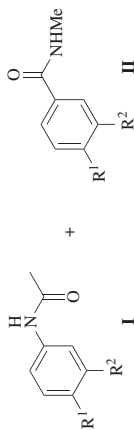
286

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
	NaN ₃ , PPA, 50°, 7 h	 (82)	54	
	HN ₃ , AlCl ₃ , PhNO ₂ , PhH, rt	 (42)	272	
	Azide, FeCl ₃ , DCE, rt	Azide	286	
		TMSN ₃ 35 min (76) NaN ₃ 3 h (68)		
	Azide, FeCl ₃ , DCE, rt	Azide	286	
		TMSN ₃ 33 min (72) NaN ₃ 2.5 h (66)		
	NaN ₃ , SiCl ₄ , MeCN, rt, 12 h	 I +  II	70	
		R		H (87) (5) 4-Cl (87) (5) 3-O ₂ N (60) (5)
	NaN ₃ , MsOH, rt, 14 h	 (82)	287	



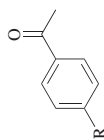
A: NaN₃, H₂SO₄, PhH, 60°
 B: NaN₃, CCl₃CO₂H, 65°



I + II (—)

59

R ¹	R ²	Conditions	I:II
H	H	A	90:10
H	H	B	90:10
O ₂ N	H	A	90:10
O ₂ N	H	B	90:10
H	O ₂ N	A	90:10
H	O ₂ N	B	90:10
MeO	H	A	80:20
MeO	H	B	80:20



NaN₃, silica sulfuric acid,^a 60°

R	Time (min)
H	25 (95)
Cl	35 (92)
O ₂ N	45 (90)
Me	25 (91)

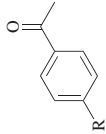
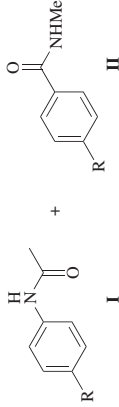
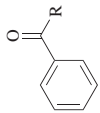
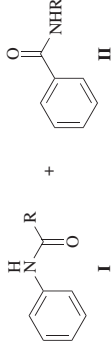

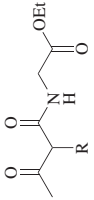
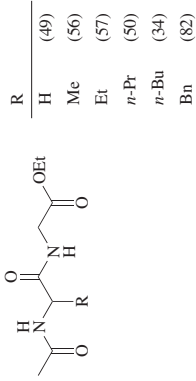
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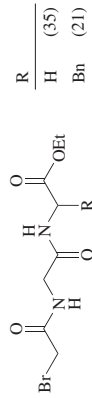
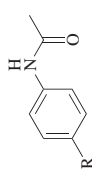
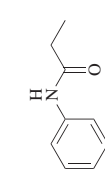
R	Time (min)
H	25 (92)
Cl	35 (91)
O ₂ N	25 (91)
Me	35 (94)

NaN₃, Fe(HSO₄)₃, grinding,
 50°

288

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																	
<p>C_{8-9}</p> 	<p>$\text{NaN}_3, \text{P}_2\text{O}_5\text{-SiO}_2, \text{MW}$</p>		289																																																	
	<table border="1"> <thead> <tr> <th>R</th> <th>Time (min)</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>8</td> <td>(90)</td> <td>1:0</td> </tr> <tr> <td>Cl</td> <td>8</td> <td>(90)</td> <td>1:0</td> </tr> <tr> <td>O_2N</td> <td>10</td> <td>(80)</td> <td>4:1</td> </tr> <tr> <td>Me</td> <td>10</td> <td>(85)</td> <td>1:0</td> </tr> <tr> <td>MeO</td> <td>10</td> <td>(83)</td> <td>1:0</td> </tr> </tbody> </table>	R	Time (min)	I + II	I:II	H	8	(90)	1:0	Cl	8	(90)	1:0	O_2N	10	(80)	4:1	Me	10	(85)	1:0	MeO	10	(83)	1:0																											
R	Time (min)	I + II	I:II																																																	
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Cl	8	(90)	1:0																																																	
O_2N	10	(80)	4:1																																																	
Me	10	(85)	1:0																																																	
MeO	10	(83)	1:0																																																	
<p>C_{8-10}</p> 	<p>$\text{NaN}_3, \text{HCl (concd)}$</p>		7																																																	
	<table border="1"> <thead> <tr> <th>R</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(81)</td> <td>95:6</td> </tr> <tr> <td>Et</td> <td>(80)</td> <td>85:15</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>(57)</td> <td>51:49</td> </tr> </tbody> </table>	R	I + II	I:II	Me	(81)	95:6	Et	(80)	85:15	<i>i</i> -Pr	(57)	51:49																																							
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<i>i</i> -Pr	(57)	51:49																																																		
<p>MeS </p>	<p>1. $\text{IN}_3, \text{CH}_2\text{Cl}_2, -78$ to -10°, 2 h 2. TFA, CHCl_3, rt, 2 h</p>	<table border="1"> <thead> <tr> <th>R</th> <th>(62)</th> <th>(77)</th> <th>(59)</th> </tr> </thead> <tbody> <tr> <td><i>t</i>-Bu</td> <td></td> <td></td> <td></td> </tr> <tr> <td><i>n</i>-C_5H_{11}</td> <td></td> <td></td> <td></td> </tr> <tr> <td><i>c</i>-C_6H_{11}</td> <td></td> <td></td> <td></td> </tr> </tbody> </table>	R	(62)	(77)	(59)	<i>t</i> -Bu				<i>n</i> - C_5H_{11}				<i>c</i> - C_6H_{11}				83																																	
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<i>c</i> - C_6H_{11}																																																				
<p>C_{8-15}</p> 	<p>$\text{HN}_3, \text{H}_2\text{SO}_4$</p>		290																																																	
		<table border="1"> <thead> <tr> <th>R</th> <th>(49)</th> <th>(56)</th> <th>(57)</th> <th>(50)</th> <th>(34)</th> <th>(82)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>Me</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>Et</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td><i>n</i>-Pr</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td><i>n</i>-Bu</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>Bn</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> </tbody> </table>	R	(49)	(56)	(57)	(50)	(34)	(82)	H							Me							Et							<i>n</i> -Pr							<i>n</i> -Bu							Bn							
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	$\text{HN}_3, \text{H}_2\text{SO}_4$	R	H (35) Bn (21)	291																																		
	C_{8-20}	A. $\text{NaN}_3, \text{AcOH}, \text{H}_2\text{SO}_4, 70^\circ, 2-6 \text{ h}$ B. $\text{NaN}_3, \text{H}_2\text{SO}_4$		<table border="1"> <thead> <tr> <th>R</th> <th>Conditions</th> </tr> </thead> <tbody> <tr><td>H</td><td>A (99)</td></tr> <tr><td>O_2N</td><td>A (70)</td></tr> <tr><td>$n\text{-C}_3\text{H}_7$</td><td>A (81)</td></tr> <tr><td>Ph</td><td>A (99)</td></tr> <tr><td>PhO</td><td>A (99)</td></tr> <tr><td>PhS</td><td>A (99)</td></tr> <tr><td>PhOS</td><td>A (60)</td></tr> <tr><td>PhO_2S</td><td>A (85)</td></tr> <tr><td>$4\text{-O}_2\text{NC}_6\text{H}_4$</td><td>A (80)</td></tr> <tr><td>$4\text{-O}_2\text{NC}_6\text{H}_4\text{O}$</td><td>A (50)</td></tr> <tr><td>$n\text{-C}_3\text{H}_7$</td><td>B (81)</td></tr> <tr><td>Bn</td><td>A (70)</td></tr> <tr><td>$n\text{-C}_7\text{H}_{15}$</td><td>B (—)</td></tr> <tr><td>$n\text{-C}_8\text{H}_{17}$</td><td>B (—)</td></tr> <tr><td>$n\text{-C}_{10}\text{H}_{21}$</td><td>A (93)</td></tr> <tr><td>$n\text{-C}_{12}\text{H}_{25}$</td><td>A (95)</td></tr> </tbody> </table>	R	Conditions	H	A (99)	O_2N	A (70)	$n\text{-C}_3\text{H}_7$	A (81)	Ph	A (99)	PhO	A (99)	PhS	A (99)	PhOS	A (60)	PhO_2S	A (85)	$4\text{-O}_2\text{NC}_6\text{H}_4$	A (80)	$4\text{-O}_2\text{NC}_6\text{H}_4\text{O}$	A (50)	$n\text{-C}_3\text{H}_7$	B (81)	Bn	A (70)	$n\text{-C}_7\text{H}_{15}$	B (—)	$n\text{-C}_8\text{H}_{17}$	B (—)	$n\text{-C}_{10}\text{H}_{21}$	A (93)	$n\text{-C}_{12}\text{H}_{25}$	A (95)
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	$\text{NaN}_3, \text{silica sulfuric acid}, 60^\circ, 0.5 \text{ h}$	I (95)		282																																		
	$\text{NaN}_3, \text{P}_2\text{O}_5\text{-SiO}_2, \text{MW}, 8 \text{ min}$	I (92)		289																																		
	$\text{NaN}_3, \text{Fe}(\text{HCO}_4)_3, 50^\circ, 30 \text{ min}$	I (93)		288																																		
C_9																																						

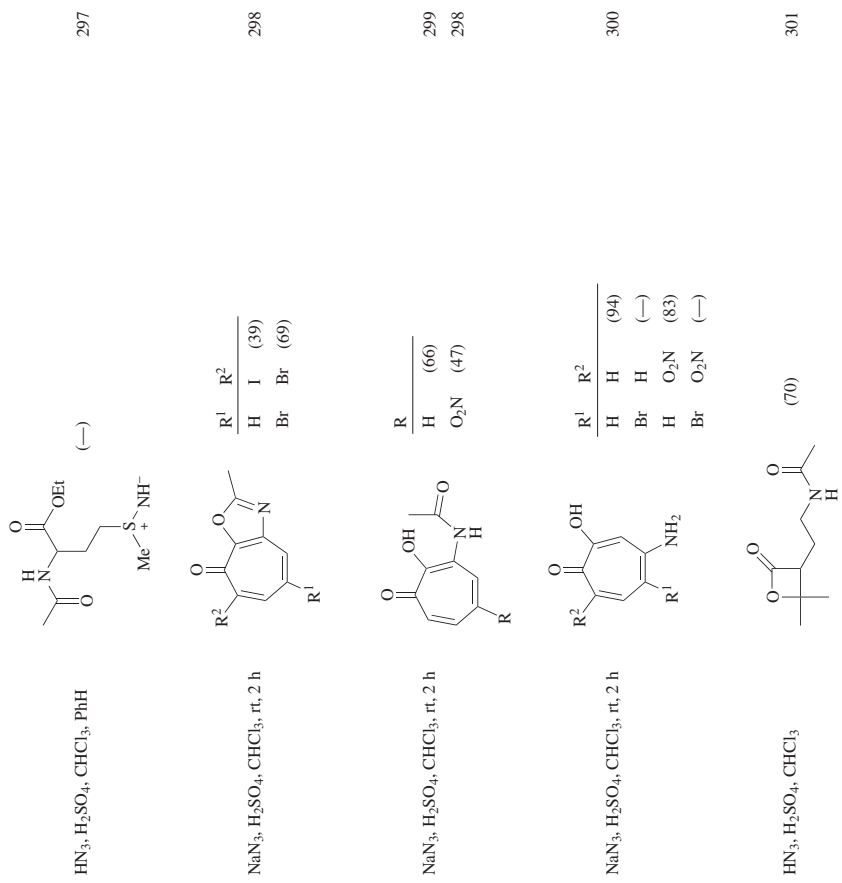
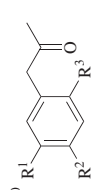
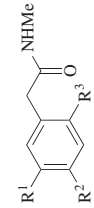
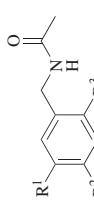
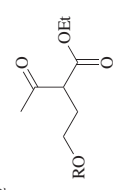
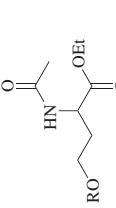

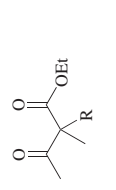
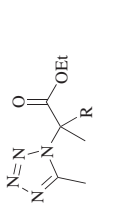

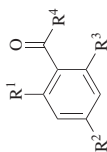
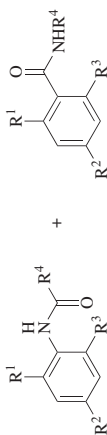


TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.																																																																												
C_9-10 	A: NaN_3 , PPA, 0° , 6 h B: NaN_3 , H_2SO_4 , PhH, rt, 6 h C: NaN_3 , H_2SO_4 , Et_2O , 0° , 6 h	I 	II 	296																																																																													
		<table border="1"> <thead> <tr> <th>R^1</th> <th>R^2</th> <th>R^3</th> <th>Conditions</th> <th>$\text{I} + \text{II}$</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>A</td> <td>(>95)</td> <td>24:76</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>B</td> <td>(>95)</td> <td>20:80</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>C</td> <td>(>95)</td> <td>60:40</td> </tr> <tr> <td>H</td> <td>H</td> <td>O_2N</td> <td>A</td> <td>(90)</td> <td>27:73</td> </tr> <tr> <td>H</td> <td>H</td> <td>O_2N</td> <td>B</td> <td>(100)</td> <td>14:86</td> </tr> <tr> <td>H</td> <td>H</td> <td>O_2N</td> <td>C</td> <td>(40)</td> <td>67:33</td> </tr> <tr> <td>H</td> <td>O_2N</td> <td>H</td> <td>A</td> <td>(90)</td> <td>15:85</td> </tr> <tr> <td>H</td> <td>O_2N</td> <td>H</td> <td>B</td> <td>(100)</td> <td>14:86</td> </tr> <tr> <td>H</td> <td>O_2N</td> <td>H</td> <td>C</td> <td>(60)</td> <td>33:67</td> </tr> <tr> <td>$-\text{OCH}_2\text{O}-$</td> <td>H</td> <td>H</td> <td>A</td> <td>(35)</td> <td>90:10</td> </tr> <tr> <td>$-\text{OCH}_2\text{O}-$</td> <td>H</td> <td>H</td> <td>B</td> <td>(-)</td> <td>—</td> </tr> <tr> <td>$-\text{OCH}_2\text{O}-$</td> <td>H</td> <td>H</td> <td>C</td> <td>(29)</td> <td>43:57</td> </tr> </tbody> </table>	R^1	R^2	R^3	Conditions	$\text{I} + \text{II}$	I:II	H	H	H	A	(>95)	24:76	H	H	H	B	(>95)	20:80	H	H	H	C	(>95)	60:40	H	H	O_2N	A	(90)	27:73	H	H	O_2N	B	(100)	14:86	H	H	O_2N	C	(40)	67:33	H	O_2N	H	A	(90)	15:85	H	O_2N	H	B	(100)	14:86	H	O_2N	H	C	(60)	33:67	$-\text{OCH}_2\text{O}-$	H	H	A	(35)	90:10	$-\text{OCH}_2\text{O}-$	H	H	B	(-)	—	$-\text{OCH}_2\text{O}-$	H	H	C	(29)	43:57	
R^1	R^2	R^3	Conditions	$\text{I} + \text{II}$	I:II																																																																												
H	H	H	A	(>95)	24:76																																																																												
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$-\text{OCH}_2\text{O}-$	H	H	C	(29)	43:57																																																																												
C_9-12 	HN_3 , H_2SO_4 , PhH, 50° , 3 h			198																																																																													
C_9-14 	TMSN_3 , ZnBr_2 , 65° , 24 h			302																																																																													

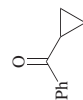
C₉₋₁₉

NaN₃, H₂SO₄, CCl₃CO₂H,
60°, 1–5 h

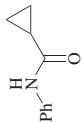


8

I		II		
R ¹	R ²	R ³	R ⁴	I + II E:II
Me	H	H	Me	(–) 99:1
HO ₂ C	H	H	Me	(65) 91:9
Cl	H	H	Ph	(100) 30:70
Br	H	H	Ph	(100) 19:81
O ₂ N	H	H	Ph	(–) 70:30
Me	H	H	Ph	(34) 12:88
MeO	H	H	Ph	(88) 50:50
HO ₂ C	H	H	Ph	(–) 98:2
Me	Me	Me	Ph	(–) 95:5
Ph	H	H	Ph	(35) 95:5

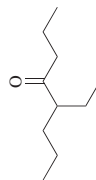
C₁₀

Azide, FeCl₃, DCE, rt

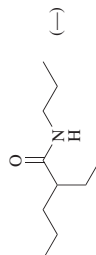
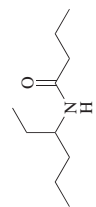


Azide	Time
TMSN ₃	45 min (81)
NaN ₃	3.5 h (73)

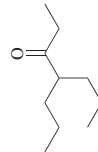
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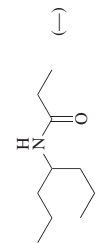
NaN₃, H₂SO₄, CHCl₃



303

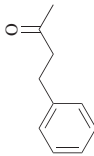

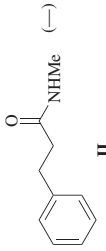
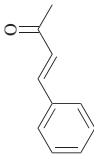
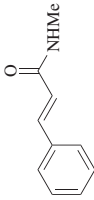
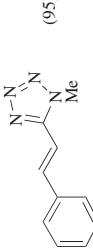
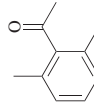
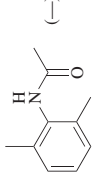
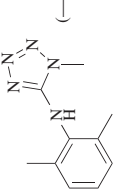
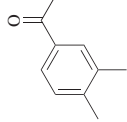
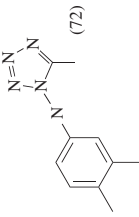


NaN₃, H₂SO₄, CHCl₃



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TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN ₃ , PPA, rt, 8 h	 (95) +  (—)	54
	NaN ₃ , silica sulfuric acid, ^a 60°, 45 min	I + II (93), I:II = 5:1	282
	NaN ₃ , P ₂ O ₅ , SiO ₂ , MW, 10 min	I + II (93), I:II = 5:1	289
	NaN ₃ , Fe(HSO ₄) ₃ , 50°, 25 min	I + II (90), I:II = 4:1	288
	NaN ₃ , PPA, rt, 8 h	 (58)	54
	SiCl ₄ , NaN ₃ , MeCN, rt, 12 h	 (95)	70
	NaN ₃ , H ₂ SO ₄ , 0° to rt, 14 h	 (—) +  (—)	304
	NaN ₃ , H ₂ SO ₄	 (72)	305

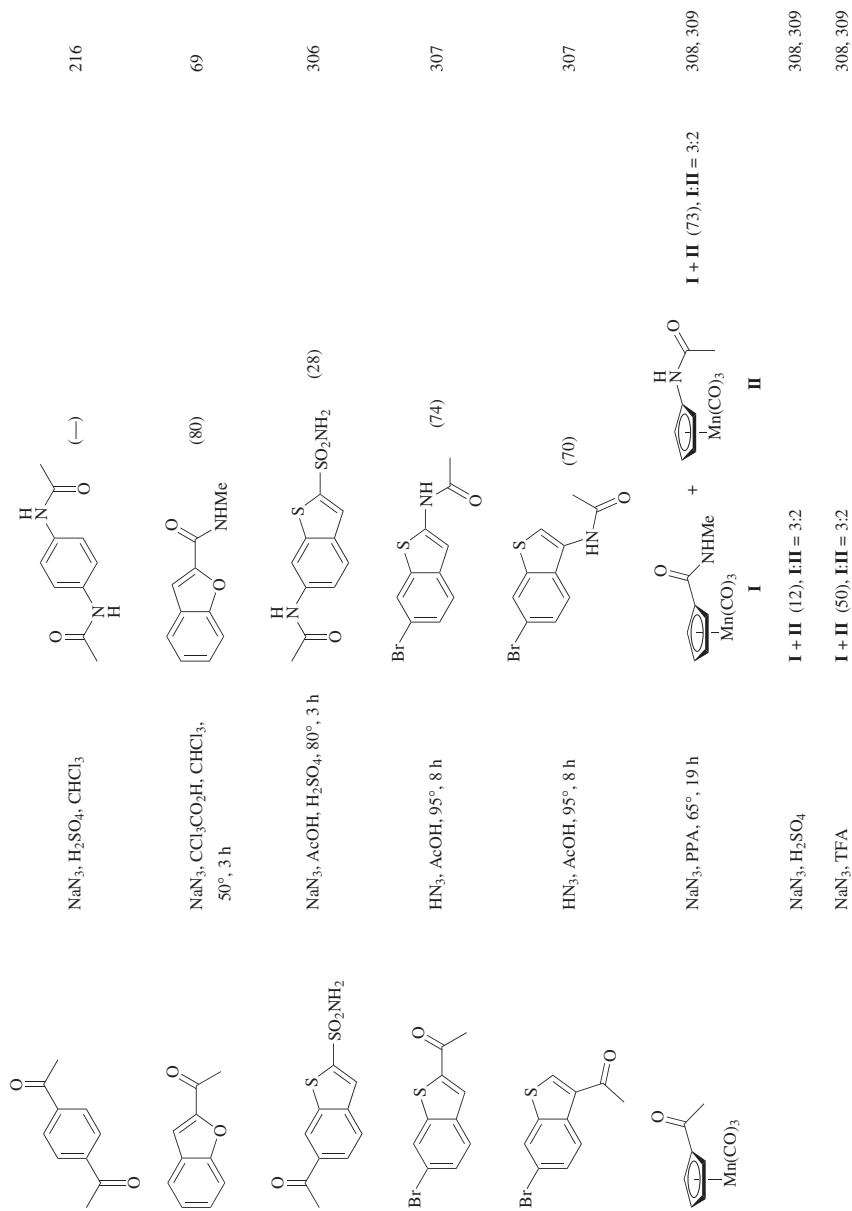
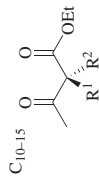
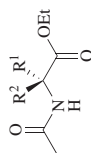


TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
<p>C₁₀₋₁₁</p>	NaN ₃ , CCl ₃ CO ₂ H	 	<table border="0"> <tr> <td>R</td> <td>I</td> <td>II</td> </tr> <tr> <td>H</td> <td>(75)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>(0)</td> <td>(86)</td> </tr> </table>	R	I	II	H	(75)	(0)	Me	(0)	(86)	7		
R	I	II													
H	(75)	(0)													
Me	(0)	(86)													
<p>C₁₀₋₁₂</p>	HN ₃ , H ₂ SO ₄ , CHCl ₃	<table border="0"> <tr> <td>R</td> <td>(89)</td> </tr> <tr> <td>H</td> <td>(89)</td> </tr> <tr> <td>Et</td> <td>(92)</td> </tr> </table>	R	(89)	H	(89)	Et	(92)	301						
R	(89)														
H	(89)														
Et	(92)														
	NaN ₃ , H ₂ SO ₄ , 0° to rt, 6 h	<table border="0"> <tr> <td>R</td> <td>(50)</td> </tr> <tr> <td>Ph</td> <td>(74)</td> </tr> <tr> <td>4-BrC₆H₄</td> <td>(74)</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>(77)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>(58)</td> </tr> <tr> <td>4-EtOC₆H₄</td> <td>(63)</td> </tr> </table>	R	(50)	Ph	(74)	4-BrC ₆ H ₄	(74)	4-MeC ₆ H ₄	(77)	4-MeOC ₆ H ₄	(58)	4-EtOC ₆ H ₄	(63)	310
R	(50)														
Ph	(74)														
4-BrC ₆ H ₄	(74)														
4-MeC ₆ H ₄	(77)														
4-MeOC ₆ H ₄	(58)														
4-EtOC ₆ H ₄	(63)														
<p>C₁₀₋₁₃</p>	HN ₃ , H ₂ SO ₄	<table border="0"> <tr> <td>R</td> <td>(48)</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>(46)</td> </tr> <tr> <td>Bn</td> <td>(46)</td> </tr> </table>	R	(48)	<i>i</i> -Bu	(46)	Bn	(46)	290						
R	(48)														
<i>i</i> -Bu	(46)														
Bn	(46)														
	NaN ₃ , H ₂ SO ₄ , CHCl ₃	<table border="0"> <tr> <td>R</td> <td>(57)</td> </tr> <tr> <td>H</td> <td>(57)</td> </tr> <tr> <td>H₂NO₂S</td> <td>(44)</td> </tr> <tr> <td>(HO)₂AsO</td> <td>(70)</td> </tr> <tr> <td>EtO</td> <td>(35)</td> </tr> <tr> <td>EtO₂C</td> <td>(50)</td> </tr> </table>	R	(57)	H	(57)	H ₂ NO ₂ S	(44)	(HO) ₂ AsO	(70)	EtO	(35)	EtO ₂ C	(50)	311
R	(57)														
H	(57)														
H ₂ NO ₂ S	(44)														
(HO) ₂ AsO	(70)														
EtO	(35)														
EtO ₂ C	(50)														



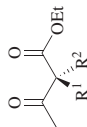
NaN₃, MsOH, HCl,
0° to reflux, 6 h



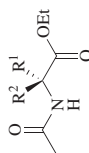
R ¹	R ²
allyl	Me (44)
<i>n</i> -Pr	Me (99)
<i>i</i> -Pr	Me (50)
<i>n</i> -Bu	Me (89)
<i>i</i> -Bu	Me (80)
allyl	Et (0)
<i>n</i> -Pr	Et (48)
<i>i</i> -Pr	Et (21)
<i>n</i> -Bu	Et (37)
<i>i</i> -Bu	Et (35)
Et	<i>i</i> -Bu (40)
H	Bn (90)
Bn	Me (95)
Bn	Et (52)

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C₁₀₋₂₀



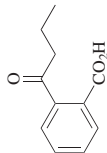
A. NaN₃, MsOH, CHCl₃,
reflux, 1 h
B. NaN₃, H₂SO₄, DME,
rt, 24 h



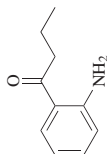
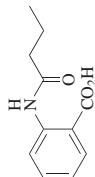
R ¹	R ²	Conditions
MeO ₂ CCH ₂	Me	A (88)
Bn	Me	A (95)
Bn	Me	B (82)
4-BrC ₆ H ₄ CH ₂	Me	B (63)
4-BrC ₆ H ₄ CH ₂	Bu	B (43)
2-C ₁₀ H ₇ -CH ₂	Me	A (89)
2-C ₁₀ H ₇ -CH ₂	Me	B (82)
2-C ₁₀ H ₇ -CH ₂	Bu	B (41)

108
108
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C₁₁



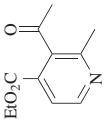
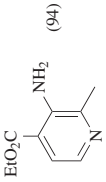
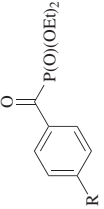
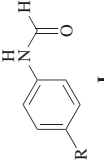
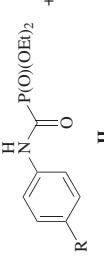
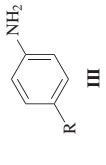
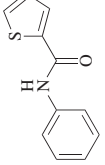
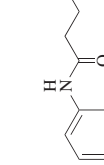
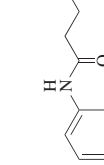
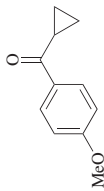
NaN₃, H₂SO₄, CHCl₃, rt, 3 h

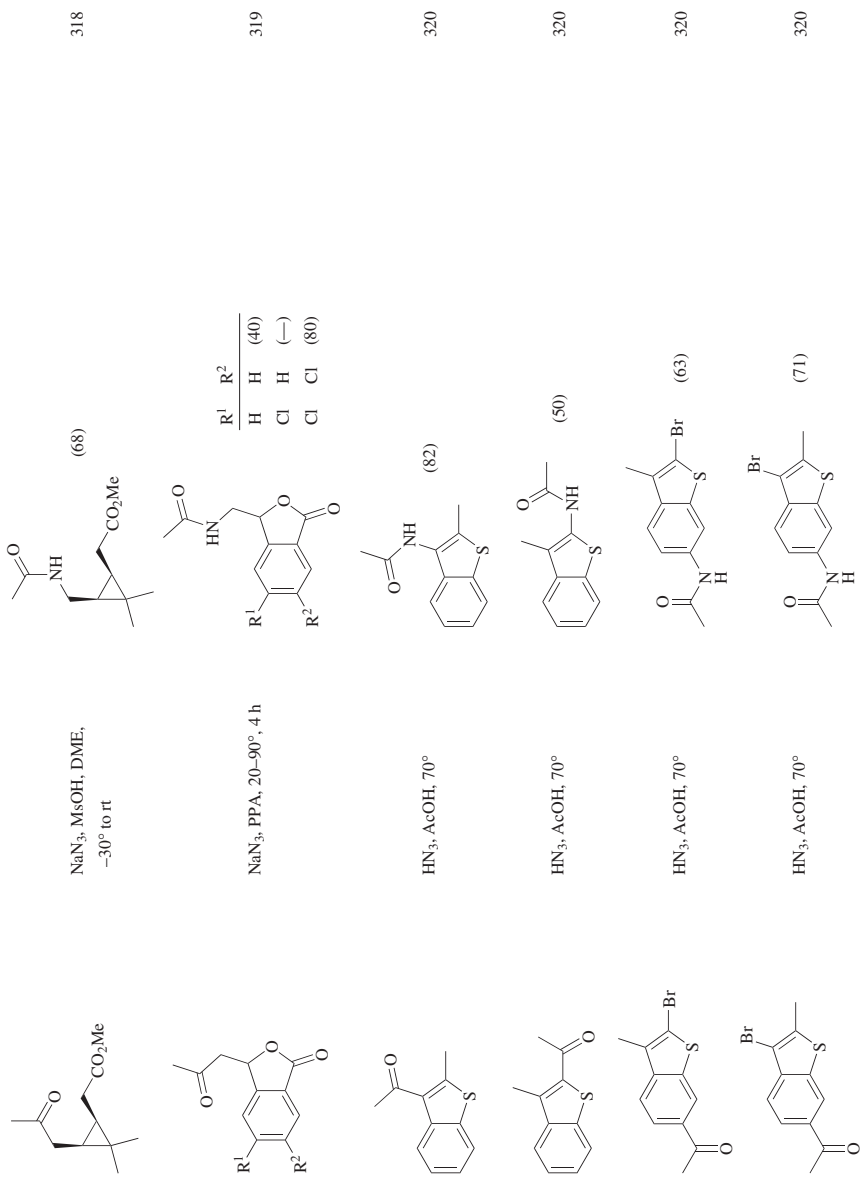


(77) + (5)

315

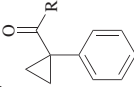
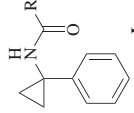
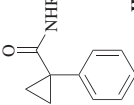
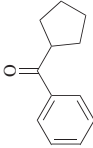
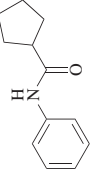
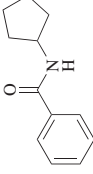
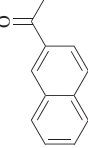
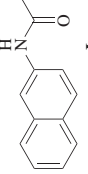





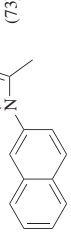
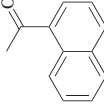
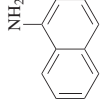
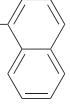
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	1. NaN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 18 h 2. H ₂ O, reflux, 1.5h	 (94)	316												
	HN ₃ , H ₂ SO ₄ , CHCl ₃	 I +  II	82												
		<table border="1"> <thead> <tr> <th>R</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(53)</td> <td>(9)</td> <td>(14)</td> </tr> <tr> <td>Cl</td> <td>(65)</td> <td>(19)</td> <td>(0)</td> </tr> </tbody> </table>	R	I	II	III	H	(53)	(9)	(14)	Cl	(65)	(19)	(0)	
R	I	II	III												
H	(53)	(9)	(14)												
Cl	(65)	(19)	(0)												
 III	NaN ₃ , H ₂ SO ₄ , CCl ₃ CO ₂ H, 50°, 3 h	 (49)	317												
 (69)	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 3 h	 (69)	315												
	Azide, FeCl ₃ , DCE, rt	<table border="1"> <thead> <tr> <th>Azide</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>TMSN₃</td> <td>49 min (78)</td> </tr> <tr> <td>NaN₃</td> <td>3.5 h (70)</td> </tr> </tbody> </table>	Azide	Time	TMSN ₃	49 min (78)	NaN ₃	3.5 h (70)	286						
Azide	Time														
TMSN ₃	49 min (78)														
NaN ₃	3.5 h (70)														



R ¹	R ²
H	H (40)
Cl	H (—)
Cl	Cl (80)

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.	
 C ₁₁₋₁₆	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , rt	 I	 II	R I + II I:II Me (81) 3.3:1 Ph (66) 1.7:1	279
 C ₁₂	NaN ₃ , ClCH ₂ CO ₂ H, 60°, 6 h	 I	 II	(-) + (-)	(-)
	NaN ₃ , MsOH, DME, -30° to rt, 3 h	 I	 (91)		56
	NaN ₃ , PPA, 55°, 12 h	 I (81)			54
	NaN ₃ , CCl ₃ CO ₂ H, 60°	 I (95)			1
	NaN ₃ , H ₂ SO ₄	 I (55)			1
	NaN ₃ , POCl ₃ , CHCl ₃	 I (42)			1
	NaN ₃ , AlCl ₃ , PhNO ₂	 (73)			1
	1. NaN ₃ , x% H ₂ SO ₄ , 0°, 8 h 2. HCl, EtOH, reflux, 24 h	 (15)	 (48)	$\frac{x}{75}$ 85 (48) 90 (70) 95 (36)	5

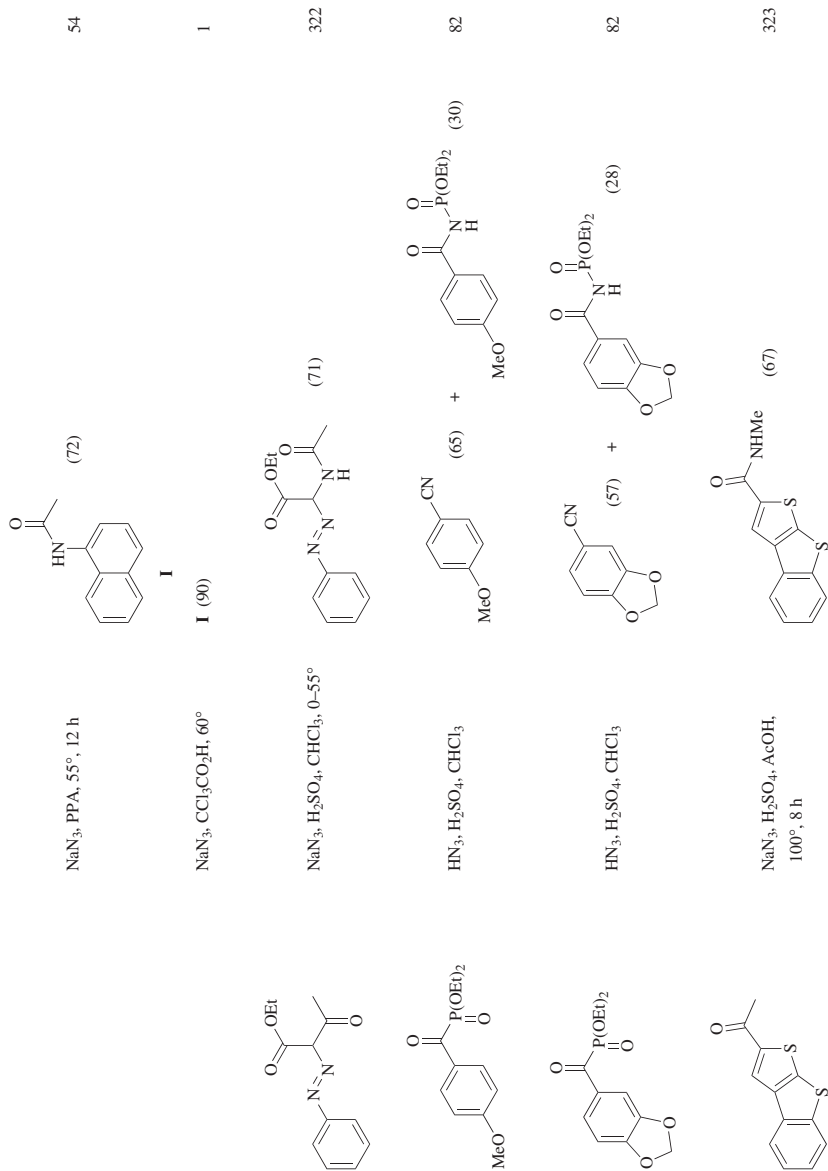
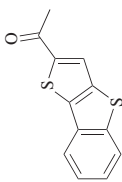
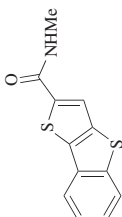
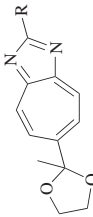
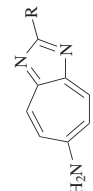
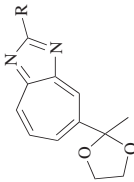
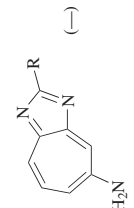
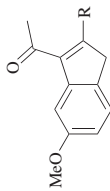
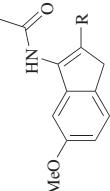
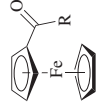
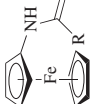


TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂ 	NaN ₃ , H ₂ SO ₄ , AcOH, 100°, 8 h	 (60)	323
C ₁₂₋₁₃ 	NaN ₃ , H ₂ SO ₄ , rt, 2 h	 R H (—) H ₂ N (80)	324
C ₁₂₋₁₃ 	NaN ₃ , H ₂ SO ₄ , rt, 2 h	 R H (—) H ₂ N MeS	324
C ₁₂₋₁₇ 	NaN ₃ , TFA, CHCl ₃ , 60°, 4 h	 R H (78) Me (80)	69
C ₁₂₋₁₇ 	NaN ₃ , PPA, 60°, 28 h	 R Me (20) (10) Ph (10) (5)	309

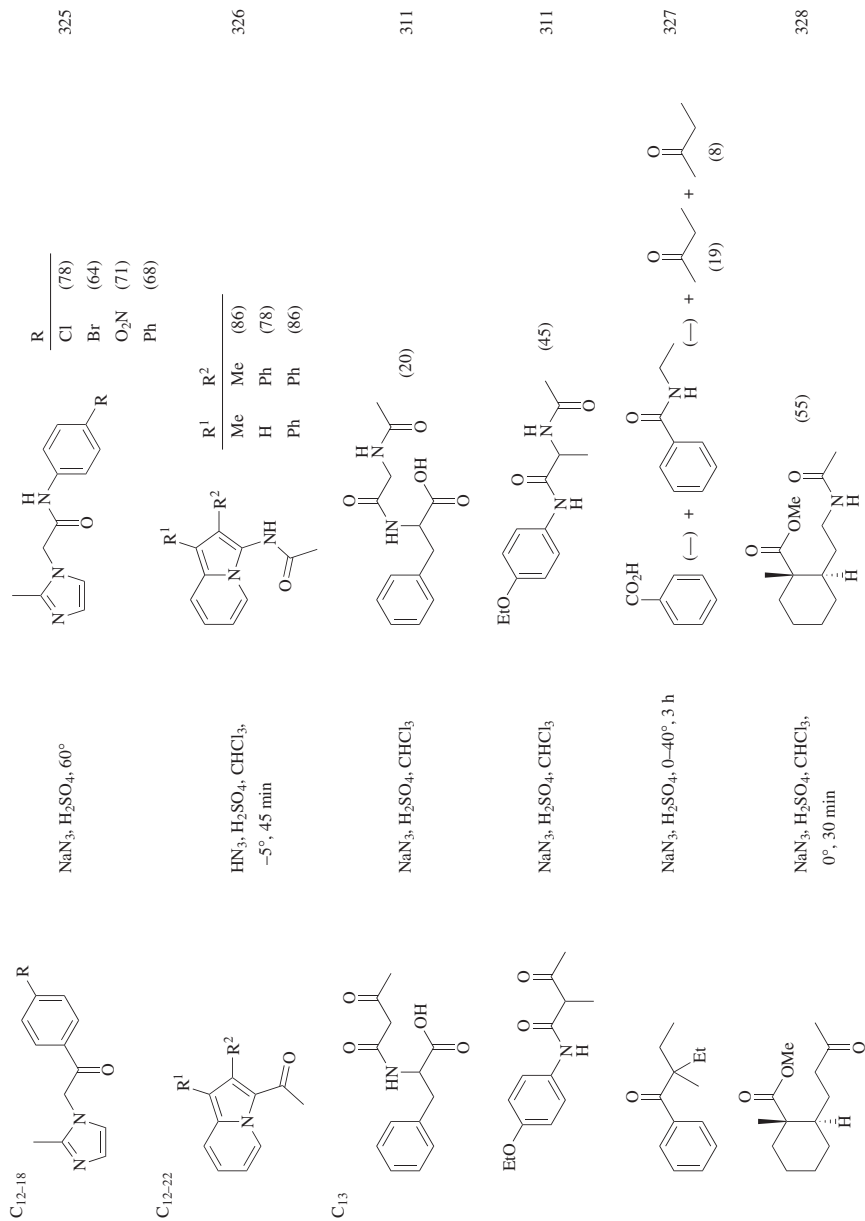
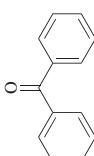
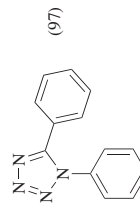
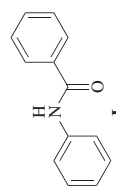
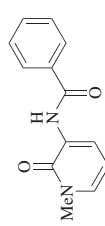
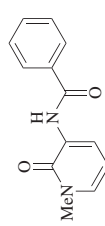
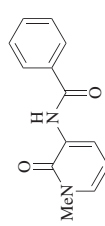
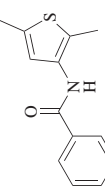
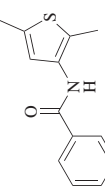
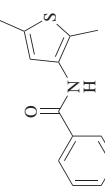
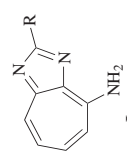
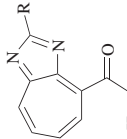
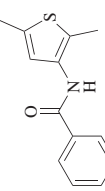
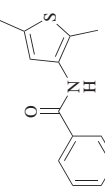
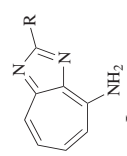
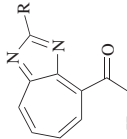
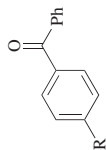
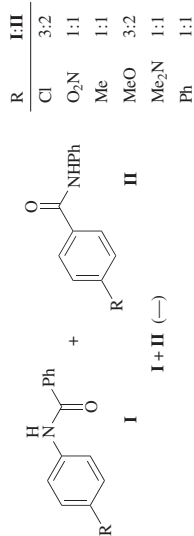


TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

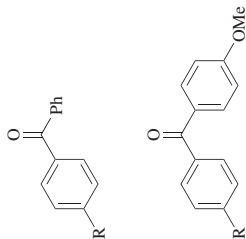
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
	SiCl ₄ , NaN ₃ , MeCN, rt, 15 h	 (97)	70								
	A. NaN ₃ , H ₂ SO ₄ , CCl ₃ CO ₂ H	A (99)	I								
	B. NaN ₃ , PPA, 50°, 8.5 h	B (99)									
	C. NaN ₃ , MeOH, DME, rt	C (57)									
	Azide, FeCl ₃ , DCE, rt	<table border="1"> <thead> <tr> <th>Azide</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>I</td> <td>TMSN₃, 32 min (79)</td> </tr> <tr> <td></td> <td>NaN₃, 2.5 h (70)</td> </tr> </tbody> </table>	Azide	Time	I	TMSN ₃ , 32 min (79)		NaN ₃ , 2.5 h (70)	286		
	Azide	Time									
I	TMSN ₃ , 32 min (79)										
	NaN ₃ , 2.5 h (70)										
	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 0–50°, 12 h	 (70)	329								
	NaN ₃ , CCl ₃ CO ₂ H, H ₂ SO ₄ , 50°, 3 h	 (58)	317								
	NaN ₃ , H ₂ SO ₄ , rt, 2 h	 (58) +  (I) +  (II)	<table border="1"> <thead> <tr> <th>R</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(34)</td> <td>(0)</td> </tr> <tr> <td>Ph</td> <td>(84)</td> <td>(15)</td> </tr> </tbody> </table>	R	I	II	Me	(34)	(0)	Ph	(84)
R	I	II									
Me	(34)	(0)									
Ph	(84)	(15)									
	NaN ₃ , H ₂ SO ₄ , rt, 2 h	 (58) +  (I) +  (II)	330								

C₁₃₋₁₉

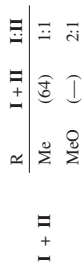
NaN₃, CCl₃CO₂H, 60°, 8 h



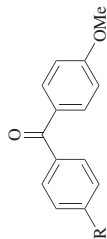
7

C₁₄

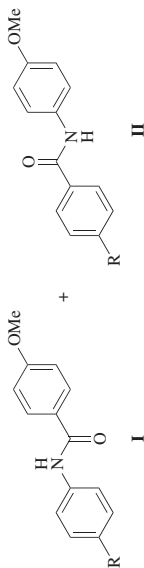
NaN₃, H₂SO₄, PhH, 50°, 8 h



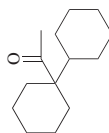
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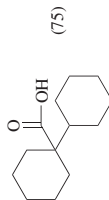
NaN₃, H₂SO₄, CCl₃CO₂H,
60°, 8 h



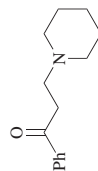
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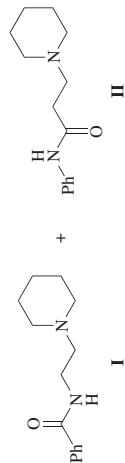
NaN₃, H₂SO₄, CHCl₃



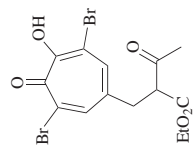
332



NaN₃, H₂SO₄



333

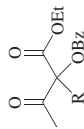


NaN₃, H₂SO₄, PhH, 0°, 1 h

(97)

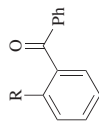
335

C₁₄₋₁₇



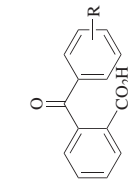
HN₃, H₂SO₄, CCl₄

336



NaN₃, CCl₃CO₂H, 60°, 12 h

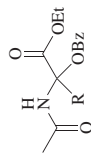
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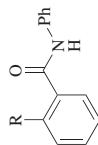
NaN₃, H₂SO₄, CHCl₃, rt, 3 h

315

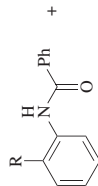
R	
Me	(58)
Et	(60)
<i>n</i> -Pr	(60)
<i>n</i> -Bu	(60)



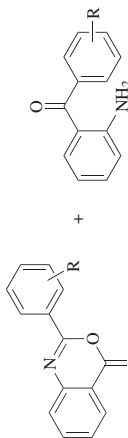
R	I + II	I:II
Me	(99)	24:76
HO ₂ C	(87)	100:0
Et	(96)	23:77
<i>i</i> -Pr	(96)	18:82



II



I



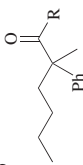
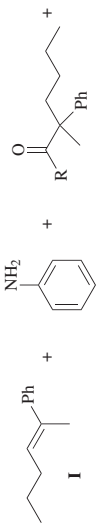
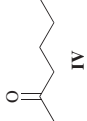
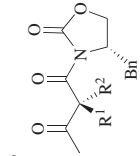
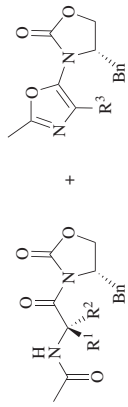

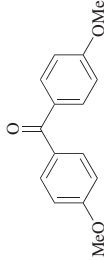
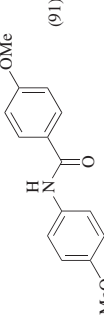

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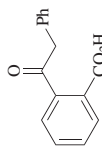
I

II

R	I	II
4-Cl	(84)	(3)
3-O ₂ N	(87)	(4)
4-MeO	(75)	(0)
2,4,6-Me ₃	(29)	(0)

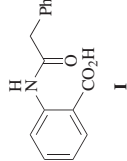
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.		
 C ₁₄₋₁₉	NaN ₃ , PPA, 50°, 8 h	  IV	337		
 C ₁₄₋₂₃	A: NaN ₃ , MeOH, DME, -30° to rt B: NaN ₃ , H ₂ SO ₄ , DME, -30° C: NaN ₃ , H ₂ SO ₄ , PhH, 5° to rt	  III	R I II III IV Me (8) (41) (25) (29) Ph (8) (24) (58) (—)	56	
 C ₁₅	NaN ₃ , PPA, 50°, 8.5 h	  III	R ¹ R ² R ³ H H H H Me Me Me H Me H Bn Bn H Bn — H Bn — Ph(CH ₂) ₂ H H (E)-PhCH=CHCH ₂ (E)-PhCH=CHCH ₂	Conditions I II A (0) (45) A (0) (91) C (14) (21) A (0) (27) B (50) (0) C (0) (0) A (0) (66) A (0) (32)	54

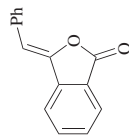


$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, \text{rt}, 3 \text{ h}$

(85)



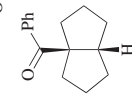
315



$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, \text{rt}, 3 \text{ h}$

I (62)

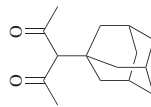
315



$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3,$
 $0^\circ, 45 \text{ min}$

(56)

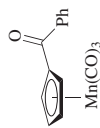
338



$\text{NaN}_3, \text{MsOH}, \text{DME},$
 $-30^\circ \text{ to rt}, 3 \text{ h}$

(87)

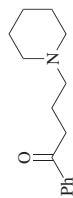
56



$\text{NaN}_3, \text{Promoter}$

Promoter	Conditions
PPA	$65^\circ, 19 \text{ h}$ (67)
H_2SO_4	— (15)
TFA	— (32)

308



$\text{NaN}_3, \text{H}_2\text{SO}_4$

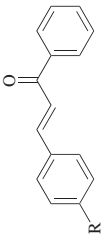
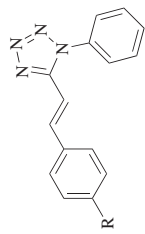
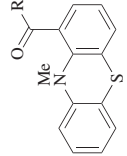
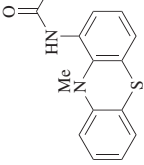
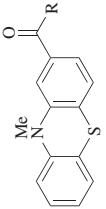
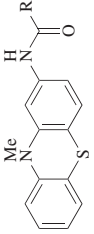
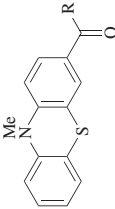
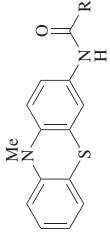
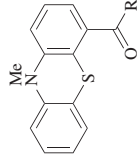
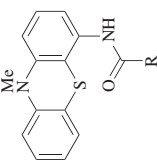


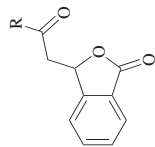
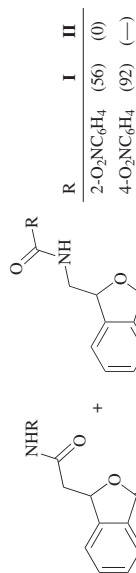
I + II (—), **I:II** = 3:7

II

333

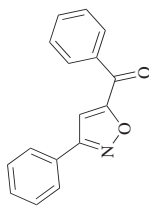
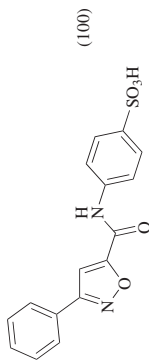
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
<p>C_{15-16}</p> 	<p>$\text{NaN}_3, \text{SiCl}_4, \text{MeCN}, \text{rt}, 12 \text{ h}$</p>	 <p>R</p> <table border="0"> <tr><td>H</td><td>(94)</td></tr> <tr><td>Cl</td><td>(95)</td></tr> <tr><td>MeO</td><td>(90)</td></tr> </table>	H	(94)	Cl	(95)	MeO	(90)	70
H	(94)								
Cl	(95)								
MeO	(90)								
<p>C_{15-20}</p> 	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH}, 0^\circ$</p>	 <p>R</p> <table border="0"> <tr><td>Me</td><td>(83)</td></tr> <tr><td>Ph</td><td>(16)</td></tr> </table>	Me	(83)	Ph	(16)	339		
Me	(83)								
Ph	(16)								
	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH}, 0^\circ$</p>	 <p>R</p> <table border="0"> <tr><td>Me</td><td>(67)</td></tr> <tr><td>Ph</td><td>(53)</td></tr> </table>	Me	(67)	Ph	(53)	339		
Me	(67)								
Ph	(53)								
	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH}, 0^\circ$</p>	 <p>R</p> <table border="0"> <tr><td>Me</td><td>(31)</td></tr> <tr><td>Ph</td><td>(63)</td></tr> </table>	Me	(31)	Ph	(63)	339		
Me	(31)								
Ph	(63)								
	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH}, 0^\circ$</p>	 <p>R</p> <table border="0"> <tr><td>Me</td><td>(72)</td><td>(0)</td></tr> <tr><td>Ph</td><td>(34)</td><td>(24)</td></tr> </table> <p style="text-align: center;"> I II </p>	Me	(72)	(0)	Ph	(34)	(24)	339
Me	(72)	(0)							
Ph	(34)	(24)							

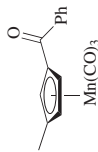
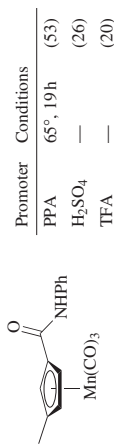
C₁₆NaN₃, PPA, 20–90°, 4 h

319

	I	II
	2-O ₂ NC ₆ H ₄	(56) (0)
	4-O ₂ NC ₆ H ₄	(92) (—)

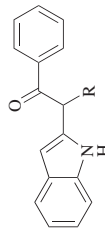
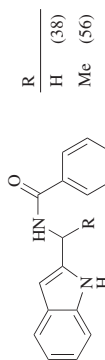
NaN₃, H₂SO₄, CHCl₃

340

NaN₃, Promoter

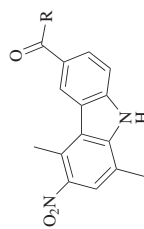
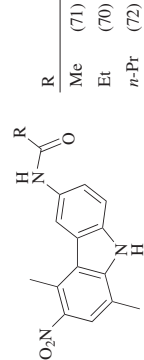
308

Promoter	Conditions
PPA	65°, 19 h (53)
H ₂ SO ₄	— (26)
TFA	— (20)

C₁₆₋₁₇NaN₃, H₂SO₄, CHCl₃, rt

341

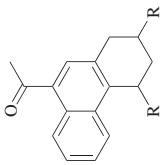
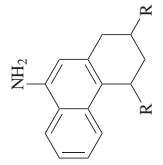
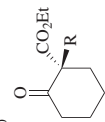
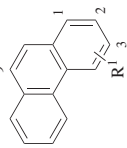
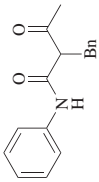
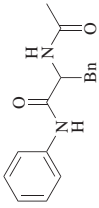
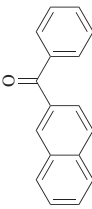
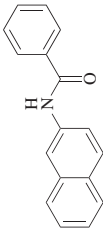
R	
H	(38)
Me	(56)

C₁₆₋₁₈NaN₃, TFA, 100°, 5 h

342

R	
Me	(71)
Et	(70)
<i>n</i> -Pr	(72)

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
<p>C_{16-18}</p> 	<p>1. NaN_3, H_2SO_4, 60°, 8 h 2. Hydrolysis</p>	 <table border="0"> <tr> <td style="text-align: center;">R</td> <td style="border-left: 1px solid black; border-right: 1px solid black;"></td> </tr> <tr> <td style="text-align: center;">H</td> <td style="border-left: 1px solid black; border-right: 1px solid black;">(81)</td> </tr> <tr> <td style="text-align: center;">Me</td> <td style="border-left: 1px solid black; border-right: 1px solid black;">(82)</td> </tr> </table>	R		H	(81)	Me	(82)	5														
R																							
H	(81)																						
Me	(82)																						
<p>C_{16-20}</p> 	<p>NaN_3, MeOH, CHCl_3, reflux, 1 h</p>	<table border="0"> <tr> <td style="text-align: center;">R</td> <td style="border-left: 1px solid black; border-right: 1px solid black;"></td> </tr> <tr> <td style="text-align: center;">Bn</td> <td style="border-left: 1px solid black; border-right: 1px solid black;">(97)</td> </tr> <tr> <td style="text-align: center;">2-$\text{C}_{10}\text{H}_7\text{CH}_2$</td> <td style="border-left: 1px solid black; border-right: 1px solid black;">(71)</td> </tr> </table>	R		Bn	(97)	2- $\text{C}_{10}\text{H}_7\text{CH}_2$	(71)	108														
R																							
Bn	(97)																						
2- $\text{C}_{10}\text{H}_7\text{CH}_2$	(71)																						
<p>C_{16-21}</p> 	<p>1. NaN_3, H_2SO_4, 60°, 8 h 2. Hydrolysis</p>	<table border="0"> <tr> <td style="text-align: center;">R¹</td> <td style="border-left: 1px solid black; border-right: 1px solid black;"></td> <td style="text-align: center;">R²</td> <td style="border-left: 1px solid black; border-right: 1px solid black;"></td> </tr> <tr> <td style="text-align: center;">2-Ac</td> <td style="border-left: 1px solid black; border-right: 1px solid black;"></td> <td style="text-align: center;">2-H₂N</td> <td style="border-left: 1px solid black; border-right: 1px solid black;">(88)</td> </tr> <tr> <td style="text-align: center;">3-Ac</td> <td style="border-left: 1px solid black; border-right: 1px solid black;"></td> <td style="text-align: center;">3-H₂N</td> <td style="border-left: 1px solid black; border-right: 1px solid black;">(80)</td> </tr> <tr> <td style="text-align: center;">9-Ac</td> <td style="border-left: 1px solid black; border-right: 1px solid black;"></td> <td style="text-align: center;">9-H₂N</td> <td style="border-left: 1px solid black; border-right: 1px solid black;">(73)</td> </tr> <tr> <td style="text-align: center;">1-Bz</td> <td style="border-left: 1px solid black; border-right: 1px solid black;"></td> <td style="text-align: center;">1-BzHN</td> <td style="border-left: 1px solid black; border-right: 1px solid black;">(93)</td> </tr> </table>	R ¹		R ²		2-Ac		2-H ₂ N	(88)	3-Ac		3-H ₂ N	(80)	9-Ac		9-H ₂ N	(73)	1-Bz		1-BzHN	(93)	5
R ¹		R ²																					
2-Ac		2-H ₂ N	(88)																				
3-Ac		3-H ₂ N	(80)																				
9-Ac		9-H ₂ N	(73)																				
1-Bz		1-BzHN	(93)																				
<p>C_{17}</p> 	<p>NaN_3, H_2SO_4, CHCl_3</p>	 (40)	311																				
	<p>NaN_3, PPA, 50°, 10 h</p>	 (72)	54																				

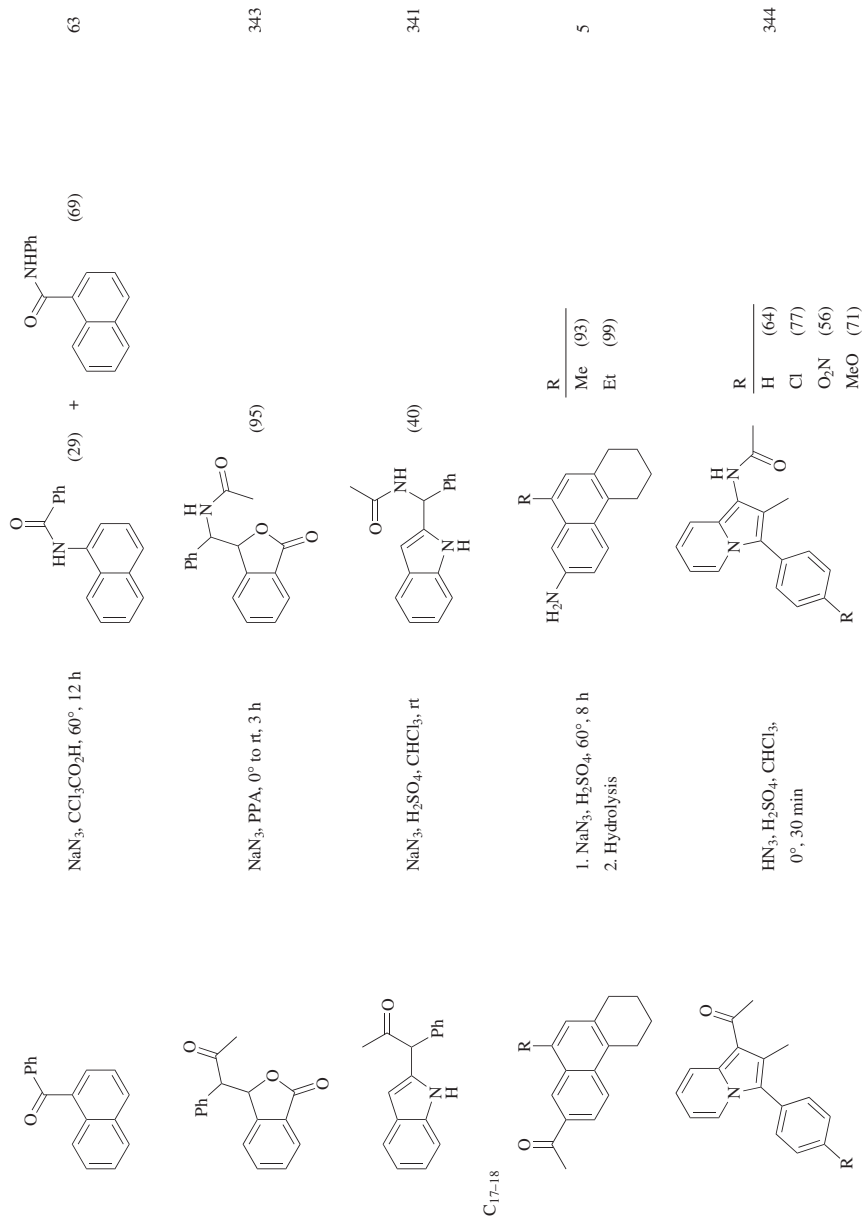
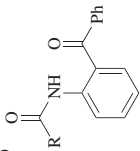
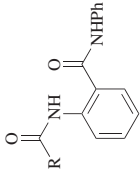
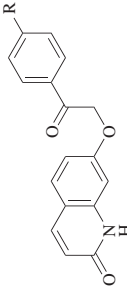
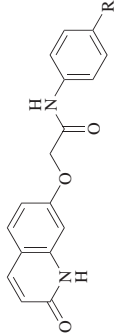
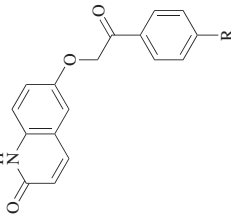
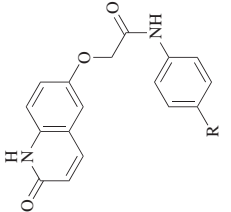
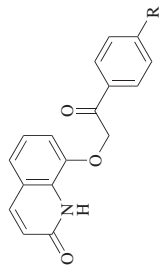
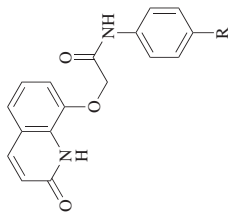


TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.											
<p>C_{17-20}</p> 	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, \text{rt}, 12 \text{ h}$</p>	<p>(-)</p> 	345											
<p>C_{17-23}</p> 	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{rt}, 10 \text{ min}$</p>		<table border="1"> <tr> <td>R</td> <td>(94)</td> </tr> <tr> <td>H</td> <td>(92)</td> </tr> <tr> <td>F</td> <td>(80)</td> </tr> <tr> <td>MeO</td> <td>(98)</td> </tr> <tr> <td>Ph</td> <td>(98)</td> </tr> </table>	R	(94)	H	(92)	F	(80)	MeO	(98)	Ph	(98)	346
R	(94)													
H	(92)													
F	(80)													
MeO	(98)													
Ph	(98)													
	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{rt}, 10 \text{ min}$</p>		<table border="1"> <tr> <td>R</td> <td>(85)</td> </tr> <tr> <td>H</td> <td>(73)</td> </tr> <tr> <td>F</td> <td>(93)</td> </tr> <tr> <td>MeO</td> <td>(95)</td> </tr> <tr> <td>Ph</td> <td>(95)</td> </tr> </table>	R	(85)	H	(73)	F	(93)	MeO	(95)	Ph	(95)	346
R	(85)													
H	(73)													
F	(93)													
MeO	(95)													
Ph	(95)													
	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{rt}, 10 \text{ min}$</p>		<table border="1"> <tr> <td>R</td> <td>(96)</td> </tr> <tr> <td>H</td> <td>(92)</td> </tr> <tr> <td>F</td> <td>(96)</td> </tr> <tr> <td>MeO</td> <td>(96)</td> </tr> <tr> <td>Ph</td> <td>(75)</td> </tr> </table>	R	(96)	H	(92)	F	(96)	MeO	(96)	Ph	(75)	346
R	(96)													
H	(92)													
F	(96)													
MeO	(96)													
Ph	(75)													

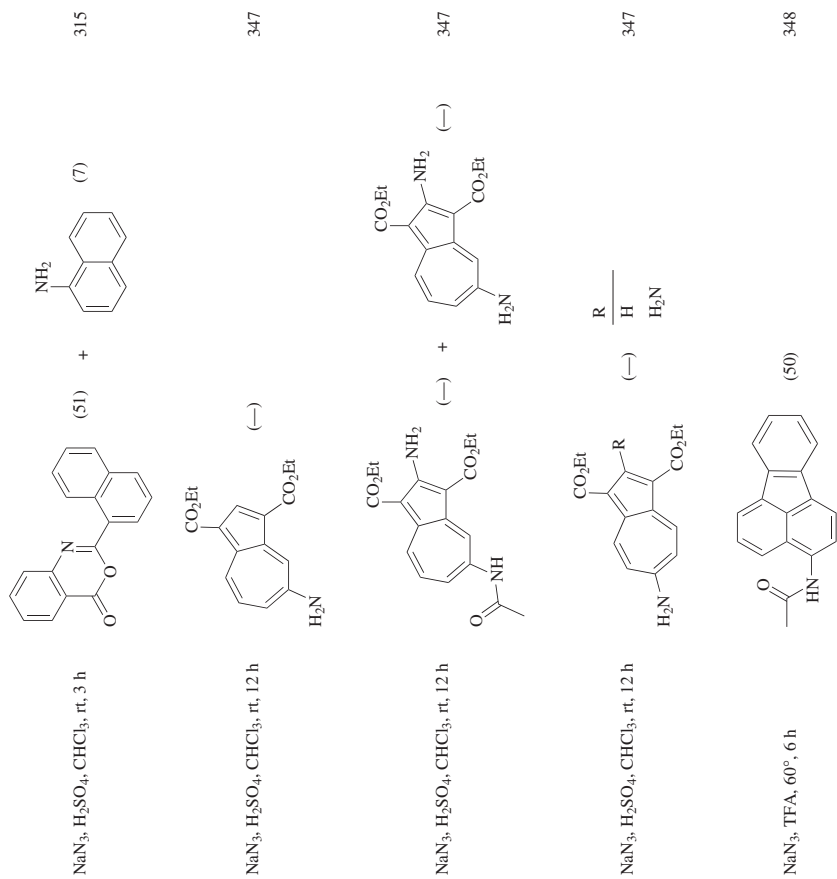
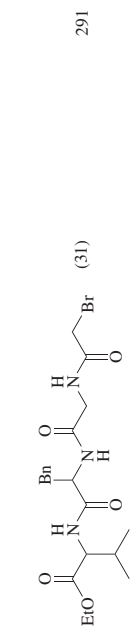
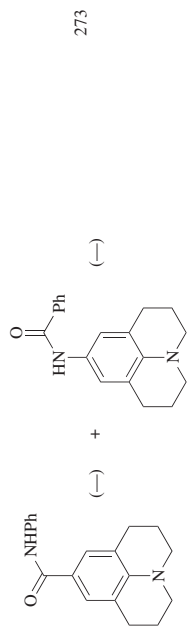


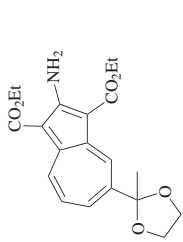
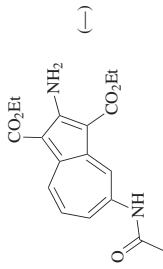
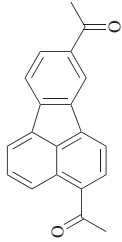
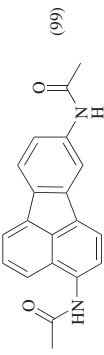
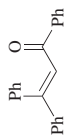
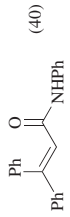
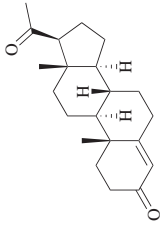
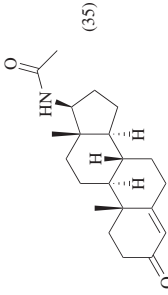
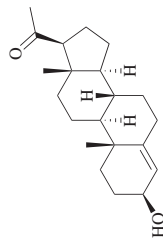
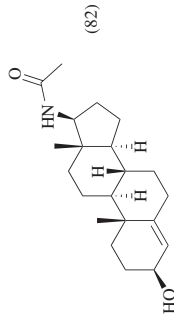
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₈</p>	<p>NaN₃, CHCl₃, 50–60°, 2 h</p>	<p>(70)</p>	349
<p>C₁₉</p>	<p>NaN₃, TiCl₄, MeCN, reflux, 5 h</p>	<p>I + II</p>	350
		<p>III + IV</p>	I + II + III + IV (71)
	<p>NaN₃, H₂SO₄, CHCl₃</p>	<p>(53)</p>	311
	<p>NaN₃, TFA, 60°, 27 h</p>	<p>(43)</p>	351

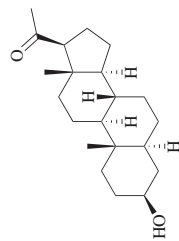


C₂₀

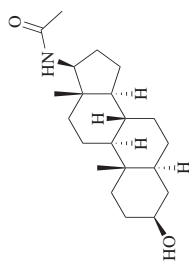
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, \text{rt}, 12 \text{ h}$	 (-)	347
	$\text{NaN}_3, \text{TFA}, 60^\circ, 6 \text{ h}$	 (99)	348
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, 35^\circ, 1 \text{ h}$	 (40)	353
	NaN_3 (1 eq), PPA, $50^\circ, 10 \text{ h}$	 (35)	354
	$\text{HN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3, \text{rt}, 30 \text{ min}$	 (82)	355

C₂₁

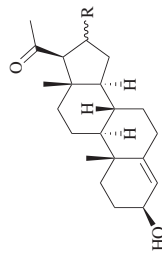


HN₃, H₂SO₄, CHCl₃, rt, 30 min

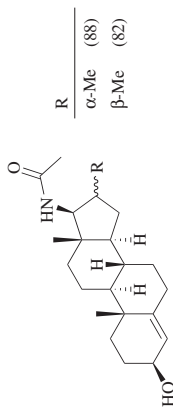


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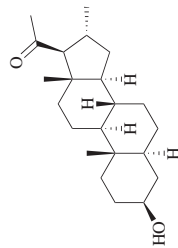
C₂₂



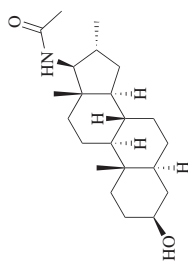
HN₃, H₂SO₄, CHCl₃, rt, 30 min



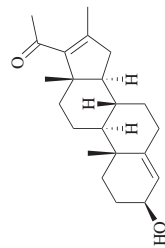
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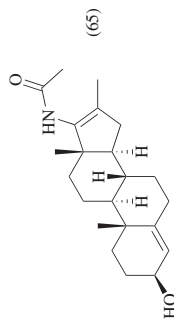
HN₃, H₂SO₄, CHCl₃, rt, 30 min



355

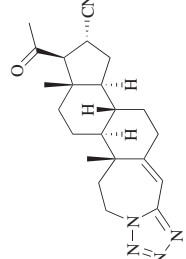
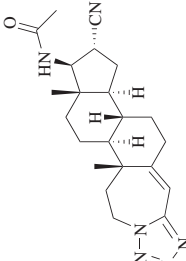
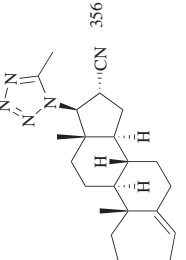
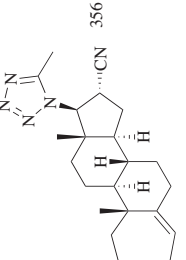
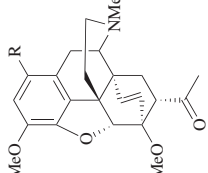
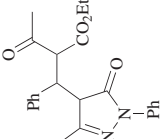
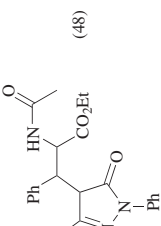


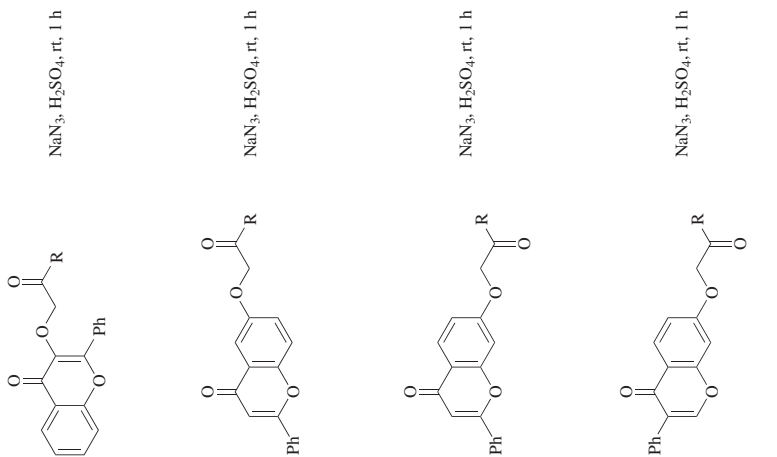
HN₃, H₂SO₄, CHCl₃, rt, 30 min



355

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
	HN_3 , $\text{BF}_3 \cdot \text{OEt}_2$, CHCl_3 , 0° to rt, 24 h	 (25)	356						
 (20)		 (23)	357						
	A. NaN_3 , perchloric acid, 75° , 5 h B. NaN_3 , HCl (concd), 60° , 6 h	<table border="1" data-bbox="585 520 665 694"> <thead> <tr> <th>R</th> <th>Conditions</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(50)</td> </tr> <tr> <td>Cl</td> <td>(23)</td> </tr> </tbody> </table>	R	Conditions	H	(50)	Cl	(23)	357
R	Conditions								
H	(50)								
Cl	(23)								
	NaN_3 , H_2SO_4 , CHCl_3 , 0 – 50° , 5 h	 (48)	263						



R	(78)
Ph	(85)
4-FC ₆ H ₄	(72)
4-MeOC ₆ H ₄	(71)
2-C ₁₀ H ₇	(65)
4-PhC ₆ H ₄	
R	(91)
Ph	(96)
4-FC ₆ H ₄	(94)
4-MeOC ₆ H ₄	(89)
2-C ₁₀ H ₇	(61)
4-PhC ₆ H ₄	
R	(87)
Ph	(85)
4-FC ₆ H ₄	(67)
4-MeOC ₆ H ₄	(77)
2-C ₁₀ H ₇	(85)
4-PhC ₆ H ₄	
R	(89)
Ph	(93)
4-FC ₆ H ₄	(91)
4-MeOC ₆ H ₄	(88)
2-C ₁₀ H ₇	(90)
4-PhC ₆ H ₄	



358

358

358

358

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p data-bbox="196 347 402 418">NaN_3, HCl (concd), rt, 12 h</p>	 <p data-bbox="196 418 402 609">(35)</p>	<p data-bbox="196 609 402 710">359</p>

^a Silica sulfuric acid is silica-bound sulfuric acid generated by treating silica gel with chlorosulfonic acid.

^b The reaction was performed in the presence of 1 equivalent of dimethyl phosphite.

^c The reaction was performed in the presence of 1 equivalent of diethyl phosphite.

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃






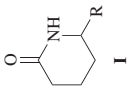

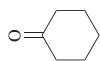
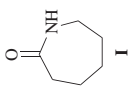


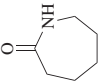
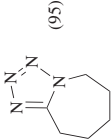

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
 C ₄	HN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 2 h	 (20)	360												
 C ₅	NaN ₃ , silica sulfuric acid, ^a 60°, 25 min	 (95)	282												
 C ₅₋₈	HN ₃ , H ₂ SO ₄ , CHCl ₃ , 5°, 1 h	 I <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R</td> <td>(80)</td> </tr> <tr> <td>H</td> <td>(75)</td> </tr> <tr> <td>Me</td> <td>(63)</td> </tr> <tr> <td>Et</td> <td>(61)</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>(46)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td></td> </tr> </table>	R	(80)	H	(75)	Me	(63)	Et	(61)	<i>n</i> -Pr	(46)	<i>i</i> -Pr		53
R	(80)														
H	(75)														
Me	(63)														
Et	(61)														
<i>n</i> -Pr	(46)														
<i>i</i> -Pr															
	NaN ₃ , PPA, 50°, 9–14 h	 I <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R</td> <td>(83)</td> </tr> <tr> <td>H</td> <td>(87)</td> </tr> <tr> <td>Me</td> <td>(82)</td> </tr> <tr> <td><i>n</i>-Pr</td> <td></td> </tr> </table>	R	(83)	H	(87)	Me	(82)	<i>n</i> -Pr		54				
R	(83)														
H	(87)														
Me	(82)														
<i>n</i> -Pr															
 C ₆	NaN ₃ , HCl	 (63)	1												
	NaN ₃ , AcOH, HBr (cat)	 I (56)	1												

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.		
		Promoter	<i>x</i>	Time (h)			
 C ₆	TMSN ₃ , Promoter (<i>x</i> eq), DCE, rt	 I (70)	FeCl ₃	1.0	0.5	(82)	286
		I (96)	FeCl ₃	0.1	12	(78)	
		I (89)	InBr ₃	0.5	3	(40)	56
		I (92)	InCl ₃	0.5	3	(30)	
		I (70)	ZrCl ₄	0.5	3	(15)	286
	NaN ₃ , FeCl ₃ (1 eq), DCE, rt, 3 h	I (96)					56
	NaN ₃ , MeOH, DMIE, -30° to rt, 3 h	I (89)					54
	NaN ₃ , PPA, 50°, 8 h	I (92)					282
	NaN ₃ , silica sulfuric acid, ^a 60°, 35 min	I (70)					289
	NaN ₃ , P ₂ O ₅ -SiO ₂ , MW, 7 min	I (88)					288
	NaN ₃ , Fe(HSO ₄) ₃ , grinding, 50°, 20 min	 (95)					70
	NaN ₃ , SiCl ₄ , MeCN, rt, 20 h	 (90)					195
	1. NaN ₃ , H ₂ SO ₄ 2. HCl						

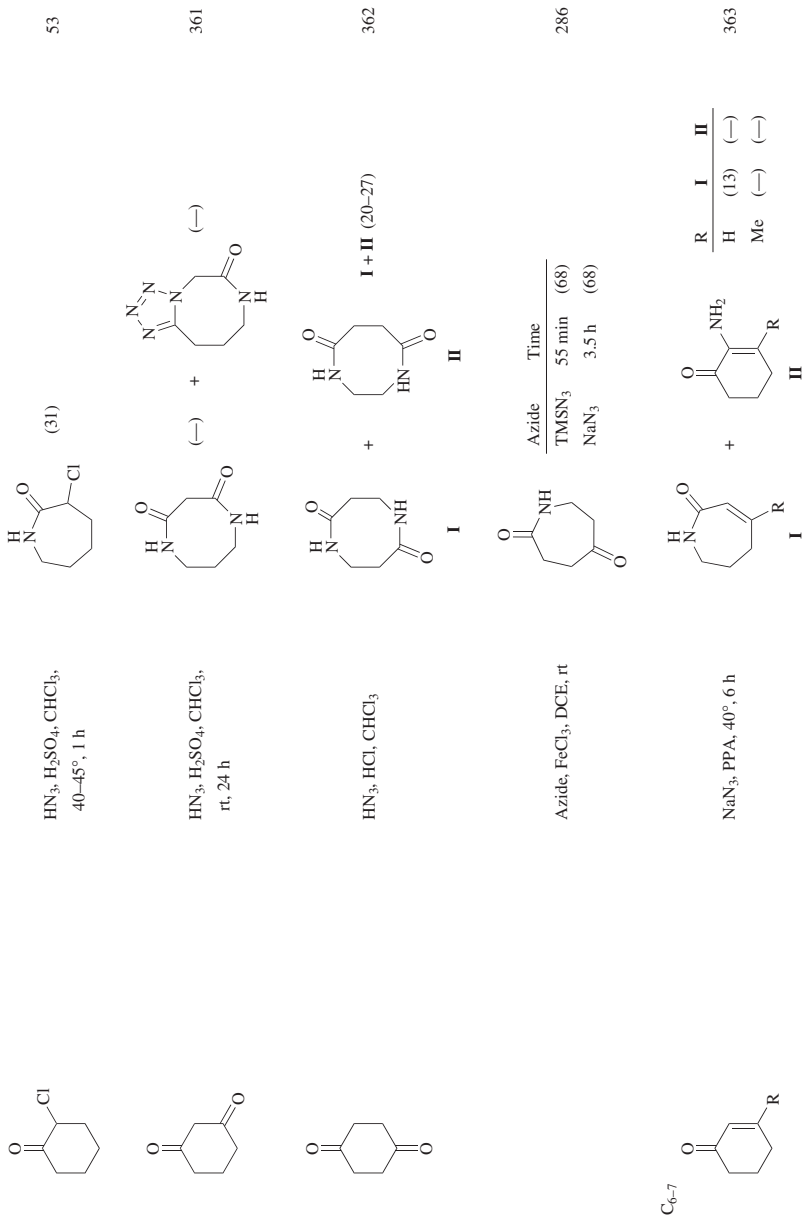
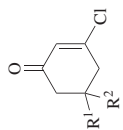
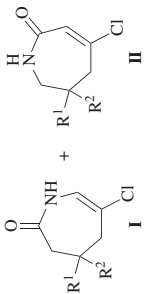

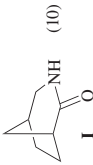

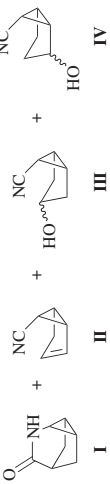
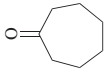
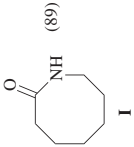
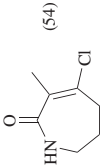
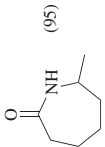
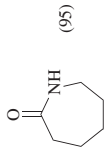


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																	
<p>C_{6-8}</p> 	<p>NaN_3, PPA, 120°, 2 h</p>		<table border="1"> <thead> <tr> <th>R^1</th> <th>R^2</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(11)</td> <td>(15)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>(17)</td> <td>(35)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(32)</td> <td>(36)</td> </tr> </tbody> </table>	R^1	R^2	I	II	H	H	(11)	(15)	Me	H	(17)	(35)	Me	Me	(32)	(36)	364 365 365
R^1	R^2	I	II																	
H	H	(11)	(15)																	
Me	H	(17)	(35)																	
Me	Me	(32)	(36)																	
<p>C_7</p> 	<p>NaN_3, H_2SO_4, PhH, 15°</p>	 <p>I (43)</p>	366																	
	<p>HN_3, H_2SO_4, P_2O_5, CHCl_3, 0° to rt, 4 h</p>	<p>I (16)</p>	367																	
	<p>NaN_3, HCl, 5°, 5 h</p>	<p>I (34)</p>	367																	
	<p>NaN_3, PPA, 60°, 2 d</p>		368																	
	<p>NaN_3, H_2SO_4, CHCl_3, 0° to rt, 12 h</p>	 <p>I (11), II (13), III + IV (33)</p>	369																	
	<p>NaN_3, PPA, 50°, 9 h</p>	 <p>I (89)</p>	54																	
	<p>NaN_3, silica sulfuric acid,^a 60°, 35 min</p>	<p>I (92)</p>	282																	

NaN ₃ , P ₂ O ₅ -SiO ₂ , MW, 7 min	I (72)	289						
NaN ₃ , Fe(HSO ₄) ₃ , grinding, 50°	I (90)	288						
Azide, FeCl ₃ , DCE, rt	<table border="1"> <thead> <tr> <th>Azide</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>TMSN₃</td> <td>45 min (80)</td> </tr> <tr> <td>NaN₃</td> <td>3 h (72)</td> </tr> </tbody> </table>	Azide	Time	TMSN ₃	45 min (80)	NaN ₃	3 h (72)	286
Azide	Time							
TMSN ₃	45 min (80)							
NaN ₃	3 h (72)							
NaN ₃ , PPA, 120°, 2 h	 (54)	370						
NaN ₃ , silica sulfuric acid, ^a 60°, 30 min	 I (95)	282						
NaN ₃ , P ₂ O ₅ -SiO ₂ , MW, 7 min	I (75)	289						
NaN ₃ , silica sulfuric acid, ^a 60°, 25 min	 I (95)	282						
NaN ₃ , P ₂ O ₅ -SiO ₂ , MW, 7 min	I (70)	289						
NaN ₃ , Fe(HSO ₄) ₃ , grinding, 50°, 20 min	I (90)	288						

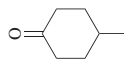
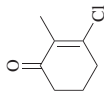
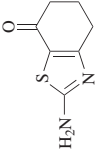
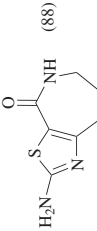
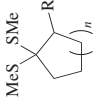

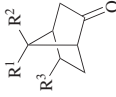
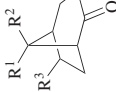
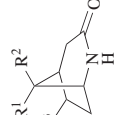
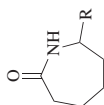


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																														
 C_7	NaN_3 , H_2SO_4 , CHCl_3 , rt, 24 h	 (88)	371																														
 C_7 - 10	1. IN_3 , CH_2Cl_2 , -78 to -10° , 2 h 2. TFA, CHCl_3 , rt, 2 h	<table border="1"> <thead> <tr> <th>n</th> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>H</td> <td>(73)</td> </tr> <tr> <td>2</td> <td>H</td> <td>(76)</td> </tr> <tr> <td>2</td> <td>Me</td> <td>(60)</td> </tr> <tr> <td>3</td> <td>H</td> <td>(59)</td> </tr> <tr> <td>4</td> <td>H</td> <td>(65)</td> </tr> </tbody> </table>	n	R	Yield (%)	1	H	(73)	2	H	(76)	2	Me	(60)	3	H	(59)	4	H	(65)	83												
n	R	Yield (%)																															
1	H	(73)																															
2	H	(76)																															
2	Me	(60)																															
3	H	(59)																															
4	H	(65)																															
 C_7 - 14	TMSN_3 , SnCl_4 , I_2 , CH_2Cl_2 , -78° to rt, 2.5 h	<table border="1"> <thead> <tr> <th>n</th> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>H</td> <td>(95)</td> </tr> <tr> <td>2</td> <td>H</td> <td>(46)</td> </tr> <tr> <td>2</td> <td>Me</td> <td>(31)</td> </tr> <tr> <td>3</td> <td>H</td> <td>(51)</td> </tr> <tr> <td>4</td> <td>H</td> <td>(38)</td> </tr> </tbody> </table>	n	R	Yield (%)	1	H	(95)	2	H	(46)	2	Me	(31)	3	H	(51)	4	H	(38)	83												
n	R	Yield (%)																															
1	H	(95)																															
2	H	(46)																															
2	Me	(31)																															
3	H	(51)																															
4	H	(38)																															
 C_7 - 14	NaN_3 , H_2SO_4 , CHCl_3 , rt, 1-36 h	 I +  II	68																														
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(35)</td> <td>100:0</td> </tr> <tr> <td>H</td> <td>MeO</td> <td>H</td> <td>(48)</td> <td>73:27</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>H</td> <td>(28)</td> <td>85:15</td> </tr> <tr> <td>H</td> <td>Br</td> <td>H</td> <td>(37)</td> <td>81:19</td> </tr> <tr> <td>H</td> <td>TsO</td> <td>H</td> <td>(52)</td> <td>35:65</td> </tr> </tbody> </table>	R ¹	R ²	R ³	I + II	I:II	H	H	H	(35)	100:0	H	MeO	H	(48)	73:27	H	Cl	H	(28)	85:15	H	Br	H	(37)	81:19	H	TsO	H	(52)	35:65	
R ¹	R ²	R ³	I + II	I:II																													
H	H	H	(35)	100:0																													
H	MeO	H	(48)	73:27																													
H	Cl	H	(28)	85:15																													
H	Br	H	(37)	81:19																													
H	TsO	H	(52)	35:65																													

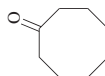
Cl	H	H	(29)	83:17
Br	H	H	(41)	100:0
TsO	H	H	(40)	36:64
MeO ₂ C	H	H	(31)	66:34
MeO ₂ C	H	Br	(52)	52:48

C₇₋₁₈

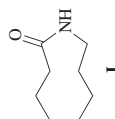


NaN₃, H₂SO₄ or PPA,
0–50°, 1–10 h

R	
Me	(96)
NC–	(76)
Et	(93)
<i>n</i> -Pr	(97)
EtO ₂ C	(80)
<i>i</i> -Bu	(77)
<i>n</i> -C ₆ H ₁₃	(16)
Bn	(49)
4-MeC ₆ H ₄ CH ₂	(45)
2-MeOC ₆ H ₄ CH ₂	(42)
4-MeOC ₆ H ₄ CH ₂	(40)
<i>n</i> -C ₁₂ H ₂₅	(25)



C₈



NaN₃, silica sulfuric acid,^a
60°, 25 min

282

NaN₃, P₂O₅-SiO₂, MW, 7 min

I (70)

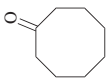
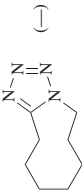
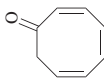
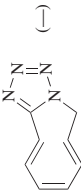
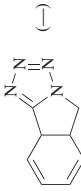
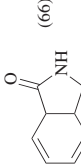
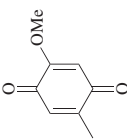
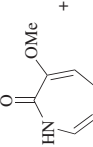
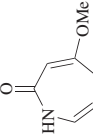
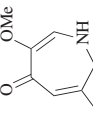
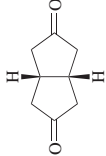
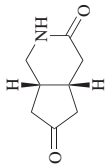
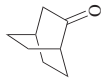
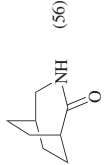
289

NaN₃, Fe(HSO₄)₃, grinding,
50°, 25 min

I (92)

288

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN ₃ , H ₂ SO ₄ , 0° to rt, 12 h	 (—)	373
	NaN ₃ , TFA, 0° to rt, 6 h	 (—) +  (—)	373
	NaN ₃ , HCl, 0° to rt, 5 h	 (66)	373
	NaN ₃ , H ₂ SO ₄ , 0–70°, 70 h	 (22) +  (16) +  (13)	374
	NaN ₃ , HCl, rt, 3 h	 (52)	116
	HN ₃ , AcOH, 0° to rt, 3 h	 (56)	375

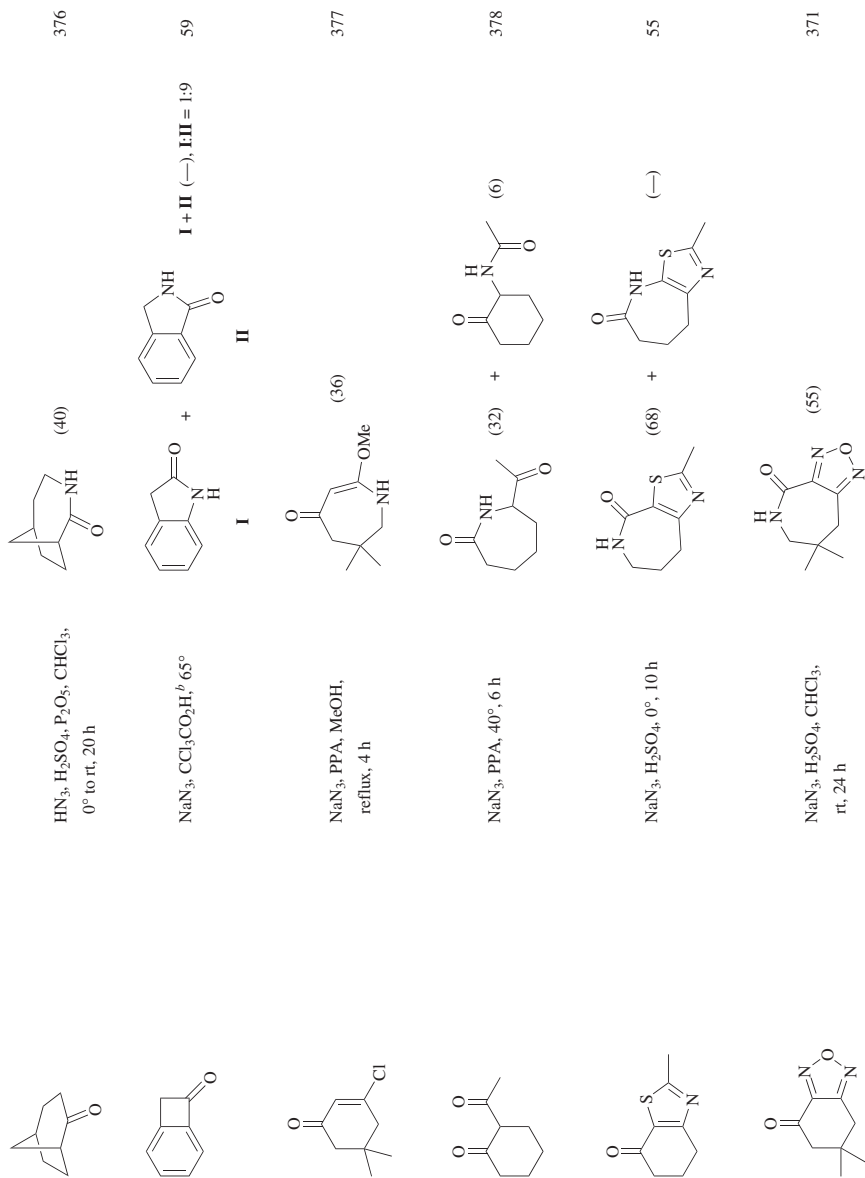
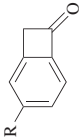
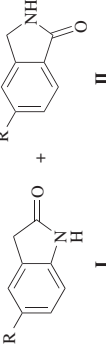
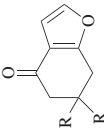
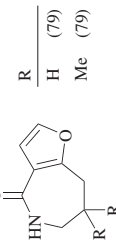
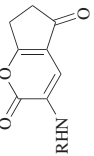
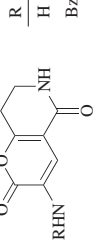
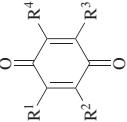
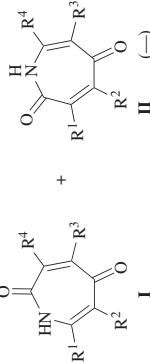
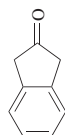


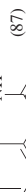
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₈₋₉	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH}, 60^\circ$</p>	 R H (—) 7:3 59 MeO (—) 1:9	
 C ₈₋₁₀	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, 0^\circ, 10 \text{ h}$</p>	 R H (79) Me (79)	379
 C ₈₋₁₅	<p>$\text{TMSN}_3, \text{H}_2\text{SO}_4, \text{CH}_2\text{Cl}_2,$ $\text{rt}, 3 \text{ h}$</p>	 R H (67) Bz (71)	380
 C ₈₋₂₁	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4$</p>	 R ¹ R ² R ³ R ⁴ I H Me H Me (80) H Me Me (80) H <i>i</i> -Pr H Me (75) Me Me Me Me (80) H H H <i>i</i> -Pr (—) H H Bn Bn (—) Me H Bn Bn (—)	71 71 71 71 381 381 381

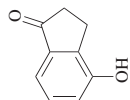
C₉



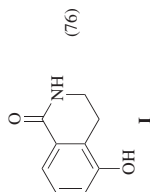
NaN₃, H₂SO₄, CHCl₃,
40°, 3 h



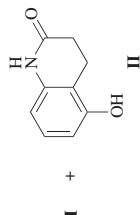
382



NaN₃, TFA, 70°, 18 h



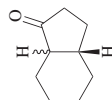
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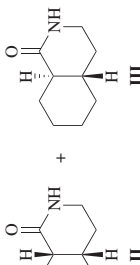
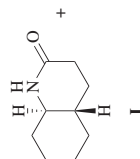
TMSN₃, MsOH, MsCl, <5°

I + II (92), I:II = 1:2.5

384

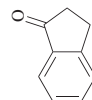


NaN₃, H₂SO₄, CHCl₃, rt, 1 h

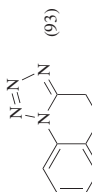


385

I + III (-), I:II:III = 3.5:2.6:1

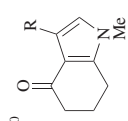
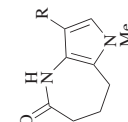
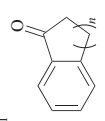
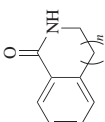
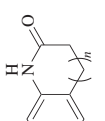
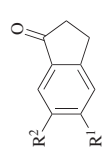
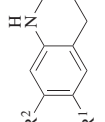
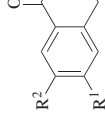


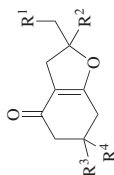
NaN₃, SiCl₄, MeCN, rt, 13 h



70

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																										
 C_9-10	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3,$ rt, 30 min	 H (40) Me (31)	392																																																										
 C_9-11	NaN_3, HCl (concd)	 I	 II	<table border="1"> <thead> <tr> <th>n</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>2</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>3</td> <td>(7)</td> <td>(87)</td> </tr> </tbody> </table>	n	I	II	1	(—)	(—)	2	(—)	(—)	3	(7)	(87)	393																																												
n	I	II																																																											
1	(—)	(—)																																																											
2	(—)	(—)																																																											
3	(7)	(87)																																																											
	A: $\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH}, 60^\circ$ B: $\text{NaN}_3, \text{CCl}_3\text{CO}_2\text{H}, 65^\circ$	 I	 II	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Conditions</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>A</td> <td>7:3</td> </tr> <tr> <td>H</td> <td>H</td> <td>B</td> <td>1:4</td> </tr> <tr> <td>H</td> <td>HO</td> <td>A</td> <td>1:4</td> </tr> <tr> <td>H</td> <td>HO</td> <td>B</td> <td>1:9</td> </tr> <tr> <td>HO</td> <td>H</td> <td>A</td> <td>9:1</td> </tr> <tr> <td>HO</td> <td>H</td> <td>B</td> <td>1:4</td> </tr> <tr> <td>H₂N</td> <td>H</td> <td>A</td> <td>1:1</td> </tr> <tr> <td>H₂N</td> <td>H</td> <td>B</td> <td>1:9</td> </tr> <tr> <td>H</td> <td>H₂N</td> <td>A</td> <td>9:1</td> </tr> <tr> <td>H</td> <td>H₂N</td> <td>B</td> <td>1:4</td> </tr> <tr> <td>Cl</td> <td>H</td> <td>A</td> <td>3:2</td> </tr> <tr> <td>Cl</td> <td>H</td> <td>B</td> <td>1:9</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>A</td> <td>4:1</td> </tr> </tbody> </table>	R ¹	R ²	Conditions	I:II	H	H	A	7:3	H	H	B	1:4	H	HO	A	1:4	H	HO	B	1:9	HO	H	A	9:1	HO	H	B	1:4	H ₂ N	H	A	1:1	H ₂ N	H	B	1:9	H	H ₂ N	A	9:1	H	H ₂ N	B	1:4	Cl	H	A	3:2	Cl	H	B	1:9	H	Cl	A	4:1	59
R ¹	R ²	Conditions	I:II																																																										
H	H	A	7:3																																																										
H	H	B	1:4																																																										
H	HO	A	1:4																																																										
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Cl	H	A	3:2																																																										
Cl	H	B	1:9																																																										
H	Cl	A	4:1																																																										



NaN₃, SiCl₄, MeCN, rt

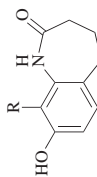
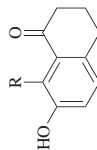


H	Cl	B	1:9
O ₂ N	H	A	9:1
O ₂ N	H	B	1:9
H	O ₂ N	A	4:1
H	O ₂ N	B	1:4
MeO	H	A	1:9
MeO	H	B	1:9
H	MeO	A	7:3
H	MeO	B	1:4
AcHN	H	A	9:1
AcHN	H	B	1:9
H	AcHN	A	9:1
H	AcHN	B	—
AcO	H	A	—
AcO	H	B	1:4
H	AcO	A	—
H	AcO	B	1:9

R ¹	R ²	R ³	R ⁴	I	II
Br	H	H	H	(68)	(—)
Br	H	Me	H	(56)	(—)
Br	Me	H	H	(89)	(—)
Br	H	Me	Me	(65)	(—)
I	H	H	H	(42)	(18)
I	H	H	Me	(44)	(14)
I	Me	H	H	(42)	(19)
I	H	Me	Me	(50)	(—)

R ¹	R ²	R ³	Conditions	I + II	I:II
H	H	H	A	(78)	10:1
H	H	H	B	(85)	3.3:1
H	H	H	C	(81)	4.5:1
H	Me	H	A	(94)	38:1
H	Me	H	B	(96)	3.2:1
H	Me	H	C	(99)	4.2:1
H	Me	H	D	(96)	20:1
Me	Me	H	A	(85)	17.5:1
Me	Me	H	C	(83)	2.3:1
H	H	Bz	B	(99)	3.9:1
H	H	Bz	D	(98)	21:1
H	Me	Bz	B	(97)	4.3:1
H	Me	Bz	D	(92)	10:1
Me	Me	Bz	A	(99)	9:1
Me	Me	Bz	B	(98)	3.1:1
Me	Me	Bz	D	(98)	18:1

C₁₀

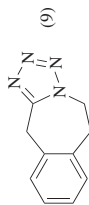
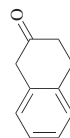


NaN₃, MeOH, 8°, 1 h



H (76)
O₂N (84)

287

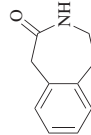


HN₃, BF₃•OEt₂, PhH, rt, 24 h

(21)

(9)

396

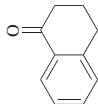
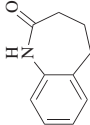

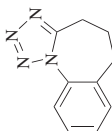
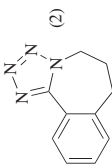


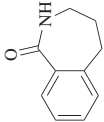
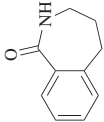
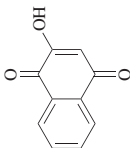
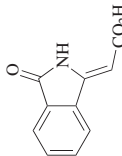
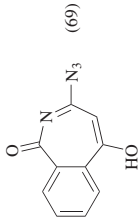


Azide Time
TMSN₃ 46 min (70)
NaN₃ 2.5 h (67)

Azide, FeCl₃, DCE, rt

286

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
	NaN ₃ , CCl ₃ CO ₂ H, ^b 60°	 I (85)	1						
	Azide, FeCl ₃ , DCE, rt	<table border="1"> <thead> <tr> <th>Azide</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>TMSN₃</td> <td>40 min (80)</td> </tr> <tr> <td>NaN₃</td> <td>2.5 h (75)</td> </tr> </tbody> </table>	Azide	Time	TMSN ₃	40 min (80)	NaN ₃	2.5 h (75)	286
Azide	Time								
TMSN ₃	40 min (80)								
NaN ₃	2.5 h (75)								
	HN ₃ , BF ₃ ·OEt ₂ , PhH, rt, 24 h	 I (5) +  (33) +  (2)  II	396						
	NaN ₃ , HCl, 0° to rt, 4 h	 I (42) +  (13) +  (13)	397						
	NaN ₃ (1.3 eq), H ₂ SO ₄ , 5° to rt, 2 h	 (80)	398						
	NaN ₃ (10 eq), H ₂ SO ₄ , 0°, 15 min	 (69)	398						

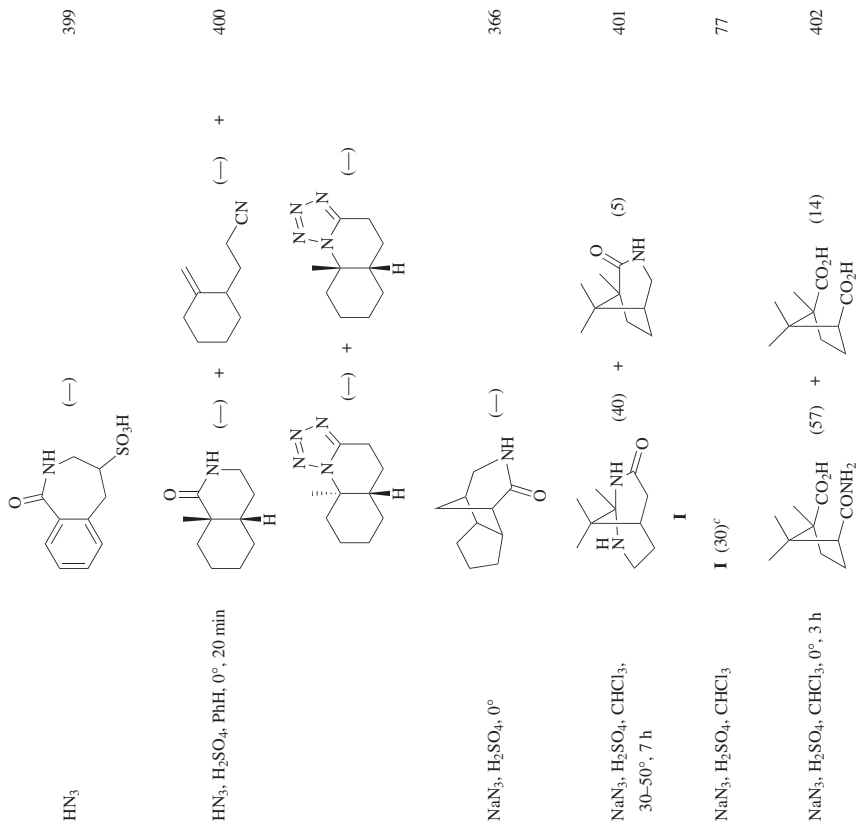
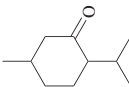
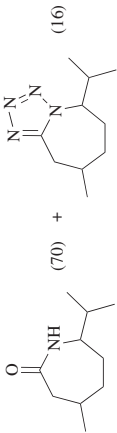

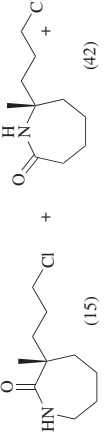
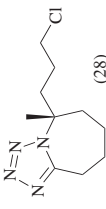
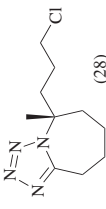
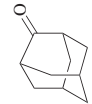
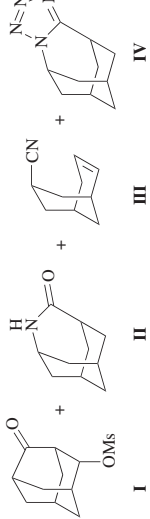


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.		
	NaN ₃ , H ₂ SO ₄ , rt, 50 h		55		
	NaN ₃ , TFA, H ₂ O		29		
					
	NaN ₃		403 403 403 403 403 404		
	Conditions	I	II	III	IV
	MsOH, rt, 50 h	(88)	(11)	(0)	(0)
	MsOH, AcOH, rt, 50 h	(3)	(33)	(61)	(0)
	TFA, rt, 3 h	(0)	(60)	(40)	(0)
	MsOH, CHCl ₃ , rt, 20 h	(36)	(34)	(10)	(8)
	MsOH, AcOH, 24 h	(0)	(70)	(30)	(0)
	AcOH, <i>p</i> -T ₂ SOH	(0)	(31)	(0)	(0)

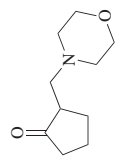
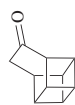
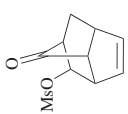
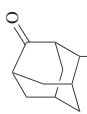
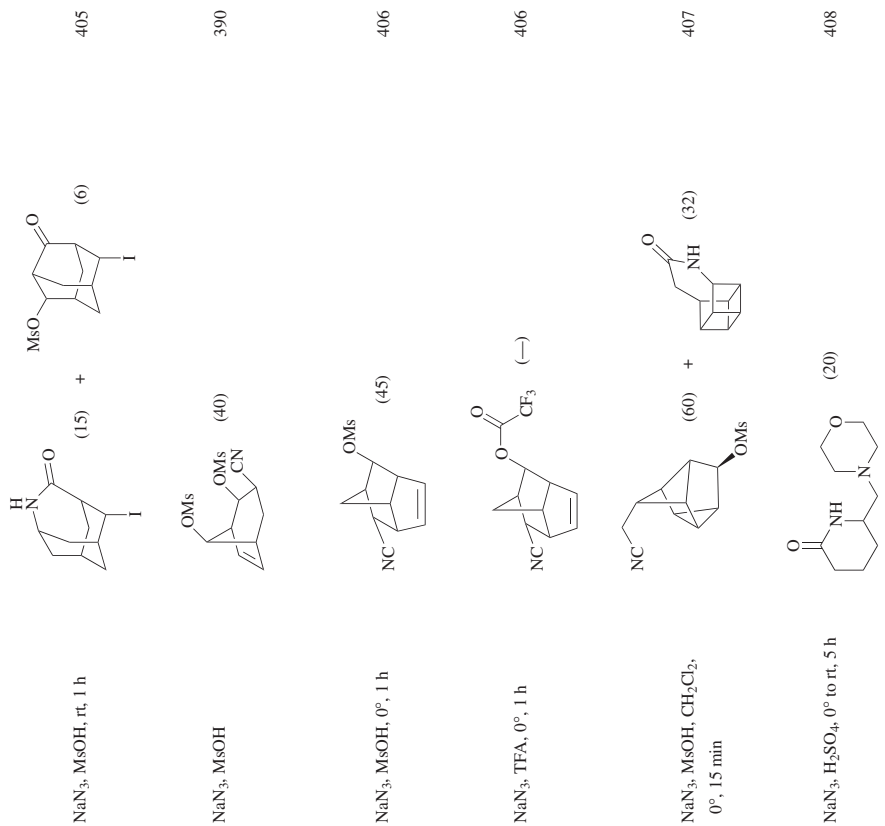
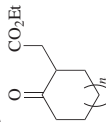
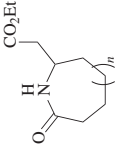
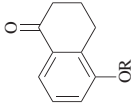
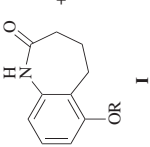
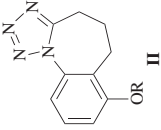
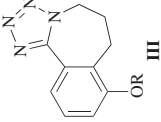
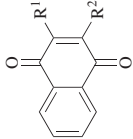
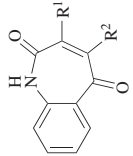
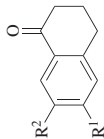
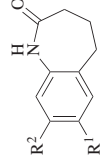
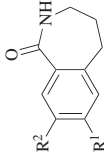
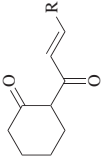
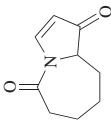
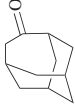
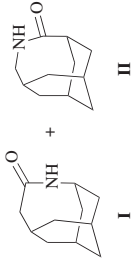
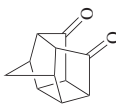
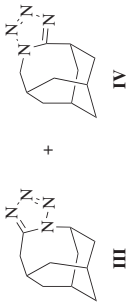
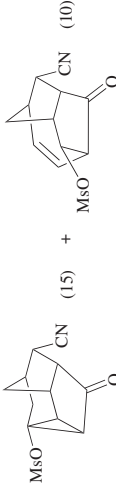
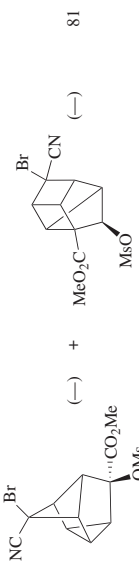
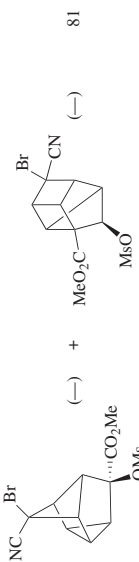
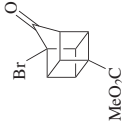
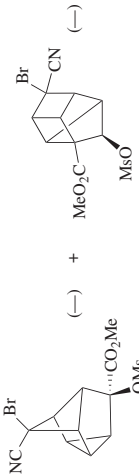


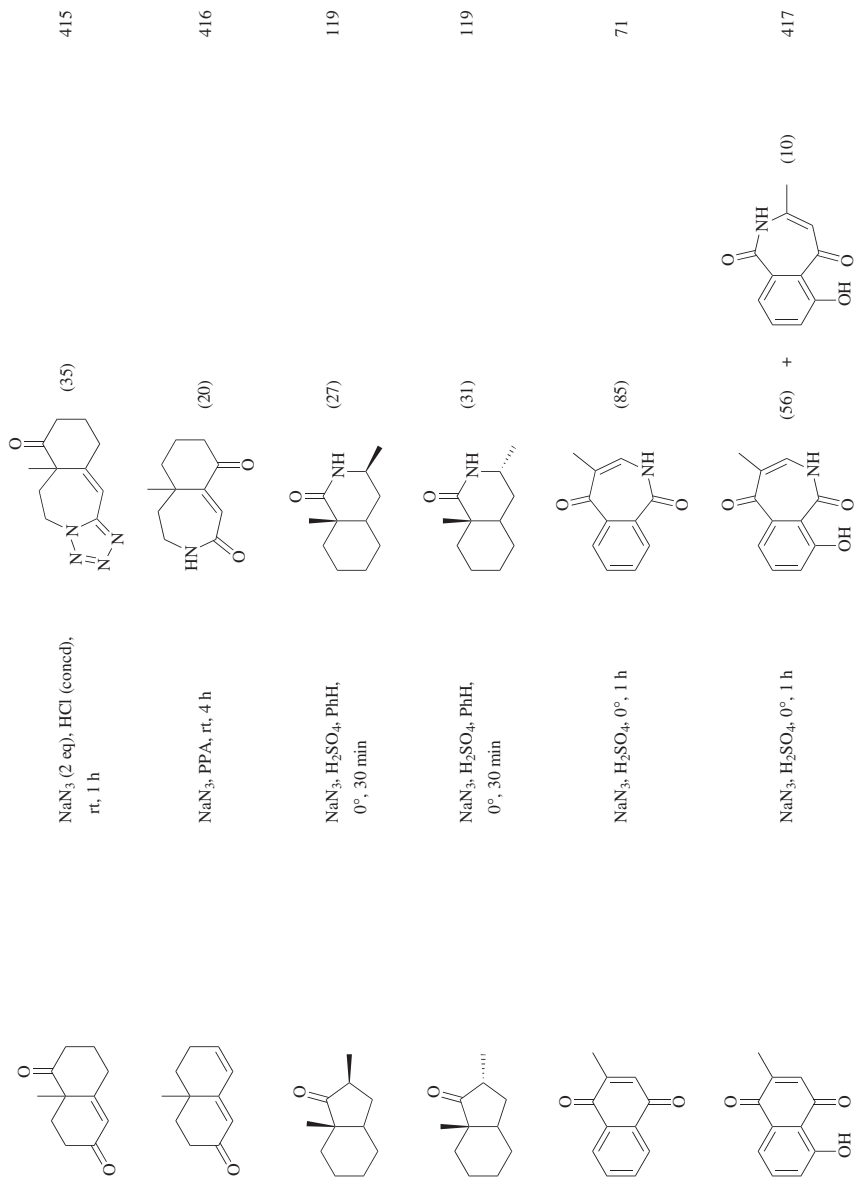
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
 C ₁₀₋₁₁	NaN ₃ , H ₂ SO ₄ , 0°, 10 h	 <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td><i>n</i></td> <td></td> </tr> <tr> <td>1</td> <td>(74)</td> </tr> <tr> <td>2</td> <td>(80)</td> </tr> </table>	<i>n</i>		1	(74)	2	(80)	409									
<i>n</i>																		
1	(74)																	
2	(80)																	
	NaN ₃ , CCl ₃ CO ₂ H, ^b reflux, 6 h	  	410															
	NaN ₃ , H ₂ SO ₄ , rt	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R¹</td> <td>R²</td> <td></td> </tr> <tr> <td>H</td> <td>Cl</td> <td>(22)</td> </tr> <tr> <td>Cl</td> <td>Cl</td> <td>(49)</td> </tr> <tr> <td>Cl</td> <td>Br</td> <td>(12)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>(50)</td> </tr> </table> 	R ¹	R ²		H	Cl	(22)	Cl	Cl	(49)	Cl	Br	(12)	H	Me	(50)	411
R ¹	R ²																	
H	Cl	(22)																
Cl	Cl	(49)																
Cl	Br	(12)																
H	Me	(50)																
 C ₁₀₋₁₂	A: NaN ₃ , H ₂ SO ₄ , PhH, 60° B: NaN ₃ , CCl ₃ CO ₂ H, ^b 65°	  I + II (—) 59	59															

R ¹	R ²	Conditions	I:H
H	H	A	4:1
H	H	B	7:3
H ₂ N	H	A	4:1
H ₂ N	H	B	4:1
H	H ₂ N	A	9:1
H	H ₂ N	B	3:2
HO	H	A	3:2
HO	H	B	2:3
H	HO	A	4:1
H	HO	B	7:3
Cl	H	A	9:1
Cl	H	B	3:2
H	Cl	A	4:1
H	Cl	B	7:3
O ₂ N	H	A	9:1
O ₂ N	H	B	4:1
H	O ₂ N	A	9:1
H	O ₂ N	B	9:1
MeO	H	A	1:1
MeO	H	B	1:1
H	MeO	A	4:1
H	MeO	B	7:3
AcHN	H	A	9:1
AcHN	H	B	2:3
H	AcHN	A	9:1
H	AcHN	B	7:3
AcO	H	A	—
AcO	H	B	7:3
H	AcO	A	—
H	AcO	B	7:3

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
 C ₁₀₋₁₆	NaN ₃ (2 eq), H ₂ SO ₄	 + RNH ₂ (—) <table border="1" style="margin-left: 20px;"> <tr> <td>R</td> <td>Yield (%)</td> </tr> <tr> <td>Me</td> <td>(76)</td> </tr> <tr> <td>Ph</td> <td>(76)</td> </tr> <tr> <td>4-O₂NC₆H₄</td> <td>(82)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>(70)</td> </tr> </table>	R	Yield (%)	Me	(76)	Ph	(76)	4-O ₂ NC ₆ H ₄	(82)	4-MeOC ₆ H ₄	(70)	412
R	Yield (%)												
Me	(76)												
Ph	(76)												
4-O ₂ NC ₆ H ₄	(82)												
4-MeOC ₆ H ₄	(70)												
 C ₁₁	NaN ₃ , MsOH, rt, 24 h	 I + II (7), I:II = 1:1 III + IV (48), III:IV = 1:1	413										
	NaN ₃ , MsOH, CH ₂ Cl ₂ , 0°, 2 h	 III + IV (48), III:IV = 1:1  (15) + (10)  (—) + (81)  (—) + (81)	414										
	NaN ₃ , MsOH, 0°, 10 min	 (—) + (81)	81										



NaN₃ (2 eq), HCl (concd),
rt, 1 h

NaN₃, PPA, rt, 4 h

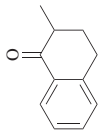
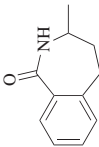
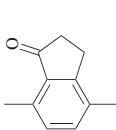
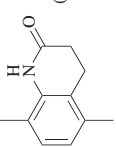
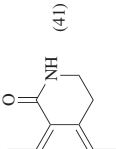
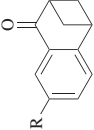
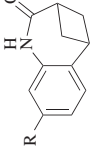
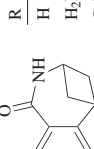
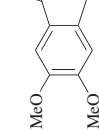
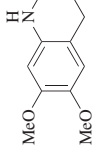
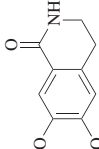
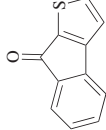
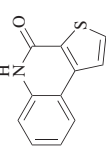
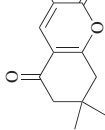
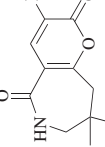
NaN₃, H₂SO₄, PhH,
0°, 30 min

NaN₃, H₂SO₄, PhH,
0°, 30 min

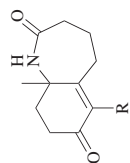
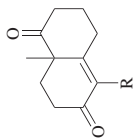
NaN₃, H₂SO₄, 0°, 1 h

NaN₃, H₂SO₄, 0°, 1 h

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

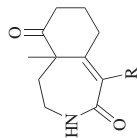
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.													
	NaN ₃ , HCl, 0° to rt, 4 h	 (34)	397													
	NaN ₃ , PPA, 60°	 (24) +  (41)	387													
	NaN ₃ , H ₂ SO ₄ , PhH, 60°, 12 h	 +  R	<table border="0" style="display: inline-table; vertical-align: middle;"> <tr> <td>R</td> <td>I</td> <td>II</td> </tr> <tr> <td>H</td> <td>(68)</td> <td>(23)</td> </tr> <tr> <td>H₂N</td> <td>(56)</td> <td>(24)</td> </tr> <tr> <td>O₂N</td> <td>(64)</td> <td>(16)</td> </tr> </table>	R	I	II	H	(68)	(23)	H ₂ N	(56)	(24)	O ₂ N	(64)	(16)	418
R	I	II														
H	(68)	(23)														
H ₂ N	(56)	(24)														
O ₂ N	(64)	(16)														
	TMSN ₃ , MsOH, MsCl, <0°	 +  II	384													
	HN ₃ , CCl ₃ CO ₂ H, H ₂ SO ₄ , 55°	 (—)	419													
	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 0° to rt, 4 h	 R	<table border="0" style="display: inline-table; vertical-align: middle;"> <tr> <td>R</td> <td>(71)</td> </tr> <tr> <td>H</td> <td>(91)</td> </tr> <tr> <td>PhCO</td> <td>(91)</td> </tr> </table>	R	(71)	H	(91)	PhCO	(91)	420						
R	(71)															
H	(91)															
PhCO	(91)															

C₁₁₋₁₂



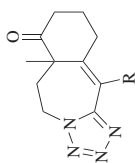
NaN₃ (2 eq), H₂SO₄, 5°, 1 h

415



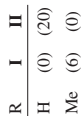
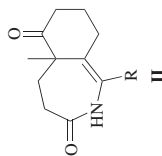
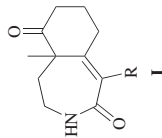
NaN₃ (1 eq), HCl (concd),
rt, 45 min

415



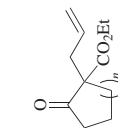
NaN₃ (2 eq), HCl (concd),
rt, 1 h

415



NaN₃ (3 eq), CCl₃CO₂H,^b
60°, 2.5 h

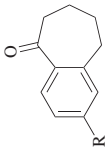
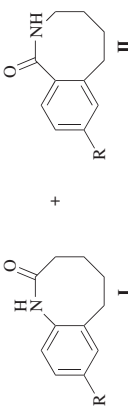
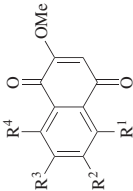
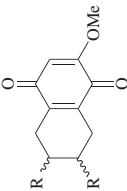
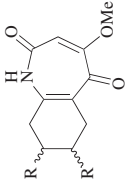
415

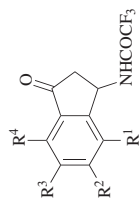
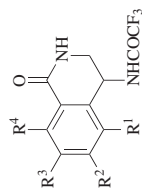


NaN₃, H₂SO₄, CHCl₃,
rt, 1 h

415a

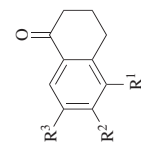
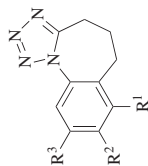
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																	
	A: NaN_3 , H_2SO_4 , PhH, 60°																																																																			
	B: NaN_3 , $\text{CCl}_3\text{CO}_2\text{H}$, 65°																																																																			
	C: NaN_3 , HCl, DME, rt																																																																			
	D: NaN_3 , concd HCl																																																																			
	NaN_3 , H_2SO_4 , 0° to rt, 24 h	<table border="1"> <thead> <tr> <th>R</th> <th>Conditions</th> <th>I + II</th> <th>EI</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>A</td> <td>(-)</td> <td>4:1</td> </tr> <tr> <td>H</td> <td>B</td> <td>(-)</td> <td>4:1</td> </tr> <tr> <td>H</td> <td>C</td> <td>(83)</td> <td>1:0</td> </tr> <tr> <td>H</td> <td>D</td> <td>(89)</td> <td>1:0</td> </tr> <tr> <td>MeO</td> <td>A</td> <td>(-)</td> <td>4:1</td> </tr> <tr> <td>MeO</td> <td>B</td> <td>(-)</td> <td>4:1</td> </tr> </tbody> </table>	R	Conditions	I + II	EI	H	A	(-)	4:1	H	B	(-)	4:1	H	C	(83)	1:0	H	D	(89)	1:0	MeO	A	(-)	4:1	MeO	B	(-)	4:1	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Me</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>Me</td> <td>H</td> <td>Me</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Me</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>Me</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Me</td> <td>H</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	H	H	H	H	H	H	H	Me	Me	H	H	H	H	Me	H	Me	H	Me	Me	H	Me	H	H	Me	Me	H	Me	H	Me	Me	H	H	59 59 421 422 59 59
		R	Conditions	I + II	EI																																																															
		H	A	(-)	4:1																																																															
		H	B	(-)	4:1																																																															
		H	C	(83)	1:0																																																															
		H	D	(89)	1:0																																																															
		MeO	A	(-)	4:1																																																															
		MeO	B	(-)	4:1																																																															
		R ¹	R ²	R ³	R ⁴																																																															
		H	H	H	H																																																															
		H	H	H	Me																																																															
		Me	H	H	H																																																															
		H	Me	H	Me																																																															
H	Me	Me	H																																																																	
Me	H	H	Me																																																																	
Me	H	Me	H																																																																	
Me	Me	H	H																																																																	
	NaN_3 , H_2SO_4 , rt, 16 h	<table border="1"> <thead> <tr> <th>R</th> <th>(19)</th> <th>(16)</th> <th>(6)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td></td> <td></td> <td></td> </tr> <tr> <td>Cl</td> <td></td> <td></td> <td></td> </tr> <tr> <td>Me</td> <td></td> <td></td> <td></td> </tr> </tbody> </table>	R	(19)	(16)	(6)	H				Cl				Me					424																																																
		R	(19)	(16)	(6)																																																															
		H																																																																		
Cl																																																																				
Me																																																																				

C₁₁₋₁₄NaN₃, TFA, reflux, 5 h

425

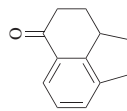
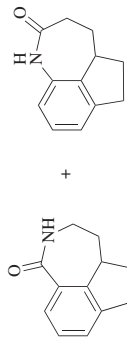
R ¹	R ²	R ³	R ⁴
H	H	H	H
H	F	H	H
H	H	F	H
Br	H	H	H
Cl	Cl	H	H
Me	H	H	H
H	Me	H	H
H	H	Me	H
Me	H	Me	H
H	H	Et	H
H	H	<i>i</i> -Pr	H

NaN₃, BF₃·OEt₂, PhH,
rt, 24 h

(50-70)

396

R ¹	R ²	R ³
H	H	MeO
H	MeO	MeO
H	MeO	EtO
H	EtO	MeO
H	EtO	EtO

C₁₂NaN₃, PPA, 80°, 5 h**I****I + II (54), I:II = 1:1.5**

426

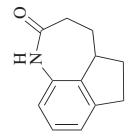

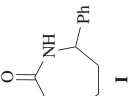
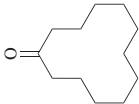
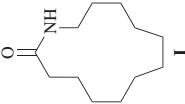
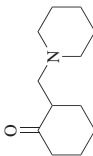
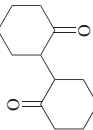
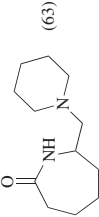
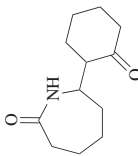
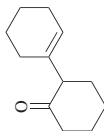
**II**

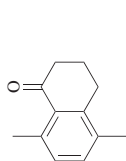
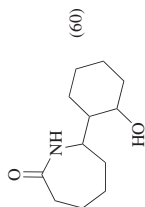
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																					
	A: NaN ₃ , PPA, rt, 18 h	 I	<table border="1"> <thead> <tr> <th>Conditions</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>(40)</td> <td>1:10</td> </tr> <tr> <td>B</td> <td>(30)</td> <td>1:3</td> </tr> <tr> <td>C</td> <td>(60)</td> <td>1:2</td> </tr> <tr> <td>D</td> <td>(40)</td> <td>0:100</td> </tr> <tr> <td>E</td> <td>(15)</td> <td>1.3:1</td> </tr> <tr> <td>F</td> <td>(15)</td> <td>100:0</td> </tr> </tbody> </table>	Conditions	I + II	I:II	A	(40)	1:10	B	(30)	1:3	C	(60)	1:2	D	(40)	0:100	E	(15)	1.3:1	F	(15)	100:0
	Conditions			I + II	I:II																			
	A			(40)	1:10																			
	B			(30)	1:3																			
	C			(60)	1:2																			
	D			(40)	0:100																			
E	(15)	1.3:1																						
F	(15)	100:0																						
B: NaN ₃ , PPA, rt to 55°	368																							
C: NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 0°, 3 h	296																							
D: NaN ₃ , PPA, 0°, 3 h	296																							
E: NaN ₃ , H ₂ SO ₄ , Et ₂ O, rt, 3 h	296																							
F: NaN ₃ , H ₂ SO ₄ , PhH, rt, 3 h	296																							
	A: NaN ₃ , silica sulfuric acid, ^a 60°, 30 min	 I	<table border="1"> <thead> <tr> <th>Conditions</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>(95)</td> </tr> <tr> <td>B</td> <td>(75)</td> </tr> <tr> <td>C</td> <td>(94)</td> </tr> </tbody> </table>	Conditions	Yield (%)	A	(95)	B	(75)	C	(94)													
	Conditions			Yield (%)																				
	A			(95)																				
B	(75)																							
C	(94)																							
B: NaN ₃ , P ₂ O ₅ , MW, 7 min	282																							
C: NaN ₃ , Fe(HSO ₄) ₃ , grinding, 50°, 30 min	289 288																							
	Azide, FeCl ₃ , DCE, rt	<table border="1"> <thead> <tr> <th>Azide</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>I TMSN₃</td> <td>65 min</td> <td>(81)</td> </tr> <tr> <td>NaN₃</td> <td>4 h</td> <td>(65)</td> </tr> </tbody> </table>	Azide	Time	Yield (%)	I TMSN ₃	65 min	(81)	NaN ₃	4 h	(65)	286												
	Azide		Time	Yield (%)																				
I TMSN ₃	65 min	(81)																						
NaN ₃	4 h	(65)																						
	NaN ₃ , HCl (concd), rt	 (63)	333																					
	NaN ₃ , PPA, 15° to rt, 15 h		 (29)	427																				



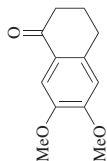
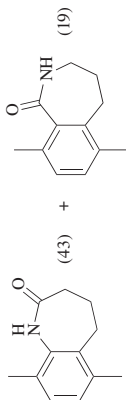
NaN_3 , PPA, 15° to rt, 1.5 h

428



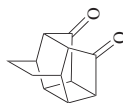
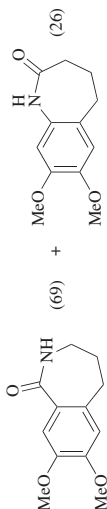
NaN_3 , PPA, 60°

387



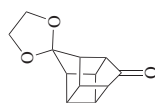
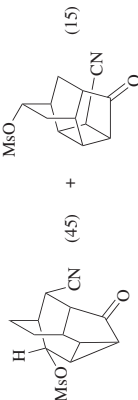
NaN_3 , HCl (concd),
0° to rt, 12 h

429



NaN_3 , MsOH, CH_2Cl_2 ,
0°, 30 min

430



NaN_3 , MsOH, 0°, 1 h

431

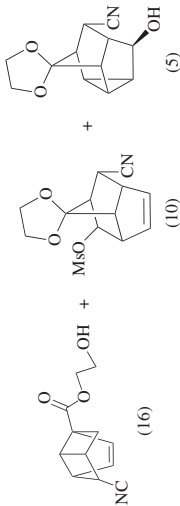
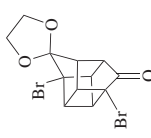
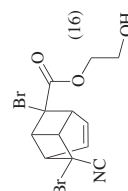
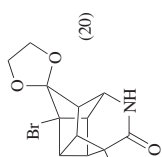

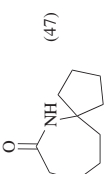
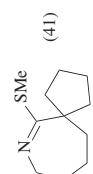
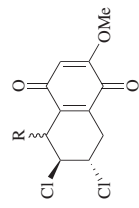
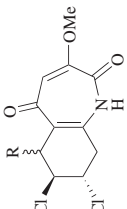
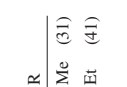
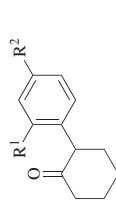
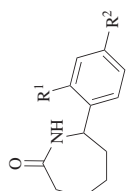
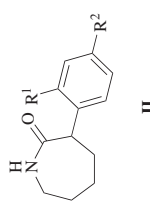
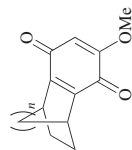


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

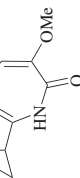
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₂	NaN_3 , MeOH , 0°, 1 h	 (16) +  (20)	431
 C ₁₂₋₁₃	1. IN_3 , CH_2Cl_2 , -78 to -10°, 2 h 2. TFA , CHCl_3 , rt, 2 h	 (47)	83
	TMSN_3 , SnCl_4 , I_2 , CH_2Cl_2 , -78°, 2.5 h	 (41)	83
 C ₁₂₋₁₃	NaN_3 , TFA , 0° to rt, 2.5 h	 (31)  (41)	424
 C ₁₂₋₁₃	A: NaN_3 , PPA , 0°, 6 h B: NaN_3 , H_2SO_4 , PhH , rt, 6 h C: NaN_3 , H_2SO_4 , Et_2O , 0°, 6 h	 I +  II	296

Conditions	R ¹	R ²	I	II
A	H	H	(66)	(—)
B	H	H	(—)	(40)
C	H	H	(—)	(30)
A	H	O ₂ N	(16)	(64)
B	H	O ₂ N	(25)	(45)
C	H	O ₂ N	(—)	(65)
A	O ₂ N	H	(17)	(68)
B	O ₂ N	H	(28)	(47)
C	O ₂ N	H	(39)	(31)
A	O ₂ N	O ₂ N	(—)	(55)
B	O ₂ N	O ₂ N	(—)	(80)
C	O ₂ N	O ₂ N	(—)	(42)
A	H	Me	(10)	(—)
B	H	Me	(40)	(5)
C	H	Me	(15)	(15)
A	H	MeO	(10)	(—)
B	H	MeO	(5)	(—)
C	H	MeO	(11)	(4)

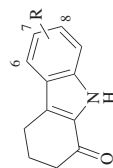
C₁₂₋₁₃



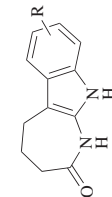
NaI₃, H₂SO₄, 0°, 2 min



424



NaI₃, PPA, 100°, 8 h

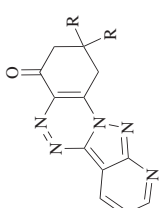
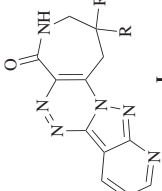
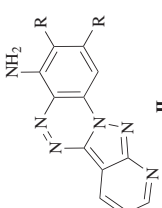

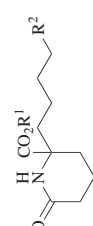

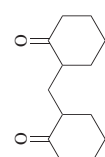
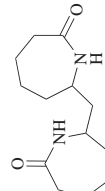

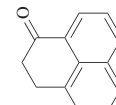
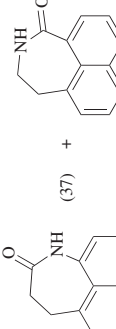
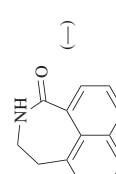
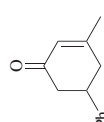
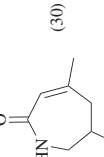


432

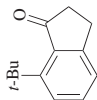
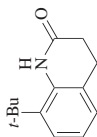
n
1 (14)
2 (31)

R
H (45)
6-Cl (57)
6-Me (49)
7-Me (44)
8-Me (58)

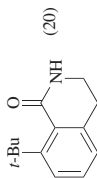
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₂₋₁₄	<p>NaIN₃, H₂SO₄, CHCl₃, rt, 3 h</p>	 I  II 433	
 C ₁₂₋₁₅	<p>NaIN₃, H₂SO₄, CHCl₃</p>	 I  II H (16) (13) Me (6) (17) R ¹ R ² Me NC- (48) Et EtO ₂ C (87) 434	
 C ₁₃	<p>A: NaN₃, HCl, 0°, 30 min B: NaN₃, PPA, rt, 24 h</p>	 A  B Conditions A (57) B (80) 435	
	<p>NaN₃, H₂SO₄, 0°</p>	 (37) +  (-) 436	
	<p>NaN₃, PPA, 0–55°, 7 h</p>	 (30) 368	

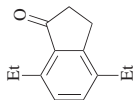
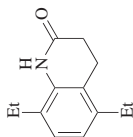
C13

NaN₃, PPA

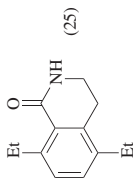
(5) +



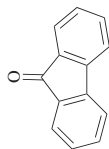
437

NaN₃, PPA, 60°

(10) +



387



A: NaN₃, PPA, 70°, 22 h
 B: NaN₃, CCl₃CO₂H,^b 60°
 C: NaN₃, H₂SO₄

Conditions

A (92)

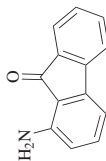
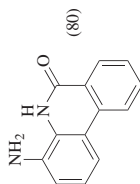
B (55)

C (99)

54

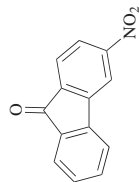
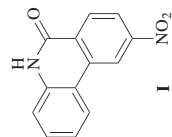
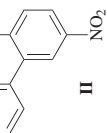
I

I

NaN₃, H₂SO₄

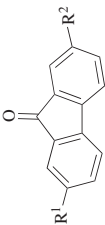
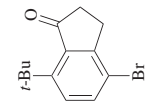
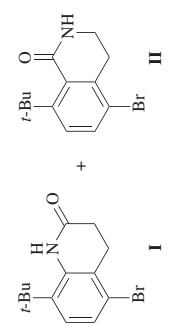
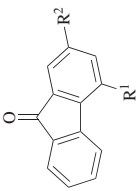
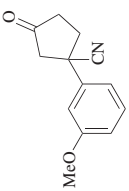
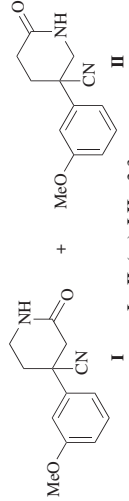
(80)

438

NaN₃, H₂SO₄, CHCl₃**I****II****I + II (98), I:II = 7:3**

439

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
	$\text{NaN}_3, \text{H}_2\text{SO}_4, 0^\circ \text{ to rt}, 24 \text{ h}$	<table border="1" data-bbox="235 477 384 876"> <thead> <tr> <th>R^1</th> <th>R^2</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>H_2N</td> <td>(61)</td> </tr> <tr> <td>Cl</td> <td>O_2N</td> <td>(80)</td> </tr> <tr> <td>Br</td> <td>H_2N</td> <td>(55)</td> </tr> <tr> <td>Br</td> <td>O_2N</td> <td>(100)</td> </tr> </tbody> </table>	R^1	R^2	Yield (%)	Cl	H_2N	(61)	Cl	O_2N	(80)	Br	H_2N	(55)	Br	O_2N	(100)	440
R^1	R^2	Yield (%)																
Cl	H_2N	(61)																
Cl	O_2N	(80)																
Br	H_2N	(55)																
Br	O_2N	(100)																
	$\text{NaN}_3, \text{PPA}, 50^\circ, 9 \text{ h}$	 <p style="text-align: center;">$\text{I} + \text{II} \text{ (47), I:II} = 85:15$</p>	387															
	$\text{NaN}_3, \text{H}_2\text{SO}_4, 0^\circ \text{ to rt}, 48 \text{ h}$	<table border="1" data-bbox="631 529 769 876"> <thead> <tr> <th>R^1</th> <th>R^2</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H_2N</td> <td>H</td> <td>(99)</td> </tr> <tr> <td>O_2N</td> <td>H</td> <td>(96)</td> </tr> <tr> <td>Cl</td> <td>O_2N</td> <td>(71)</td> </tr> </tbody> </table>	R^1	R^2	Yield (%)	H_2N	H	(99)	O_2N	H	(96)	Cl	O_2N	(71)	440			
R^1	R^2	Yield (%)																
H_2N	H	(99)																
O_2N	H	(96)																
Cl	O_2N	(71)																
	$\text{NaN}_3, \text{CCl}_3\text{CO}_2\text{H}^b$	 <p style="text-align: center;">$\text{I} + \text{II} \text{ (-), I:II} = 2:3$</p>	441															
	$\text{NaN}_3, 80\% \text{H}_2\text{SO}_4, \text{PhH}$	$\text{I} + \text{II} \text{ (-), I:II} = 100:0$	441															

C₁₃

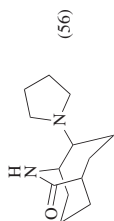
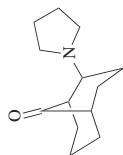
441

I + II (—), **I:II** = 2:3NaN₃, 98% H₂SO₄, PhH

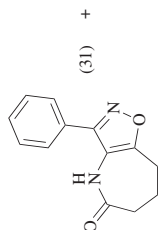
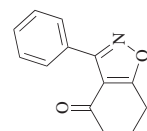
441

I + II (—), **I:II** = 100:0NaN₃, 98% H₂SO₄, CHCl₃

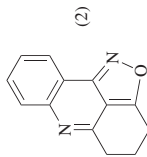
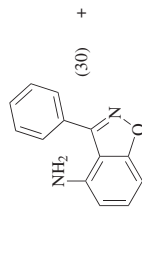
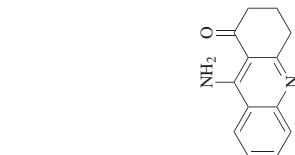
441

I + II (—), **I:II** = 1:1NaN₃, PPANaN₃, H₂SO₄, CHCl₃,
50°, 1 h

442

NaN₃, H₂SO₄, CH₂Cl₂,
rt, 3 h

443

NaN₃, H₂SO₄, CHCl₃,
rt, 8 h

444

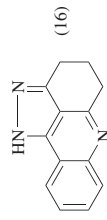
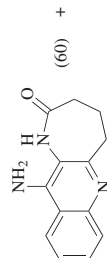
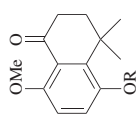
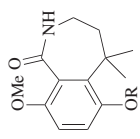
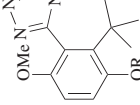
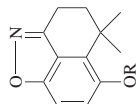
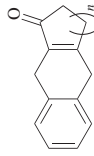
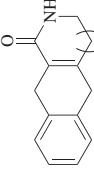
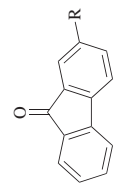
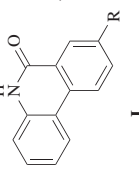
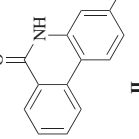
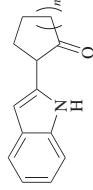
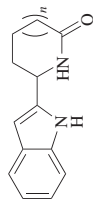


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.									
	<p>NaN₃, H₂SO₄, CHCl₃, 70°, 8 h</p>	<p>    </p>	<p>445</p>									
	<p>NaN₃, PPA, 100°, 3 h</p>	<p>  </p>	<p>446</p>									
	<p>NaN₃, H₂SO₄, CHCl₃, rt, 1 h</p>	<p>   </p>	<p> <table border="1"> <tr> <td>R</td> <td>I + II</td> <td>III</td> </tr> <tr> <td>O₂N</td> <td>(—)</td> <td>1:1</td> </tr> <tr> <td>MeO</td> <td>(—)</td> <td>19:1</td> </tr> </table> </p>	R	I + II	III	O ₂ N	(—)	1:1	MeO	(—)	19:1
R	I + II	III										
O ₂ N	(—)	1:1										
MeO	(—)	19:1										
	<p>NaN₃, H₂SO₄, CHCl₃, rt</p>	<p>  </p>	<p>341</p>									

C₁₄

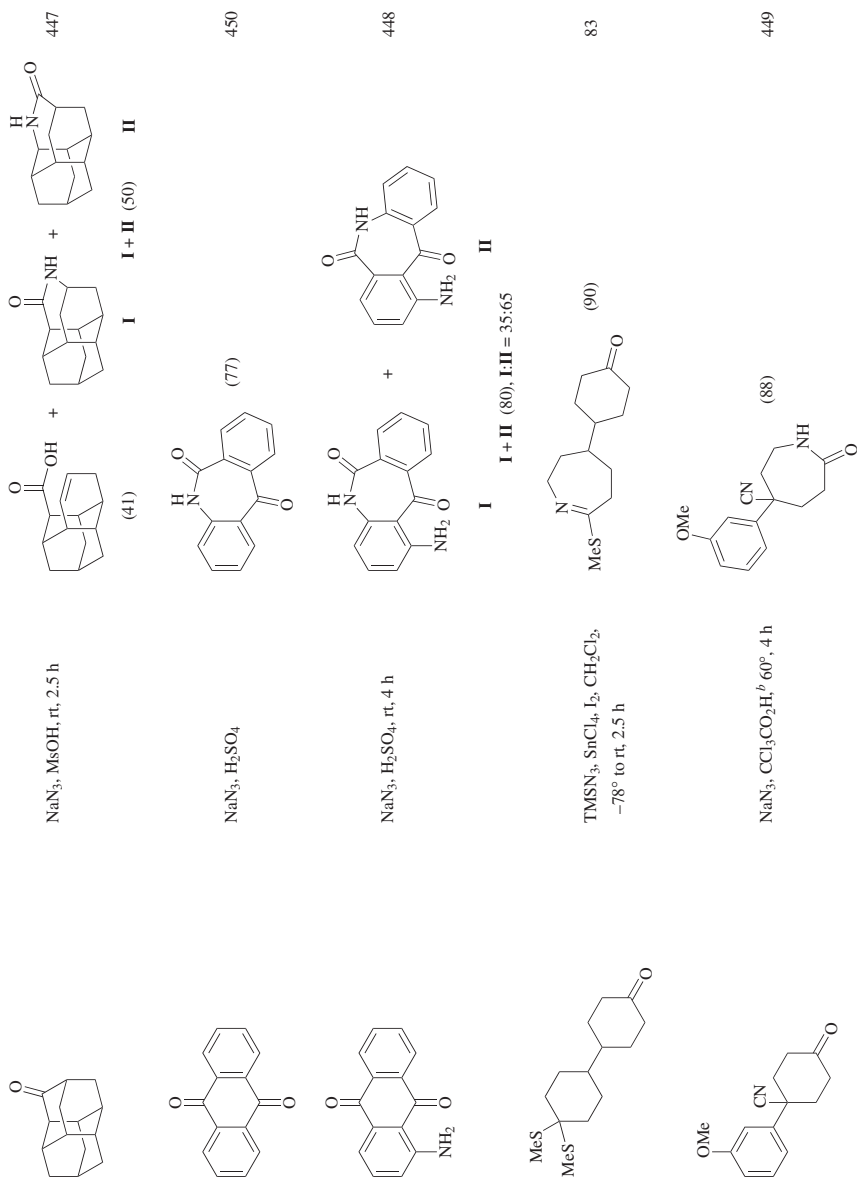
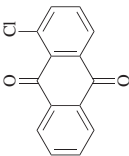
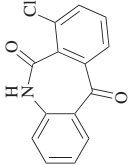
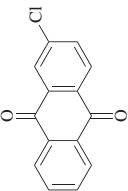
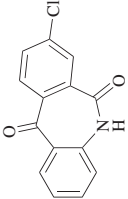
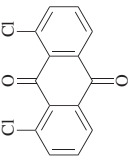
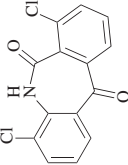
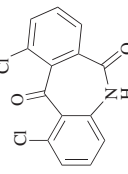
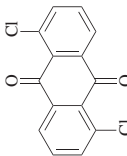
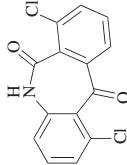
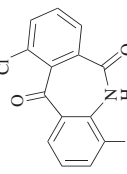
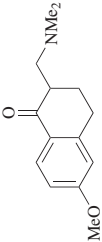
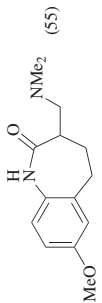


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>NaN₃, H₂SO₄, CH₂Cl₂, rt, 12 h</p>	 (10) + isomers (4)	450
	<p>NaN₃, H₂SO₄, CH₂Cl₂, rt, 12 h</p>	 (8) + isomers (8)	450
	<p>NaN₃, H₂SO₄, 50°, 4 h</p>	 I +  II	I + II (90) 451
	<p>NaN₃, H₂SO₄, 50°, 4 h</p>	 I +  II	I + II (95) 451
	<p>NaN₃, H₂SO₄, rt, 16 h</p>	 (55)	62

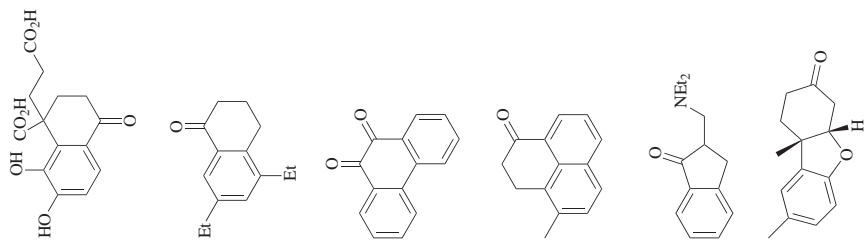
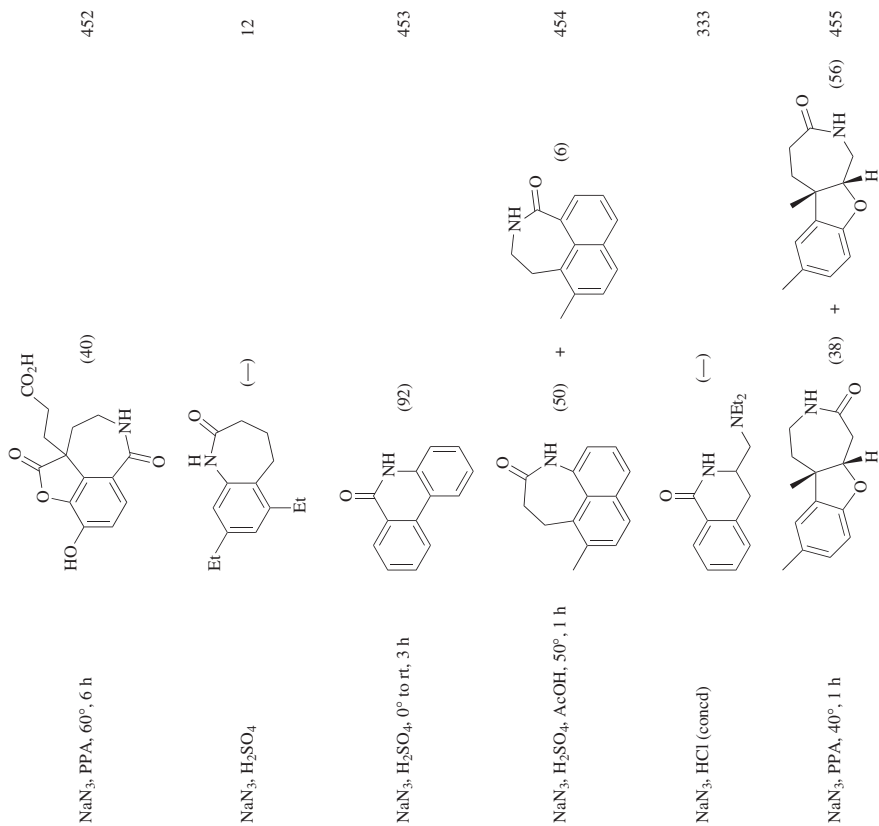
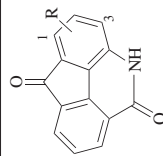
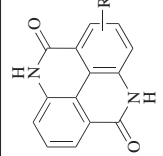
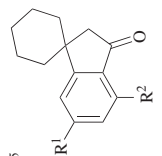
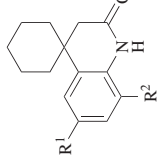
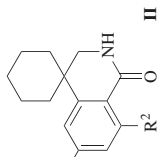
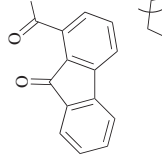
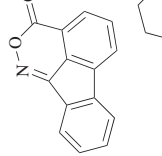
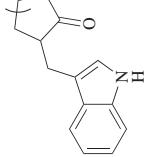
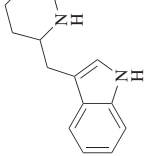
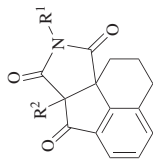


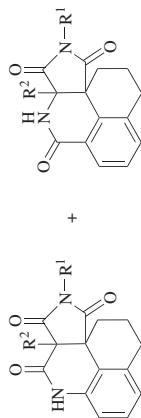
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₄	NaIN ₃ , H ₂ SO ₄ , 50°, 4 h	 R H (86) 1-O ₂ N (—) 3-O ₂ N (—)	456
 C ₁₄₋₁₅	A: NaIN ₃ , H ₂ SO ₄ , PhH, 60° B: NaIN ₃ , CCl ₃ CO ₂ H, ^b 65°	 +  I + II R ¹ R ² Conditions I + II I:II H H A (83) 7:3 H H B (—) 1:4 MeO H A (78) 1:9 MeO H B (—) 1:9 H MeO A (66) 1:9 H MeO B (—) 1:9	457 59 457 59 457 59
	NaIN ₃ , H ₂ SO ₄	 R HO (—) MeO (—)	458
	NaIN ₃ , H ₂ SO ₄ , 0 to 50°, 5 h	 $\frac{n}{1}$ (70) $\frac{2}{2}$ (74)	459

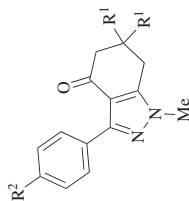
C₁₄₋₁₆

A: NaN₃, H₂SO₄, rt
 B: NaN₃, PPA, 80°, 15 h

460

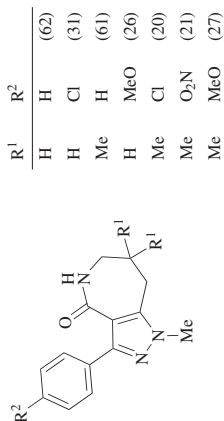
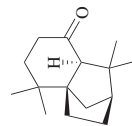
**II**

R ¹	R ²	Conditions	I	II
H	H	A	(91)	(0)
H	H	B	(45)	(30)
Me	H	A	(87)	(0)
Me	H	B	(47)	(48)
Me	Me	A	(74)	(0)
Me	Me	B	(43)	(28)

C₁₄₋₁₇

HN₃, H₂SO₄, PPA, rt, 0.5 h

461

C₁₅

NaN₃, H₂SO₄, CHCl₃,
 0°, 45 min

462

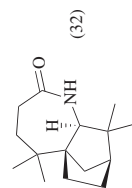


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 0°, 45 min		462						
	A: NaN ₃ , PPA, rt, 3 h B: NaN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 48 h	<table border="1"> <thead> <tr> <th>Conditions</th> <th>Product(s) and Yield(s) (%)</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>(74)</td> </tr> <tr> <td>B</td> <td>(26)</td> </tr> </tbody> </table>	Conditions	Product(s) and Yield(s) (%)	A	(74)	B	(26)	463
Conditions	Product(s) and Yield(s) (%)								
A	(74)								
B	(26)								
	NaN ₃ , H ₂ SO ₄ , CH ₂ Cl ₂ , rt, 12 h		(19) + isomers (23)						
	NaN ₃ , H ₂ SO ₄ , CH ₂ Cl ₂ , rt, 12 h		(20) + isomers (18)						
	NaN ₃ , H ₂ SO ₄ , CH ₂ Cl ₂ , rt, 12 h		(63)						

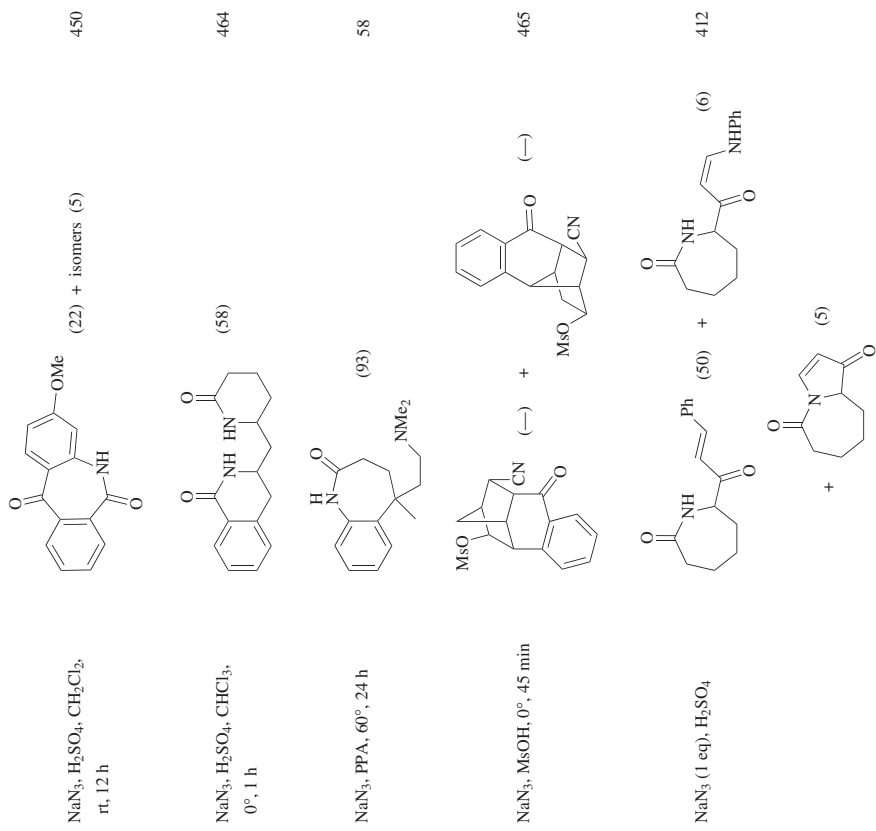
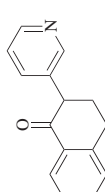
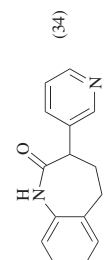
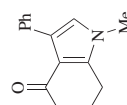
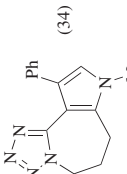
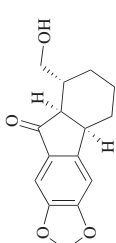
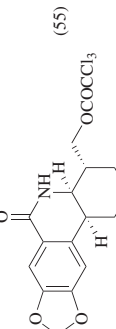
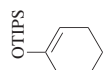
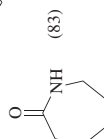
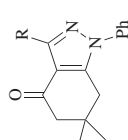
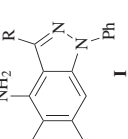
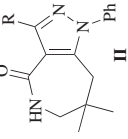
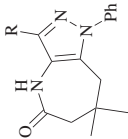
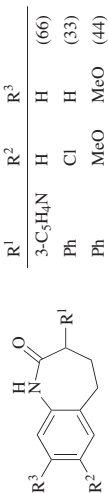


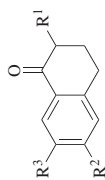
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
C_{15} 	NaN_3 , H_2SO_4 , AcOH , 50°, 0.5 h; rt, 1 h	 (34)	466								
	NaN_3 , H_2SO_4 , CHCl_3 , rt, 30 min	 (34)	392								
	NaN_3 , $\text{CCl}_3\text{CO}_2\text{H}$, ^b 60°, 60 h	 (55)	467								
	1. TMSN_3 , Dowex, CH_2Cl_2 , rt, 48 h 2. <i>h</i> v, $c\text{-C}_6\text{H}_{12}$, 0°, 3.5 h	 (83)	468								
C_{15-18} 	NaN_3 , PPA, 60°, 12 h	 I +  II +  III I + II + III (—)	<table border="1"> <thead> <tr> <th>R</th> <th>I:II:III</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>0:100:0</td> </tr> <tr> <td>Me</td> <td>18:61:21</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>17:67:16</td> </tr> </tbody> </table>	R	I:II:III	H	0:100:0	Me	18:61:21	<i>i</i> -Pr	17:67:16
R	I:II:III										
H	0:100:0										
Me	18:61:21										
<i>i</i> -Pr	17:67:16										

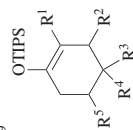


NaN₃, AcOH, 50°, 2 h

470

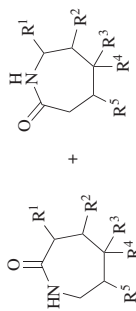


C₁₅₋₁₉

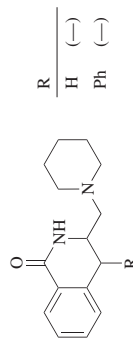


1. TMSN₃, PPTS, CH₂Cl₂,
rt, 2 d
2. /iv, *c*-C₆H₁₂, 0°, 1 h

74

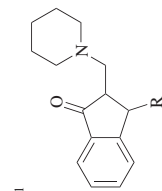


I					II				
R ¹	R ²	R ³	R ⁴	R ⁵	R ¹	R ²	R ³	R ⁴	R ⁵
H	H	H	H	H	H	H	H	H	H
Me	H	H	H	H	H	H	H	H	(0)
H	H	H	H	Me	H	H	H	Me	(12)
H	H	Me	H	H	H	Me	H	H	(36)
H	H	Me	Me	H	H	H	H	H	(68)
H	H	Me	Me	Me	H	H	Me	H	(60)
H	H	-O(CH ₂) ₂ O-	H	H	H	H	-O(CH ₂) ₂ O-	H	(77)
H	H	<i>t</i> -Bu	H	H	H	H	H	H	(63)

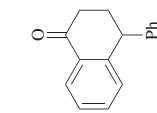


NaN₃, HCl

333



C₁₅₋₂₁



C₁₆

NaN₃, AcOH, 50°, 2 h

470

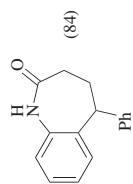
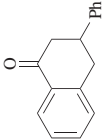
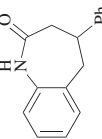
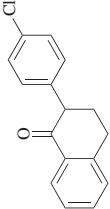
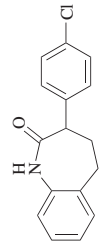
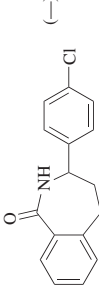
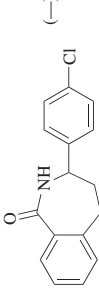
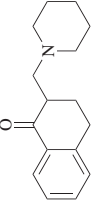
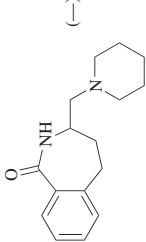
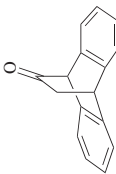
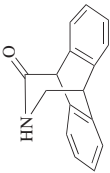
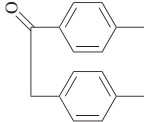
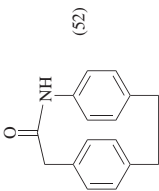


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3 , H_2SO_4 , AcOH, 50°, 45 min	 (61)	471
	NaN_3 , AcOH, rt to 50°, 3 h	 (42) +	472
		 (-)	
	NaN_3 , HCl (concd)	 (-)	333
	NaN_3 , $\text{CCl}_3\text{CO}_2\text{H}$, ^b 60°	 (10) +	473
	NaN_3 , H_2SO_4 , dioxane, 15–45°, 45 min	 (52)	474

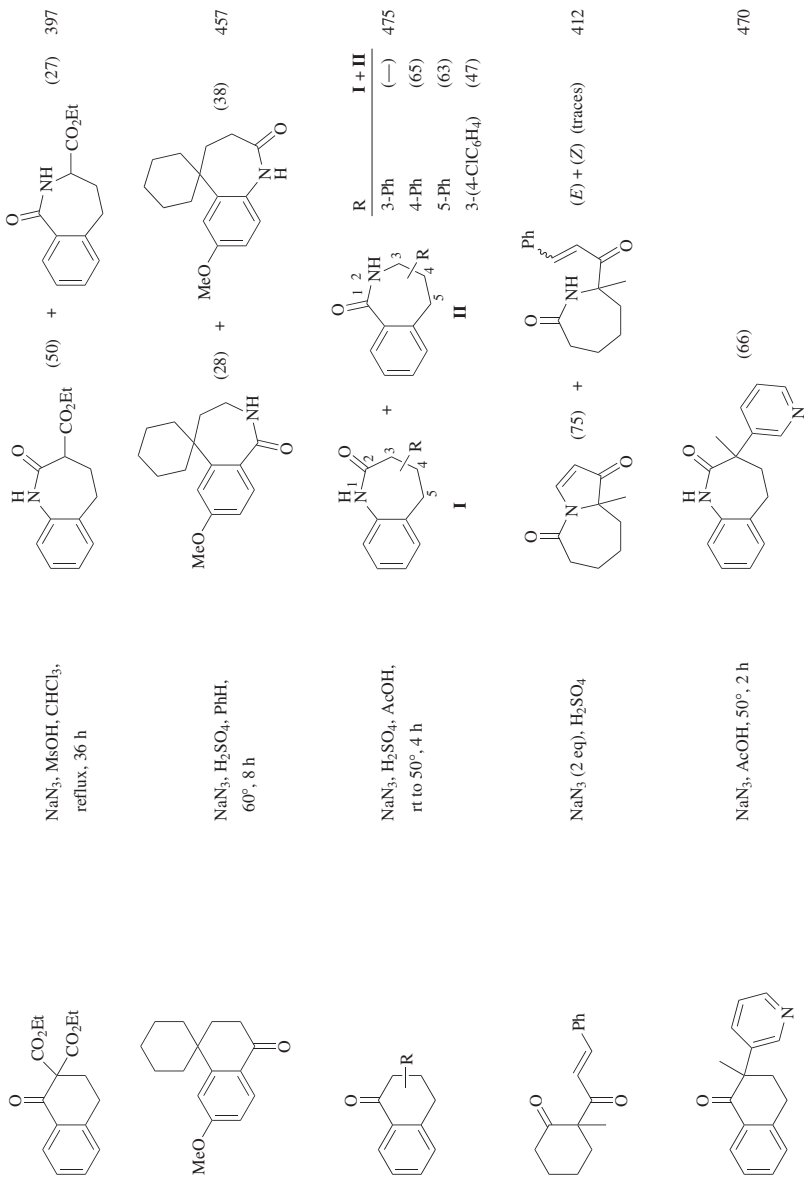
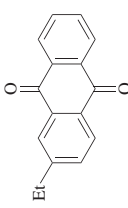
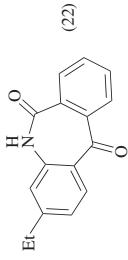
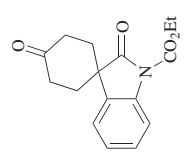
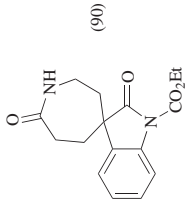
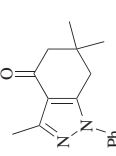
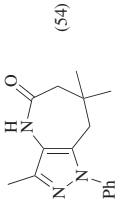
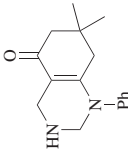
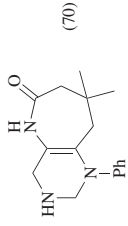
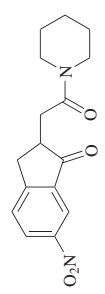
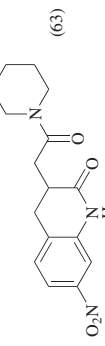
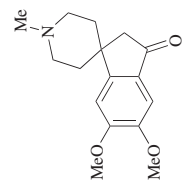


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

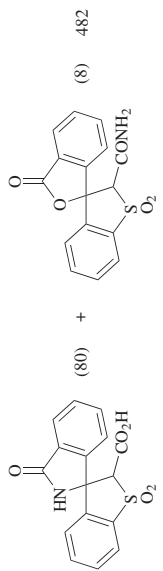
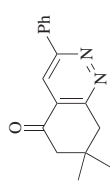
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <chem>CC1=CC=C2C(=O)NCC2=C1</chem> (22)	NaN_3 , H_2SO_4 , CH_2Cl_2 , rt, 12 h	 (22)	450
 <chem>CC1=CC=C2C(=O)NCC2=C1</chem> (90)	NaN_3 , H_2SO_4 , CHCl_3 , -10° to rt	 (90)	476
 <chem>CC1=CC=C2C(=O)NCC2=C1</chem> (54)	NaN_3 , PPA, 100° , 5 h	 (54)	477
 <chem>CC1=CC=C2C(=O)NCC2=C1</chem> (70)	NaN_3 , H_2SO_4 , CHCl_3 , 0° to rt, 5 h	 (70)	478
 <chem>CC1=CC=C2C(=O)NCC2=C1</chem> (63)	NaN_3 , H_2SO_4 , PhH, 40° , 15 min	 (63)	479



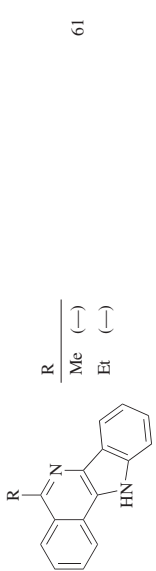
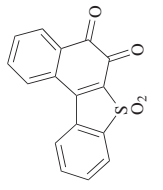
NaN₃, H₂SO₄, 60°, 45 min



NaN₃, H₂SO₄, rt, 2 h

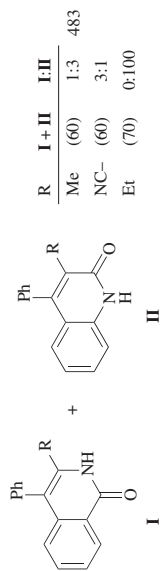
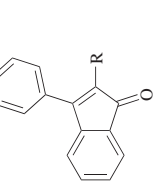


NaN₃, H₂SO₄, 45°, 30 min



HN₃

C₁₆₋₁₇



NaN₃, AcOH, 50°, 1 h

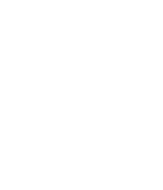
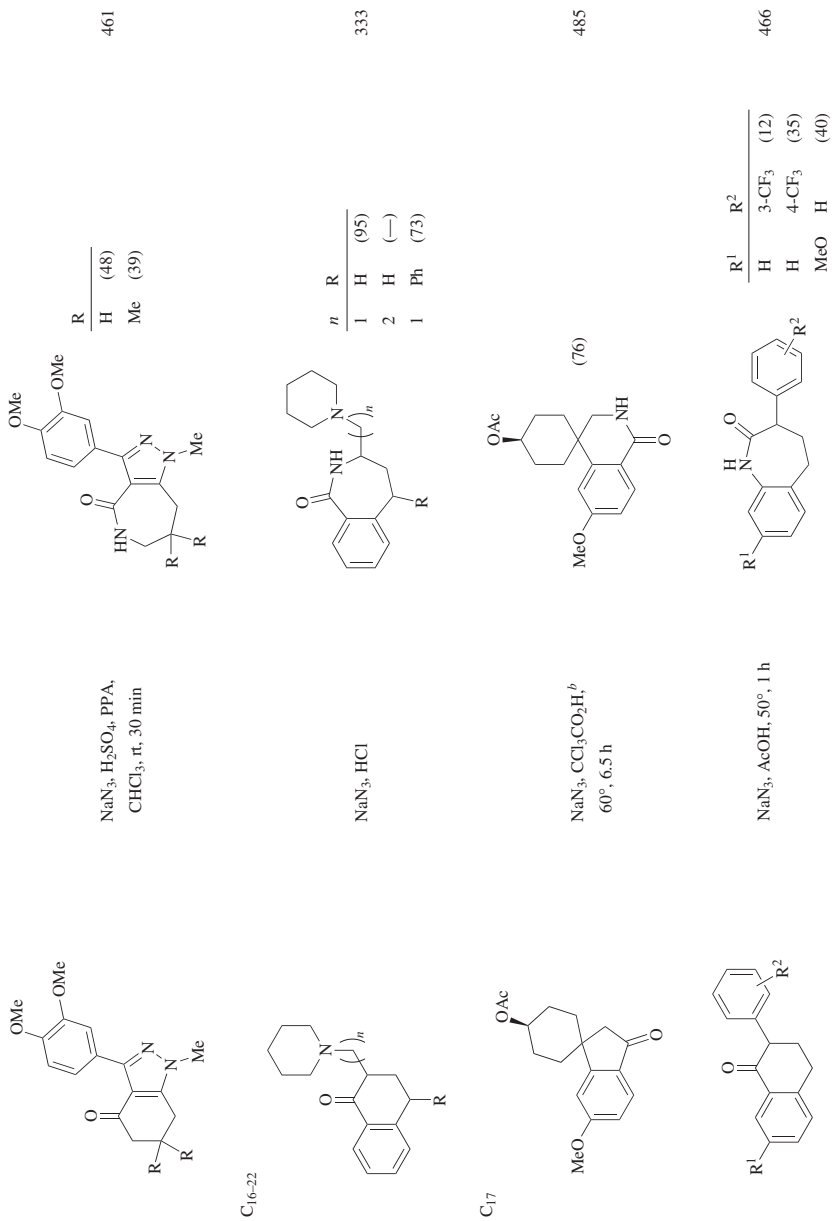


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
<p>C_{16-17}</p>	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{rt to } 55^\circ, 4.5 \text{ h}$</p>	<p style="text-align: center;">n</p> <p style="text-align: center;">1 (82) 2 (63)</p>	464												
	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{AcOH}, 50^\circ, 2 \text{ h}$</p>	<p style="text-align: center;">I</p> <p style="text-align: center;">+ <p style="text-align: center;">II</p> </p>	470												
		<table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;">R^1</th> <th style="text-align: left;">R^2</th> <th style="text-align: left;">I</th> <th style="text-align: left;">II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td><i>n</i>-C_6H_{13}</td> <td>(45)</td> <td>(38)</td> </tr> <tr> <td>Ph</td> <td>MeO</td> <td>(36)</td> <td>(25)</td> </tr> </tbody> </table>	R^1	R^2	I	II	H	<i>n</i> - C_6H_{13}	(45)	(38)	Ph	MeO	(36)	(25)	
R^1	R^2	I	II												
H	<i>n</i> - C_6H_{13}	(45)	(38)												
Ph	MeO	(36)	(25)												
<p>C_{16-18}</p>	<p>$\text{NaN}_3, \text{AcOH}, \text{rt}, 1 \text{ h}$</p>	<p style="text-align: center;">R</p> <p style="text-align: center;">H₂N (40) EtO (30)</p>	484												
	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{rt}, 1 \text{ h}$</p>	<p style="text-align: center;">R</p> <p style="text-align: center;">H₂N (50) EtO (40)</p>	484												



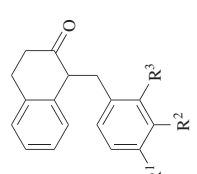
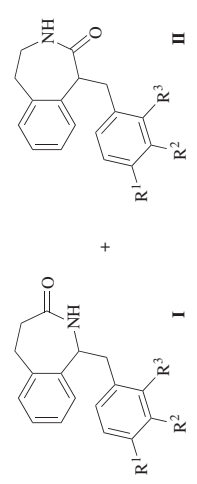
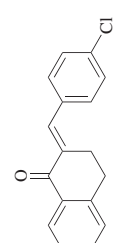
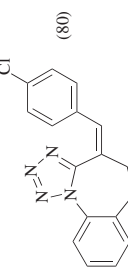
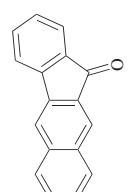
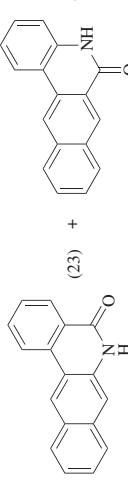
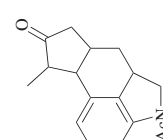
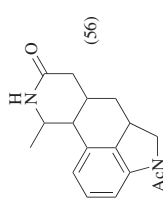
NaI₃, H₂SO₄, PPA,
CHCl₃, rt, 30 min

NaI₃, HCl

NaI₃, CCl₃CO₂H,^b
60°, 6.5 h

NaI₃, AcOH, 50°, 1 h

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
 <p>C₁₇</p>	<p>NaN₃, PPA, 40°, 5 h</p>	 <p>II</p> <p>461</p>																					
		<table border="1" data-bbox="401 503 528 781"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(20)</td> <td>(—)</td> </tr> <tr> <td>Cl</td> <td>H</td> <td>H</td> <td>(47)</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>H</td> <td>O₂N</td> <td>(30)</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	I	II	H	H	H	(20)	(—)	Cl	H	H	(47)	(—)	H	H	O ₂ N	(30)	(—)	
R ¹	R ²	R ³	I	II																			
H	H	H	(20)	(—)																			
Cl	H	H	(47)	(—)																			
H	H	O ₂ N	(30)	(—)																			
	<p>NaN₃, SiCl₄, MeCN, rt, 18 h</p>	 <p>(80)</p> <p>70</p>																					
	<p>NaN₃, H₂SO₄, CCl₃CO₂H,^b 100°, 4 h</p>	 <p>(23) +</p> <p>(21)</p> <p>486</p>																					
	<p>NaN₃, H₂SO₄, AcOH, 40°</p>	 <p>(56)</p> <p>487</p>																					

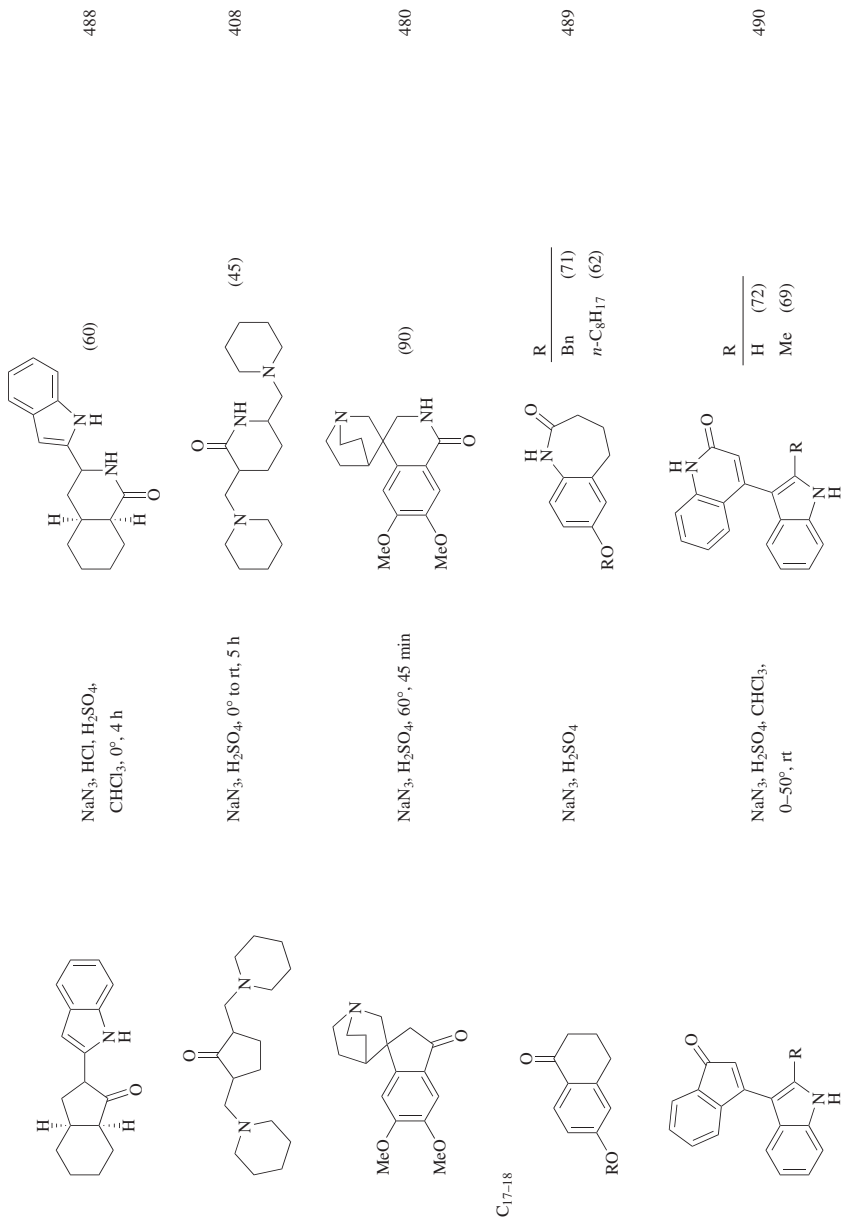
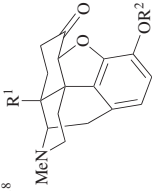
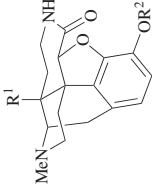
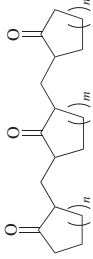
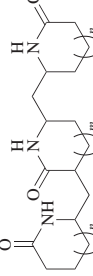
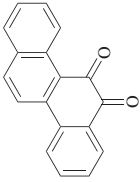
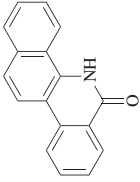
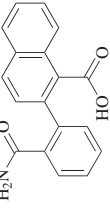
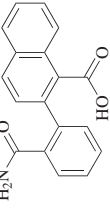
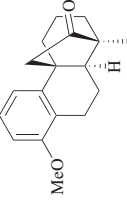
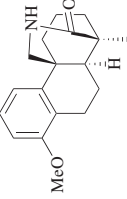


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
<p>C₁₇₋₁₈</p> 	NaN ₃ , PPA, 65°	 <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(40)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>(52)</td> </tr> <tr> <td>HO</td> <td>Me</td> <td>(23)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	H	H	(40)	H	Me	(52)	HO	Me	(23)	491			
R ¹	R ²	Yield (%)																
H	H	(40)																
H	Me	(52)																
HO	Me	(23)																
<p>C₁₇₋₂₀</p> 	NaN ₃ , H ₂ SO ₄ , 0 to 55°, 5 h	 <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>n</th> <th>m</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>1</td> <td>(70)</td> </tr> <tr> <td>1</td> <td>2</td> <td>(59)</td> </tr> <tr> <td>2</td> <td>1</td> <td>(66)</td> </tr> <tr> <td>2</td> <td>2</td> <td>(63)</td> </tr> </tbody> </table>	n	m	Yield (%)	1	1	(70)	1	2	(59)	2	1	(66)	2	2	(63)	492
n	m	Yield (%)																
1	1	(70)																
1	2	(59)																
2	1	(66)																
2	2	(63)																
<p>C₁₈</p> 	NaN ₃ , H ₂ SO ₄	 (100)	262															
	NaN ₃ , H ₂ SO ₄ , 50°, 1 h	 (70)	262															
	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , -10°, 1 h	 (14)	493															

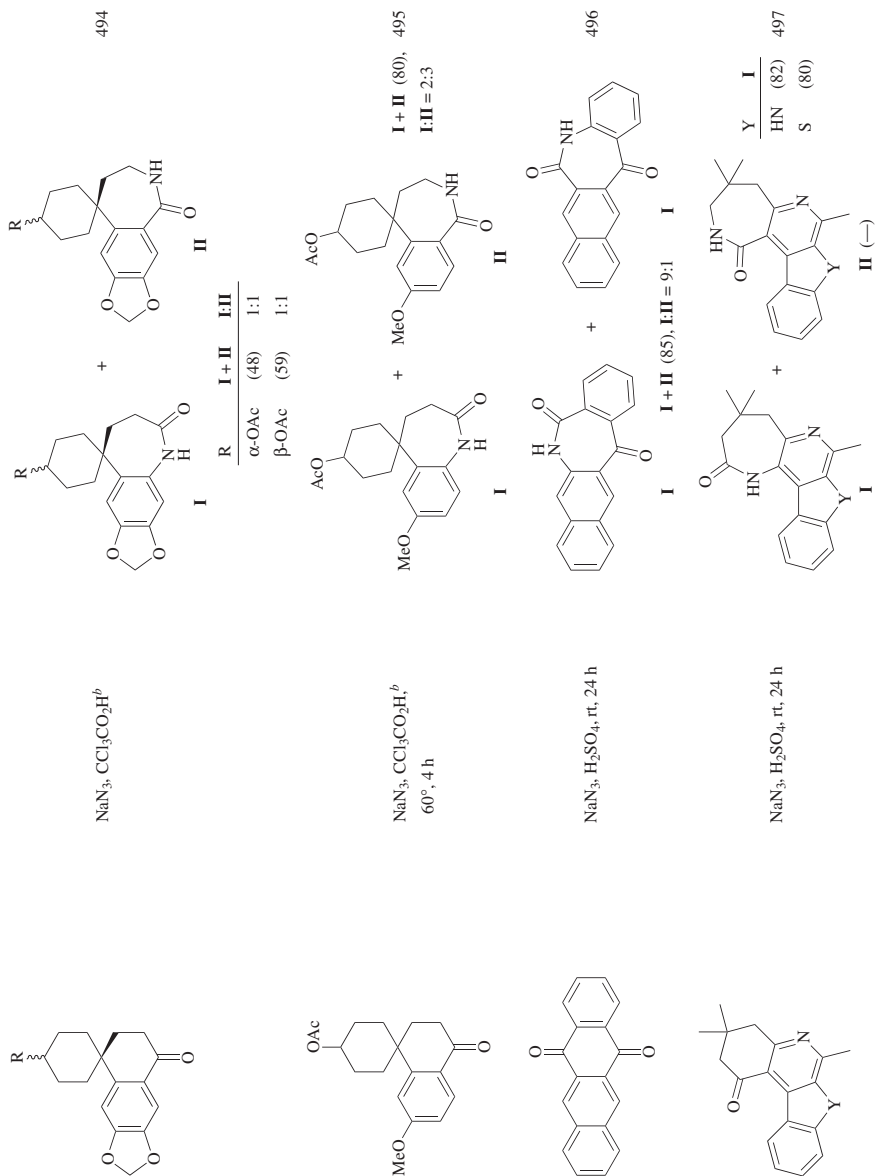
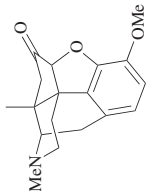
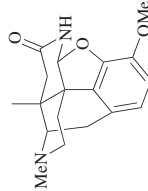
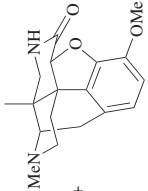
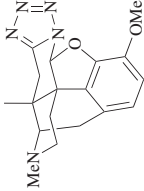
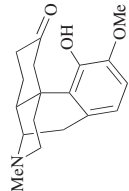
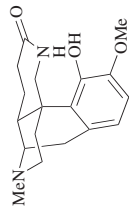
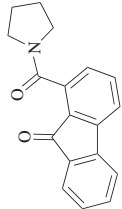
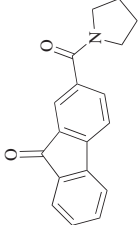
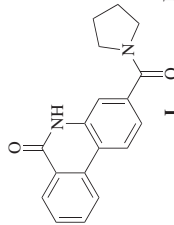
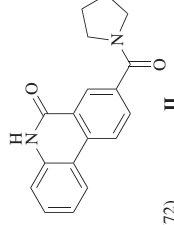
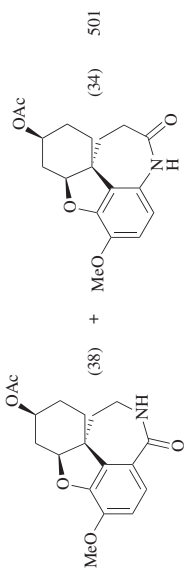


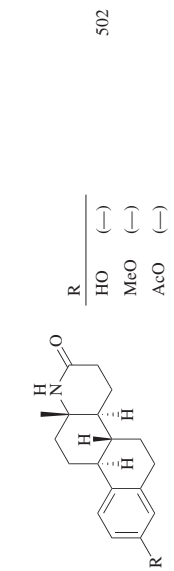
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>NaN₃, P₂O₅, MsOH, 65°, 24 h</p>	 (9) +  (3) + 498  (15)	
	<p>NaN₃, PPA, 65°</p>	 (16)	491
	<p>NaN₃, H₂SO₄</p>	<p>(-)</p>	499
	<p>NaN₃, H₂SO₄, CHCl₃, rt, 1 h</p>	 I +  II (72)	500



NaI, $\text{CCl}_3\text{CO}_2\text{H}^b$

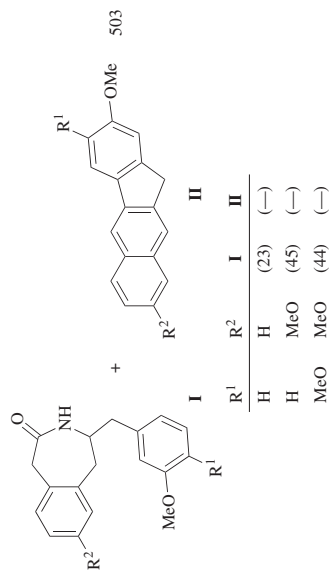
501



$\text{HN}_3, \text{H}_2\text{SO}_4, \text{PhI}, \text{rt}$

502

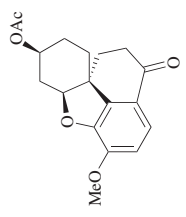
R	(-)
HO	(-)
MeO	(-)
AcO	(-)



NaI, PPA, $70^\circ, 2 \text{ h}$

503

R ¹	R ²	I	II
H	H	(23)	(-)
H	MeO	(45)	(-)
MeO	MeO	(44)	(-)



C₁₈₋₂₀

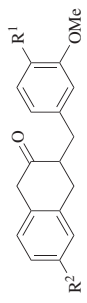
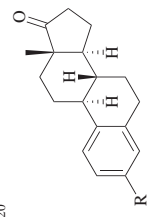
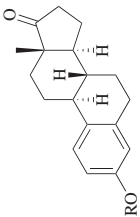
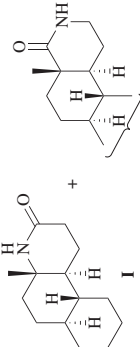
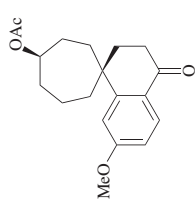
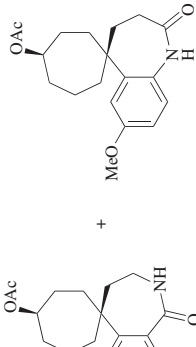
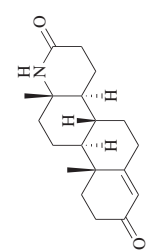


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
 <p>C_{18-23}</p>	<p>A: NaN_3, PPA, 60°, 10 h B: HN_3, H_2SO_4, rt, 2 h</p>	 <p>I II</p>	504																				
 <p>C_{19}</p>	<p>NaN_3, $\text{CCl}_3\text{CO}_2\text{H}$, 60°, 4 h</p>	 <p>I II</p>	505																				
 <p>(35)</p>	<p>NaN_3, PPA, 0°, 20 min</p>	<p>I + II (79), I:II = 2:3</p>	506																				
		<table border="1"> <thead> <tr> <th>R</th> <th>Conditions</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>A</td> <td>(-)</td> <td>2:1</td> </tr> <tr> <td>Me</td> <td>A</td> <td>(-)</td> <td>1:0</td> </tr> <tr> <td>Ac</td> <td>A</td> <td>(-)</td> <td>1:0</td> </tr> <tr> <td><i>c</i>-C_5H_9</td> <td>B</td> <td>(-)</td> <td>1:0</td> </tr> </tbody> </table>	R	Conditions	I + II	I:II	H	A	(-)	2:1	Me	A	(-)	1:0	Ac	A	(-)	1:0	<i>c</i> - C_5H_9	B	(-)	1:0	
R	Conditions	I + II	I:II																				
H	A	(-)	2:1																				
Me	A	(-)	1:0																				
Ac	A	(-)	1:0																				
<i>c</i> - C_5H_9	B	(-)	1:0																				

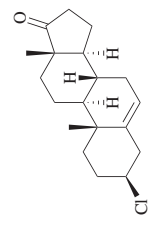
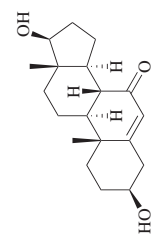
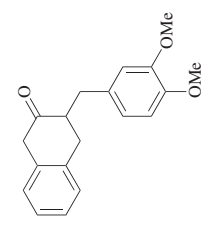
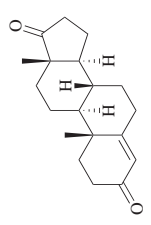
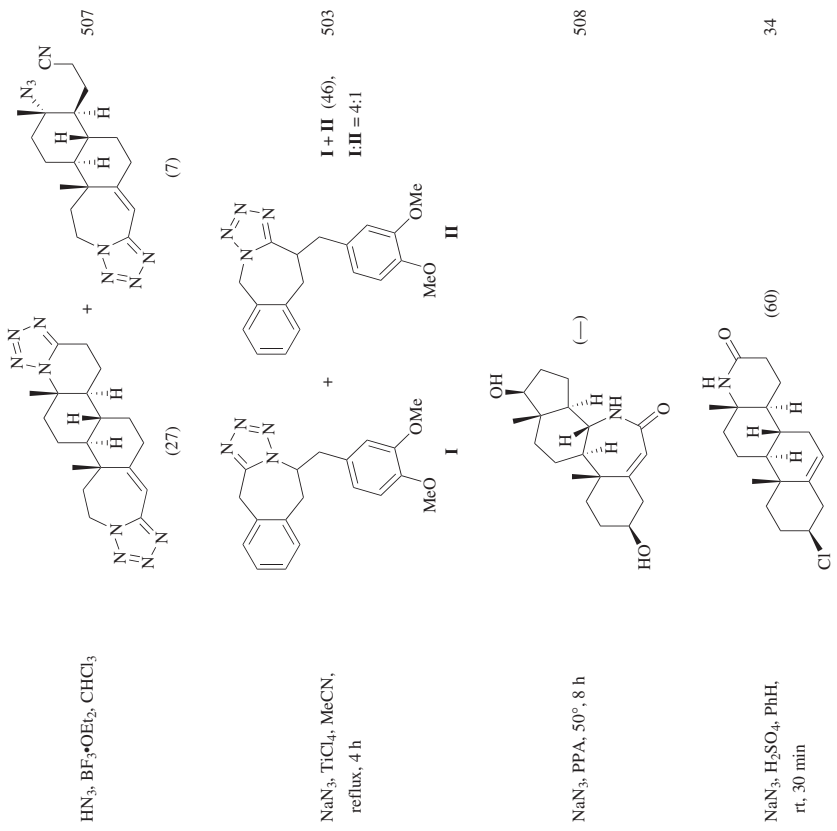
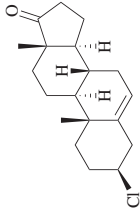
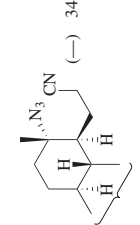
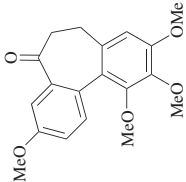
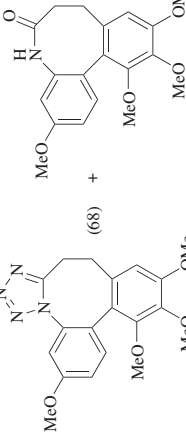
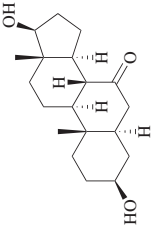
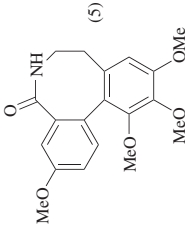
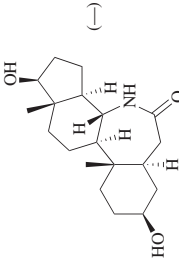
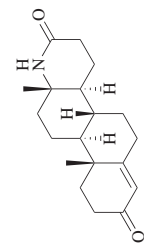


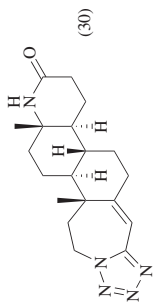
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>HN₃, BF₃·OEt₂, PhH, 0°, 5 h</p>	 <p>(-) + (-) 34</p>	
	<p>TMSN₃, TFA, rt, 24 h</p>	 <p>(68) + (13) + 509</p>	
	<p>NaN₃, PPA, 50°, 8 h</p>	 <p>(5)</p>  <p>(-)</p>	508

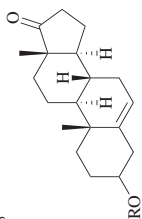


HN₃, BF₃•OEt₂, CHCl₃,
0° to rt, 24 h

509a

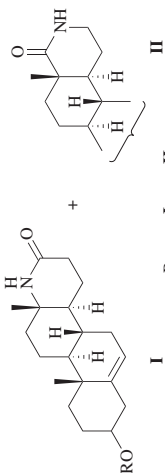


C₁₉₋₂₆

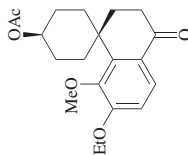


NaN₃, H₂SO₄, CHCl₃, 10°

510

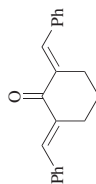
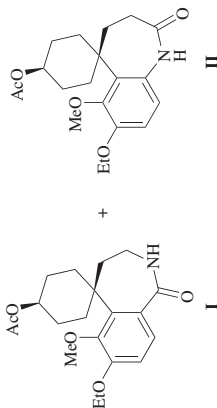


C₂₀



NaN₃, CCl₃CO₂H, PhH,
60°, 8 h

511



NaN₃, SiCl₄, MeCN,
rt, 14 h

70

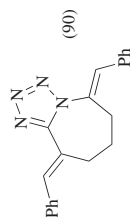
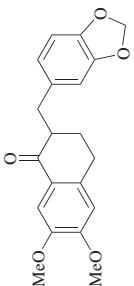
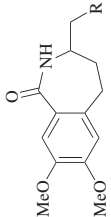
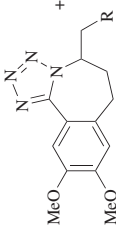
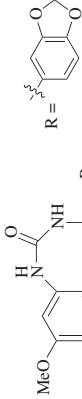
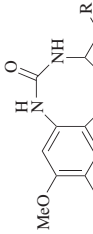

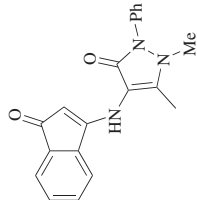
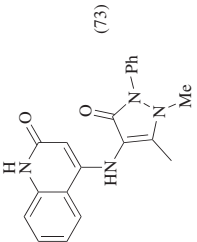
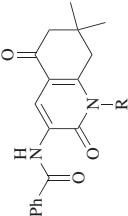
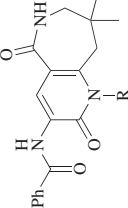

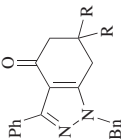
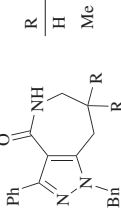

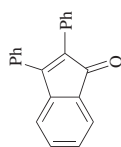


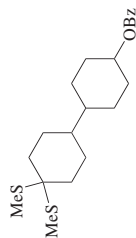
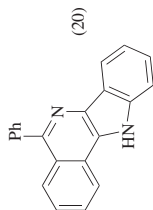
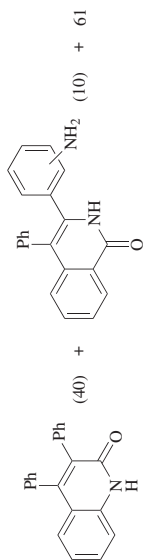
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>NaN₃, CCl₃CO₂H,^b 57°, 15 h</p>	 +  (12)	512
		 (2)	<p>R = </p>
	<p>NaN₃, H₂SO₄, CHCl₃, 0 to 50°, 5 h</p>	 (73)	490
	<p>NaN₃, H₂SO₄, CHCl₃, 0° to rt, 4 h</p>	 (80)  (84)	420
	<p>HN₃, H₂SO₄, CHCl₃, rt, 30 min</p>	 (10)  (10)	461

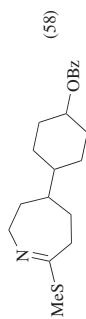
C₂₁



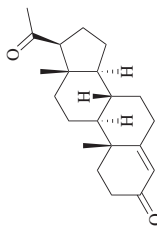
NaN₃, AcOH, H₂SO₄



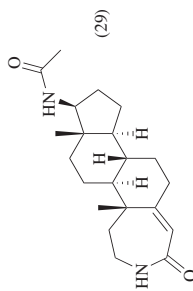
TMSN₃, SnCl₄, I₂, CH₂Cl₂,
-78° to rt, 2.5 h



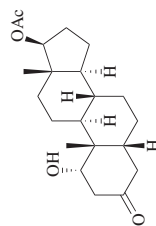
83



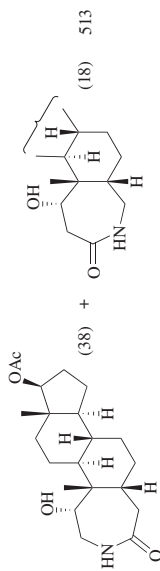
NaN₃, PPA, 50°, 10 h



354

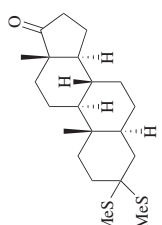
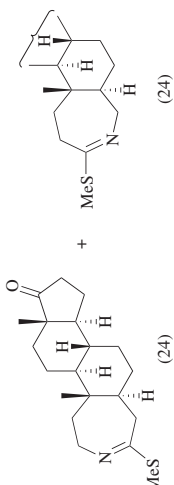
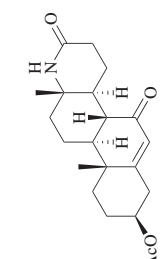
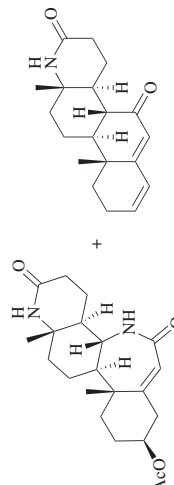
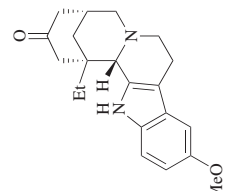
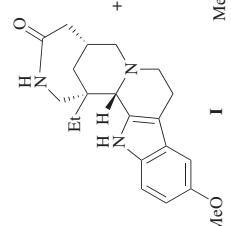
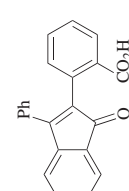
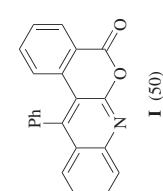


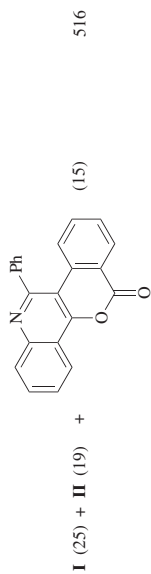
HN₃, H₂SO₄, CHCl₃,
0°, 20 min



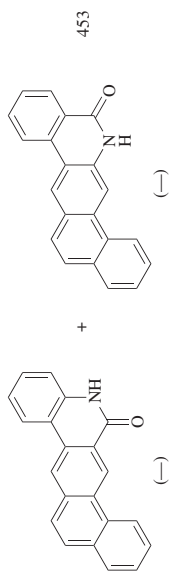
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TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

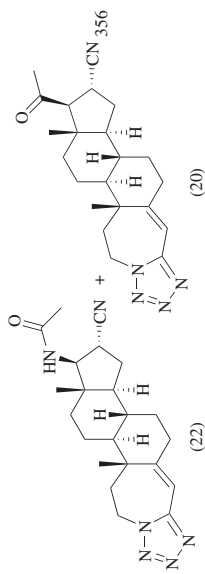
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 MeS	$\text{TMSN}_3, \text{SnCl}_4 \cdot \text{I}_2, \text{CH}_2\text{Cl}_2,$ -78° to rt, 2.5 h	 MeS (24)	83
 AcO	$\text{NaN}_3, \text{PPA}, 60^\circ, 10 \text{ h}$	 (13)	514
 Et MeO	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3$	 Et MeO I	I + II (85), 515 I:II = —
 Ph CO_2H	$\text{NaN}_3, \text{AcOH}, 80^\circ, 1 \text{ h}$	 Ph CO_2H I (50)	II (23) 516



$\text{NaN}_3, \text{AcOH}, \text{H}_2\text{SO}_4,$
 $40^\circ, 45 \text{ min}$



$\text{NaN}_3, \text{H}_2\text{SO}_4$



$\text{HN}_3, \text{BF}_3 \cdot \text{OEt}_2,$
 $\text{CHCl}_3, 0^\circ \text{ to rt}, 24 \text{ h}$

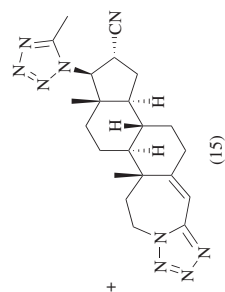
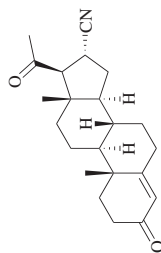
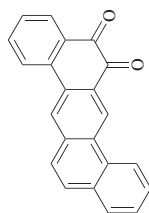
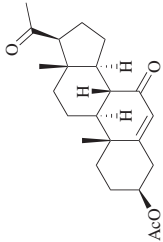
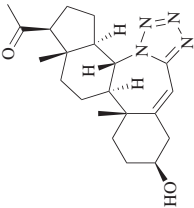
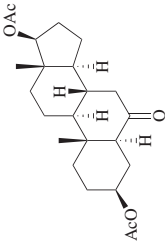
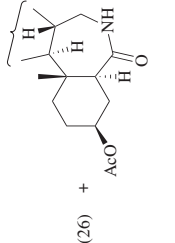
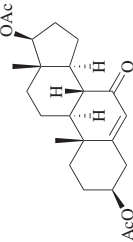
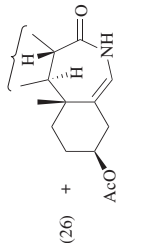
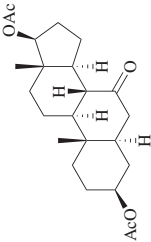
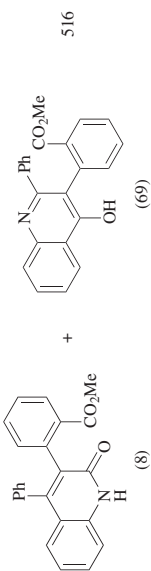


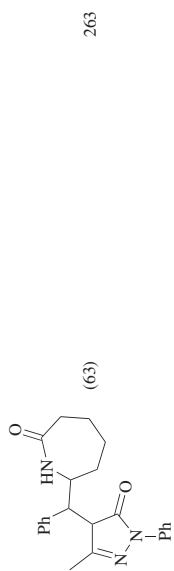
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 (50)	HN ₃ , BF ₃ ·OEt ₂ , CHCl ₃ , rt, 20 h	 (26)	517
 (26)	NaN ₃ , H ₂ SO ₄ , PhH, 20°, 2 h	 (22)	508
 (26)	NaN ₃ , PPA, 50°, 8 h	 (22)	508
 (26)	NaN ₃ , PPA, 50°, 8 h	(—)	508

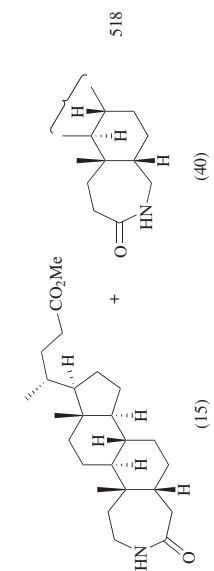
C₂₃



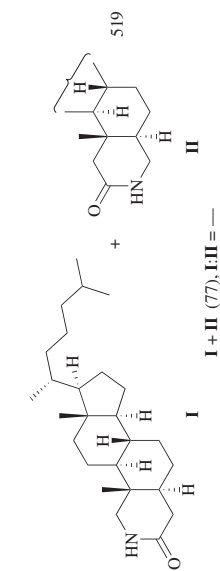
NaN₃, AcOH, H₂SO₄,
40°, 45 min



NaN₃, H₂SO₄, CHCl₃,
0–50°, 5 h



NaN₃, H₂SO₄, CHCl₃,
0°, 30 min



NaN₃, PPA, 60°, 10 h

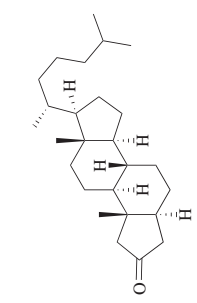
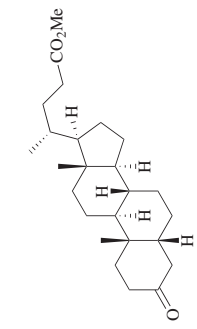
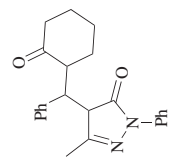
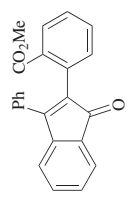
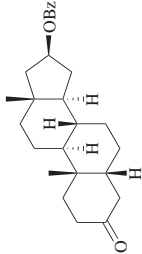
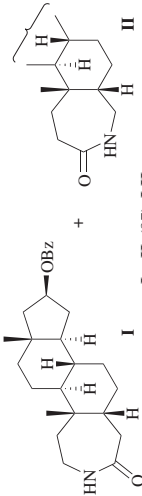
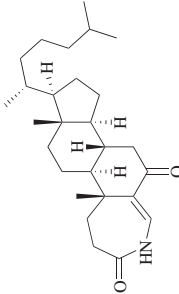
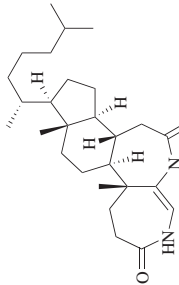
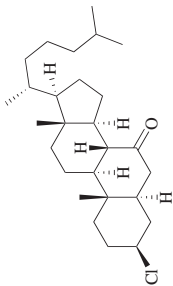
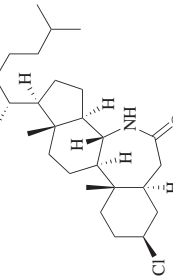
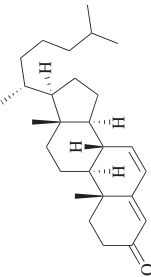
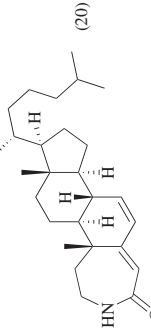
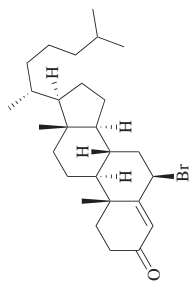


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

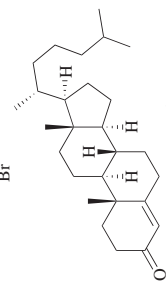
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C₂₆</p>	$\text{HN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3,$ $0^\circ, 20 \text{ min}$	 <p>I + II (97), I:II = —</p> <p>520</p>	520
 <p>(48)</p>	$\text{NaN}_3, \text{PPA}, 60^\circ, 1 \text{ h}$	 <p>(48)</p>	521
 <p>C₂₇</p>	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH},$ $\text{rt}, 1 \text{ h}$	 <p>(50)</p>	522
 <p>(20)</p>	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH},$ $\text{rt}, 1 \text{ h}$	 <p>I (75)</p>	523
	$\text{NaN}_3, \text{PPA}, \text{rt}, 2 \text{ h}$		416



NaI₃, H₂SO₄, PhH,
rt, 1 h

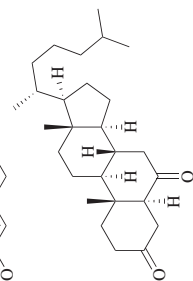
I (20)

523



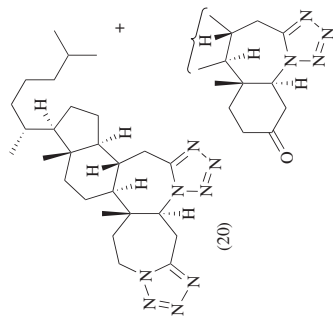
NaI₃, PPA, 50°, 10 h

354



NaI₃, PPA, 65°, 12 h

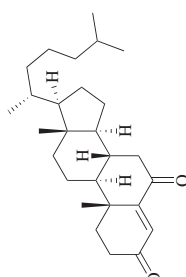
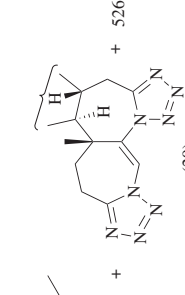
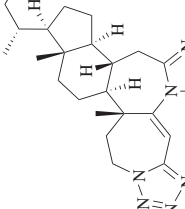
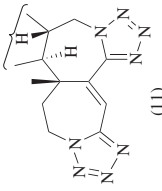
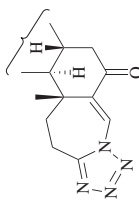
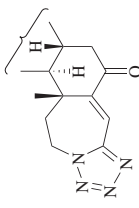
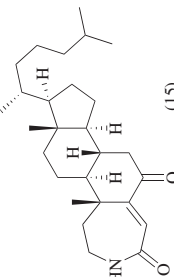
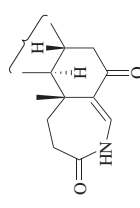
524



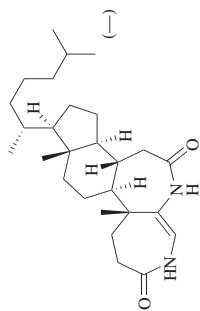
HN₃, BF₃·OEt₂, PhH,
rt, 5 h

525

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

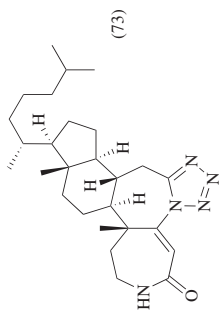
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>HN₃, BF₃·OEt₂, CHCl₃, 40°, 10 h</p>	<p>  + 526  I (33)  (11) </p>	(29)
	<p>HN₃, BF₃·OEt₂, PhH, rt, 5 h</p>	<p>  + 525  I (5) + (20) </p>	(10)
	<p>NaN₃ (1 eq), PPA, 55°, 10 h</p>	<p>  + 15  + 25 </p>	(25)

C₂₇



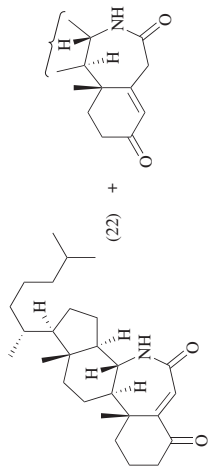
521

NaN₃ (2 eq), PPA, 55°, 10 h



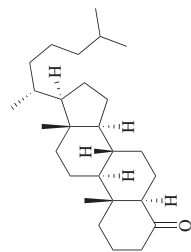
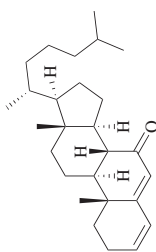
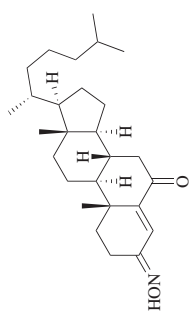
527

HN₃, BF₃·OEt₂, CHCl₃,
0° to rt, 24 h



416

NaN₃, PPA, rt, 2 h



528

NaN₃, PPA, 50°, 6 h

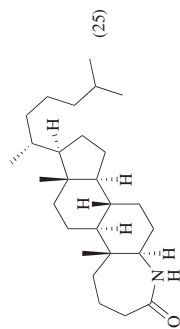
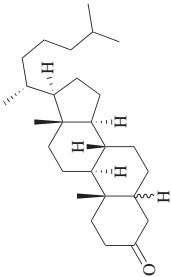
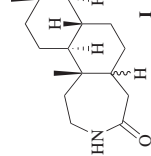
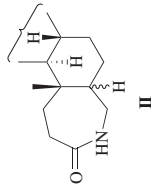
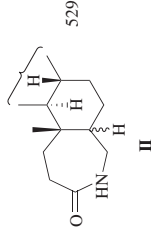


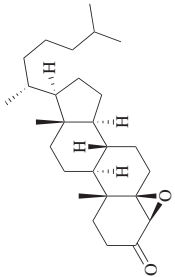
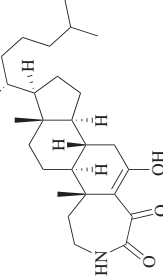
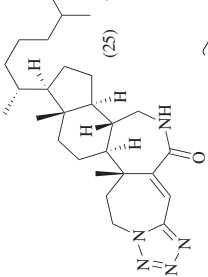
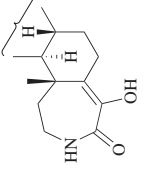
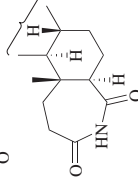


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>NaN_3, PPA, 65°, 12 h</p>	<p>   +  529 </p>	
		<p>   I + II <hr/> α (67) 1:1 β (86) 1:1 </p>	
	<p>NaN_3, PPA, 50°, 6 h</p>	<p>  (40) 528 </p>	
	<p>HN_3, $\text{BF}_3 \cdot \text{OEt}_2$, PhH, rt, 3 d</p>	<p>  (25) +  (-) + 530  (10) </p>	

C₂₇

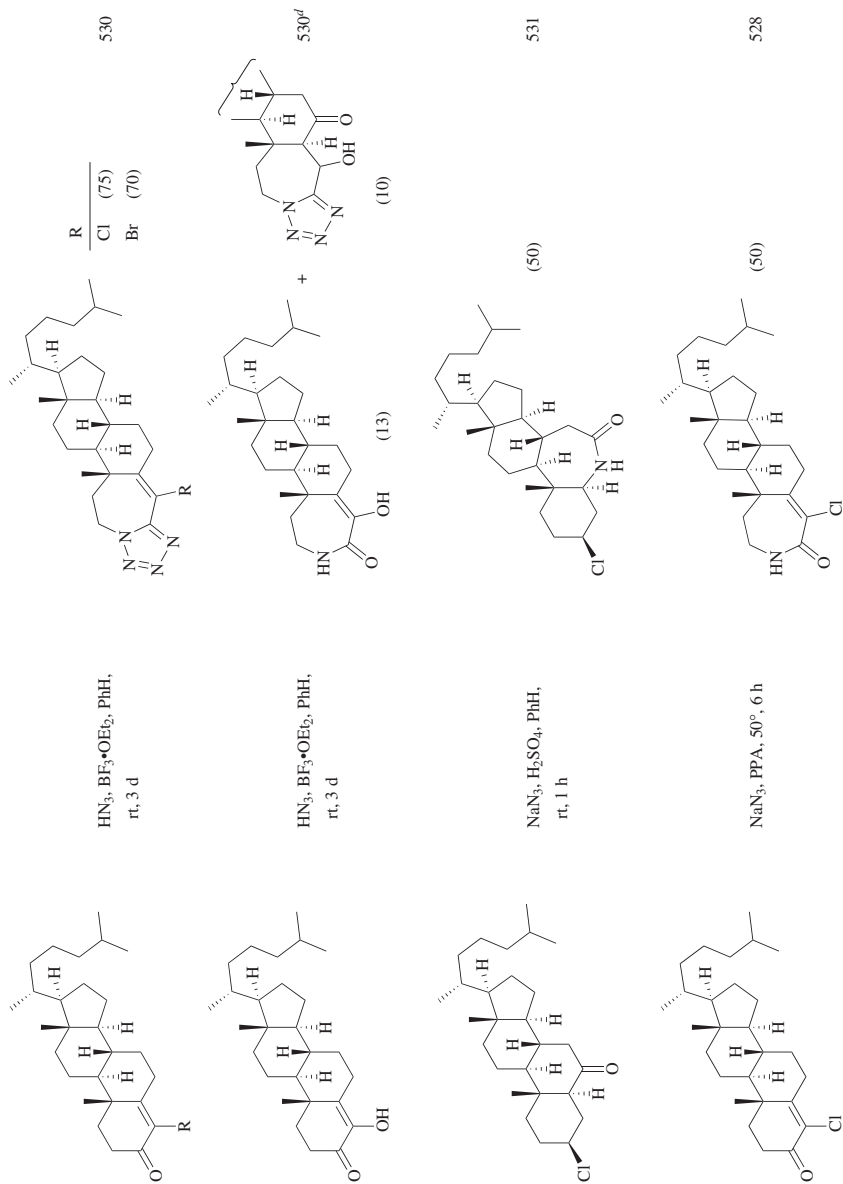
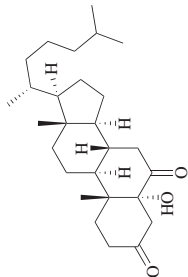
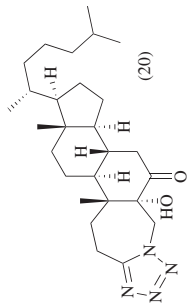
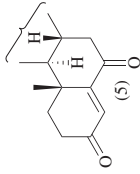
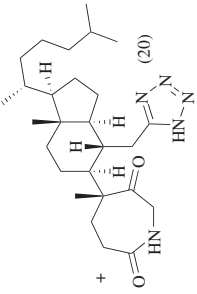
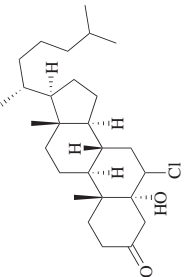
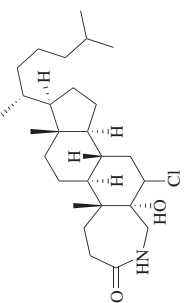
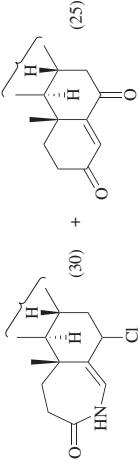
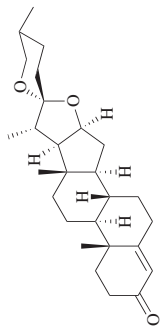


TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

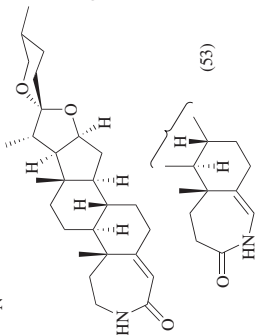
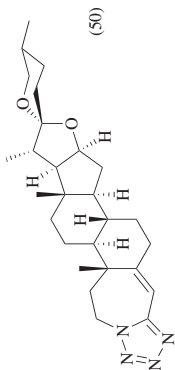
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>HN₃, BF₃·OEt₂, PhH, rt, 5 h</p>	 (20) +  (5) +  (20)	525
	<p>HN₃, BF₃·OEt₂, PhH, rt, 24 h</p>	 (30) +  (25)	532 ^d

C₂₇



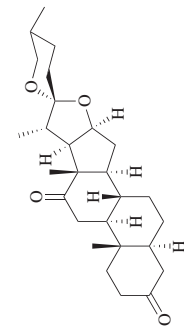
HN₃, BF₃•OEt₂, CHCl₃,
0° to rt, 20 h

533



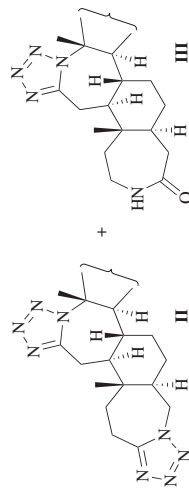
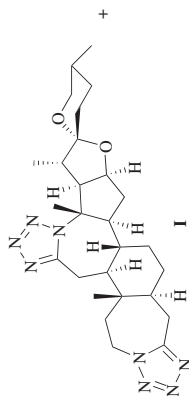
NaN₃, H₂SO₄

534



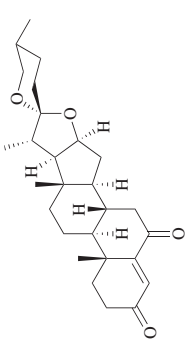
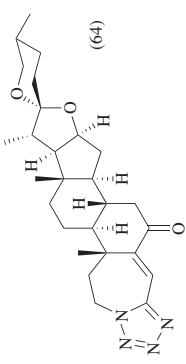
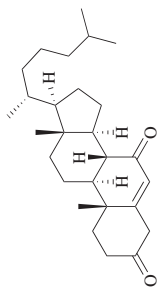
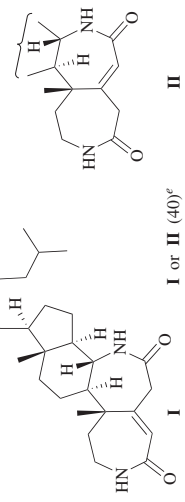
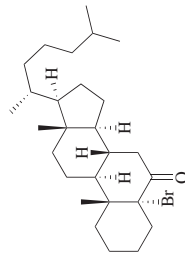
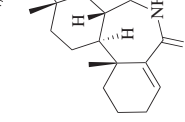
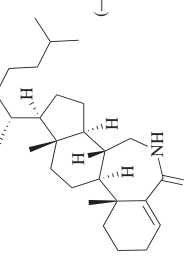
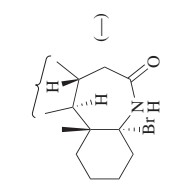
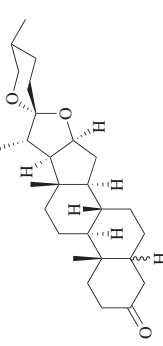
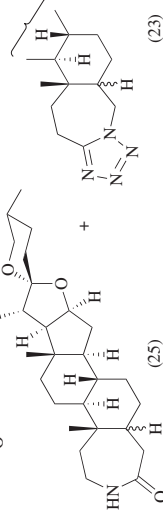
HN₃, BF₃•OEt₂, CHCl₃,
0° to rt, 24 h

535



I + II + III (20), I:II:III = 3:2:1

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C27</p>	HN ₃ , BF ₃ •OEt ₂ , CHCl ₃ , 0° to rt, 24 h	 <p>(64)</p>	526
	NaN ₃ , PPA, 60°, 10 h	 <p>I or II (40)^e</p>	536
	HN ₃ , BF ₃ •OEt ₂ , CHCl ₃ , 0° to rt, 24 h	 <p>I or II (18)^e</p>	536
	NaN ₃ , H ₂ SO ₄ , PhH, rt, 1 h	 <p>(–) + (–)</p>	537
	HN ₃ , 70°	 <p>(25) + (23)</p>	538

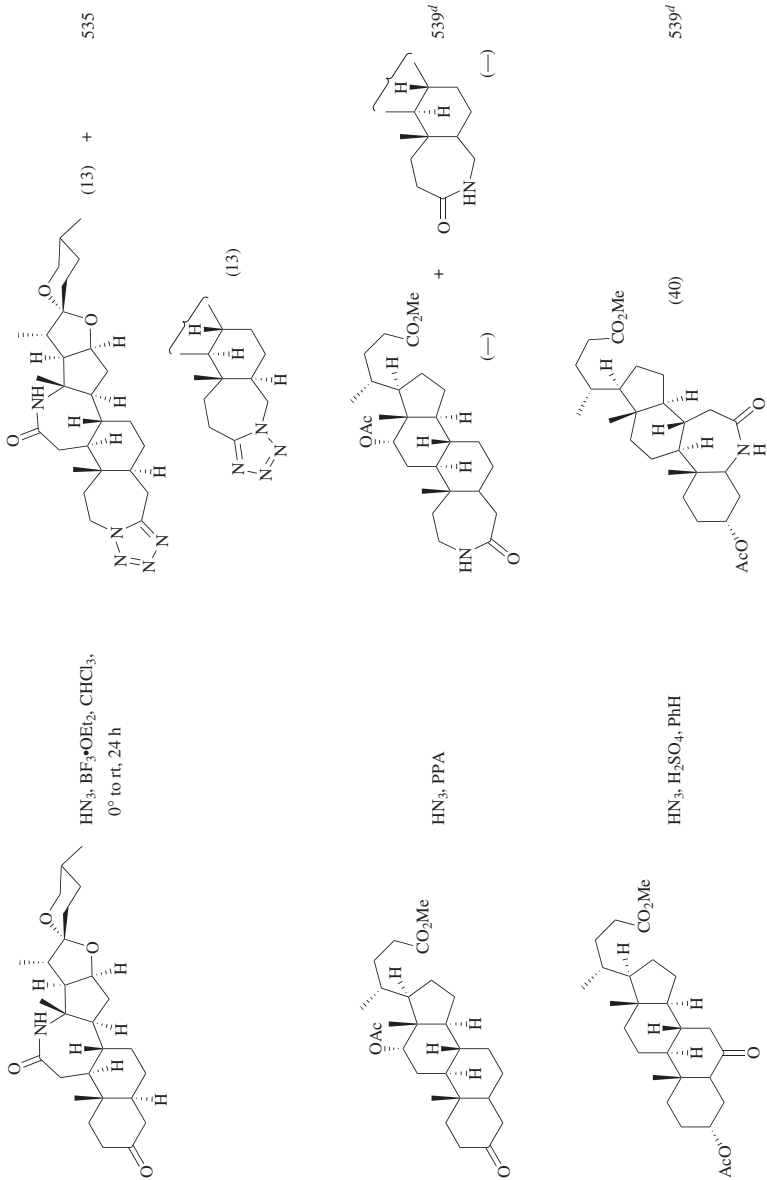
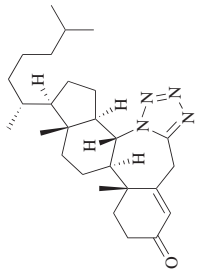
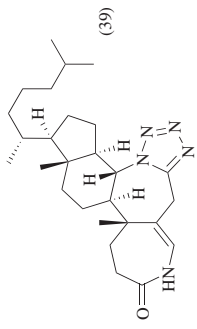
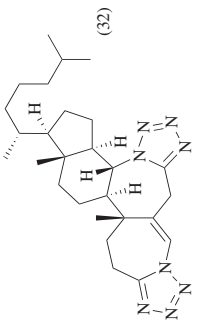
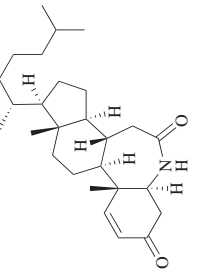
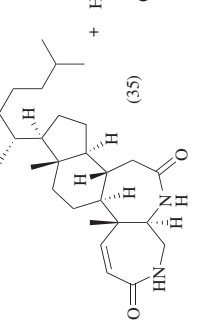
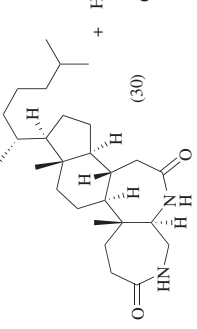
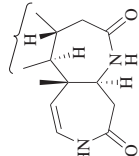
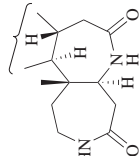
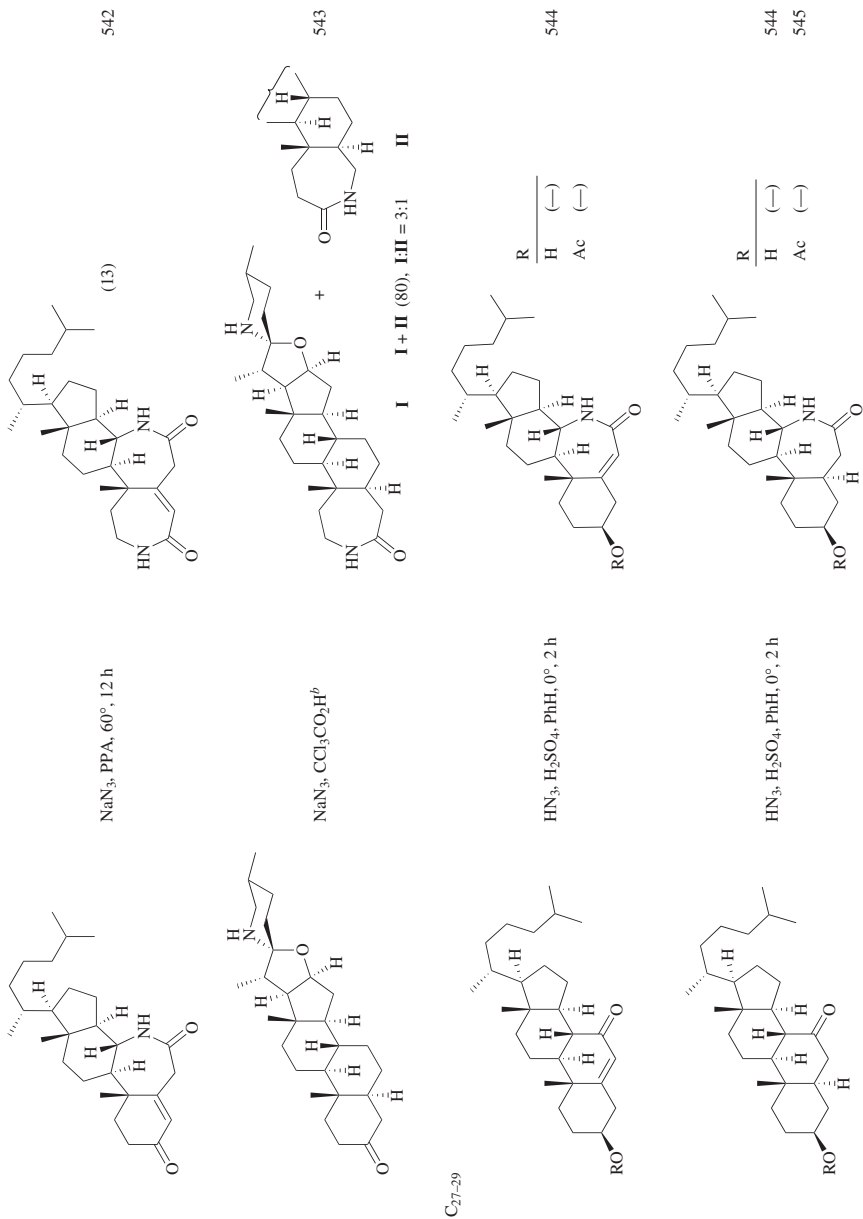


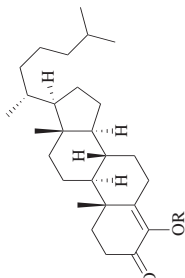
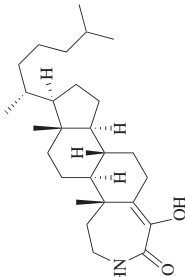
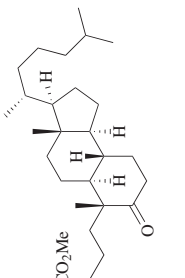
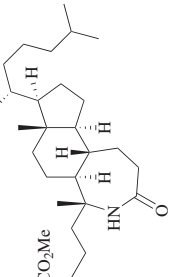
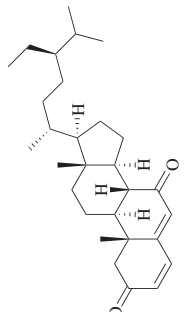
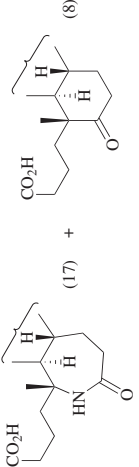
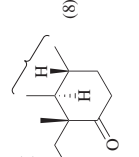
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

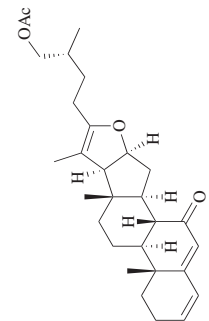
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C₂₇</p>	NaN ₃ , PPA, 50°, 10 h	 <p>(39)</p>	540
	HN ₃ , BF ₃ ·OEt ₂ , CHCl ₃ , 0° to rt, 28 h	 <p>(32)</p>	540
	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 1 h	 <p>(35)</p>	541
	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 1.5 h	 <p>(30)</p>	541
		 <p>(10)</p>	541
		 <p>(35)</p>	541



C₂₇₋₂₉

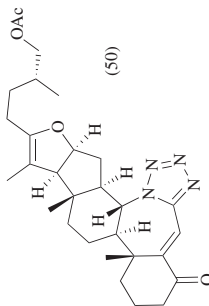
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C_{27-29}</p>	<p>NaN_3, PPA, 50°, 6 h</p>	 <p>R H (58) Ac (58)</p>	528
 <p>C_{28}</p>	<p>NaN_3, PPA, 60°, 10 h</p>	 <p>(30) +</p>	546
	<p>NaN_3, H_2SO_4</p>	 <p>(17) +</p>  <p>(8)</p>	547

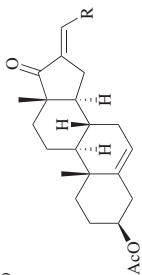


HN₃, BF₃•OEt₂, PhH, rt, 80 h

548

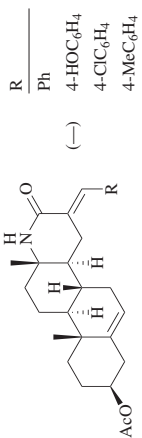


C₃₈₋₂₉



NaN₃, H₂SO₄, PhH, rt, 1 h

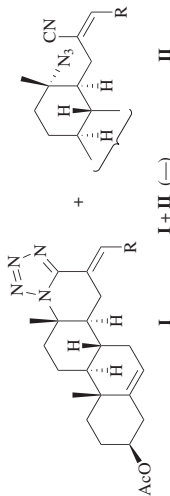
549



R —————
 Ph
 4-HOC₆H₄
 4-ClC₆H₄
 4-MeC₆H₄
 4-MeOC₆H₄

HN₃, BF₃•OEt₂, PhH,
 0° to rt, 24 h

549



R —————
 Ph
 4-HOC₆H₄
 4-ClC₆H₄
 4-MeC₆H₄
 4-MeOC₆H₄

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

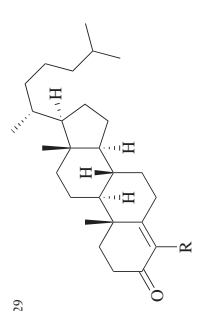
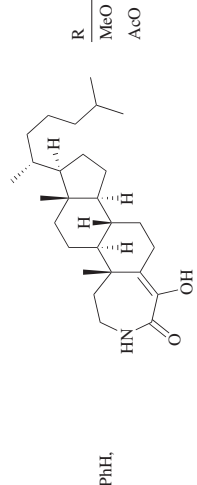
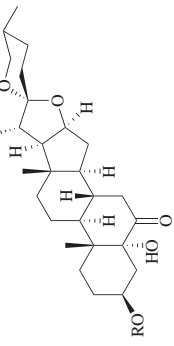
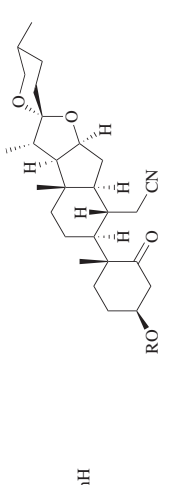
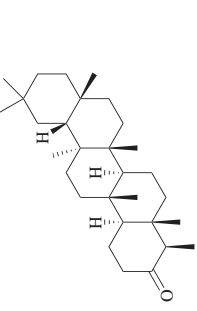
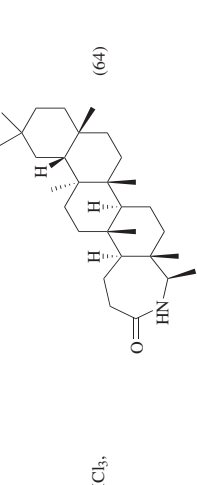
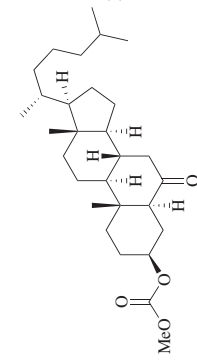
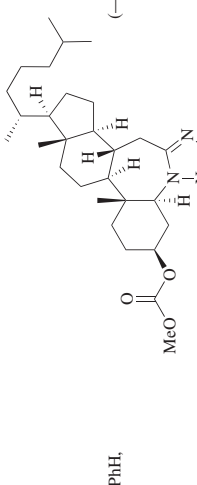
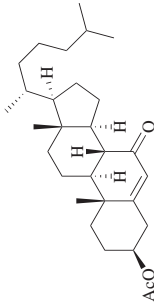
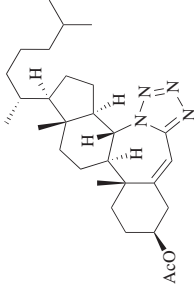
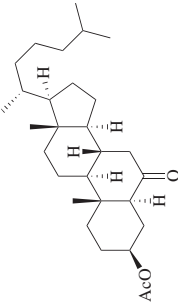
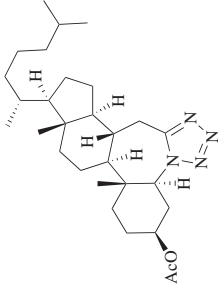
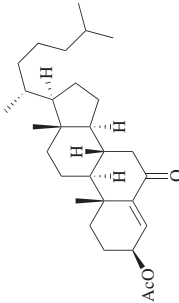
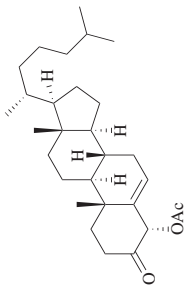
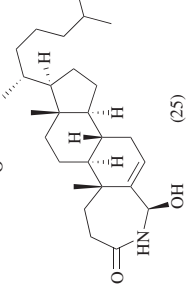
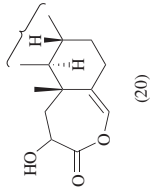
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{28-29}	$\text{HN}_3, \text{BF}_3 \cdot \text{OEt}_2, \text{PhH},$ rt, 3 d	 R MeO (60) AcO (50)	530
 C_{29}	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH}$	 R Me (—) Et (—)	550
 C_{29}	$\text{HN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3,$ $0^\circ, 2 \text{ h}$	 (64)	551
 C_{29}	$\text{HN}_3, \text{BF}_3 \cdot \text{OEt}_2, \text{PhH},$ $0^\circ \text{ to rt}, 35 \text{ h}$	 (—)	552

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	HN ₃ , BF ₃ ·OEt ₂ , PhH, 0° to rt, 5 h	 (—)	553
	HN ₃ , BF ₃ ·OEt ₂ , PhH, 0° to rt, 35 h	 (—)	554
	NaN ₃ , PPA, 60°, 8 h	(15)	531
	HN ₃ , BF ₃ ·OEt ₂ , PhH, rt, 24 h	 (25) +  (20)	532

C₂₉

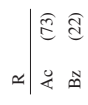
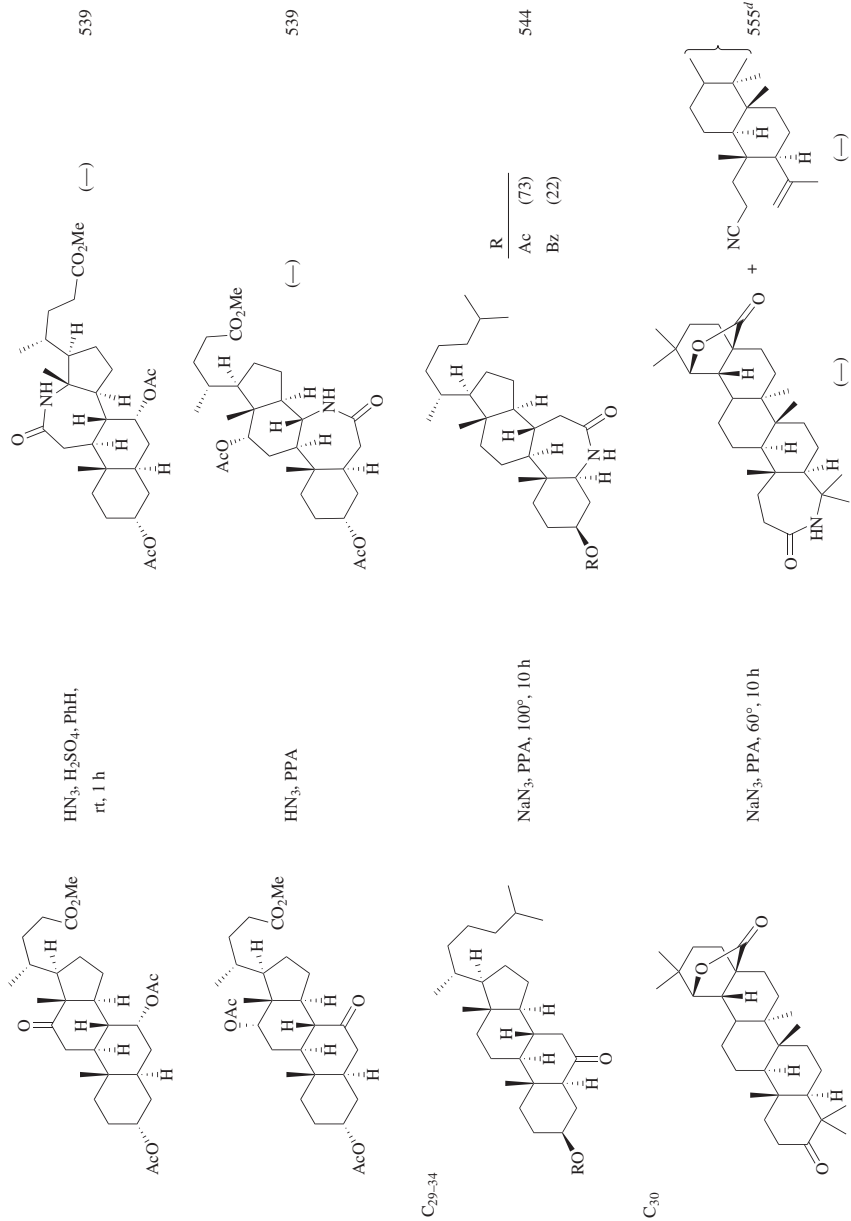
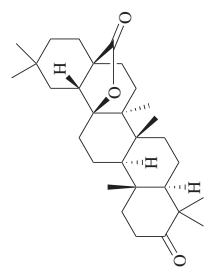
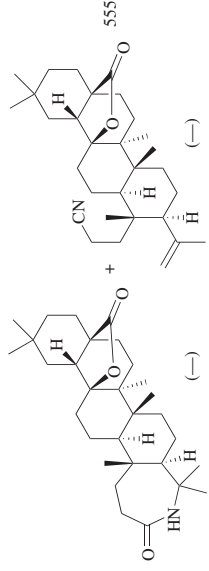
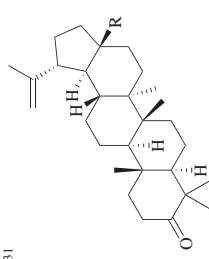
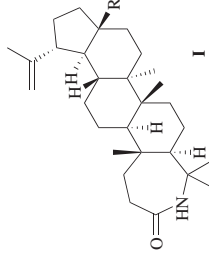
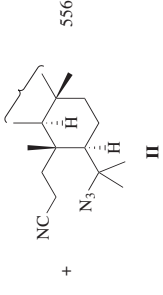
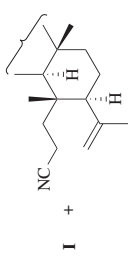
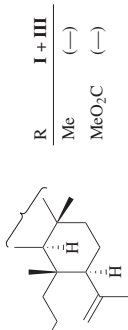
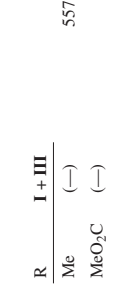
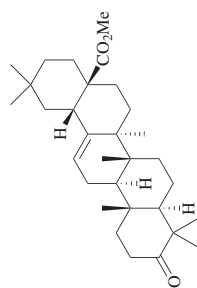


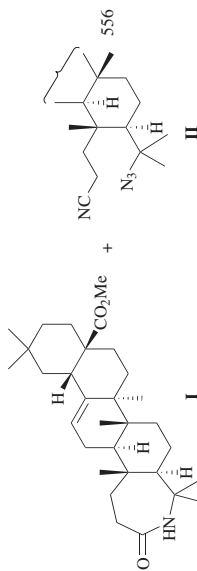
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
 <p>C₃₀</p>	NaN ₃ , PPA, 60°, 10 h	 <p>555</p>	(—)																				
 <p>C₃₀₋₃₁</p>	<p>A: HN₃, BF₃•OEt₂, PhH, rt, 16 h</p> <p>B: HN₃, H₂SO₄, PhH, rt, 16 h</p>	 <p>I</p>  <p>556</p> <p>II</p>	(—)																				
		<table border="1"> <thead> <tr> <th>R</th> <th>Conditions</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>A</td> <td>(—)</td> <td>(45)</td> </tr> <tr> <td>Me</td> <td>B</td> <td>(57)</td> <td>(—)</td> </tr> <tr> <td>MeO₂C</td> <td>A</td> <td>(—)</td> <td>(45)</td> </tr> <tr> <td>MeO₂C</td> <td>B</td> <td>(57)</td> <td>(—)</td> </tr> </tbody> </table>	R	Conditions	I	II	Me	A	(—)	(45)	Me	B	(57)	(—)	MeO ₂ C	A	(—)	(45)	MeO ₂ C	B	(57)	(—)	
R	Conditions	I	II																				
Me	A	(—)	(45)																				
Me	B	(57)	(—)																				
MeO ₂ C	A	(—)	(45)																				
MeO ₂ C	B	(57)	(—)																				
 <p>I</p>	NaN ₃ , H ₂ SO ₄ , AcOH, 30–70°, 12 h	 <p>I + III</p>	<p>Me (—)</p> <p>MeO₂C (—)</p>																				
		 <p>III</p>	557, 555																				

C₃₁

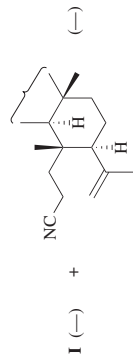


A: HN_3 , $\text{BF}_3 \cdot \text{OEt}_2$, PhH,
rt, 16 h
B: HN_3 , H_2SO_4 , PhH,
rt, 16 h



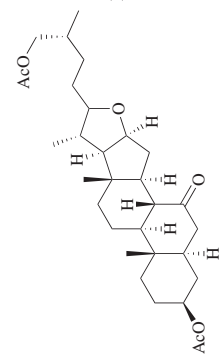
556

Conditions I II
A (–) (45)
B (57) (–)



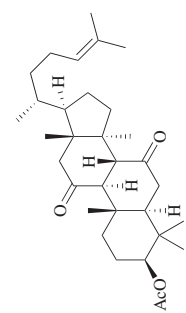
NaN_3 , H_2SO_4 , AcOH,
30–70°, 12 h

557



HN_3 , $\text{BF}_3 \cdot \text{OEt}_2$, PhH,
rt, 80 h

548^d

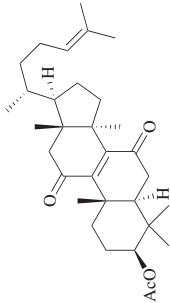
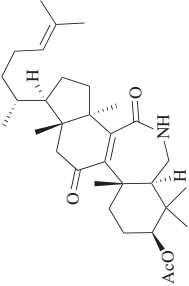
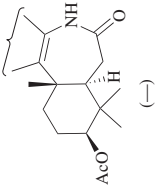
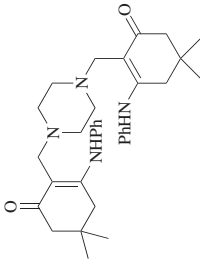
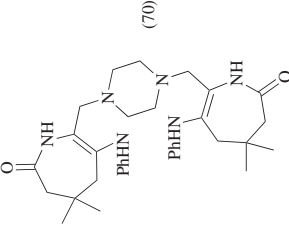


NaN_3 , H_2SO_4 , 0°, 15 min

558

(44)

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₃₁	NaN_3 , H_2SO_4 , 0° , 30 min	 (50) +  (-)	558
 C ₃₄	NaN_3 , H_2SO_4 , CHCl_3 , 0° to rt, 5 h	 (70) (-)	478

^a Silica sulfuric acid is silica-bound sulfuric acid generated by treating silica with chlorosulfonic acid.

^b Molten trichloroacetic acid (mp 57°) was used as solvent.

^c The structure was initially assigned incorrectly. It has been corrected here, see reference 401.

^d The stereochemistry of the substrate was not specified in the reference.

^e A single isomer of unassigned structure was obtained.

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN₃

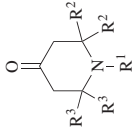
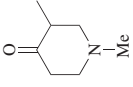

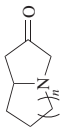
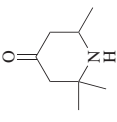
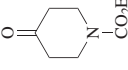
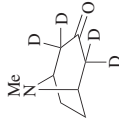
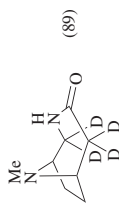
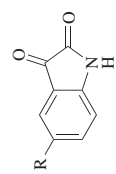
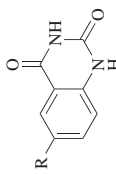
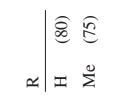
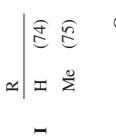
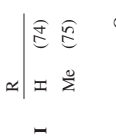
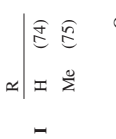
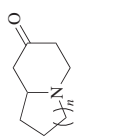
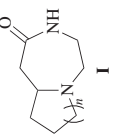
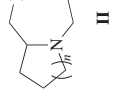
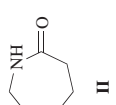
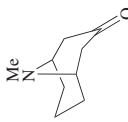
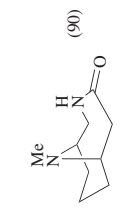
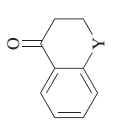
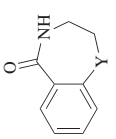
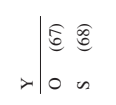
Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.
		R ¹	R ²	R ³		
<p>C₅₋₉</p> 	<p>NaN₃, H₂SO₄, CHCl₃, 0°, 45 min</p>	<p>H</p>	<p>H</p>	<p>H</p>	<p>(88)</p>	<p>559</p>
		<p>Me</p>	<p>H</p>	<p>H</p>	<p>(53)</p>	
		<p>H</p>	<p>Me</p>	<p>Me</p>	<p>(51)</p>	
<p>C₇</p> 	<p>NaN₃, H₂SO₄, 0°, 1 h</p>				<p>(38)</p>	<p>57</p>
	<p>HN₃, P₂O₅, H₂SO₄, CHCl₃, 30°, 6 h</p>				<p>(73)</p>	<p>560</p>
<p>C₇₋₈</p> 	<p>NaN₃, H₂SO₄, CHCl₃, 0–50°, 2 h</p>				<p>n</p>	<p>561</p>
					<p>1</p>	<p>(44)</p>
					<p>2</p>	<p>(65)</p>
<p>C₈</p> 	<p>NaN₃, H₂SO₄, 0°, 1 h</p>				<p>(64)</p>	<p>57</p>
	<p>NaN₃, H₂SO₄, 0°, 3 h</p>				<p>(70)</p>	<p>562</p>

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
 C ₈	NaN ₃ , D ₂ SO ₄ , 0–50°, 3 h	 (89)	563						
 C ₈₋₉	TMSN ₃ , FeCl ₃ , DCE, rt, 30–35 min	 (80)  (75)	286						
 I	NaN ₃ , FeCl ₃ , DCE, rt, 2.5 h	 (74)  (75)	286						
 C ₉	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 0–50°, 2 h	 (90)  I  II " <table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>1</td> <td>(22)</td> <td>(0)</td> </tr> <tr> <td>2</td> <td>(20)</td> <td>(—)</td> </tr> </table>	1	(22)	(0)	2	(20)	(—)	561
1	(22)	(0)							
2	(20)	(—)							
 C ₉	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 0–50°, 4 h	 (90)	564						
 C ₉	HN ₃ , P ₂ O ₅ , CHCl ₃ , 20°, 4 h	 (67)  (68)	560						

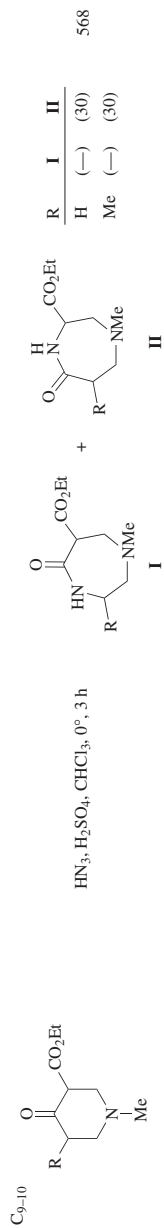
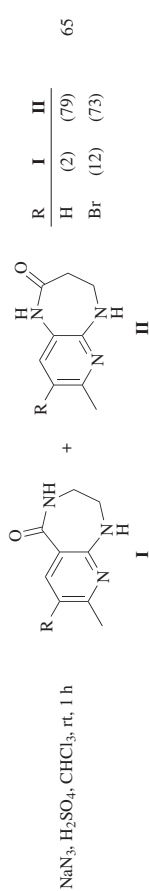
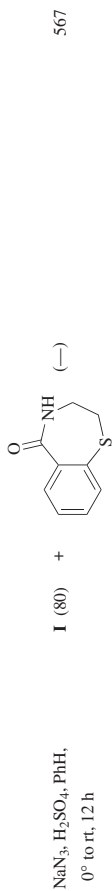
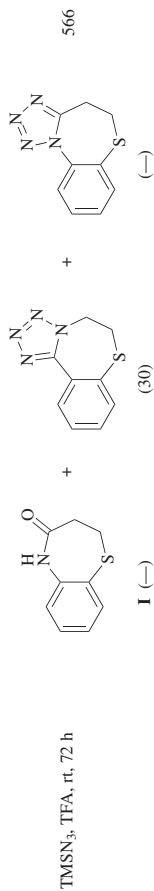
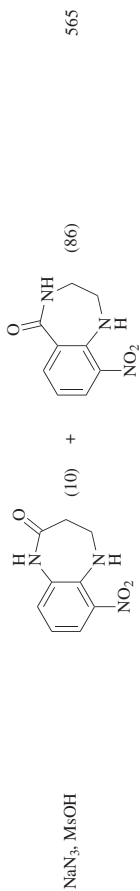
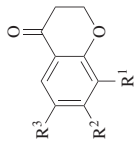
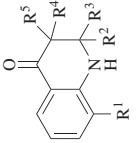
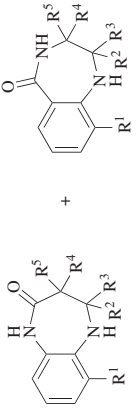
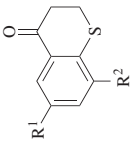
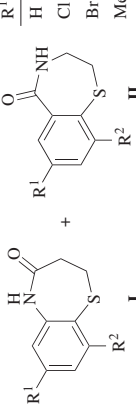
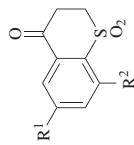
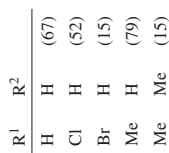


TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																										
<p>C₉-10</p> 	<p>NaN₃, H₂SO₄, 0° to rt, 12 h</p>	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>Cl</td> </tr> <tr> <td>H</td> <td>H</td> <td>Br</td> </tr> <tr> <td>Cl</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>Me</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>MeO</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>MeO</td> </tr> </tbody> </table>	R ¹	R ²	R ³	H	H	H	H	H	Cl	H	H	Br	Cl	H	H	H	H	Me	Me	H	H	H	MeO	H	H	H	MeO	62															
R ¹	R ²	R ³																																											
H	H	H																																											
H	H	Cl																																											
H	H	Br																																											
Cl	H	H																																											
H	H	Me																																											
Me	H	H																																											
H	MeO	H																																											
H	H	MeO																																											
<p>C₉-11</p> 	<p>NaN₃, H₂SO₄, rt, 2 h</p>	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>R⁵</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>(30)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>(52)</td> <td>(0)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Me</td> <td>H</td> <td>(45)</td> <td>(27)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Me</td> <td>H</td> <td>H</td> <td>(77)</td> <td>(0)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Me</td> <td>Me</td> <td>(0)</td> <td>(79)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	R ⁵	I	II	H	H	H	H	H	(30)	(0)	Me	H	H	H	H	(52)	(0)	H	H	H	Me	H	(45)	(27)	H	Me	Me	H	H	(77)	(0)	H	H	H	Me	Me	(0)	(79)	569
R ¹	R ²	R ³	R ⁴	R ⁵	I	II																																							
H	H	H	H	H	(30)	(0)																																							
Me	H	H	H	H	(52)	(0)																																							
H	H	H	Me	H	(45)	(27)																																							
H	Me	Me	H	H	(77)	(0)																																							
H	H	H	Me	Me	(0)	(79)																																							
	<p>NaN₃, H₂SO₄</p>	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(42)</td> <td>(21)</td> </tr> <tr> <td>Cl</td> <td>H</td> <td>(78)</td> <td>(0)</td> </tr> <tr> <td>Br</td> <td>H</td> <td>(84)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>(36)</td> <td>(44)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(21)</td> <td>(33)</td> </tr> </tbody> </table>	R ¹	R ²	I	II	H	H	(42)	(21)	Cl	H	(78)	(0)	Br	H	(84)	(0)	Me	H	(36)	(44)	Me	Me	(21)	(33)	570																		
R ¹	R ²	I	II																																										
H	H	(42)	(21)																																										
Cl	H	(78)	(0)																																										
Br	H	(84)	(0)																																										
Me	H	(36)	(44)																																										
Me	Me	(21)	(33)																																										

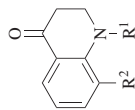


NaN₃, H₂SO₄

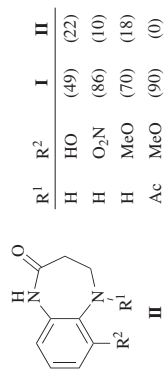


570

C₉-12



NaN₃, MeOH



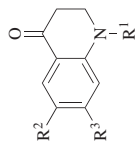
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565

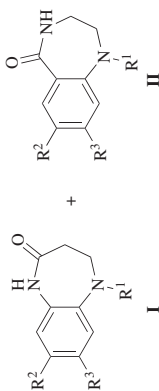
571

571

C₉-15

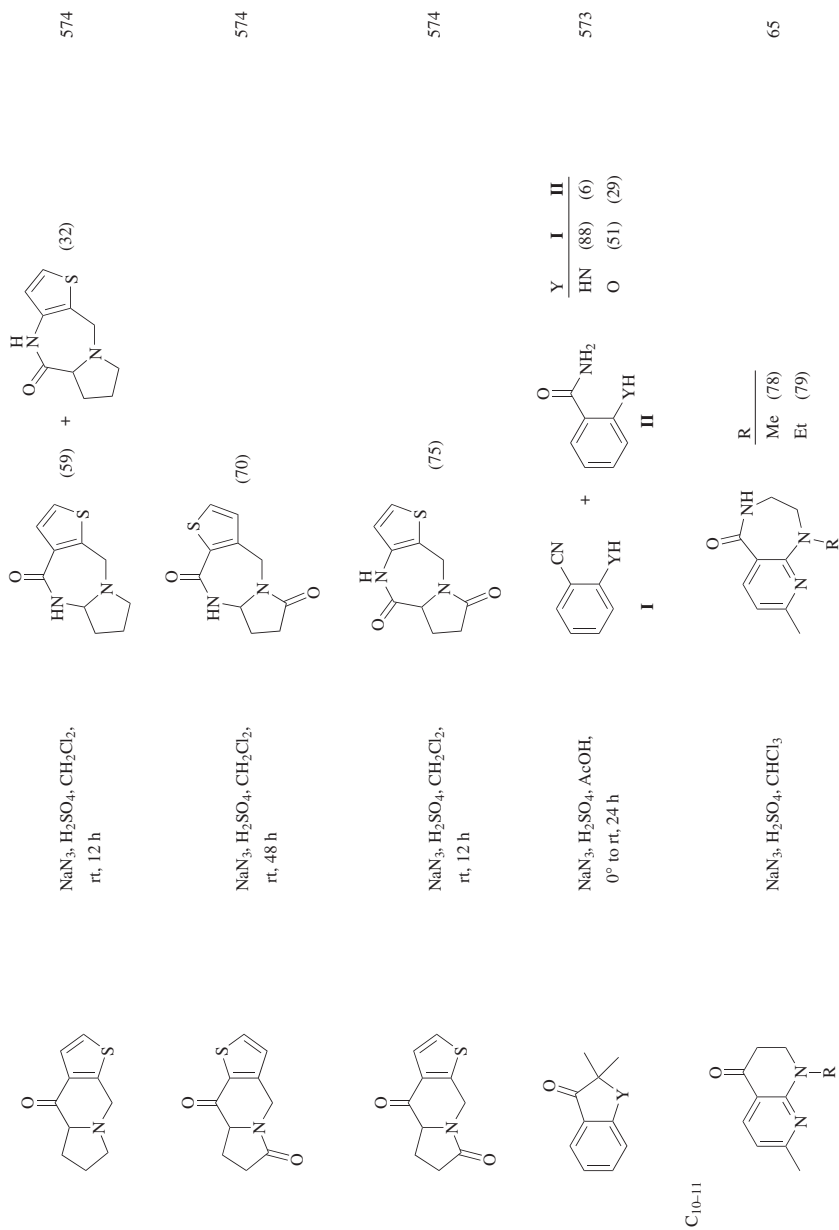


NaN₃, H₂SO₄, CHCl₃, rt, 2 h



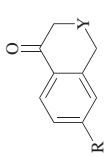
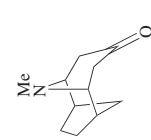
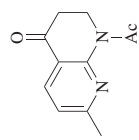
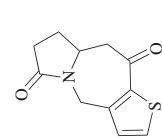
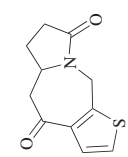
572

R ¹	R ²	R ³	I + II	I:II	R ¹	R ²	R ³	I + II	I:II
H	H	H	(88)	1:4	Me	H	MeO	(92)	1:2
H	Cl	H	(92)	1:2	Ac	H	H	(85)	19:1
H	H	MeO	(95)	3:7	Ac	Cl	H	(80)	9:1
Me	H	H	(82)	1:3	Ac	H	MeO	(90)	9:1
Me	Cl	H	(91)	1:3	Ph	H	H	(82)	1:3



C₁₀₋₁₁

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
		R	Y		
<p>C_{10-14}</p> 	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{PhH},$ 0° to rt, 12 h</p>	<p>MeO</p> <p>H</p> <p>MeO</p>	<p>S</p> <p>EtN</p> <p>EtN</p>	<p>(—)</p> <p>(—)</p> <p>(63)</p>	575
<p>C_{11}</p> 	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4$</p>			(93)	576
	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CHCl}_3,$ rt, 1 h</p>			(69)	65
	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CH}_2\text{Cl}_2,$ rt, 24 h</p>			(65)	66
	<p>$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CH}_2\text{Cl}_2,$ rt, 24 h</p>			(70)	66

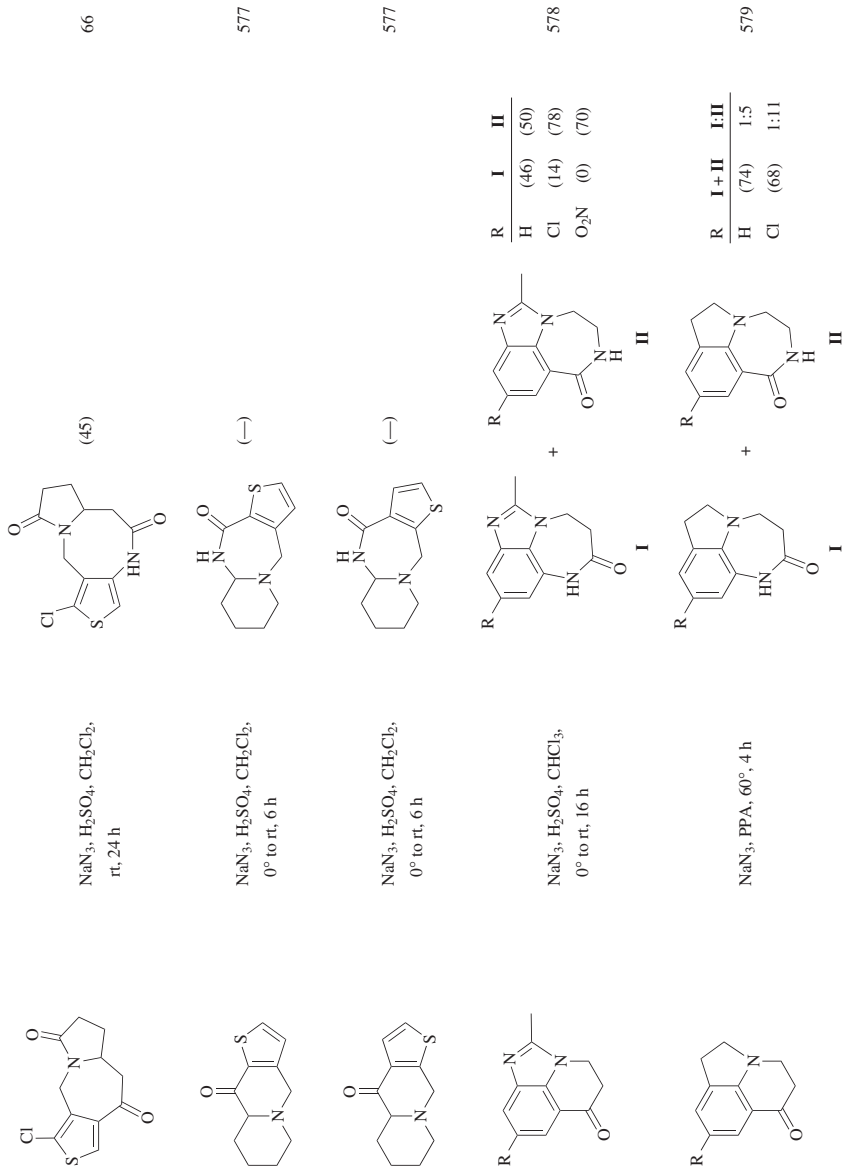
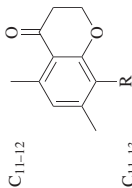
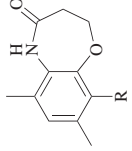
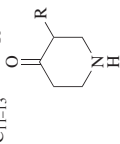
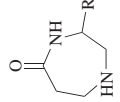
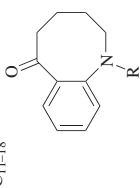
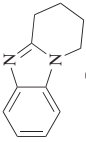
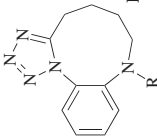
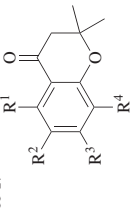
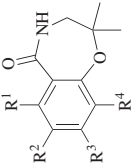
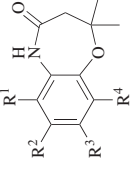
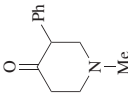
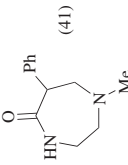
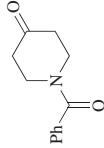
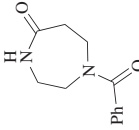
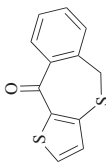
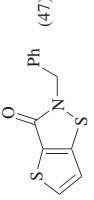
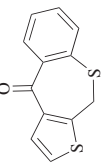
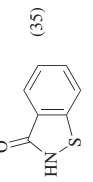
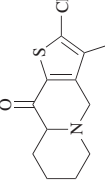
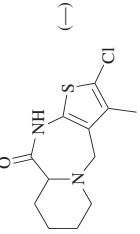
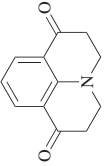
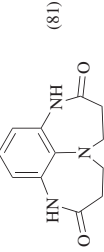


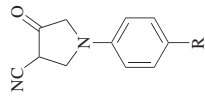
TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₁₋₁₂	NaN ₃ , H ₂ SO ₄ , rt, 16 h	 R H (5) Me (5)	62
 C ₁₁₋₁₃	HN ₃ , H ₂ SO ₄ , CHCl ₃ , 0°, 1.5 h	 R Ph (71) Bn (74) BnCH ₂ (74)	568
 C ₁₁₋₁₈	NaN ₃ , H ₂ SO ₄ , AcOH, 0° to rt, 24 h	 I +  II R H (54) (23) Ac (50) (20) Ts (50) (20)	573
 C ₁₁₋₂₇	NaN ₃ , H ₂ SO ₄ , AcOH, 50°, 3 h	 I +  II R ¹ R ² R ³ R ⁴ R ⁴ R ⁴ R ⁴ H H MeO MeO MeO MeO MeO MeO (57) (47) (53) (55) (0) (49) (54) (0) (54)	580

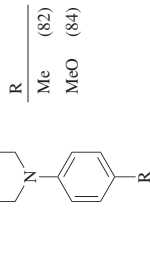
H	H	NCCH ₂ O	H	(45)	(0)
H	H	HO ₂ CCH ₂ O	H	(64)	(0)
H	H	H ₂ NCOCH ₂ O	H	(51)	(0)
Me	H	MsO	H	(0)	(47)
H	H	HO ₂ CCH ₂ O	Me	(75)	(0)
H	H	EtO ₂ CCH ₂ O	H	(71)	(0)
H	H	EtO ₂ CCH ₂ O	Me	(73)	(0)
H	H	PhSO ₃	H	(35)	(0)
H	H	BnO	H	(71)	(0)
H	HO	BnO	H	(42)	(0)
H	H	2-ClC ₆ H ₄ CH ₂ O	H	(52)	(0)
H	H	4-ClC ₆ H ₄ CH ₂ O	H	(61)	(0)
H	H	PNBO	H	(91)	(0)
H	H	4-BrC ₆ H ₄ CH ₂ O	H	(48)	(0)
H	H	TsO	H	(47)	(0)
Me	H	BnO	H	(0)	(59)
Me	H	2-ClC ₆ H ₄ CH ₂ O	H	(0)	(58)
Me	H	PNBO	H	(0)	(46)
Me	H	4-BrC ₆ H ₄ CH ₂ O	H	(0)	(44)
H	H	PhNHCOCH ₂ O	H	(46)	(0)
H	H	2-ClC ₆ H ₄ NHCOCH ₂ O	H	(61)	(0)
H	H	3-ClC ₆ H ₄ NHCOCH ₂ O	H	(87)	(0)
H	H	2-BrC ₆ H ₄ NHCOCH ₂ O	H	(62)	(0)
H	H	3-BrC ₆ H ₄ NHCOCH ₂ O	H	(61)	(0)
H	H	2,6-Cl ₂ C ₆ H ₃ NHCOCH ₂ O	H	(48)	(0)
Me	H	PhNHCOCH ₂ O	H	(0)	(57)
H	H	PhNHCOCH ₂ O	Me	(62)	(0)
H	H	2-MeC ₆ H ₄ NHCOCH ₂ O	H	(54)	(0)
H	H	2-Me-6-EtC ₆ H ₃ NHCOCH ₂ O	H	(52)	(0)
H	PhSO ₂ O	PhSO ₂ O	H	(42)	(0)
H	TsO	TsO	H	(45)	(0)
H	4-MeC ₆ H ₄ COHNCH ₂ O	BnO	H	(39)	(0)

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3 , H_2SO_4 , CHCl_3 , 10° , 30 min	 (41)	581
	HN_3 , P_2O_5 , H_2SO_4 , CH_2Cl_2 , 20° , 4 h	 (72)	560
	NaN_3 , H_2SO_4 , CH_2Cl_2 , rt, 3 h	 (47)	582
	NaN_3 , H_2SO_4 , CH_2Cl_2 , rt, 3 h	 (35)	582
	NaN_3 , H_2SO_4 , CH_2Cl_2 , 0° to rt, 6 h	 (−)	169
	NaN_3 , H_2SO_4 , CHCl_3 , 0° , 15 min	 (81)	583

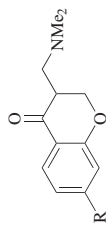


NaN₃, CHCl₃, concd H₂SO₄

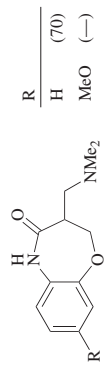


584

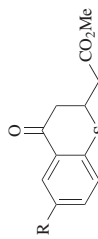
C₁₂₋₁₃



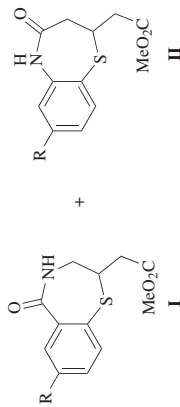
NaN₃, H₂SO₄, rt, 16 h



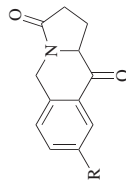
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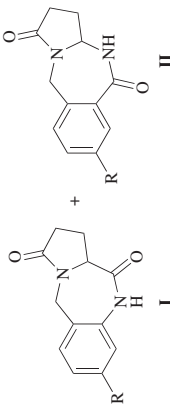
NaN₃, H₂SO₄, PhH,
0° to rt, 12 h



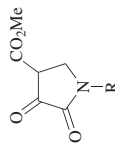
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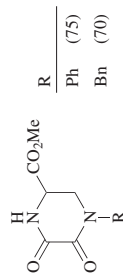
NaN₃, H₂SO₄, CH₂Cl₂,
0°, 3 h



169



NaN₃, H₂SO₄



322

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.	
		R ¹	R ²		
C ₁₂₋₁₄ 	NaN ₃ , H ₂ SO ₄ , PhH, rt, 12 h	H H H Me Et	H HO Cl H H	(52) (15) (34) (57) (46)	586
C ₁₃ 	NaN ₃ , H ₂ SO ₄ , rt to 50°, 37 h	(64)	(-)	(-)	55
	NaN ₃ , H ₂ SO ₄ , CHCl ₃	(28)	(54)	(54)	587
	NaN ₃ , SiCl ₄ , MeCN, rt, 12 h	(40)	(40)	(40)	70
	NaN ₃ , CCl ₃ CO ₂ H, CHCl ₃ , rt, 12 h	(100)	(100)	(100)	588

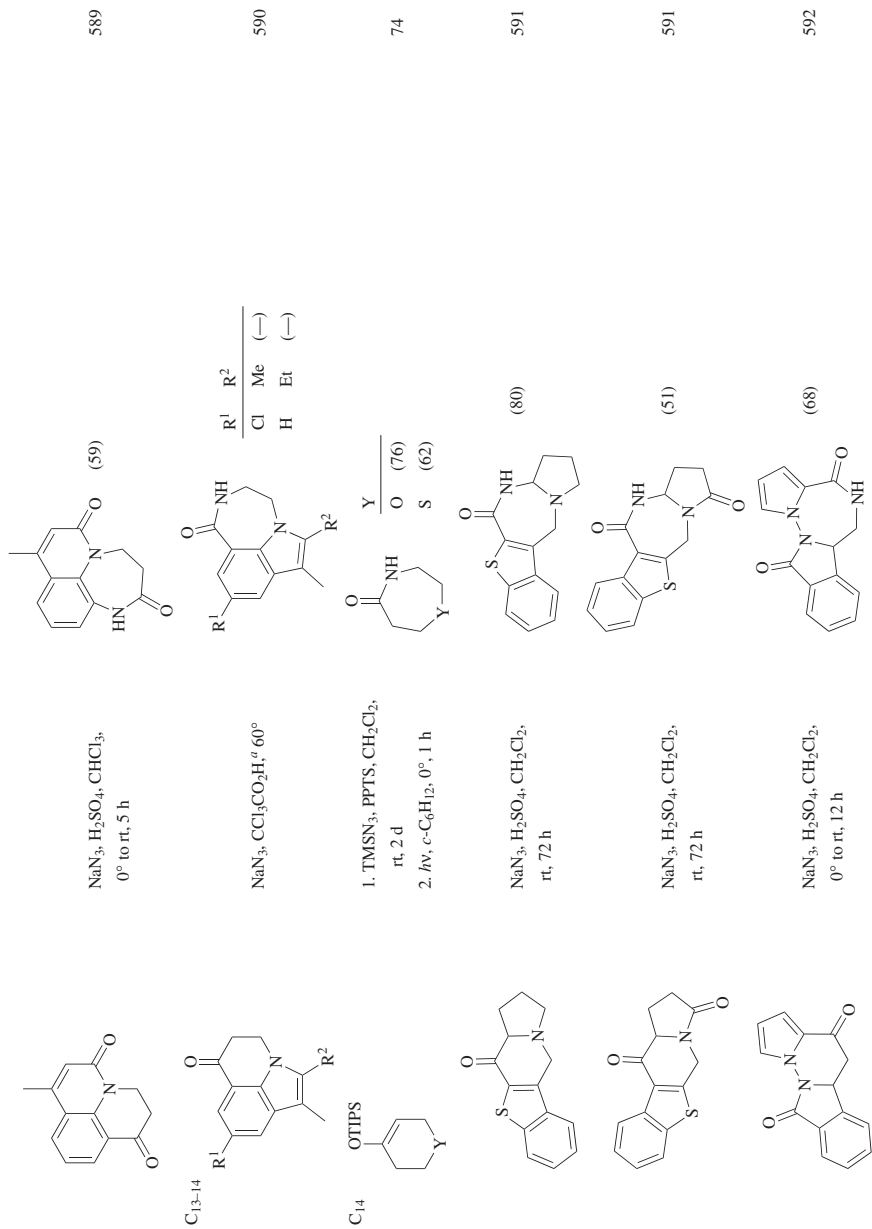
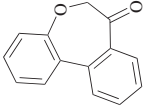
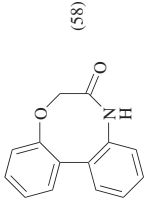
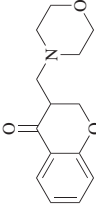
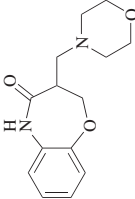
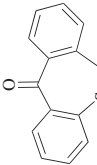
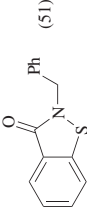
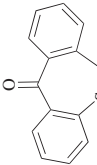
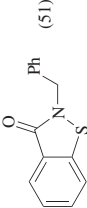
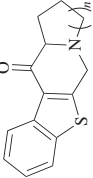
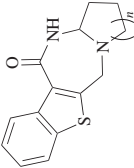
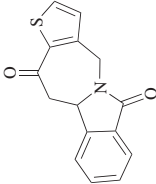
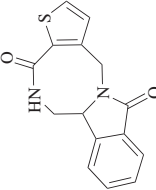
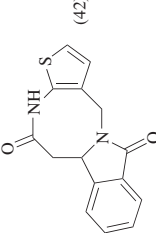


TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{NaN}_3, \text{H}_2\text{SO}_4, 0^\circ$ to rt, 2 h	 I (58)	593
	$\text{NaN}_3, \text{PPA}, 50^\circ$, 4 h	 (20)	593
	$\text{NaN}_3, \text{H}_2\text{SO}_4$, rt, 16 h	 (51)	62
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CH}_2\text{Cl}_2$, rt, 3 h	 (51)	582
	$\text{NaN}_3, \text{H}_2\text{SO}_4, \text{CH}_2\text{Cl}_2$, rt, 72 h	 n 1 (65) 2 (51)	591
	$\text{NaN}_3, \text{H}_2\text{SO}_4$	 (32) +  (42)	594

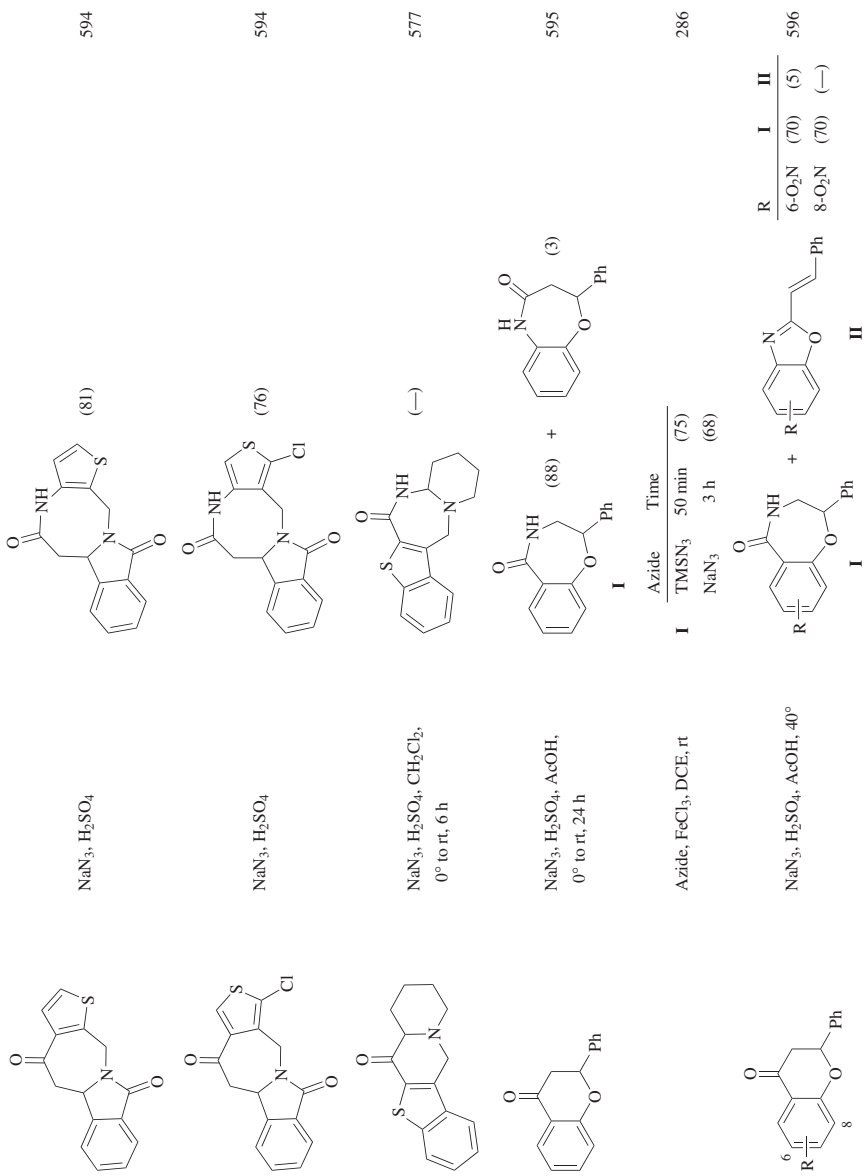
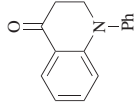
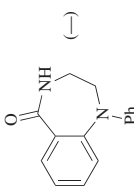
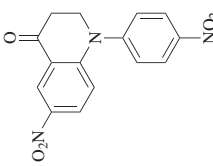
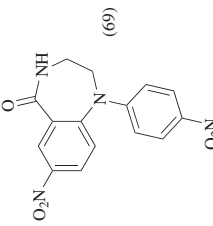
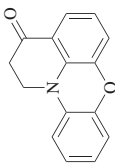
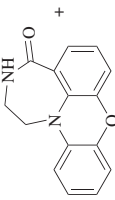
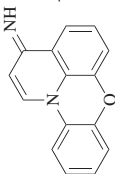
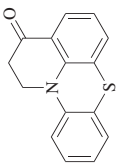
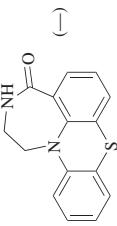
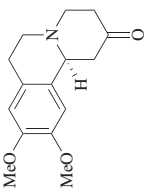
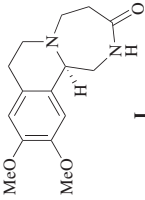
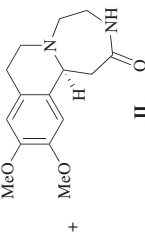


TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 3 h	 (—)	597
	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 3 h	 (69)	597
	NaN ₃ , CCl ₃ CO ₂ H, or CHCl ₃ , 70°, 5 h	 +  (13)	598
	NaN ₃ , CCl ₃ CO ₂ H, or 60°, 5 h	 (20) (—)	599
	NaN ₃ , H ₂ SO ₄ , CH ₂ Cl ₂ , rt, 4 h	 +  (90)	600

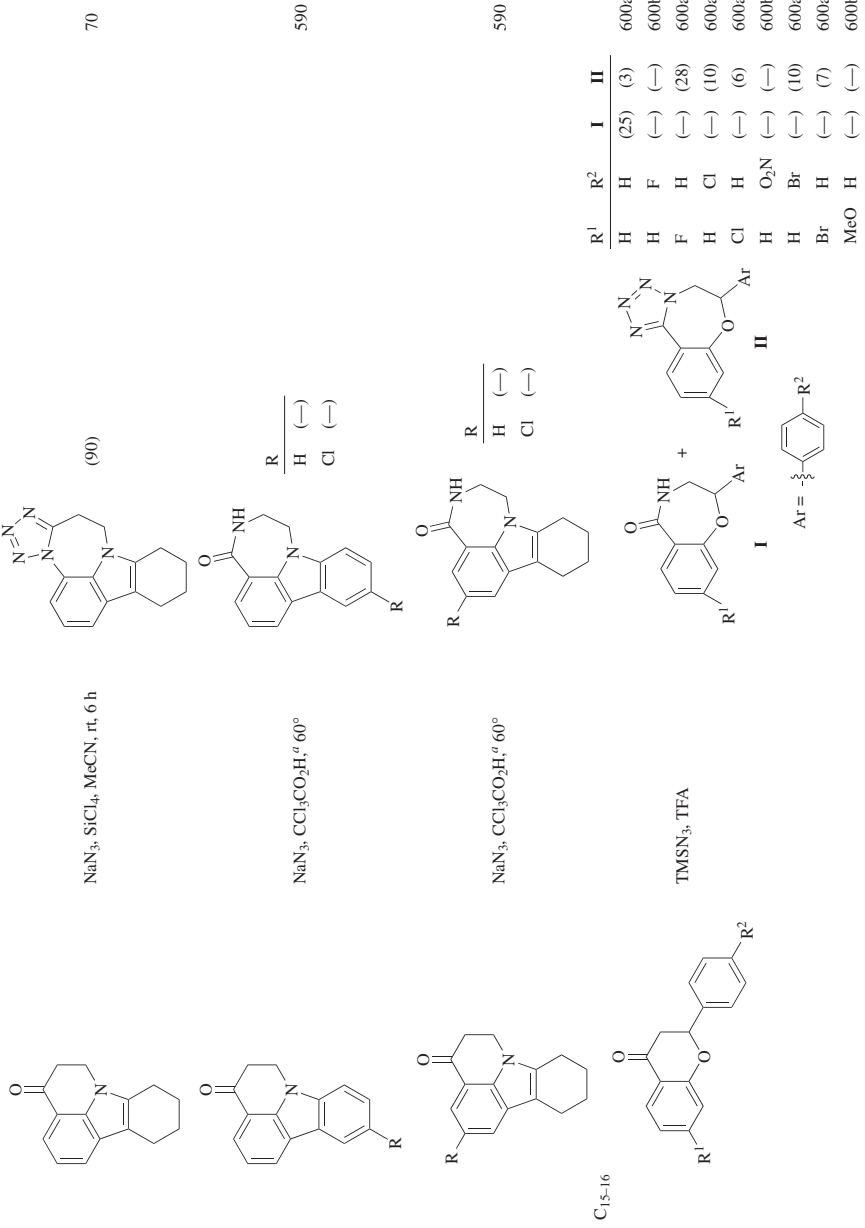
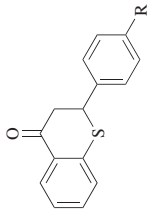
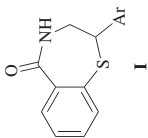
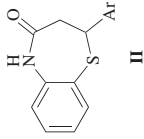
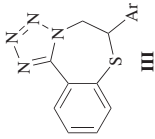
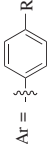
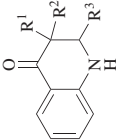
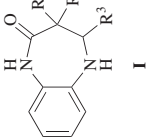
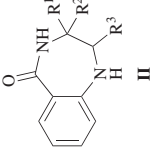
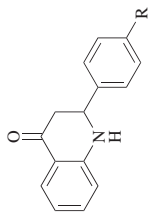
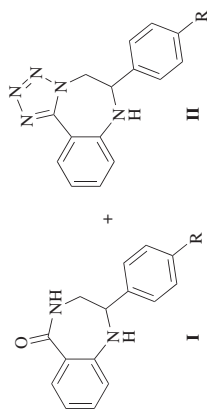


TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																														
<p>C₁₅₋₁₆</p> 	TMSN ₃ , TFA, rt, 72 h	  	566																														
		<table border="1"> <thead> <tr> <th>R</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(40)</td> <td>(20)</td> <td>(22)</td> </tr> <tr> <td>F</td> <td>(35)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>Cl</td> <td>(33)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>Br</td> <td>(28)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>MeO</td> <td>(—)</td> <td>(—)</td> <td>(—)</td> </tr> </tbody> </table> 	R	I	II	III	H	(40)	(20)	(22)	F	(35)	(—)	(—)	Cl	(33)	(—)	(—)	Br	(28)	(—)	(—)	MeO	(—)	(—)	(—)							
R	I	II	III																														
H	(40)	(20)	(22)																														
F	(35)	(—)	(—)																														
Cl	(33)	(—)	(—)																														
Br	(28)	(—)	(—)																														
MeO	(—)	(—)	(—)																														
<p>C₁₅₋₁₇</p> 	NaN ₃ , H ₂ SO ₄ , rt, 2 h	 	601																														
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>Ph</td> <td>(81)</td> <td>(0)</td> </tr> <tr> <td>H</td> <td>H</td> <td>4-ClC₆H₄</td> <td>(79)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Ph</td> <td>(0)</td> <td>(73)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Ph</td> <td>(0)</td> <td>(84)</td> </tr> <tr> <td>Et</td> <td>H</td> <td>Ph</td> <td>(0)</td> <td>(76)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	I	II	H	H	Ph	(81)	(0)	H	H	4-ClC ₆ H ₄	(79)	(0)	Me	H	Ph	(0)	(73)	Me	Me	Ph	(0)	(84)	Et	H	Ph	(0)	(76)	
R ¹	R ²	R ³	I	II																													
H	H	Ph	(81)	(0)																													
H	H	4-ClC ₆ H ₄	(79)	(0)																													
Me	H	Ph	(0)	(73)																													
Me	Me	Ph	(0)	(84)																													
Et	H	Ph	(0)	(76)																													

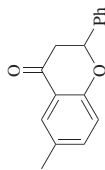
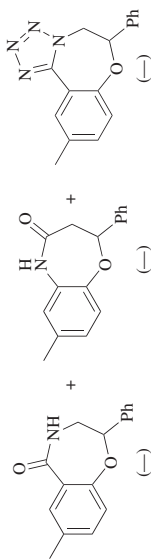
C₁₅₋₂₁

A: NaN₃, H₂SO₄, AcOH,
50°, 4 h
B: TMSN₃, TFA, rt, 5 d
C: NaN₃, SnCl₄, CH₂Cl₂,
rt, 5 d
D: NaN₃, TFA, rt, 5 d

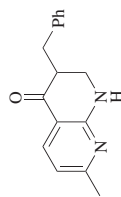
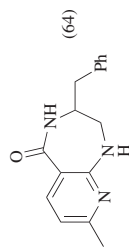


73

R	Conditions	I	II	R	Conditions	I	II
H	A	(35)	(30)	Me	C	(4)	(65)
H	B	(28)	(30)	Me	D	(5)	(40)
H	C	(5)	(60)	Ph	A	(30)	(30)
H	D	(5)	(38)	Ph	B	(35)	(30)
Me	A	(40)	(38)	Ph	C	(5)	(62)
Me	B	(35)	(35)	Ph	D	(5)	(40)

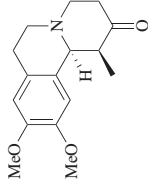
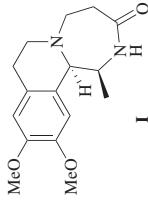
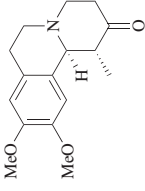
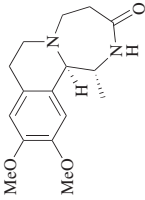
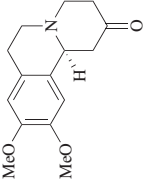
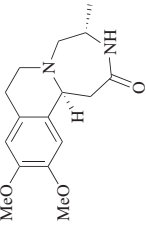
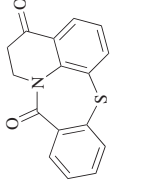
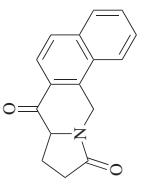
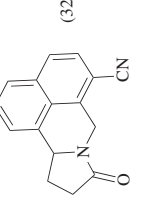
C₁₆NaN₃, AcOH, 40°

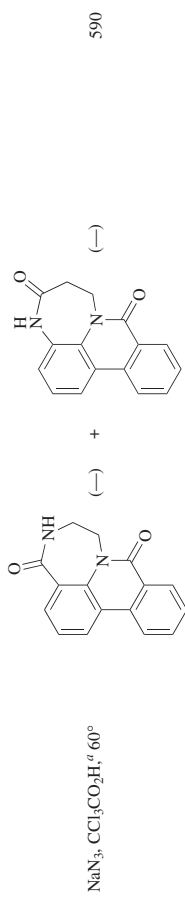
596

NaN₃, H₂SO₄, CHCl₃

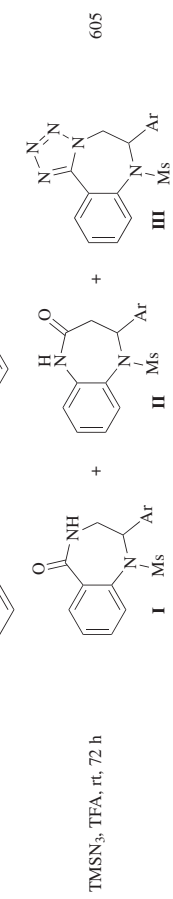
602

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₆	NaN ₃ , H ₂ SO ₄ , CH ₂ Cl ₂ , rt, 4 h	 I + II (69), I:II = —	600
 I	NaN ₃ , H ₂ SO ₄ , CH ₂ Cl ₂ , rt, 4 h	 II (67)	600
 II	NaN ₃ , H ₂ SO ₄ , CH ₂ Cl ₂ , rt, 4 h	 (82)	600
 (77)	A: NaN ₃ , H ₃ PO ₄ , 65°, 5 h B: NaN ₃ , CCl ₃ CO ₂ H, ^a 80°, 20 h C: NaN ₃ , PPA, 65°, 5 h D: NaN ₃ , H ₂ SO ₄ , rt, 3 h	A (77) B (60) C (39) D (28)	603
 (32)	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 0° to rt, 3 h	 (32)	604

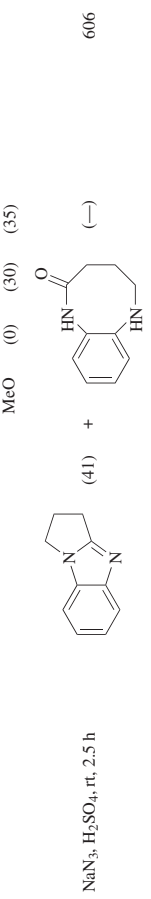
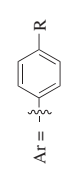


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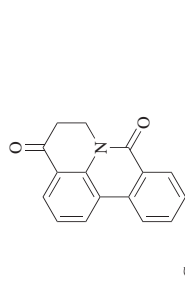


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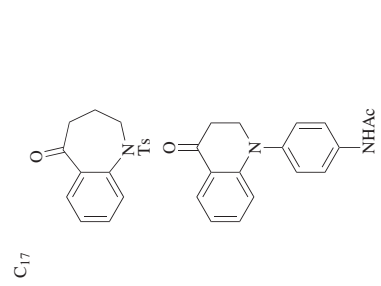
R	I	II	III
H	(35)	(25)	(20)
F	(30)	(10)	(20)
Cl	(35)	(20)	(30)
Br	(40)	(25)	(20)
MeO	(0)	(30)	(35)



606



C₁₆₋₁₇

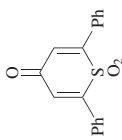
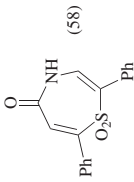
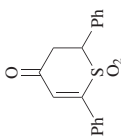
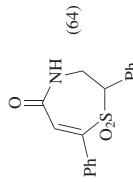
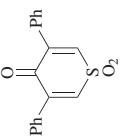
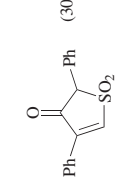
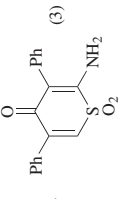
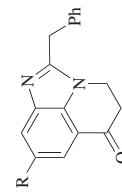
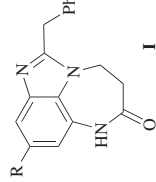
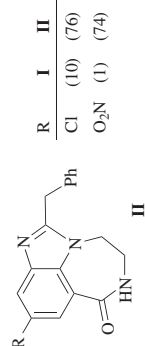
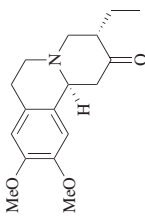
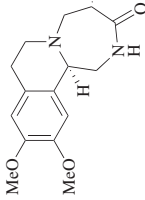
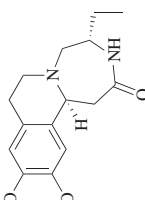


C₁₇

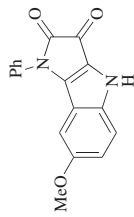


597

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN₃ (Continued)

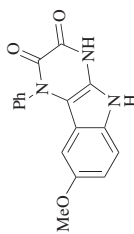
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN ₃ , H ₂ SO ₄ , 0° to rt	 (58)	607
	NaN ₃ , H ₂ SO ₄ , 0° to rt	 (64)	607
	NaN ₃ , H ₂ SO ₄ , 0° to rt	 (30) +  (3)	607
	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 0° to rt, 16 h	 I +  II	578
	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 0°	 (2) +  (90)	608

C₁₇



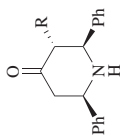
NaN₃, H₂SO₄, CHCl₃

(65)



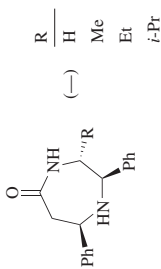
322

C₁₇₋₂₀



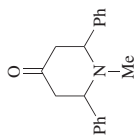
NaN₃, H₂SO₄, CHCl₃,
rt, 1.5 h

(-)



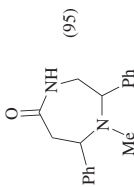
609

C₁₈

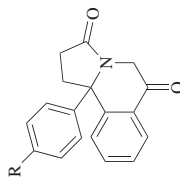


HN₃, H₂SO₄, CHCl₃,
0°, 1.5 h

(95)

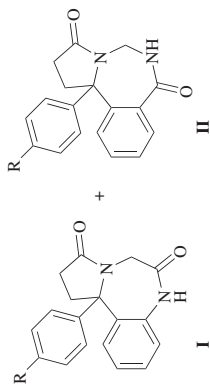


568



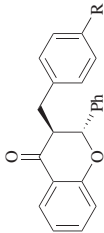
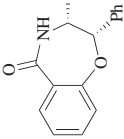
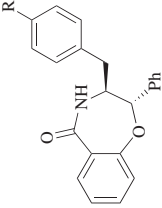
NaN₃, H₂SO₄, CHCl₃,
50°, 1.5 h

610



R	I	II
H	(41)	(4)
Cl	(55)	(4)

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	<p>NaN₃, AcOH/H₂SO₄ (5:1), 55°, 12 h</p>	<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;">  <p>I</p> </div> <div style="margin: 0 10px;">+</div> <div style="text-align: center;">  <p>II</p> </div> </div>	611												
		<table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>R</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(80)</td> <td>9:1</td> </tr> <tr> <td>Cl</td> <td>(72)</td> <td>1:0</td> </tr> <tr> <td>MeO</td> <td>(63)</td> <td>9:1</td> </tr> </tbody> </table>	R	I + II	I:II	H	(80)	9:1	Cl	(72)	1:0	MeO	(63)	9:1	
R	I + II	I:II													
H	(80)	9:1													
Cl	(72)	1:0													
MeO	(63)	9:1													

^a Mollen trichloroacetic acid (mp 57°) was used as solvent.

TABLE 6. SCHMIDT REACTIONS OF ALCOHOLS AND ALKENES WITH HN₃


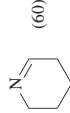

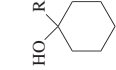
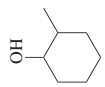

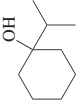
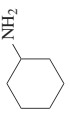
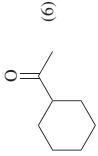
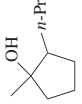
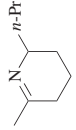
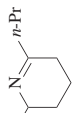
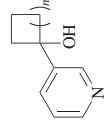
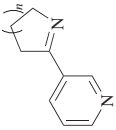
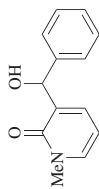
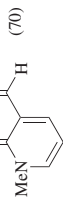
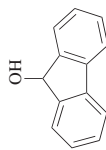
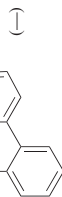
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅ 	HN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 2 h	 (60)	612
C ₆₋₉ 	1. HN ₃ , BF ₃ •OEt ₂ 2. H ₂ SO ₄ , CHCl ₃	R Me (—) <i>n</i> -Pr (93) <i>n</i> -Bu (—)	39
C ₆₋₁₂ 	NaN ₃ , H ₂ SO ₄ , rt, 2 h	R H (—) Me (22) Et (—) <i>c</i> -C ₆ H ₁₁ (—)	613 614 614 614
C ₇ 	HN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 2 h	 (30)	612
C ₉ 	NaN ₃ , H ₂ SO ₄ , rt, 2 h	 (—) +  (6)	614
	1. HN ₃ , BF ₃ •OEt ₂ 2. H ₂ SO ₄ , CHCl ₃	 (—) +  (—)	39
C ₉₋₁₀ 	HN ₃ , H ₂ SO ₄ , CH ₂ Cl ₂	 (—) n 1 (65) 2 (75)	615

TABLE 6. SCHMIDT REACTIONS OF ALCOHOLS AND ALKENES WITH HN₃ (Continued)

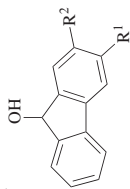
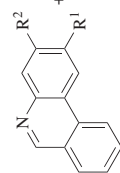
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉₋₁₅ 	1. HN ₃ , BF ₃ ·OEt ₂ , PhH 2. H ₂ SO ₄ , CHCl ₃ , 0°	 R Me (90) allyl (95) Ph (95) Bn (85)	616
C ₁₀ 	HN ₃ , H ₂ SO ₄ , CHCl ₃ , rt, 2 h	 (14) +	612
C ₁₀₋₁₆ 	HN ₃ , H ₂ SO ₄ , PhH	 R Me (35) Bn (30)	41
C ₁₁₋₁₂ 	1. HN ₃ , BF ₃ ·OEt ₂ , PhH, 0°, 10 min 2. H ₂ SO ₄ , PhH	 I n 1 (85) 2 (90)	616
C ₁₂ 	HN ₃ , H ₂ SO ₄ , PhH	 I n 1 (85) 2 (90)	616
	NaN ₃ , H ₂ SO ₄ , rt, 2 h	 (42) + (71)	614

C₁₃NaN₃, H₂SO₄, CHCl₃

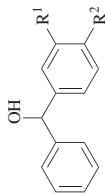
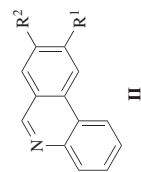
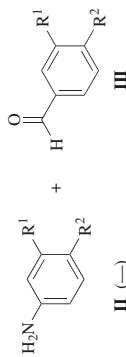
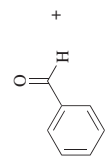
329

NaN₃, H₂SO₄, CHCl₃,
0–50°, 12 h

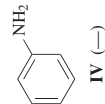
617

C_{13–14}NaN₃, H₂SO₄, CHCl₃, rt, 12 h

R ¹	R ²	I	II
O ₂ N	H	(2)	(90)
H	O ₂ N	(5)	(83) 170
H ₂ N	H	(0)	(33)
MeO	H	(11)	(21)
H	MeO	(—)	(—)
Me	H	(40)	(40)
H	Me	(54)	(14)

1. HN₃, Cl₃CCO₂H, CHCl₃
2. concd H₂SO₄, 0–55°

R ¹	R ²	I + III ^a	I:III
H	H	(—)	— 617
H	Cl	(41)	1.0:1.3 618
Cl	H	(53)	1.0:3.7 618
H	Br	(73)	1.7:1.0 618
H	Me	(80)	3.4:1.0 618
H	MeO	(46)	6.3:1.0 618



IV (—)

TABLE 6. SCHMIDT REACTIONS OF ALCOHOLS AND ALKENES WITH HN₃ (Continued)

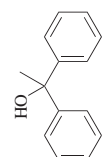
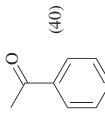
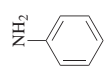
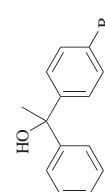
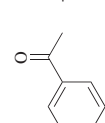
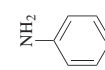
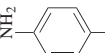
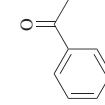
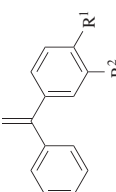
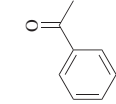
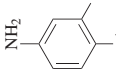
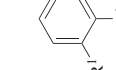
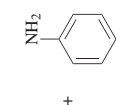
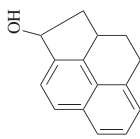
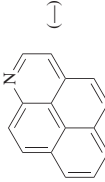

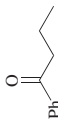
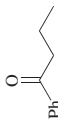
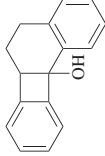
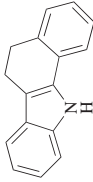
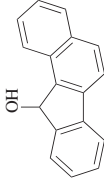
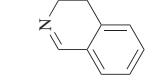
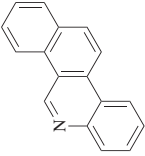
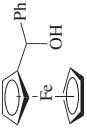
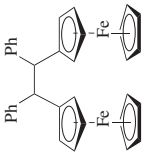
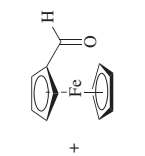
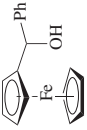
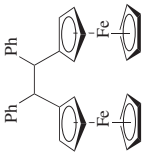
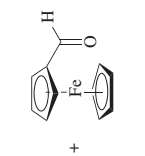
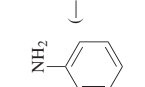
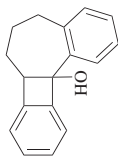
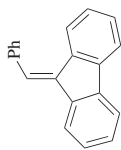
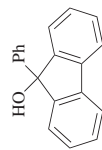
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																												
C ₁₄ 	NaN ₃ , H ₂ SO ₄ , rt	 (40) +  (65)	619																												
C ₁₄₋₁₅ 	HN ₃ , CCl ₃ CO ₂ H, PhH	 +  (I) +  (III) +  (IV)	620																												
		<table border="1"> <thead> <tr> <th>R</th> <th>I + III^b</th> <th>II (-)</th> <th>III</th> <th>IV (-)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(25)</td> <td>3:1</td> <td></td> <td></td> </tr> <tr> <td>Br</td> <td>(48)</td> <td>3:1</td> <td></td> <td></td> </tr> <tr> <td>Me</td> <td>(43)</td> <td>1:4</td> <td></td> <td></td> </tr> <tr> <td>MeO</td> <td>(37)</td> <td>0:1</td> <td></td> <td></td> </tr> </tbody> </table>	R	I + III ^b	II (-)	III	IV (-)	Cl	(25)	3:1			Br	(48)	3:1			Me	(43)	1:4			MeO	(37)	0:1						
R	I + III ^b	II (-)	III	IV (-)																											
Cl	(25)	3:1																													
Br	(48)	3:1																													
Me	(43)	1:4																													
MeO	(37)	0:1																													
C ₁₄₋₁₆ 	NaN ₃ , H ₂ SO ₄ , CHCl ₃ , 0° to rt	 +  (I) +  (II (-)) +  (III)	621 621 621 621 621 42																												
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>F</td> <td>H</td> <td>(46)</td> <td>(26)</td> </tr> <tr> <td>Br</td> <td>H</td> <td>(16)</td> <td>(30)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>(34)</td> <td>(15)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(37)</td> <td>(7)</td> </tr> <tr> <td>Et</td> <td>H</td> <td>(45)</td> <td>(10)</td> </tr> <tr> <td>EtO</td> <td>H</td> <td>(-)^c</td> <td>(-)^c</td> </tr> </tbody> </table>	R ¹	R ²	I	III	F	H	(46)	(26)	Br	H	(16)	(30)	H	Me	(34)	(15)	Me	Me	(37)	(7)	Et	H	(45)	(10)	EtO	H	(-) ^c	(-) ^c	
R ¹	R ²	I	III																												
F	H	(46)	(26)																												
Br	H	(16)	(30)																												
H	Me	(34)	(15)																												
Me	Me	(37)	(7)																												
Et	H	(45)	(10)																												
EtO	H	(-) ^c	(-) ^c																												

TABLE 6. SCHMIDT REACTIONS OF ALCOHOLS AND ALKENES WITH HN₃ (Continued)

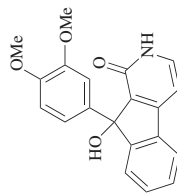
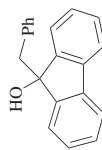
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅ 	1. NaN ₃ , MsOH, rt, 18 h 2. 10% Pd/C	 (—)	624
C ₁₆ 	NaN ₃ , H ₂ SO ₄ , rt	 (57) +  (64)	619
	1. HN ₃ , BF ₃ ·OEt ₂ , PhH 2. H ₂ SO ₄ , PhH	 (92)	616
C ₁₇ 	HN ₃ , H ₂ SO ₄ , PhH	 I (92) +  II	616
	1. NaN ₃ , CCl ₃ CO ₂ H, CHCl ₃ , rt, 2 h 2. H ₂ SO ₄ , CHCl ₃	 I +  II = 2.9:1	388
	1. HN ₃ , CCl ₃ CO ₂ H, PhH 2. AcOH, rt, 18 h	 (—) +  (—) +  (—)	625



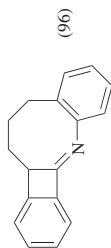
C₁₉



C₂₀

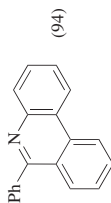


1. HN₃, BF₃•OEt₂, PhH
2. H₂SO₄, CHCl₃



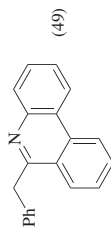
616

NaN₃, H₂SO₄, CHCl₃, rt, 1.5 h



170

NaN₃, H₂SO₄, CHCl₃, rt, 1.5 h



170

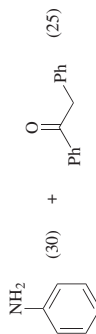
NaN₃, H₂SO₄, CHCl₃, rt, 1.5 h

I

I (40)

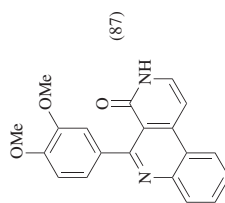
170

NaN₃, H₂SO₄, rt



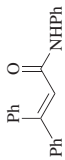
619

NaN₃, PPA, 25–45°, 12 h



329

TABLE 6. SCHMIDT REACTIONS OF ALCOHOLS AND ALKENES WITH HN₃ (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$ \begin{array}{c} \text{Ph} \quad \text{OH} \\ \diagdown \quad / \\ \text{C} \\ / \quad \backslash \\ \text{Ph} \quad \text{C} \equiv \text{C} \text{---} \text{Ph} \end{array} $	HN ₃ , H ₂ SO ₄ , CHCl ₃ , 0°, 1.5 h	 (15)	353

^a The products were isolated as mixtures of the corresponding carboxylic acids after oxidation.

^b The products were isolated as mixtures of the corresponding amine hydrochlorides.

^c The ratio of **I** and **II** was 6.2:1.

TABLE 7. SCHMIDT REACTIONS OF NITRO COMPOUNDS WITH HN_3


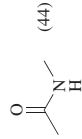
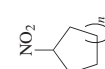
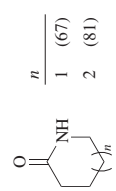
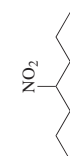
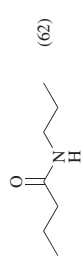

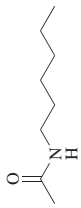
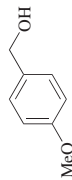
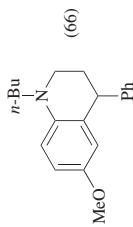
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_3	1. NaN_3 , NaOH , H_2O , heat 2. H_2SO_4 , CHCl_3 , rt	 (44)	84
 C_{5-6}	1. NaN_3 , NaOH , H_2O , heat 2. H_2SO_4 , CHCl_3 , rt	 n 1 (67) 2 (81)	84
 C_7	1. NaN_3 , NaOH , H_2O , heat 2. H_2SO_4 , CHCl_3 , rt	 (62)	84
 C_8	1. NaN_3 , NaOH , H_2O , reflux 2. H_2SO_4 , CHCl_3 , rt	 (47)	84

TABLE 8. SCHMIDT REACTIONS OF CARBOCATIONS WITH ALKYL AND ACYL AZIDES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄₋₈ 	 Pd/C, PPh ₃ , CuI, Et ₃ N, EtOH, 80°, 12 h	R HO(CH ₂) ₂ (82) HOCHMe ₂ (82) HO(CH ₂) ₃ (85) MeCH(OH)CH ₂ (60) Cl(CH ₂) ₃ (56) HO(CH ₂) ₄ (55) NC(CH ₂) ₃ (73) <i>n</i> -C ₆ H ₁₃ (44)	626
C ₄₋₉ 	 Pd/C, PPh ₃ , CuI, Et ₃ N, EtOH, 80°, 12 h	R HO(CH ₂) ₂ (78) HO(CH ₂) ₃ (84) NC(CH ₂) ₃ (65) <i>n</i> -C ₆ H ₁₃ (85) Ph (43) 4-MeC ₆ H ₄ (40)	626
C ₆ 	1. RN ₃ , TfOH, CH ₂ Cl ₂ 2. NaBH ₄ , MeOH	R <i>n</i> -Bu (95) Bn (86)	24
C ₈ 	 TfOH, CH ₂ Cl ₂ , 0° to rt	(>95)	627



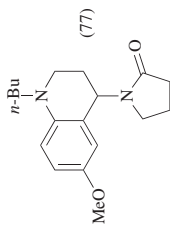
Ph
 CH_2Cl_2 , *n*-BuN₃, TIOH,
 CH_2Cl_2 , rt, 12 h



628

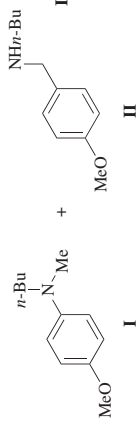


n-BuN₃, TIOH, CH_2Cl_2 , rt, 12 h



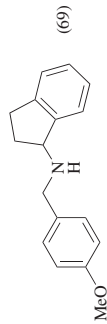
628

n-Bu
 NH*n*-Bu
 I + II (97), I:II = 1:2 17

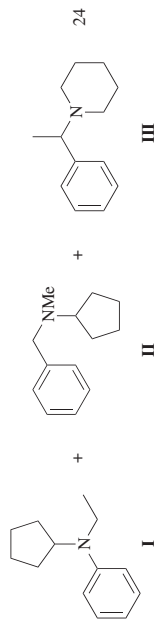


1. *n*-BuN₃, SnCl₄, CH_2Cl_2
 2. NaBH₄, MeOH

1.
 SnCl₄, CH_2Cl_2
 2. NaBH₄, MeOH



17


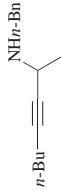

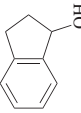
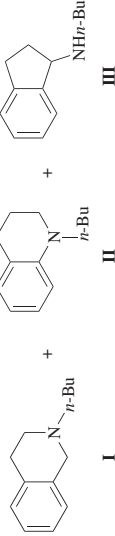
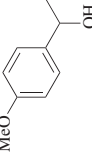
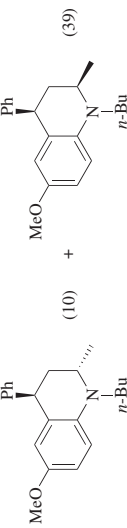


1. *c*-C₃H₆N₃, SnCl₄, CH_2Cl_2
 2. NaBH₄, MeOH

I + II + III (57), I:II:III = 2.5:1:2

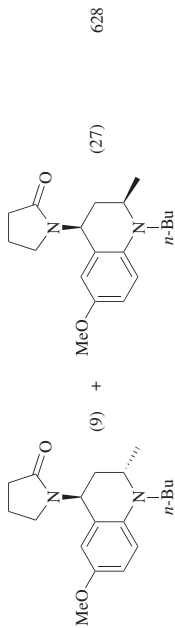
24

TABLE 8. SCHMIDT REACTIONS OF CARBOCATIONS WITH ALKYL AND ACYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
<p>C₈</p> 	<p>1. <i>n</i>-BuN₃, TfOH, CH₂Cl₂ 2. NaBH₄, MeOH</p>	<p>(48)</p> 	24																																				
<p>C₈₋₁₃</p> 	<p>1. <i>n</i>-BuN₃, SnCl₄ or TfOH, CH₂Cl₂ 2. NaBH₄, MeOH</p>	<p>Ar-C(OH)(R)-C(NH<i>n</i>-Bu)(R') + Ar-C(OH)(R)-C(<i>n</i>-Bu)(R')-N(R')-R'</p> <p>I II III</p> <table border="1" data-bbox="436 494 677 902"> <thead> <tr> <th>Aryl</th> <th>R</th> <th>I + II + III</th> <th>I:II:III</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>Me</td> <td>(81)</td> <td>4.5:1:1</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>H</td> <td>(61)</td> <td>1:6:0</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>H</td> <td>(97)</td> <td>1:2:0</td> </tr> <tr> <td>3,4-(OCH₂O)C₆H₃</td> <td>H</td> <td>(100)</td> <td>1:2:0</td> </tr> <tr> <td>3,4-(MeO)₂C₆H₃</td> <td>H</td> <td>(98)</td> <td>1:1.5:0</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>Me</td> <td>(97)</td> <td>12.5:2.5:1</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td><i>i</i>-Pr</td> <td>(91)</td> <td>3.5:0:1</td> </tr> <tr> <td>4-PhC₆H₄</td> <td>H</td> <td>(77)</td> <td>1:3:0</td> </tr> </tbody> </table>	Aryl	R	I + II + III	I:II:III	Ph	Me	(81)	4.5:1:1	4-MeC ₆ H ₄	H	(61)	1:6:0	4-MeOC ₆ H ₄	H	(97)	1:2:0	3,4-(OCH ₂ O)C ₆ H ₃	H	(100)	1:2:0	3,4-(MeO) ₂ C ₆ H ₃	H	(98)	1:1.5:0	4-MeOC ₆ H ₄	Me	(97)	12.5:2.5:1	4-MeOC ₆ H ₄	<i>i</i> -Pr	(91)	3.5:0:1	4-PhC ₆ H ₄	H	(77)	1:3:0	24
Aryl	R	I + II + III	I:II:III																																				
Ph	Me	(81)	4.5:1:1																																				
4-MeC ₆ H ₄	H	(61)	1:6:0																																				
4-MeOC ₆ H ₄	H	(97)	1:2:0																																				
3,4-(OCH ₂ O)C ₆ H ₃	H	(100)	1:2:0																																				
3,4-(MeO) ₂ C ₆ H ₃	H	(98)	1:1.5:0																																				
4-MeOC ₆ H ₄	Me	(97)	12.5:2.5:1																																				
4-MeOC ₆ H ₄	<i>i</i> -Pr	(91)	3.5:0:1																																				
4-PhC ₆ H ₄	H	(77)	1:3:0																																				
<p>C₉</p> 	<p>1. <i>n</i>-BuN₃, TfOH, PhH 2. NaBH₄</p>	<p>I + II + III</p> 	24																																				
	<p>Ph-C≡C-<i>n</i>-BuN₃, SnCl₄, PhH, reflux, 12 h</p>	<p>(10) + (39)</p> 	628																																				

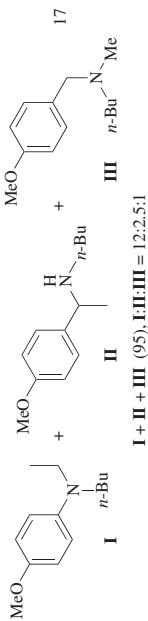


n-BuN₃, TfOH, CH₂Cl₂, rt, 12 h



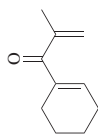
628

1. *n*-BuN₃, SnCl₄, CH₂Cl₂
2. NaBH₄, MeOH

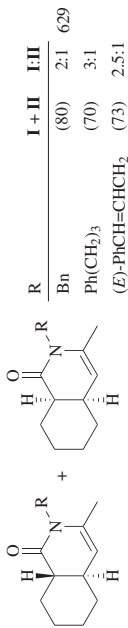


I + II + III (95), I:II:III = 12:2.5:1

C₁₀



RN₃, BF₃•OEt₂, NaHCO₃,
CH₂Cl₂, 0°, 0.5 h

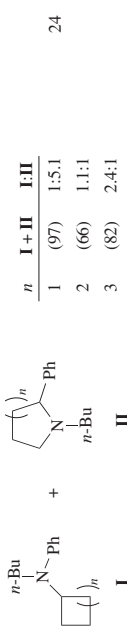


R	I + II (80)	I:II (70)	I:III (73)
Bn	2:1	2:1	629
Ph(CH ₂) ₃	(70)	3:1	
(<i>E</i>)-PhCH=CHCH ₂	(73)	2.5:1	

C₁₀₋₁₂

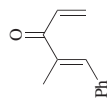


1. *n*-BuN₃, TfOH, CH₂Cl₂
2. NaBH₄, MeOH

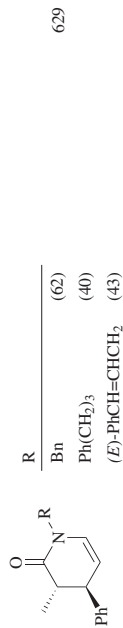


n	I + II (97)	I:II (66)	I:II (82)
1	1:5.1	1.1:1	2.4:1
2	(66)	1.1:1	
3	(82)	2.4:1	

C₁₂



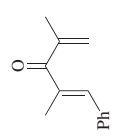
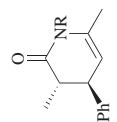
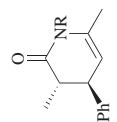
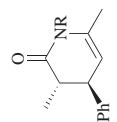
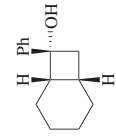
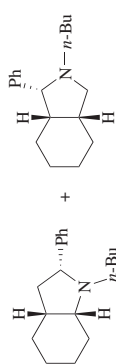
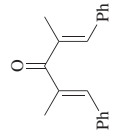
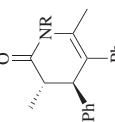
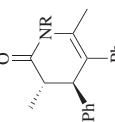
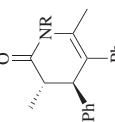

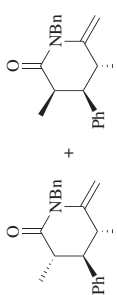
RN₃, BF₃•OEt₂, NaHCO₃,
CH₂Cl₂, 0°, 1 h



R	(62)	(40)	(43)
Bn	(62)	(40)	
Ph(CH ₂) ₃	(40)		
(<i>E</i>)-PhCH=CHCH ₂	(43)		

629

TABLE 8. SCHMIDT REACTIONS OF CARBOCATIONS WITH ALKYL AND ACYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.													
 C ₁₃	RN ₃ , BF ₃ •OEt ₂ , NaHCO ₃ , CH ₂ Cl ₂ , -78°, 0.5 h	<table border="0"> <tr> <td rowspan="3">  </td> <td>R</td> <td>(75)</td> </tr> <tr> <td>Bn</td> <td>(80)</td> </tr> <tr> <td>Ph(CH₂)₃</td> <td>(E)-PhCH=CHCH₂ (72)</td> </tr> </table>		R	(75)	Bn	(80)	Ph(CH ₂) ₃	(E)-PhCH=CHCH ₂ (72)	629						
	R	(75)														
	Bn	(80)														
	Ph(CH ₂) ₃	(E)-PhCH=CHCH ₂ (72)														
 C ₁₄	1. <i>n</i> -BuN ₃ , SnCl ₄ or TfOH, CH ₂ Cl ₂ 2. NaBH ₄ , MeOH	 I + II (91), I:II = 1:1	24													
 C ₁₉	RN ₃ , BF ₃ •OEt ₂ , NaHCO ₃ , CH ₂ Cl ₂ , -78°, 10 min	<table border="0"> <tr> <td rowspan="4">  </td> <td>R</td> <td>I + II</td> <td>I:II</td> </tr> <tr> <td>Bn</td> <td>(82)</td> <td>2:1</td> </tr> <tr> <td>Ph(CH₂)₃</td> <td>(78)</td> <td>2.3:1</td> </tr> <tr> <td>(E)-PhCH=CHCH₂</td> <td>(85)</td> <td>2:1</td> </tr> </table>		R	I + II	I:II	Bn	(82)	2:1	Ph(CH ₂) ₃	(78)	2.3:1	(E)-PhCH=CHCH ₂	(85)	2:1	629
	R	I + II		I:II												
	Bn	(82)		2:1												
	Ph(CH ₂) ₃	(78)		2.3:1												
	(E)-PhCH=CHCH ₂	(85)	2:1													
 C ₁₉	BnN ₃ , BF ₃ •OEt ₂ , CH ₂ Cl ₂ , -78°, 30 min; 0°, 15 min	 I + II (72), I:II = 1:1	629													

^aThe azide was derived from Merrifield resin.

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES



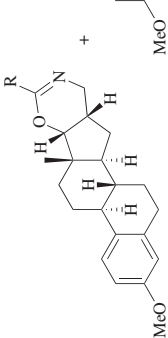

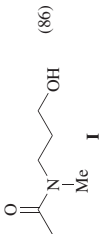

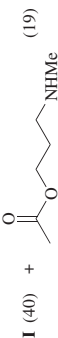


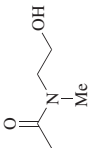

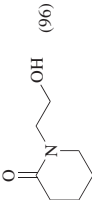



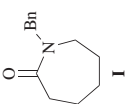
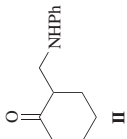
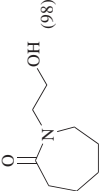
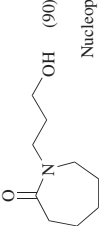
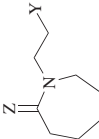
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₋₇ 	 BF ₃ •OEt ₂ , CH ₂ Cl ₂ , 0° to rt, 1 h	 I R Me (74) (13) Ph (66) (10) 4-O ₂ NC ₆ H ₄ (70) (22)	630
C ₃ 	1. N ₃ CH ₂ CH ₂ CH ₂ OH, BF ₃ •OEt ₂ , CH ₂ Cl ₂ , rt, 30 min 2. NaHCO ₃ , rt, 30 min	 I (86)	95
C ₃ 	1. N ₃ CH ₂ CH ₂ CH ₂ OH, BF ₃ •OEt ₂ , CH ₂ Cl ₂ 2. KOH	 I (40) + 	48
C ₃ 	1. N ₃ CH ₂ CH ₂ CH ₂ OH, BF ₃ •OEt ₂ , CH ₂ Cl ₂ 2. KOH	 I (87)	48
C ₅ 	1. N ₃ CH ₂ CH ₂ CH ₂ OH, BF ₃ •OEt ₂ , CH ₂ Cl ₂ , rt, 3 h 2. NaHCO ₃ , rt, 30 min	 I (96)	95

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$n\text{-C}_6\text{H}_{13}\text{N}_3$, TiCl_4 , CH_2Cl_2 , rt, 16 h	 (<5)	85
	BnN_3 , Promoter, CH_2Cl_2	 I +  II	I:II:BnN_3^a 45:39:16 85:15:0 0:11:89 0:11:89 0:8:92
	1. $\text{N}_3\text{CH}_2\text{CH}_2\text{OH}$, $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , rt, 3 h 2. NaHCO_3 , rt, 30 min	 (98)	95
	1. $\text{N}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , rt, 3 h 2. NaHCO_3 , rt, 30 min	 (90)	95
	1. $\text{N}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , rt, 3 h 2. Nucleophile	 Y Z	Y Z
		Nucleophile	
		NaOH	O (98)
		$\text{Bu}_4\text{N}^+\text{Ph}_3\text{SiF}_2^-$	O (64)
		Bu_4NI	O (55)
		NaN_3	O (85)
		NaCN	O (82)
		$\text{NaCH}(\text{CO}_2\text{Me})_2$	O (34)
		NaOPh	O (74)
		NaSPh	O (95)
		$\text{NaCH}(\text{SO}_2\text{Ph})_2$	O (54)
		$\text{NaCH}(\text{CN})_2$	O (71)

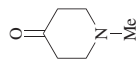
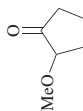
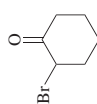
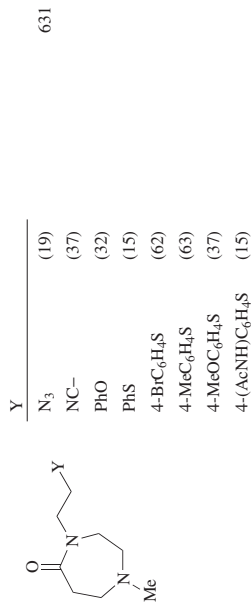
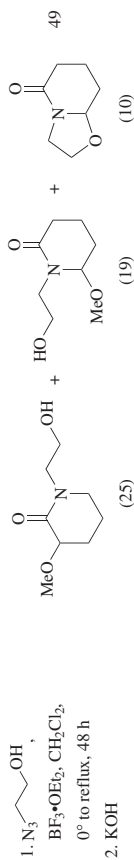
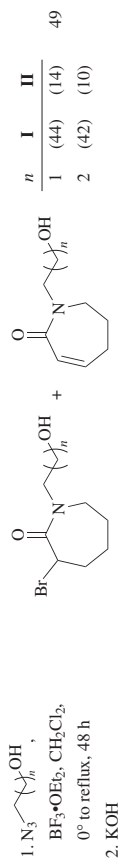
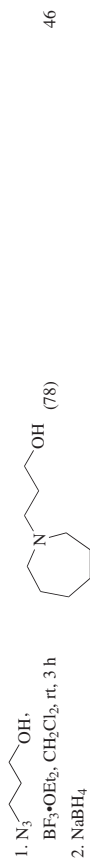

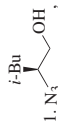
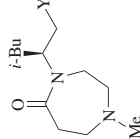
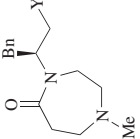
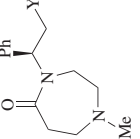
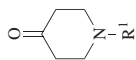


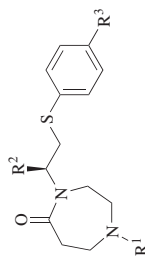
TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	i -Bu  1. N_3 , $BF_3 \cdot OEt_2$, CH_2Cl_2 , 0° to rt, 12 h 2. NaY, DMF, 70°, 24 h	 Y N_3 (8) NC- (34) PhO (20) PhS (7) 4-BrC ₆ H ₄ S (20) 4-MeC ₆ H ₄ S (58) 4-MeOC ₆ H ₄ S (34) 4-(AcNH)C ₆ H ₄ S (35)	631
		 Y N_3 (63) NC- (40) PhO (44) PhS (18) 4-BrC ₆ H ₄ S (44) 4-MeC ₆ H ₄ S (62) 4-MeOC ₆ H ₄ S (40) 4-(AcNH)C ₆ H ₄ S (62)	631
		 Y N_3 (58) NC- (22) PhO (23) PhS (8) 4-BrC ₆ H ₄ S (22) 4-MeC ₆ H ₄ S (16) 4-MeOC ₆ H ₄ S (20) 4-(AcNH)C ₆ H ₄ S (18)	631

C₆₋₈

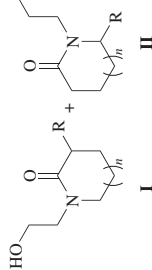
1. N₃-CH(OH)-R²,
BF₃·OEt₂, CH₂Cl₂,
0° to rt, 12 h
2. KS-
DMF, 70°, 24 h

R ¹	R ²	R ³	b	c
Me	H	Me	(58)	(61)
Me	H	MeO	(55)	(56)
Me	<i>i</i> -Bu	Me	(38)	(55)
Me	<i>i</i> -Bu	MeO	(85)	(47)
<i>n</i> -Pr	H	Me	(46)	(49)
<i>n</i> -Pr	H	MeO	(57)	(52)
<i>n</i> -Pr	<i>i</i> -Bu	Me	(56)	(58)
<i>n</i> -Pr	<i>i</i> -Bu	MeO	(47)	(52)

C₆₋₁₂

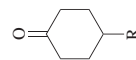
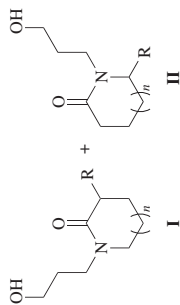
1. N₃-CH(OH)-R,
BF₃·OEt₂, CH₂Cl₂, rt, 3 h
2. KOH

OH	R	n	I + II	I:II
Me	Me	1	(89)	53:47
Me	Me	2	(83)	45:55
MeO	MeO	2	(52)	91:9
Et	Et	2	(85)	42:58
<i>i</i> -Pr	<i>i</i> -Pr	2	(80)	21:79
<i>i</i> -Bu	<i>i</i> -Bu	2	(11)	13:87
Ph	Ph	2	(93)	47:53



1. N₃-CH(OH)-R,
BF₃·OEt₂, CH₂Cl₂, rt, 3 h
2. KOH

OH	R	n	I + II	I:II
Me	Me	1	(86)	88:12
MeO	MeO	1	(76)	91:9
Me	Me	2	(95)	55:45
Et	Et	2	(94)	57:43
<i>i</i> -Bu	<i>i</i> -Bu	2	(0)	—
Ph	Ph	2	(92)	95:5


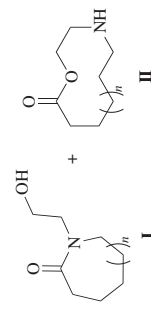
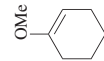
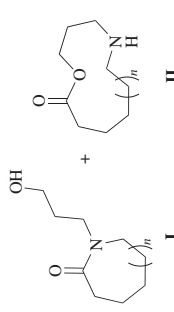
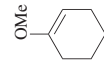
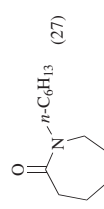


1. N₃-C₆H₁₃-R,
BF₃·OEt₂, CH₂Cl₂, rt, 3 h
2. KOH

R	(80)
H	(63)
<i>i</i> -Bu	(48)
Ph	(48)

85

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.																																																	
C_6-12 	1. $N_3-CH_2-CH_2-OH$, $BF_3 \cdot OEt_2$, CH_2Cl_2 2. Base		<table border="1"> <thead> <tr> <th>Base</th> <th>n</th> <th>I (%)</th> <th>II (%)</th> </tr> </thead> <tbody> <tr> <td>KOH</td> <td>1</td> <td>(96)</td> <td>(0)</td> </tr> <tr> <td>$NaHCO_3$</td> <td>1</td> <td>(97)</td> <td>(0)</td> </tr> <tr> <td>KOH</td> <td>2</td> <td>(68)</td> <td>(0)</td> </tr> <tr> <td>$NaHCO_3$</td> <td>2</td> <td>(27)</td> <td>(43)</td> </tr> <tr> <td>KOH</td> <td>3</td> <td>(29)</td> <td>(0)</td> </tr> <tr> <td>KOH</td> <td>4</td> <td>(88)</td> <td>(0)</td> </tr> <tr> <td>$NaHCO_3$</td> <td>4</td> <td>(26)</td> <td>(64)</td> </tr> <tr> <td>KOH</td> <td>5</td> <td>(51)</td> <td>(19)</td> </tr> <tr> <td>$NaHCO_3$</td> <td>5</td> <td>(30)</td> <td>(64)</td> </tr> <tr> <td>KOH</td> <td>7</td> <td>(50)</td> <td>(30)</td> </tr> <tr> <td>$NaHCO_3$</td> <td>7</td> <td>(8)</td> <td>(79)</td> </tr> </tbody> </table>	Base	n	I (%)	II (%)	KOH	1	(96)	(0)	$NaHCO_3$	1	(97)	(0)	KOH	2	(68)	(0)	$NaHCO_3$	2	(27)	(43)	KOH	3	(29)	(0)	KOH	4	(88)	(0)	$NaHCO_3$	4	(26)	(64)	KOH	5	(51)	(19)	$NaHCO_3$	5	(30)	(64)	KOH	7	(50)	(30)	$NaHCO_3$	7	(8)	(79)	48
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C_7 	1. $N_3-CH_2-CH_2-CH_2-OH$, $BF_3 \cdot OEt_2$, CH_2Cl_2 2. Base		<table border="1"> <thead> <tr> <th>Base</th> <th>n</th> <th>I (%)</th> <th>II (%)</th> </tr> </thead> <tbody> <tr> <td>KOH</td> <td>1</td> <td>(95)</td> <td>(0)</td> </tr> <tr> <td>$NaHCO_3$</td> <td>1</td> <td>(91)</td> <td>(0)</td> </tr> <tr> <td>KOH</td> <td>2</td> <td>(99)</td> <td>(0)</td> </tr> <tr> <td>$NaHCO_3$</td> <td>2</td> <td>(21)</td> <td>(70)</td> </tr> <tr> <td>KOH</td> <td>3</td> <td>(3)</td> <td>(28)</td> </tr> <tr> <td>KOH</td> <td>4</td> <td>(23)</td> <td>(40)</td> </tr> <tr> <td>$NaHCO_3$</td> <td>4</td> <td>(46)</td> <td>(49)</td> </tr> <tr> <td>KOH</td> <td>5</td> <td>(25)</td> <td>(54)</td> </tr> <tr> <td>$NaHCO_3$</td> <td>5</td> <td>(29)</td> <td>(67)</td> </tr> <tr> <td>KOH</td> <td>7</td> <td>(36)</td> <td>(45)</td> </tr> <tr> <td>$NaHCO_3$</td> <td>7</td> <td>(5)</td> <td>(93)</td> </tr> </tbody> </table>	Base	n	I (%)	II (%)	KOH	1	(95)	(0)	$NaHCO_3$	1	(91)	(0)	KOH	2	(99)	(0)	$NaHCO_3$	2	(21)	(70)	KOH	3	(3)	(28)	KOH	4	(23)	(40)	$NaHCO_3$	4	(46)	(49)	KOH	5	(25)	(54)	$NaHCO_3$	5	(29)	(67)	KOH	7	(36)	(45)	$NaHCO_3$	7	(5)	(93)	94
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C_7 	1. $n-C_6H_{13}N_3$, $TiOH$, CH_2Cl_2 2. NaI , acetone		94																																																	

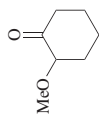
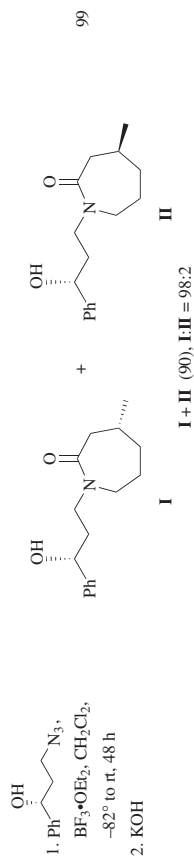
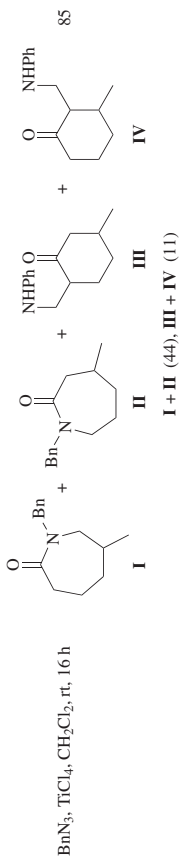
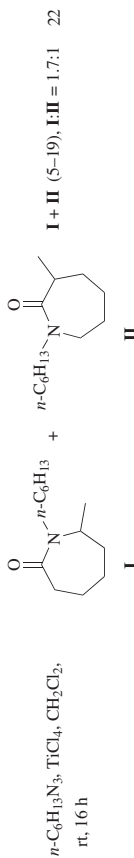
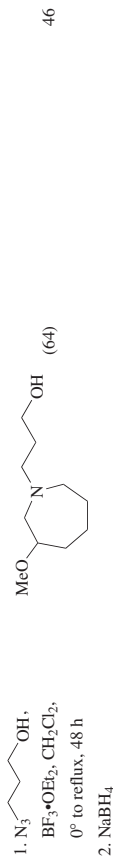
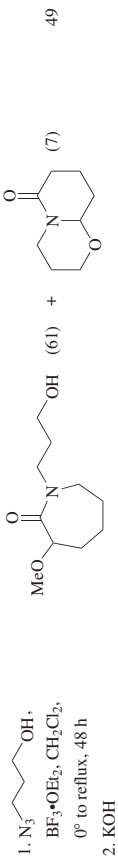
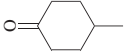
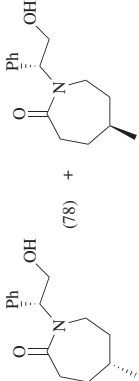
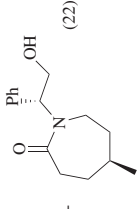
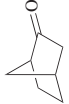


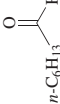
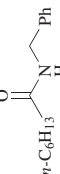

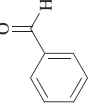
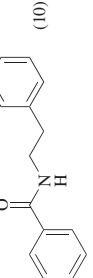
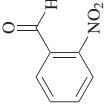
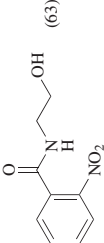
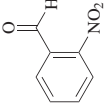
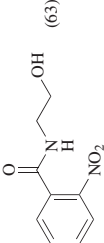
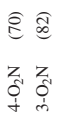
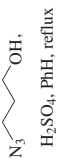
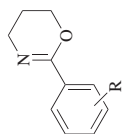
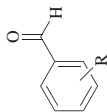
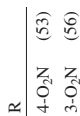
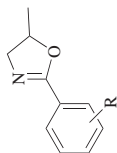


TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
	1. N_3 -CH(Ph)-CH ₂ -OH, BF ₃ ·OEt ₂ , <i>n</i> -pentane, -20°, 23 h 2. KOH	 (78) +  (22)	98										
	RN_3 , TiCl ₄ , CH ₂ Cl ₂ , rt, 16 h	 I +  II	<table border="1" data-bbox="396 373 464 564"> <tr> <td>R</td> <td>I + II</td> <td>I:II</td> </tr> <tr> <td><i>n</i>-C₆H₁₃</td> <td>(40)</td> <td>1:5</td> </tr> <tr> <td>Bn</td> <td>(46)</td> <td>1:2</td> </tr> </table>	R	I + II	I:II	<i>n</i> -C ₆ H ₁₃	(40)	1:5	Bn	(46)	1:2	22
R	I + II	I:II											
<i>n</i> -C ₆ H ₁₃	(40)	1:5											
Bn	(46)	1:2											
	N_3 -CH ₂ -Ph, promoter, 17–19 h	 I +  II	<table border="1" data-bbox="533 355 591 546"> <tr> <td>Promoter</td> <td>I</td> <td>II</td> </tr> <tr> <td>TFA</td> <td>trace</td> <td>trace</td> </tr> <tr> <td>TiCl₄</td> <td>(16)</td> <td>(10)</td> </tr> </table>	Promoter	I	II	TFA	trace	trace	TiCl ₄	(16)	(10)	632
Promoter	I	II											
TFA	trace	trace											
TiCl ₄	(16)	(10)											
	N_3 -CH ₂ -CH ₂ -Ph, H ₂ SO ₄ , 75°	 (10)	21										
	N_3 -CH ₂ -CH ₂ -OH, H ₂ SO ₄ , 75°	 (63)	21										
	N_3 -CH ₂ -CH ₂ -OH, H ₂ SO ₄ , 80°, 15 min	 (63)	21										

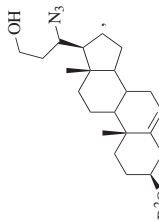
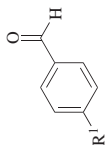


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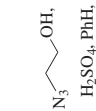
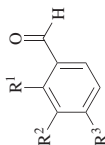
C_{7-8}



R^1	R^2
H	H
H	Ac
Cl	H
Cl	Ac
Br	H
Br	Ac
O_2N	H
O_2N	Ac
MeO	H
MeO	Ac

633

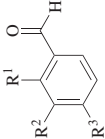
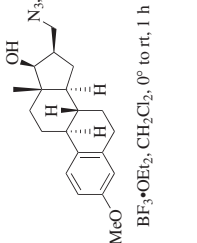
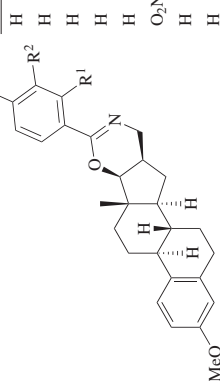

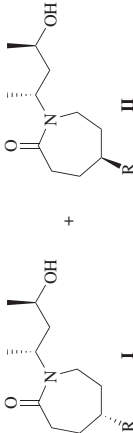
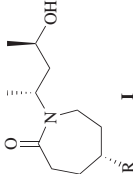
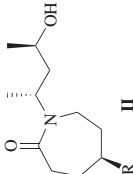
C_{7-9}

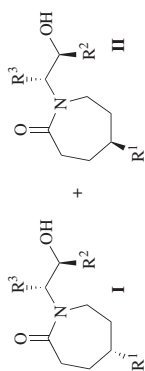
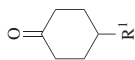


R^1	R^2	R^3
H	H	H
HO	H	H
H	H	HO
Cl	H	Cl
H	H	Cl
H	H	O_2N
H	O_2N	H
H	H	Me_2N

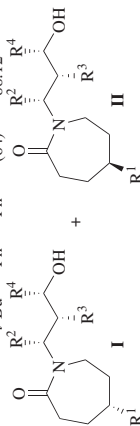
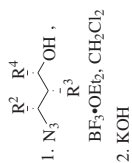
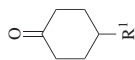
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TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , 0° to rt, 1 h		R ¹ H (82) R ² H (82) R ³ F (82) R ¹ HO (30) R ² HO (30) R ³ O ₂ N (92) R ¹ H (65) R ² O ₂ N (65) R ³ H (30) R ¹ H (88) R ² H (88) R ³ Cl (62) R ¹ H (26) R ² Cl (26) R ³ H (78) R ¹ H (78) R ² Br (78) R ³ H (30) R ¹ Me (30) R ² H (59) R ³ NC- (59) R ¹ H (49) R ² CHO (49) R ³ H (73) R ¹ MeO (73) R ² H (22) R ³ Me ₂ N (22) R ¹ H (87) R ² H (87) R ³ AcO (87)
	 1. N ₃ -CH(CH ₃)-CH ₂ -OH, $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 2. KOH	 	R I + II 98 Me (98) 59:41 <i>t</i> -Bu (98) 60:40




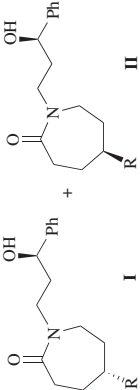
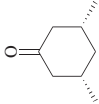
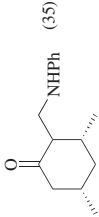
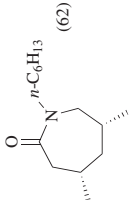
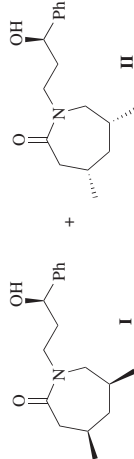

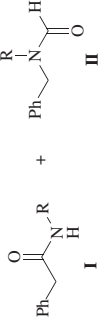
98

C₇₋₁₂

98

R ¹	R ²	R ³	R ⁴	I + II	I:II
Me	H	Ph	H	(97)	78:22
Me	Ph	Ph	Me	(51)	87:13
<i>t</i> -Bu	H	Ph	<i>i</i> -Pr	(83)	85:15
<i>t</i> -Bu	Ph	H	H	(73)	56:44
<i>t</i> -Bu	Ph	Ph	Ph	(64)	88:12
R ² , R ⁴	R ³	R ³	R ³	(93)	78:22
Me	H	Me	H	(98)	98:2
Me	H	<i>i</i> -Pr	H	(88)	88:12
Me	Ph	H	H	(96)	89:11
Me	H	Ph	H	(93)	60:40
Me	H	H	Ph	(98)	93:7
<i>t</i> -Bu	H	Me	H	(98)	74:26
<i>t</i> -Bu	Me	H	Me	(94)	94:6
<i>t</i> -Bu	H	<i>i</i> -Pr	H	(85)	88:12
<i>t</i> -Bu	Ph	H	H	(94)	90:10
<i>t</i> -Bu	H	Ph	H	(98)	60:40
<i>t</i> -Bu	H	H	Ph	(100)	95:5
<i>t</i> -Bu	3,4,5-(MeO) ₃ C ₆ H ₂	H	H	(94)	90:10
Ph	H	H	Ph	(99)	96:4

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₇₋₁₂</p> 	<p>1. N₃-CH₂-CH(OH)-CH₂-Ph, BF₃•OEt₂, CH₂Cl₂, -82° to rt, 48 h</p> <p>2. KOH</p>	<p>  I + II </p> <p>R I + II I:II Me (98) 93:7 99 t-Bu (100) 98:2</p>	
<p>C₈</p> 	<p>BnN₃, TiCl₄, CH₂Cl₂, rt, 16 h</p>	<p>  (52) </p>	85
	<p>n-C₆H₁₃N₃, TiCl₄, CH₂Cl₂, rt, 16 h</p>	<p>  (62) </p>	85
	<p>1. N₃-CH₂-CH(OH)-CH₂-Ph, BF₃•OEt₂, CH₂Cl₂, -82° to rt, 48 h</p> <p>2. KOH</p>	<p>  I + II (86), I:II = 99:1 </p>	98
	<p>RN₃, promoter, 17–19 h</p>	<p>  I + II </p>	632

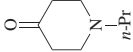
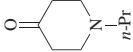
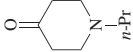
R	Promoter	I	II
<i>n</i> -C ₆ H ₁₃	TFA	(19)	(13)
<i>n</i> -C ₆ H ₁₃	TiCl ₄	(29)	(26)
Bn	TFA	trace	trace
Bn	TiCl ₄	(21)	(10)
PhCH ₂ CH ₂	TFA	(16)	(16)
PhCH ₂ CH ₂	TiCl ₄	(22)	(19)

R	I	II
Bn	(45)	(13)
<i>n</i> -C ₆ H ₁₃	(58)	(40)
3-MeOC ₆ H ₄ CH ₂	(36)	(60)
4-MeOC ₆ H ₄ CH ₂	(27)	(35)
4-MeO ₂ CC ₆ H ₄ CH ₂	(38)	(43)
4-BrC ₆ H ₄ CH ₂	(45)	(34)

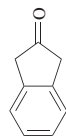
Y	I + II (40), I:II = 2:1	I + II (40), I:II = 3.2:1
N ₃	(24)	116
NC-	(28)	
PhO	(40)	
PhS	(4)	
4-BrC ₆ H ₄ S	(40)	
4-MeC ₆ H ₄ S	(15)	
4-MeOC ₆ H ₄ S	(28)	
4-(AcNH)C ₆ H ₄ S	(34)	

Y	I + II (40), I:II = 2:1
N ₃	(24)
NC-	(28)
PhO	(40)
PhS	(4)
4-BrC ₆ H ₄ S	(40)
4-MeC ₆ H ₄ S	(15)
4-MeOC ₆ H ₄ S	(28)
4-(AcNH)C ₆ H ₄ S	(34)

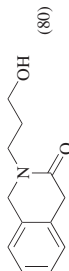
TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>1. N_3-CH(OH)-CH(<i>i</i>-Bu) $BF_3 \cdot OEt_2$, CH_2Cl_2, 0° to rt, 12 h</p> <p>2. NaY, DMF, 70°, 24 h</p>	<p>Y N_3 (22)</p> <p>NC- (33)</p> <p>PhO (41)</p> <p>PhS (12)</p> <p>4-BrC_6H_4S (41)</p> <p>4-MeC_6H_4S (17)</p> <p>4-$MeOC_6H_4S$ (33)</p> <p>4-(AcNH)C_6H_4S (22)</p>	631
		<p>Y N_3 (35)</p> <p>NC- (36)</p> <p>PhO (37)</p> <p>PhS (14)</p> <p>4-BrC_6H_4S (37)</p> <p>4-MeC_6H_4S (43)</p> <p>4-$MeOC_6H_4S$ (36)</p> <p>4-(AcNH)C_6H_4S (43)</p>	631
		<p>Y N_3 (37)</p> <p>NC- (26)</p> <p>PhO (17)</p> <p>PhS (22)</p> <p>4-BrC_6H_4S (33)</p> <p>4-MeC_6H_4S (24)</p> <p>4-$MeOC_6H_4S$ (16)</p> <p>4-(AcNH)C_6H_4S (27)</p>	631
	<p>1. N_3-CH(OH)-CH(Bn) $BF_3 \cdot OEt_2$, CH_2Cl_2, 0° to rt, 12 h</p> <p>2. NaY, DMF, 70°, 24 h</p>	<p>Y N_3 (35)</p> <p>NC- (36)</p> <p>PhO (37)</p> <p>PhS (14)</p> <p>4-BrC_6H_4S (37)</p> <p>4-MeC_6H_4S (43)</p> <p>4-$MeOC_6H_4S$ (36)</p> <p>4-(AcNH)C_6H_4S (43)</p>	631
		<p>Y N_3 (37)</p> <p>NC- (26)</p> <p>PhO (17)</p> <p>PhS (22)</p> <p>4-BrC_6H_4S (33)</p> <p>4-MeC_6H_4S (24)</p> <p>4-$MeOC_6H_4S$ (16)</p> <p>4-(AcNH)C_6H_4S (27)</p>	631
		<p>Y N_3 (37)</p> <p>NC- (26)</p> <p>PhO (17)</p> <p>PhS (22)</p> <p>4-BrC_6H_4S (33)</p> <p>4-MeC_6H_4S (24)</p> <p>4-$MeOC_6H_4S$ (16)</p> <p>4-(AcNH)C_6H_4S (27)</p>	631
	<p>1. N_3-CH(OH)-CH(Ph) $BF_3 \cdot OEt_2$, CH_2Cl_2, 0° to rt, 12 h</p> <p>2. NaY, DMF, 70°, 24 h</p>	<p>Y N_3 (37)</p> <p>NC- (26)</p> <p>PhO (17)</p> <p>PhS (22)</p> <p>4-BrC_6H_4S (33)</p> <p>4-MeC_6H_4S (24)</p> <p>4-$MeOC_6H_4S$ (16)</p> <p>4-(AcNH)C_6H_4S (27)</p>	631
		<p>Y N_3 (37)</p> <p>NC- (26)</p> <p>PhO (17)</p> <p>PhS (22)</p> <p>4-BrC_6H_4S (33)</p> <p>4-MeC_6H_4S (24)</p> <p>4-$MeOC_6H_4S$ (16)</p> <p>4-(AcNH)C_6H_4S (27)</p>	631
		<p>Y N_3 (37)</p> <p>NC- (26)</p> <p>PhO (17)</p> <p>PhS (22)</p> <p>4-BrC_6H_4S (33)</p> <p>4-MeC_6H_4S (24)</p> <p>4-$MeOC_6H_4S$ (16)</p> <p>4-(AcNH)C_6H_4S (27)</p>	631

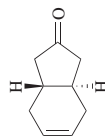
C₉



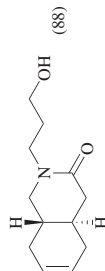
1. N₃CH₂CH₂CH₂OH,
BF₃·OEt₂, CH₂Cl₂, rt, 3 h
2. NaHCO₃, rt, 30 min



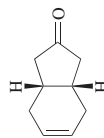
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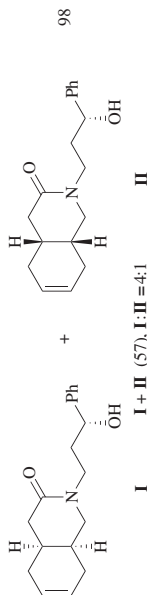
1. N₃CH₂CH₂CH₂OH,
BF₃·OEt₂, CH₂Cl₂, rt, 3 h
2. NaHCO₃, rt, 30 min



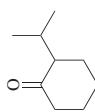
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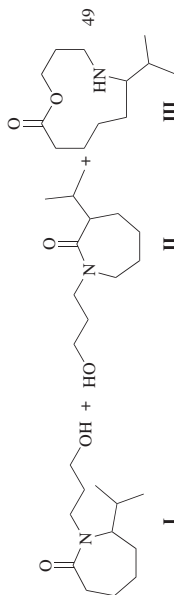
1. N₃CH₂CH₂CH₂CH(OH)Ph,
BF₃·OEt₂, CH₂Cl₂,
-82° to rt, 48 h
2. KOH



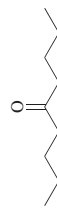
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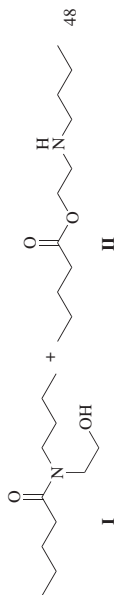
1. N₃CH₂CH₂CH₂OH,
BF₃·OEt₂, CH₂Cl₂,
0° to reflux, 48 h
2. KOH



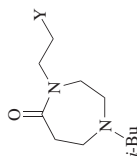
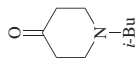
49



1. N₃CH₂CH₂CH₂OH,
BF₃·OEt₂, CH₂Cl₂
2. Base



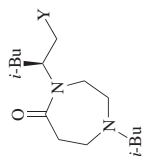
48



Y	
N ₃	(29)
NC-	(34)
PhO	(45)
PhS	(19)
4-BrC ₆ H ₄ S	(45)
4-MeC ₆ H ₄ S	(50)
4-MeOC ₆ H ₄ S	(34)
4-(AcNH)C ₆ H ₄ S	(39)

1. N₃-CH₂-CH₂-OH, BF₃·OEt₂, CH₂Cl₂, 0° to rt, 12 h
2. NaY, DMF, 70°, 24 h

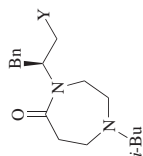
1. N₃-CH(OH)-CH₂-OH, BF₃·OEt₂, CH₂Cl₂, 0° to rt, 12 h
2. NaY, DMF, 70°, 24 h



Y	
N ₃	(10)
NC-	(60)
PhO	(49)
PhS	(36)
4-BrC ₆ H ₄ S	(49)
4-MeC ₆ H ₄ S	(28)
4-MeOC ₆ H ₄ S	(60)
4-(AcNH)C ₆ H ₄ S	(36)

2. NaY, DMF, 70°, 24 h

1. N₃-CH(OH)-CH₂-OH, BF₃·OEt₂, CH₂Cl₂, 0° to rt, 12 h
2. NaY, DMF, 70°, 24 h



Y	
N ₃	(50)
NC-	(35)
PhO	(36)
PhS	(19)
4-BrC ₆ H ₄ S	(36)
4-MeC ₆ H ₄ S	(43)
4-MeOC ₆ H ₄ S	(35)
4-(AcNH)C ₆ H ₄ S	(34)

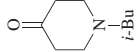

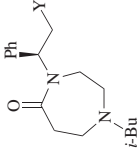

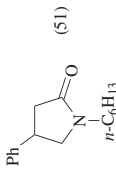

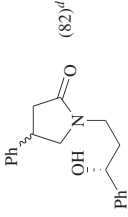

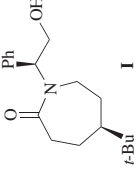
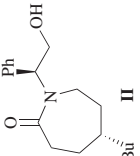
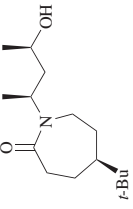
2. NaY, DMF, 70°, 24 h

631

631

631

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_9	 1. N_3 , $BF_3 \cdot OEt_2$, CH_2Cl_2 , 0° to rt, 12 h 2. NaY , DMF, 70° , 24 h	 Y N_3 (53) NC^- (18) PhO (27) PhS (10) $4-BrC_6H_4S$ (12) $4-MeC_6H_4S$ (19) $4-MeOC_6H_4S$ (23) $4-(AcNH)C_6H_4S$ (21)	631
 C_{10}	$n-C_6H_{13}N_3$, $TiCl_4$, CH_2Cl_2 , rt, 16 h	 (51)	85
	 1. Ph , $BF_3 \cdot OEt_2$, CH_2Cl_2 , -82° to rt, 48 h 2. KOH	 (82) ^d	98
 1. N_3 , $BF_3 \cdot OEt_2$, <i>n</i> -pentane, -20° , 23 h 2. KOH	 I  II	I + II (70), I:II = 7.2:1	95
	1. N_3 , $BF_3 \cdot OEt_2$, CH_2Cl_2 2. KOH	 (90-94)	95

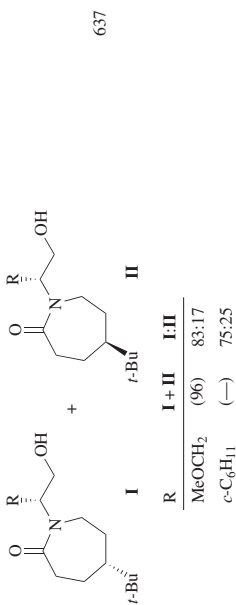
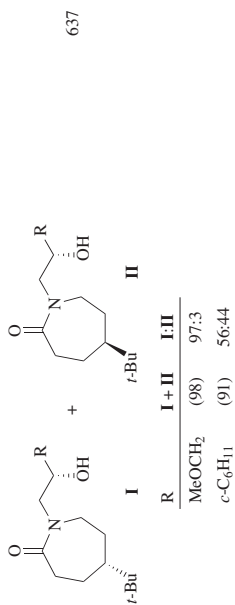
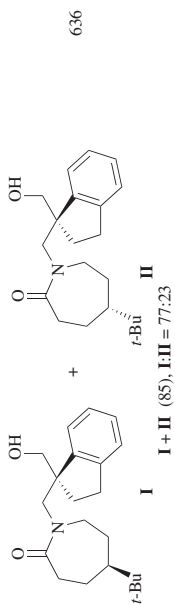

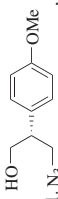
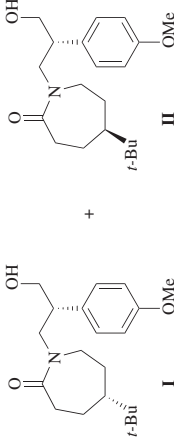
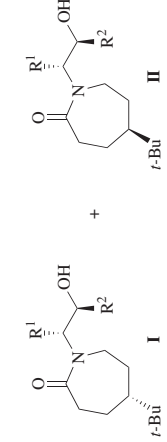
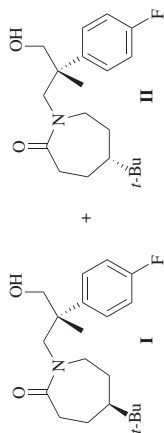
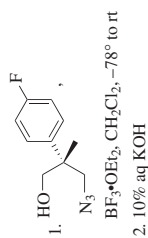


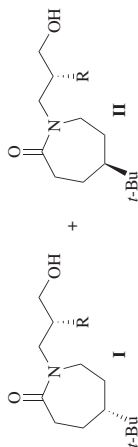
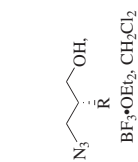
TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																								
 C_{10}	 1. N_3 $BF_3 \cdot OEt_2$, -78° to rt 2. 10% aq KOH	 I + II	638																								
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>pentane/CH_2Cl_2</td> <td>(78)</td> <td>47:53</td> </tr> <tr> <td>toluene</td> <td>(97)</td> <td>47:53</td> </tr> <tr> <td>Et_2O</td> <td>(98)</td> <td>54:47</td> </tr> <tr> <td>diglyme</td> <td>(99)</td> <td>72:28</td> </tr> <tr> <td>CH_2Cl_2</td> <td>(99)</td> <td>47:53</td> </tr> </tbody> </table>	Solvent	I + II	I:II	pentane/ CH_2Cl_2	(78)	47:53	toluene	(97)	47:53	Et_2O	(98)	54:47	diglyme	(99)	72:28	CH_2Cl_2	(99)	47:53							
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		<table border="1"> <thead> <tr> <th>R^1</th> <th>R^2</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td><i>c</i>-C_6H_{11}</td> <td>(91)</td> <td>56:44</td> </tr> <tr> <td><i>c</i>-C_6H_{11}</td> <td>H</td> <td>(85)</td> <td>75:25</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(89)</td> <td>85:15</td> </tr> <tr> <td>4-$O_2NC_6H_4$</td> <td>H</td> <td>(97)</td> <td>66:34</td> </tr> <tr> <td>3,4,5-(MeO)$_3C_6H_2$</td> <td>H</td> <td>(96)</td> <td>86:14</td> </tr> </tbody> </table>	R^1	R^2	I + II	I:II	H	<i>c</i> - C_6H_{11}	(91)	56:44	<i>c</i> - C_6H_{11}	H	(85)	75:25	Ph	H	(89)	85:15	4- $O_2NC_6H_4$	H	(97)	66:34	3,4,5-(MeO) $_3C_6H_2$	H	(96)	86:14	
R^1	R^2	I + II	I:II																								
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638

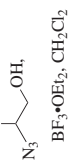
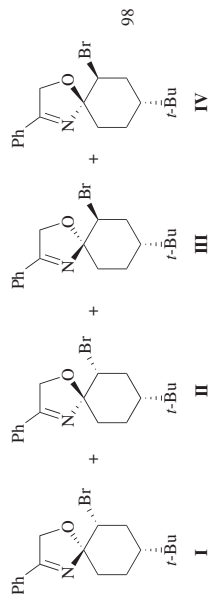
I + II (93), I:II = 93:7



636

I + II I:II

R	I + II	I:II
Me	(-)	74:26
<i>i</i> -Pr	(-)	88:12
Ph	(85)	64:36
4- FC_6H_4	(73)	69:31
4- $\text{O}_2\text{NC}_6\text{H}_4$	(86)	76:24
4- BrC_6H_4	(90)	68:32
4- MeOC_6H_4	(95)	47:53
3,4,5-(MeO) $_3\text{C}_6\text{H}_2$	(99)	43:57



98

I + II + III + IV (47), I:II:III:IV = -

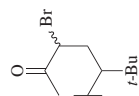
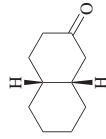
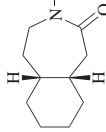
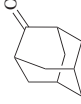
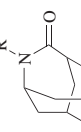
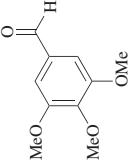
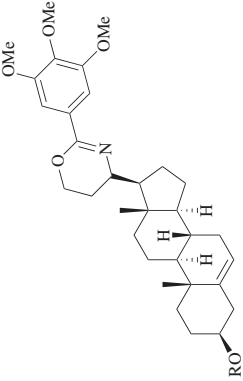
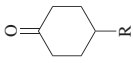
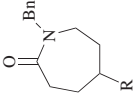
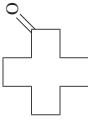
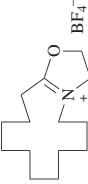
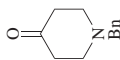
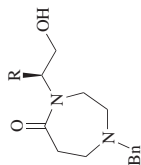


TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

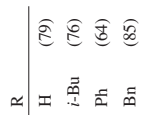
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₀	$n\text{-C}_6\text{H}_{13}\text{N}_3$, TiCl_4 , CH_2Cl_2 , rt, 16 h	 (25)	85
	RN_3 , TiCl_4 , CH_2Cl_2 , rt, 16 h	 $\frac{\text{R}}{n\text{-C}_6\text{H}_{13}}$ (100) $\frac{\text{R}}{\text{Bn}}$ (98)	85
	$\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , 0° , 2 h	 $\frac{\text{R}}{\text{H}}$ (65) $\frac{\text{R}}{\text{Ac}}$ (80)	633
 C ₁₀₋₁₂	BnN_3 , TiCl_4 , CH_2Cl_2 , rt, 16 h	 $\frac{\text{R}}{n\text{-Bu}}$ (65) $\frac{\text{R}}{\text{Ph}}$ (70)	85
 C ₁₂	N_3 -CH ₂ -CH ₂ -OH, $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , -5° , 3 h; reflux, 192 h	 (90)	639



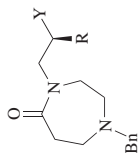
1. ,
BF₃·OEt₂, CH₂Cl₂, 0° to rt
2. NaHCO₃



631




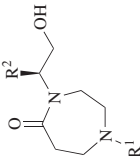
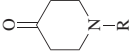
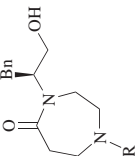
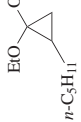
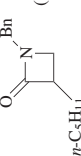
1. ,
BF₃·OEt₂, CH₂Cl₂, 0° to rt
2. NaY, DMF, 70°

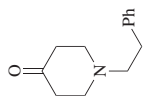


640

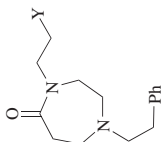
R	Y
H	N ₃ (81)
H	PhO (67)
H	PhS (80)
H	NC- (79)
<i>i</i> -Pr	N ₃ (60)
<i>i</i> -Pr	PhO (55)
<i>i</i> -Pr	PhS (58)
<i>i</i> -Pr	NC- (63)
<i>i</i> -Bu	N ₃ (66)
<i>i</i> -Bu	PhO (63)
<i>i</i> -Bu	PhS (62)
<i>i</i> -Bu	NC- (69)
Ph	N ₃ (74)
Ph	PhO (62)
Ph	PhS (70)
Ph	NC- (70)
Bn	N ₃ (66)
Bn	PhO (58)
Bn	PhS (60)
Bn	NC- (74)
4-BnOC ₆ H ₄ CH ₂	N ₃ (55)
4-BnOC ₆ H ₄ CH ₂	PhO (40)
4-BnOC ₆ H ₄ CH ₂	PhS (52)
4-BnOC ₆ H ₄ CH ₂	NC- (52)

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₂₋₂₀</p> 	<p>1. N₃-CH(OH)-R², BF₃•OEt₂, TfOH, CH₂Cl₂ 2. KOH, aq NaHCO₃</p>	<p>R¹ R²</p>  <p>Bn <i>i</i>-Pr (89) Bn <i>i</i>-Bu (87) Bn 4-BnOC₆H₄CH₂ (63) Bn CbzNH(CH₂)₃ (84) Bn CbzNH(CH₂)₄ (88) Bn MeS(CH₂)₂ (55) Bn BnO₂C (62) Cbz <i>i</i>-Bu (52) CbzNHCH₂CO <i>i</i>-Bu (79) Fmoc <i>i</i>-Pr (63) Fmoc <i>i</i>-Bu (68)</p>	641
	<p>1. N₃-CH(OH)-Bn, 2. KOH, promoter</p>	<p>R Promoter</p>  <p>Bn BF₃•OEt₂ (52) Bn TfOH (84) Cbz BF₃•OEt₂ (46) Cbz TfOH (51) Fmoc BF₃•OEt₂ (74) Fmoc TfOH (55)</p>	641
<p>C₁₃</p> 	<p>BnN₃, BF₃•OEt₂, CH₂Cl₂, MW, 135°, 10 min</p>	<p>(12) +</p>  <p><i>n</i>-C₅H₁₁ BF₃•OEt₂ (5)</p>	634

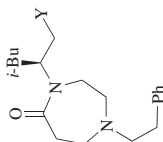
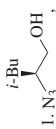


1. N_3 -CH₂-CH₂-OH, $BF_3 \cdot OEt_2$, CH_2Cl_2 , 0° to rt, 12 h
2. NaY, DMF, 70°, 24 h



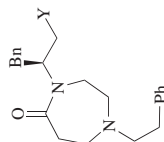
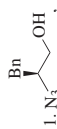
Y	
N_3	(32)
NC-	(29)
PhO	(32)
PhS	(18)
4-BrC ₆ H ₄ S	(42)
4-MeC ₆ H ₄ S	(41)
4-MeOC ₆ H ₄ S	(29)
4-(AcNH)C ₆ H ₄ S	(18)

631



Y	
N_3	(8)
NC-	(28)
PhO	(33)
PhS	(20)
4-BrC ₆ H ₄ S	(23)
4-MeC ₆ H ₄ S	(29)
4-MeOC ₆ H ₄ S	(18)
4-(AcNH)C ₆ H ₄ S	(20)

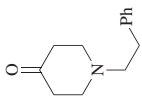

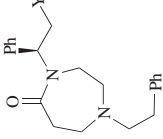
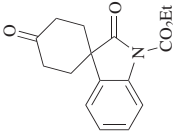

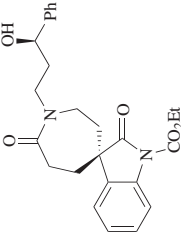
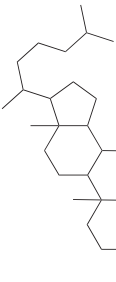
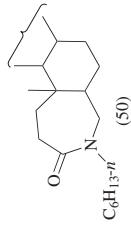
631



Y	
N_3	(41)
NC-	(22)
PhO	(30)
PhS	(12)
4-BrC ₆ H ₄ S	(26)
4-MeC ₆ H ₄ S	(42)
4-MeOC ₆ H ₄ S	(22)
4-(AcNH)C ₆ H ₄ S	(42)

631

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₃	 1. N ₃ -CH(OH)-CH ₂ -Ph BF ₃ ·OEt ₂ , CH ₂ Cl ₂ , 0° to rt, 12 h 2. NaY, DMF, 70°, 24h	 Y N ₃ (23) NC- (17) PhO (4) PhS (8) 4-BrC ₆ H ₄ S (7) 4-MeC ₆ H ₄ S (20) 4-MeOC ₆ H ₄ S (17) 4-(AcNH)C ₆ H ₄ S (13)	631
 C ₁₆	 1. N ₃ -CH(OH)-CH ₂ -Ph, BF ₃ ·OEt ₂ , CH ₂ Cl ₂ , -80° to rt 2. NaHCO ₃	 I I + II (98), II = 87:13	476
 C ₂₇	<i>n</i> -C ₆ H ₁₃ N ₃ , TiCl ₄ , CH ₂ Cl ₂ , rt, 16 h	 (50) + C ₆ H _{13-n}	85 ^e

^a The ratios were calculated on the basis of ¹H NMR integrations of the crude reaction mixtures and were normalized to 100 with the recovered azide.

^b Yields were obtained from reactions run on a Bodan Mimiblock XT automated synthesizer.

^c Yields were obtained from reactions run on a Chemspeed SLT100 automated synthesizer.

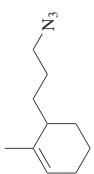
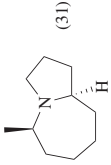
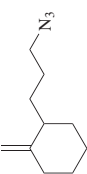
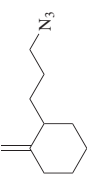
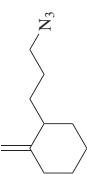
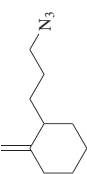
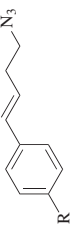
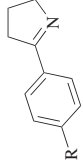
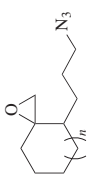
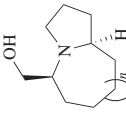
^d The ratio of the two diastereomers was 65:35. The stereochemistry was not determined.

^e The stereochemistry of the substrate was not specified in the reference.

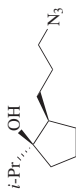
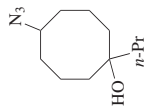
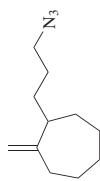
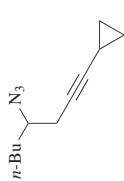
TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																								
	<p>(dppm)Au₂Cl₂ (2.5 mol %), AgSbF₆ (5 mol %), CH₂Cl₂, 33°</p>	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td><i>n</i>-Bu</td> <td>(76)</td> </tr> <tr> <td>H</td> <td>2-C₄H₉O</td> <td>(61)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>(68)</td> </tr> <tr> <td>H</td> <td>4-IC₆H₄</td> <td>(87)</td> </tr> <tr> <td>H</td> <td>2-MeOC₆H₄</td> <td>(88)</td> </tr> <tr> <td>H</td> <td>3-CF₃C₆H₄</td> <td>(93)</td> </tr> <tr> <td><i>n</i>-Bu</td> <td><i>n</i>-Bu</td> <td>(82)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	H	<i>n</i> -Bu	(76)	H	2-C ₄ H ₉ O	(61)	H	Ph	(68)	H	4-IC ₆ H ₄	(87)	H	2-MeOC ₆ H ₄	(88)	H	3-CF ₃ C ₆ H ₄	(93)	<i>n</i> -Bu	<i>n</i> -Bu	(82)	105
R ¹	R ²	Yield (%)																									
H	<i>n</i> -Bu	(76)																									
H	2-C ₄ H ₉ O	(61)																									
H	Ph	(68)																									
H	4-IC ₆ H ₄	(87)																									
H	2-MeOC ₆ H ₄	(88)																									
H	3-CF ₃ C ₆ H ₄	(93)																									
<i>n</i> -Bu	<i>n</i> -Bu	(82)																									
	<p>1. TfOH, PhH 2. NaBH₄, MeOH</p>		51																								
	<p>1. Promoter, CH₂Cl₂ 2. NaBH₄</p>	<table border="1"> <thead> <tr> <th>Promoter</th> <th>Temp (°)</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>TfOH</td> <td>-40</td> <td>(25)</td> </tr> <tr> <td>TMSOTf</td> <td>-78</td> <td>(21)</td> </tr> <tr> <td>BF₃•OEt₂</td> <td>-78</td> <td>(50)</td> </tr> <tr> <td>TiCl₄</td> <td>-25</td> <td>(43)</td> </tr> <tr> <td>EtAlCl₂</td> <td>-78</td> <td>(63)</td> </tr> </tbody> </table>	Promoter	Temp (°)	Yield (%)	TfOH	-40	(25)	TMSOTf	-78	(21)	BF ₃ •OEt ₂	-78	(50)	TiCl ₄	-25	(43)	EtAlCl ₂	-78	(63)	104						
Promoter	Temp (°)	Yield (%)																									
TfOH	-40	(25)																									
TMSOTf	-78	(21)																									
BF ₃ •OEt ₂	-78	(50)																									
TiCl ₄	-25	(43)																									
EtAlCl ₂	-78	(63)																									
	<p>BF₃•OEt₂, air, -78 to 0°</p>		642																								
	<p>1. Hg(ClO₄)₂•3H₂O, THF 2. NaBH₄</p>		50																								

TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
	1. Hg(ClO ₄) ₂ ·3H ₂ O, CH ₂ Cl ₂ 2. NaBH ₄		50										
	1. Hg(OTf) ₂ , THF 2. NaBH ₄	I (45)	50										
	1. TfOH, CH ₂ Cl ₂ 2. NaBH ₄	I + II (79), I:II = 1:1	51										
	1. Hg(OTf) ₂ , CH ₂ Cl ₂ 2. NaBH ₄	I (87)	50										
	1. Hg(ClO ₄) ₂ ·3H ₂ O, CH ₂ Cl ₂ 2. NaBH ₄	I (84)	50										
	1. TfOH, CH ₂ Cl ₂ , 0°, 30 min 2. Et ₃ N, rt, 15 min	 R <table border="1" style="margin-left: 20px;"> <tr><td>H</td><td>(48)</td></tr> <tr><td>Cl</td><td>(50)</td></tr> <tr><td>Br</td><td>(40)</td></tr> <tr><td>Me</td><td>(62)</td></tr> <tr><td>MeO</td><td>(72)</td></tr> </table>	H	(48)	Cl	(50)	Br	(40)	Me	(62)	MeO	(72)	643
H	(48)												
Cl	(50)												
Br	(40)												
Me	(62)												
MeO	(72)												
	1. Et ₂ AlCl, CH ₂ Cl ₂ , -78°, 45 min 2. NaBH ₄	 n <table border="1" style="margin-left: 20px;"> <tr><td>1</td><td>(42)</td></tr> <tr><td>2</td><td>(47)</td></tr> </table>	1	(42)	2	(47)	644						
1	(42)												
2	(47)												

C11



(dppm)Au₂Cl₂ (2.5 mol %),
AgSbF₃ (5 mol %), CH₂Cl₂, 35°

1. Hg(ClO₄)₂·3H₂O, THF
2. NaBH₄

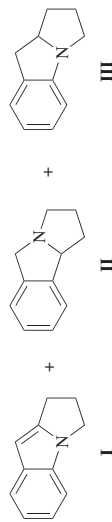
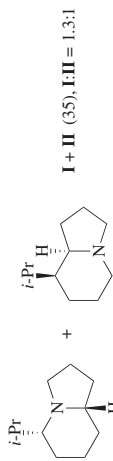
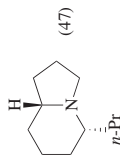
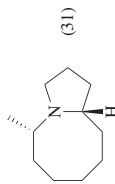
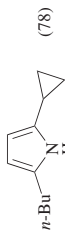
1. TfOH, Tf₂O, PhH
2. NaBH₄

1. TfOH, PhH
2. BH₃·SMe₂

1. TfOH, PhH
2. NaBH₄

1. TfOH, PhH
2. BH₃·SMe₂

1. Hg(OTf)₂
2. BH₃·SMe₂



I + II + III (48), E:III = 3:1.3:1

II + III (49), II:III = 1:1.5

I + II (50), I:II = 1.5:1

105

50

51

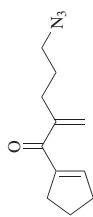
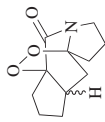

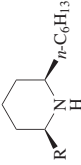
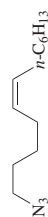

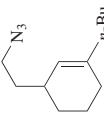
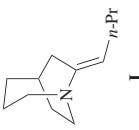
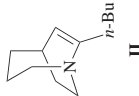

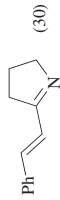
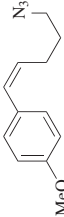
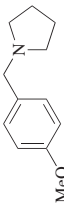
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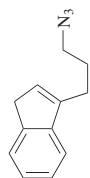
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102

50

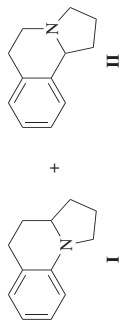
TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₁	BF ₃ ·OEt ₂ , air, -78 to 0°	 (60) dr = 2:1	642
 C ₁₁₋₁₃	1. Hg(ClO ₄) ₂ ·3H ₂ O, THF 2. NaBH ₄	 R H (58) Et (44)	50
 C ₁₂	1. Hg(ClO ₄) ₂ ·3H ₂ O, THF 2. NaBH ₄	 (73)	50
	1. TfOH, PhH 2. NaOH	 I +  II I + II (37), I:II = 1.1:1	51
	1. TfOH, CH ₂ Cl ₂ , 0°, 30 min 2. Et ₃ N, rt, 15 min	 (30)	643
	1. Hg(ClO ₄) ₂ ·3H ₂ O, THF 2. NaBH ₄	 (43)	50

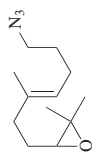


1. TfOH, PhH
2. NaBH₄

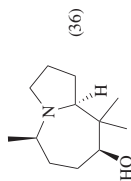
I + II (92), I:II = 2.3:1



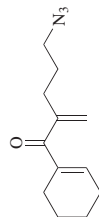
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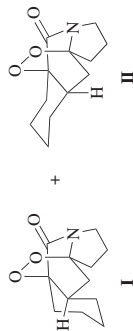
1. Et₂AlCl, CH₂Cl₂, -78°, 45 min
2. NaBH₄



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BF₃·OEt₂, air, -78 to 0°



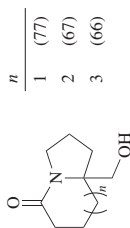
642

I + II (60), I:II = 2:1

C₁₂₋₁₄

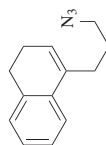


TfCl₄, CH₂Cl₂, -78° to rt

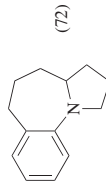


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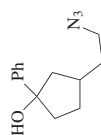
C₁₃



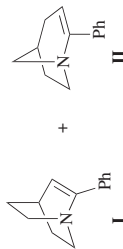
1. TfOH, PhH
2. NaBH₄



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1. TfOH, PhH
2. NaBH₄, MeOH

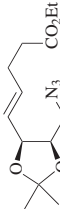
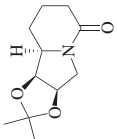
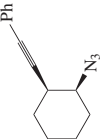
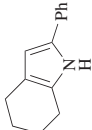
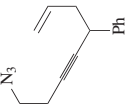
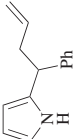
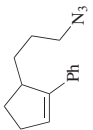
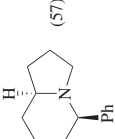
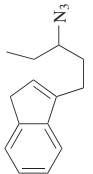
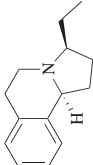


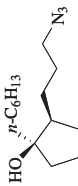
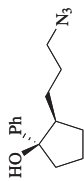
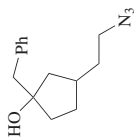
I + II (76), I:II = 1.8:1

51

TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (Continued)

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Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{13}	1. $Hg(ClO_4)_2 \cdot 3H_2O$, THF 2. $NaBH_4$	 (34)	50
 C_{14}	$(dppm)Au_2Cl_2$ (2.5 mol %), $AgSbF_6$ (5 mol %), CH_2Cl_2 , 35°	 (73)	105
	$(dppm)Au_2Cl_2$ (2.5 mol %), $AgSbF_6$ (5 mol %), CH_2Cl_2 , 35°	 (41)	105
	1. $TiOH$, PhH, 15° , 5 min 2. $NaBH_4$, MeOH, 0° to rt, 24h	 (57)	101
	1. $TiOH$, PhH 2. $NaBH_4$	 I + II + III (72), I:II:III = 2:1:1	102



1. TfOH, PhH
2. NaOH

1. TfOH, PhH
2. NaBH₄, EtOH

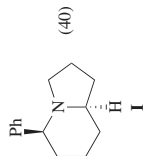
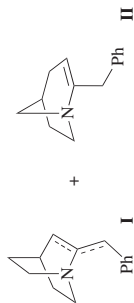
1. SnCl₄
2. NaBH₄

1. TfOH
2. NaBD₄

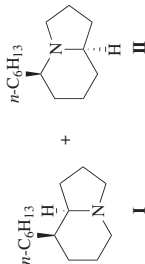
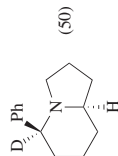
1. TfOH, PhH
2. NaBH₄, MeOH

1. SnCl₄, CH₂Cl₂
2. BH₃•Me₂S

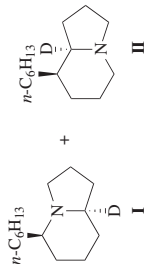
1. TfOH
2. NaBD₄



I (63)



I + II (47), **I:II** = 1:1.7



I + II (25), **I:II** = 1:3:1

51

I + II (21), **I:II** = 4.3:1

51

101

101

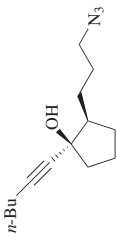
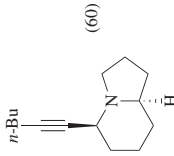
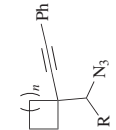
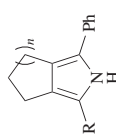
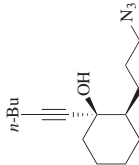
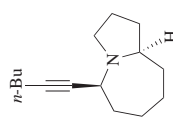
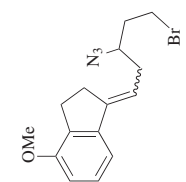
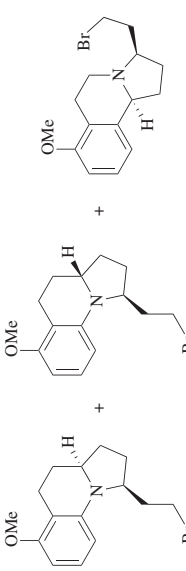
17

I + II (25), **I:II** = 1.4:1

17

101

TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL-ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.									
<p>C₁₄</p> 	<p>1. SnCl₄, CH₂Cl₂, -78°, 10 min 2. NaBH₄, MeOH, rt, 20 h</p>	<p>(60)</p> 	101									
<p>C₁₄₋₂₁</p> 	<p>(dppm)Au₂Cl₂ (2.5 mol %), AgSbF₆ (5 mol %), CH₂Cl₂, 35°</p>	<table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>R</th> <th>n</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>1</td> <td>(80)</td> </tr> <tr> <td>Ph</td> <td>2</td> <td>(84)</td> </tr> </tbody> </table> 	R	n	Yield (%)	H	1	(80)	Ph	2	(84)	105
R	n	Yield (%)										
H	1	(80)										
Ph	2	(84)										
<p>C₁₅</p> 	<p>1. SnCl₄, CH₂Cl₂, -78°, 10 min 2. NaBH₄, MeOH, rt, 20 h</p>	<p>(44)</p> 	101									
	<p>1. TfOH, PhH 2. NaBH₄</p>	<p>I + II + III (72), I:II:III = 1:1:0.6</p> 	102									

102

I + II + III (60), E:II:III = 2:1:1

1. TiOH, PhH

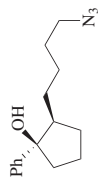
2. DIBAL-H

102

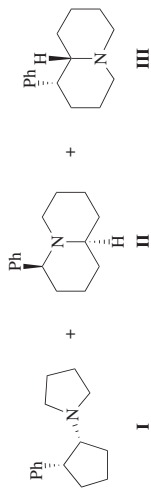
I + II + III (55), E:II:III = 4.5:0:1

1. TiOH, PhH

2. L-Selectride

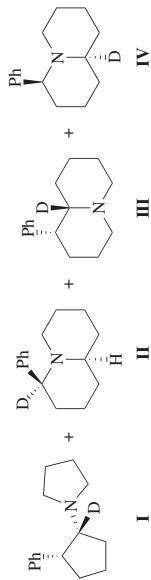


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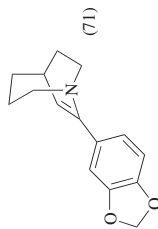
I + II + III (36), E:II:III = 2.3:1.9:1

101



I + II + III + IV (25), E:II:III:IV = 4.3:5.2:1

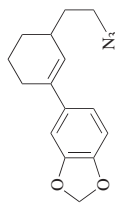
1. TiOH, PhH, 15°, 5 min

2. NaBD₄, MeOD, 0°, 24 h

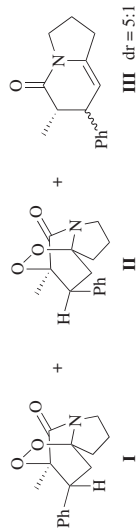
23

1. TiOH, CH₂Cl₂, 0°, 5 min

2. NaOH




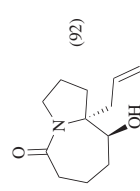
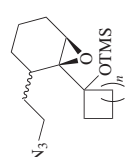
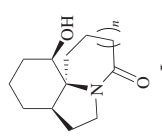
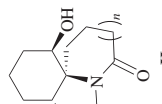
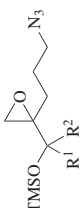
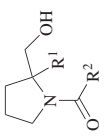
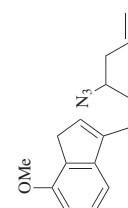
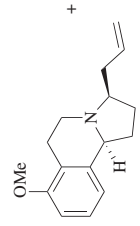
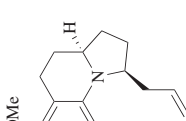
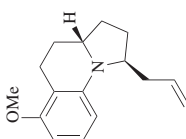
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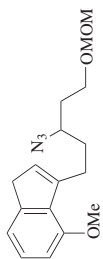
BF₃·OEt₂, airt., -78 to 0°

I + II + III (72), E:II:III = 5:5:1

III dr = 5:1

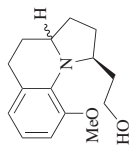
TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
 C ₁₅	TiCl ₄ , CH ₂ Cl ₂ , -78° to 0°	 (92)	645												
 C ₁₅₋₁₆	TiCl ₄ , CH ₂ Cl ₂ , -78° to 0°	 I +  II <table border="1" data-bbox="424 416 516 590"> <thead> <tr> <th>n</th> <th>I + II (%)</th> <th>II (%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>78</td> <td>7:1</td> </tr> <tr> <td>2</td> <td>92</td> <td>8:1</td> </tr> </tbody> </table>	n	I + II (%)	II (%)	1	78	7:1	2	92	8:1	645			
n	I + II (%)	II (%)													
1	78	7:1													
2	92	8:1													
 C ₁₅₋₁₇	TiCl ₄ , CH ₂ Cl ₂ , -78° to rt	 I <table border="1" data-bbox="585 538 700 763"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>(80)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(95)</td> </tr> <tr> <td>3-MeOC₆H₄</td> <td>Me</td> <td>(77)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	Ph	H	(80)	Ph	Me	(95)	3-MeOC ₆ H ₄	Me	(77)	645
R ¹	R ²	Yield (%)													
Ph	H	(80)													
Ph	Me	(95)													
3-MeOC ₆ H ₄	Me	(77)													
 C ₁₆	1. TfOH, PhH 2. NaBH ₄	 I +  II +  III I + II + III (86), I:II:III = 4:2:1	102												
	1. Hg(OTf) ₂ 2. NaBH ₄	I + II + III (45), I:II:III = 0:2:1	50												

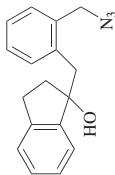
C₁₇

1. TiOH, PhH
2. NaBH₄

(47) dr = 1.2:1

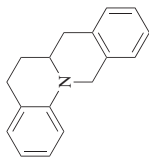


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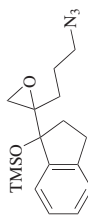


1. TiOH, PhH
2. BH₃·SMe₂

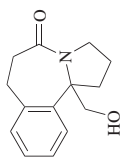
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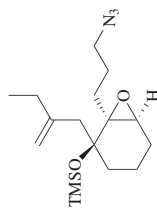
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TiCl₄, CH₂Cl₂, -78° to rt

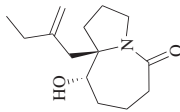
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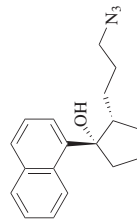
645

TiCl₄, CH₂Cl₂, -78 to 0°

(68)

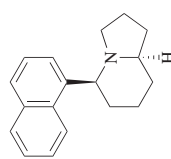


646

C₁₈

1. SnCl₄, CH₂Cl₂, -78°, 12 min
2. BH₃·SMe₂, THF, rt, 12 h

(68)



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TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₈₋₁₉</p>	<ol style="list-style-type: none"> 1. SnCl₄, CH₂Cl₂, -78°, 12 min 2. BH₃·SMe₂, THF, rt, 12 h 	 	103
<p>C₂₂</p>	<p>(dppm)Au₂Cl₂ (5 mol %), AgSbF₆ (10 mol %), MeNO₂, rt</p>		105
<p>C₃₀</p>	<ol style="list-style-type: none"> 1. Hg(OTf)₂, THF 2. NaBH₄, MeOH 3. MeONa, MeOH, reflux 		50
<p>C₃₂</p>	<ol style="list-style-type: none"> 1. Hg(ClO₄)₂·3H₂O, THF 2. NaBH₄, MeOH 		50

TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES


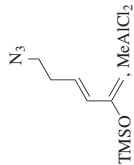
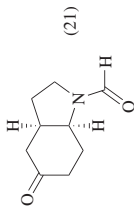
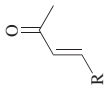
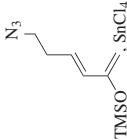
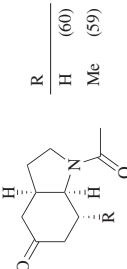

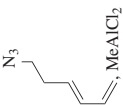
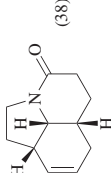
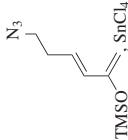
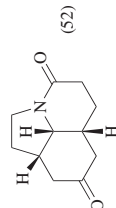
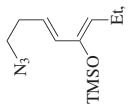
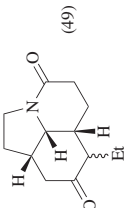

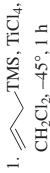

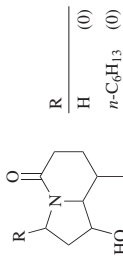

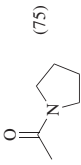

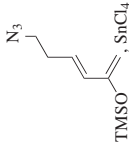
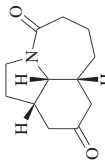
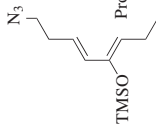
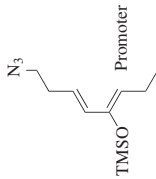
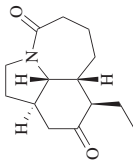
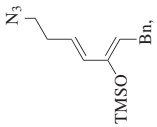
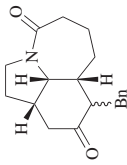
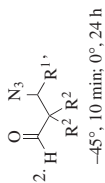
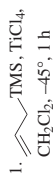
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_3	 N_3 TMSO, $MeAlCl_2$	 (36) + (21)	647
 C_{4-5}	 N_3 TMSO, $SnCl_4$	 $\frac{R}{H}$ (60) $\frac{Me}{H}$ (59)	647
 C_5	 N_3 $MeAlCl_2$	 (38)	647
	 N_3 TMSO, $SnCl_4$	 (52)	647
	 N_3 TMSO, $BF_3 \cdot OEt_2$, CH_2Cl_2 , -78° to rt	 (49)	648

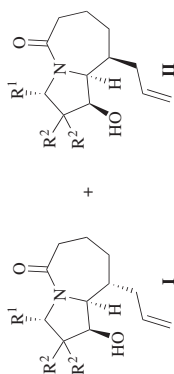
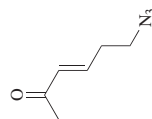
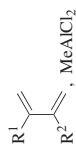
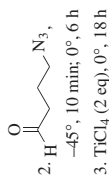
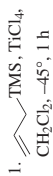
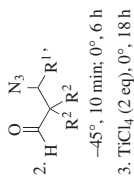
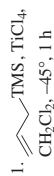
TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₅</p> 	<p>1.  TMS, TiCl₄, CH₂Cl₂, -45°, 1 h</p> <p>2.  R, -45°, 10 min; 0°, 6 h</p> <p>3. TiCl₄ (2 eq), 0°, 18 h</p>	 R H <i>n</i> -C ₆ H ₁₃ (0)	649
<p>C₆</p> 	TFA, CH ₂ Cl ₂ , rt, 16 h	 (75)	29
	TMSO,  SnCl ₄	 I + II (82), II = 3.4:1	647
	TMSO,  Promoter	 I + II Promoter TMSOTf (70) 3:1 BF ₃ •OEt ₂ (30) 0:100	650
	BF ₃ •OEt ₂ , CH ₂ Cl ₂ , -78° to rt	 (56)	648

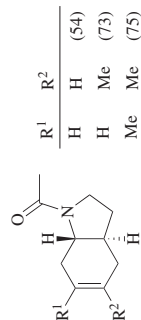
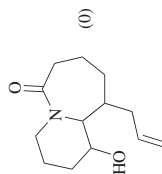
Conditions A:



Conditions B:



R ¹	R ²	Conditions	I:II
H	H	A	(38) 6.4:1
H	H	B	(59) 2.6:1
H	Me	A	(42) 1:0
H	Me	B	(56) 1:0
<i>n</i> -C ₆ H ₁₃	H	A	(36) 4.0:1
<i>n</i> -C ₆ H ₁₃	H	B	(59) 1.8:1

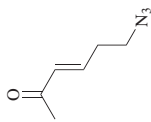

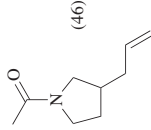
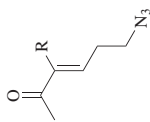

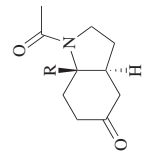
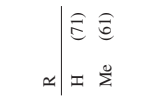
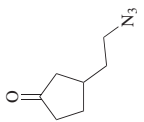
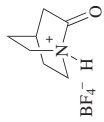
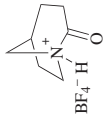
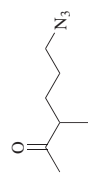
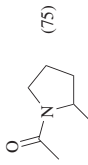
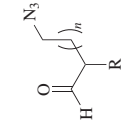
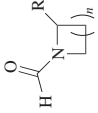
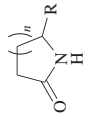


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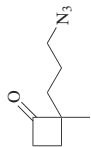
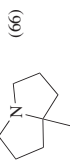
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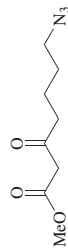
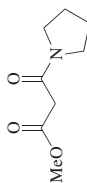
TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₆	1.  , TiCl ₄ , CH ₂ Cl ₂ , -78°, 3 h; 0°, 5 h 2. MeOH (5 eq), rt, 45 min	 (46)	649
 C ₆₋₇	 , MeAlCl ₂	 (71)  (61)	647
 C ₇	HBF ₄ ·Et ₂ O, 20°	 I +  II	I + II (38), I:II = 76:24 91
 C ₇₋₁₃	TFA	 (75)	651
 C ₇₋₁₃	Promoter, rt, 17–19 h	 I +  II	632

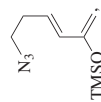
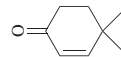
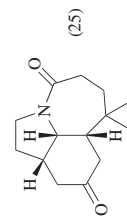
<i>n</i>	R	Promoter		I	II
		TFA	TiCl ₄		
1	allyl	TFA		(-)	(63)
1	allyl	TiCl ₄		(-)	(90)
2	allyl	TFA		(60)	(-)
2	allyl	TiCl ₄		(96)	(-)
3	allyl	TFA		(53)	(-)
3	allyl	TiCl ₄		(41)	(-)
1	Bn	TFA		(-)	(77)
1	Bn	TiCl ₄		(-)	(94)
2	Bn	TFA		(68)	(-)
2	Bn	TiCl ₄		(85)	(-)
3	Bn	TFA		(71)	(-)
3	Bn	TiCl ₄		(49)	(-)

C₈TFA, CH₂Cl₂, rt

29

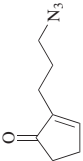

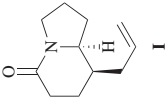
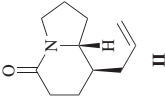
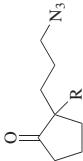

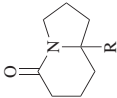
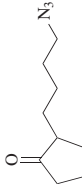
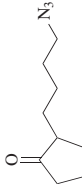

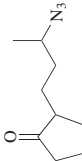

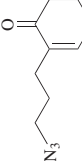

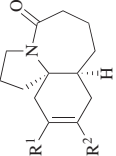
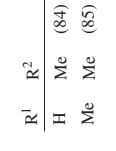
Promoter, CH₂Cl₂, rt

3

BF₃•OEt₂, CH₂Cl₂, -78° to rt

648

TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	1.  , TiCl_4 , CH_2Cl_2 , -78° , 3 h; 0° , 5 h 2. <i>t</i> -BuOH (5 eq), rt, 45 min	 I  II I + II (50), I:II = 64:36	649												
	1.  , TiCl_4 , CH_2Cl_2 , -78° , 3 h; 0° , 5 h 2. aq NH_4Cl 3. TFA	 II (47)	649												
	Promoter, CH_2Cl_2 , rt	<table border="1"> <thead> <tr> <th>R</th> <th>Promoter</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>TFA</td> <td>40 min (83)</td> </tr> <tr> <td>MeO_2C</td> <td>TFA</td> <td>16 h (66)</td> </tr> <tr> <td>MeO_2C</td> <td>TiCl_4</td> <td>20 min (70)</td> </tr> </tbody> </table>	R	Promoter	Time	H	TFA	40 min (83)	MeO_2C	TFA	16 h (66)	MeO_2C	TiCl_4	20 min (70)	3 29 3
R	Promoter	Time													
H	TFA	40 min (83)													
MeO_2C	TFA	16 h (66)													
MeO_2C	TiCl_4	20 min (70)													
	TiCl_4 , CH_2Cl_2 , rt, 16 h	 (56)	29												
	TiCl_4 , CH_2Cl_2 , rt, 16 h	 (68)	29												
	 , MeAlCl_2	 (84)  (85)	647												

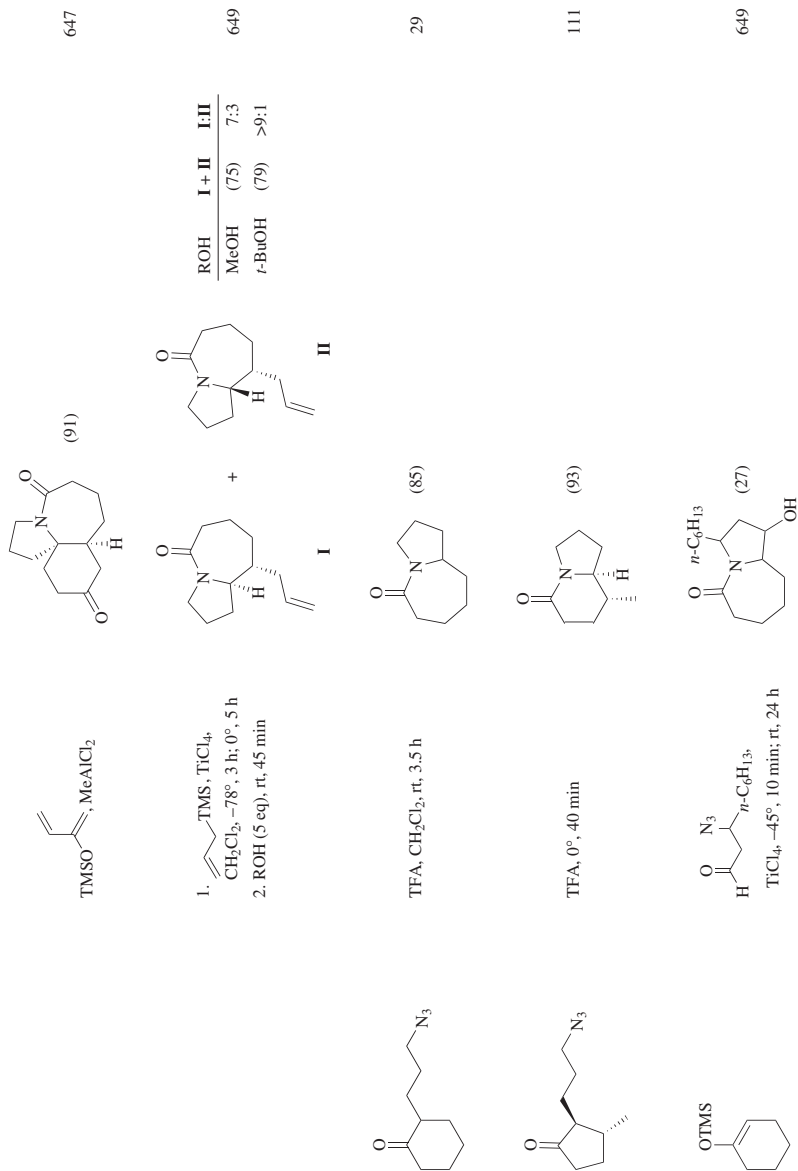
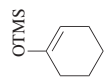
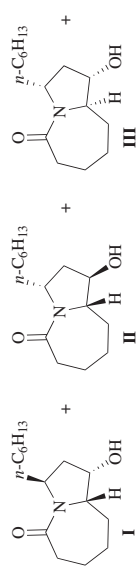
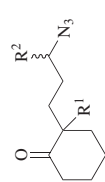
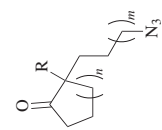
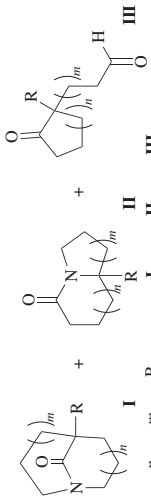
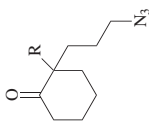
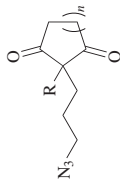


TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (Continued)

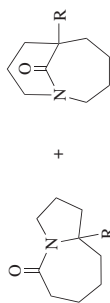
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
<p>C₉</p> 	<p>1. TiCl₄, CH₂Cl₂, rt, 3 min 2. H₂N-CH₂-CHO, n-C₆H₁₃, -45°, 10 min; rt, 24 h</p>	 <p>I + II + III + IV (56), I:(II+III+IV) = 56:44</p>	649												
<p>C₉₋₁₂</p> 	TFA, CH ₂ Cl ₂ , rt	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>10 min (90)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>20 min (74)</td> </tr> <tr> <td>EtO₂C</td> <td>H</td> <td>1 h (93)</td> </tr> </tbody> </table>	R ¹	R ²	Time	H	H	10 min (90)	H	Me	20 min (74)	EtO ₂ C	H	1 h (93)	3
R ¹	R ²	Time													
H	H	10 min (90)													
H	Me	20 min (74)													
EtO ₂ C	H	1 h (93)													
<p>C₉₋₁₅</p> 	TfOH, CH ₂ Cl ₂ , 0°		652												



C₉-17



TfOH, CH₂Cl₂, 0°



R I + II
H (85) >95:5
Ph (96) >95:5

652

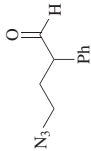
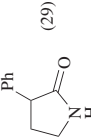

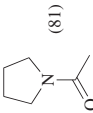
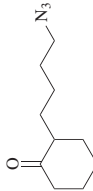
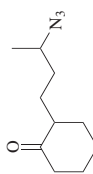
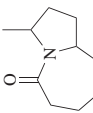
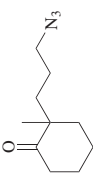
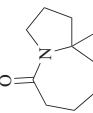

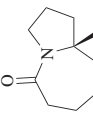
n	R	Promoter	x	Solvent	Time (h)
1	Me	BF ₃ •OEt ₂	4	Et ₂ O	24 (65)*
1	Me	TiCl ₄	2.5	Et ₂ O	1 (89)
1	Me	EtAlCl ₂	2.5	Et ₂ O	6 (83)
1	Me	CuOTf	2.5	THF	72 (—)
1	Me	ZnCl ₂	2.5	Et ₂ O	72 (—)
1	Me	Yb(OTf) ₃	—	THF	72 (—)
2	Me	BF ₃ •OEt ₂	4	Et ₂ O	24 (52)
2	Me	BF ₃ •OEt ₂	2.5	Et ₂ O	24 (85)
2	Me	TiCl ₄	1.1	Et ₂ O	1 (67)
2	Me	EtAlCl ₂	1.1	Et ₂ O	24 (60)
2	Me	EtAlCl ₂	2.5	Et ₂ O	6 (80)
3	Bn	EtAlCl ₂	2.5	Et ₂ O	24 (87)

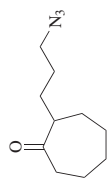
Promoter, rt, 72 h

653

n	R	Promoter	Solvent	% er
1	Me	L-menthylaluminum dichloride	hexane/toluene (1:1)	(35) 0
1	Me	(S)-BINOLAlCl	toluene	(18) 53.0:47.0
2	Me	L-menthylaluminum dichloride	hexane/toluene (1:1)	(50) 52.5:47.5
2	Me	(S)-BINOLAlCl	toluene	(25) 52.0:48.0
3	Bn	L-menthylaluminum dichloride	hexane/toluene (1:1)	(27) 0
3	Bn	(S)-BINOLAlCl	toluene	(10) 0

TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
<p>C₁₀</p> 	TFA, CH ₂ Cl ₂	 (29)	29								
	1. TMSOTf, CH ₂ Cl ₂ , rt, 16 h 2. NaI, acetone	 (81)	94								
	Promoter, CH ₂ Cl ₂ , rt, 16 h	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <th colspan="2">Promoter</th> </tr> <tr> <td>TFA</td> <td>(0)</td> </tr> <tr> <td>BF₃•OEt₂</td> <td>(29)</td> </tr> <tr> <td>TiCl₄</td> <td>(91)</td> </tr> </table>	Promoter		TFA	(0)	BF ₃ •OEt ₂	(29)	TiCl ₄	(91)	29
Promoter											
TFA	(0)										
BF ₃ •OEt ₂	(29)										
TiCl ₄	(91)										
	TFA, CH ₂ Cl ₂ , 15 min	 (74)	29								
	TFA, CH ₂ Cl ₂ , 15 min	 (87)	29								
 91% ee	TFA, CH ₂ Cl ₂ , 1 h	 (87) 94.5:5.5 er	651								



TFA, CH₂Cl₂, 3 h

(80)

29



Promoter, CH₂Cl₂

Promoter	Time
TFA	16 h (66)
TiCl ₄	30 min (70)

29



TiCl₄, CH₂Cl₂, 0° to rt

(89)

654

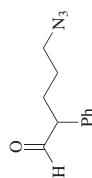
C₁₁



TFA, CH₂Cl₂, rt, 16 h

(77)

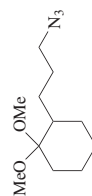
29



Promoter, CH₂Cl₂

Promoter	I	II
TFA	(81)	(8)
AlCl ₃	(69)	(8)
SnCl ₄	(59)	(15)
ZnCl ₂	(48)	(17)
TMSOTf	(61)	(22)

29



1. TFA, CH₂Cl₂, rt, 16 h
2. NaI, acetone

(72)

94

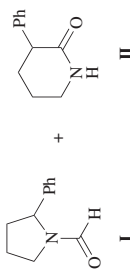
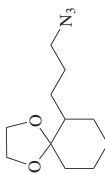
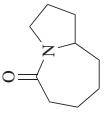
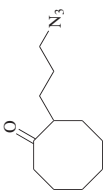
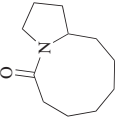

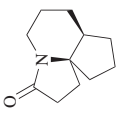
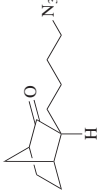
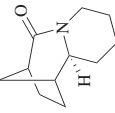
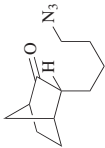
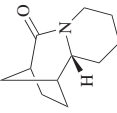
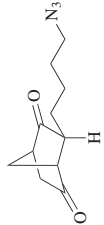
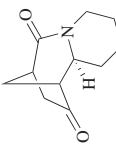


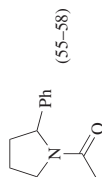
TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₁	1. TFA, CH ₂ Cl ₂ , rt, 16 h 2. NaI, acetone	 (35)	94
	TFA, CH ₂ Cl ₂ , 16 h	 (96)	29
	TiCl ₄ , CH ₂ Cl ₂ , rt	 (39)	3
	TiCl ₄ , CH ₂ Cl ₂	 (82)	655
	TiCl ₄ , CH ₂ Cl ₂	 (92)	655
	TiCl ₄ , CH ₂ Cl ₂	 (50-75)	655

C₁₂

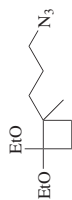


TiCl₄ or TfOH,
CH₂Cl₂, 0°, 15 min

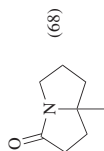


90

(55–58)

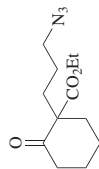


TFA, CH₂Cl₂, rt, 16 h

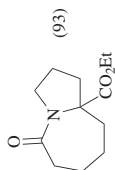


94

(68)

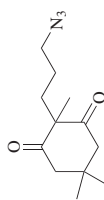


TFA, CH₂Cl₂, rt, 1 h

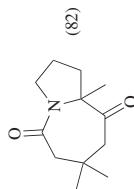


29

(93)

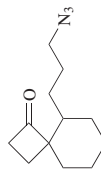


TFA, CH₂Cl₂

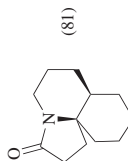


29

(82)

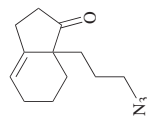


TiCl₄, CH₂Cl₂, rt

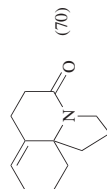


3

(81)



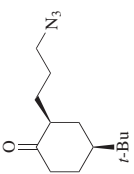
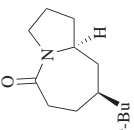
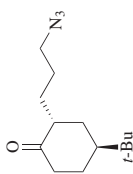
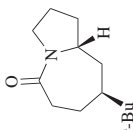
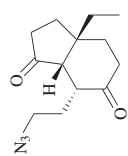
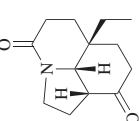
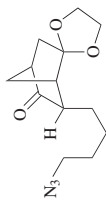
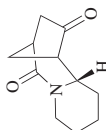
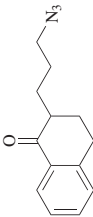
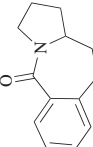
BF₃·OEt₂, rt



656

(70)

TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFA, CH ₂ Cl ₂	 (96)	29
	TiCl ₄ , CH ₂ Cl ₂	 (92)	29
	TiCl ₄ , CH ₂ Cl ₂	 (82)	114
	TiCl ₄ , CH ₂ Cl ₂ , reflux	 (62)	115
	TfOH, CH ₂ Cl ₂	 (45)	29

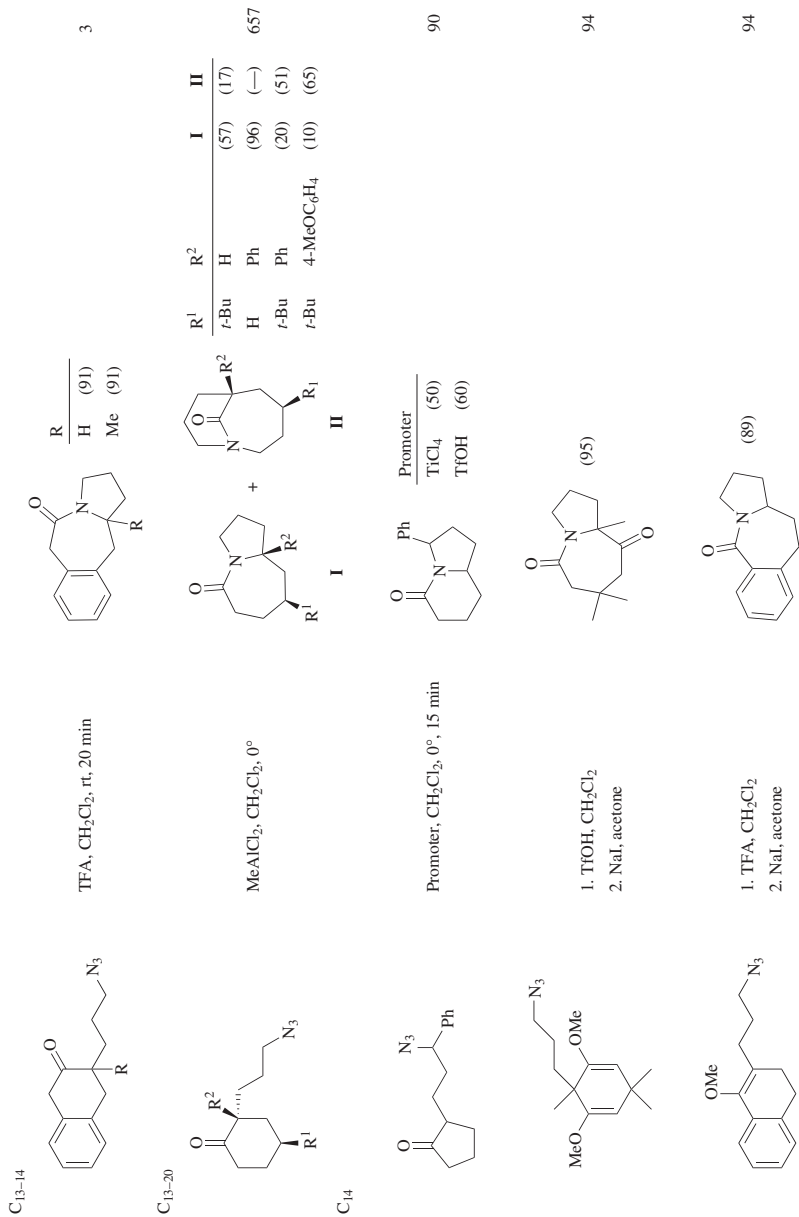
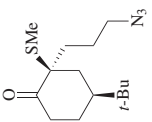
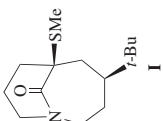
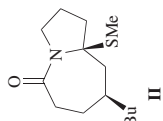
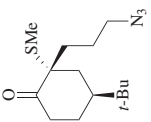
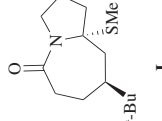
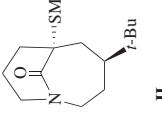
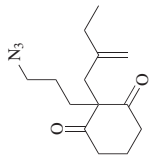
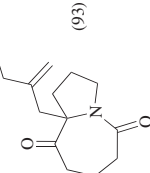
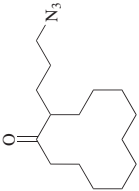
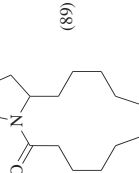


TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₄	TfOH, CH ₂ Cl ₂ , 0°	 I +  II I + II (74), I:II = 86:14	652
 C ₁₄	TfOH, CH ₂ Cl ₂ , 0°	 I +  II I + II (75), I:II = >95:5	652
 C ₁₅	TiCl ₄ , CH ₂ Cl ₂ , -78°, 15 min; rt	 (93)	658
 C ₁₅	TFA, CH ₂ Cl ₂ , 2 h	 (89)	29

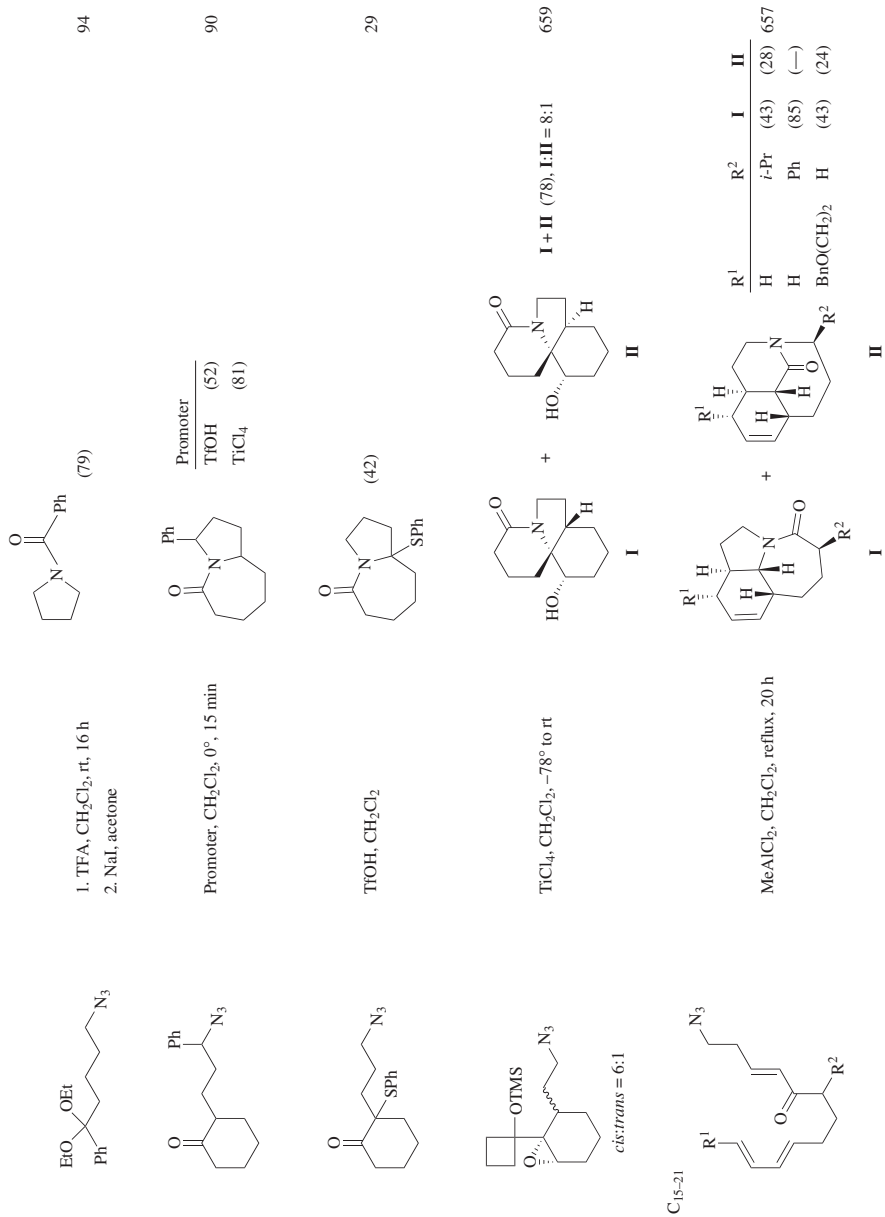


TABLE 1.1. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₆</p>	<p>TfOH, CH₂Cl₂, 0°, 30 min</p>	<p>(79)</p>	660
	<p>TfOH, CH₂Cl₂, -5° to 0°, 15 min</p>	<p>(54)</p>	661, 662
<p>C₁₇</p>	<p>TMSOTf, CH₂Cl₂, 0° to rt, 40 min</p>	<p>(94)</p>	94
	<p>TiCl₄, CH₂Cl₂, 0°, 40 min</p>	<p>(75)</p>	658
<p>C₁₇₋₁₉</p>	<p>TFA, CH₂Cl₂, rt, 6 h</p>	<p>(81)</p> <p> <p>(85)</p> </p>	110

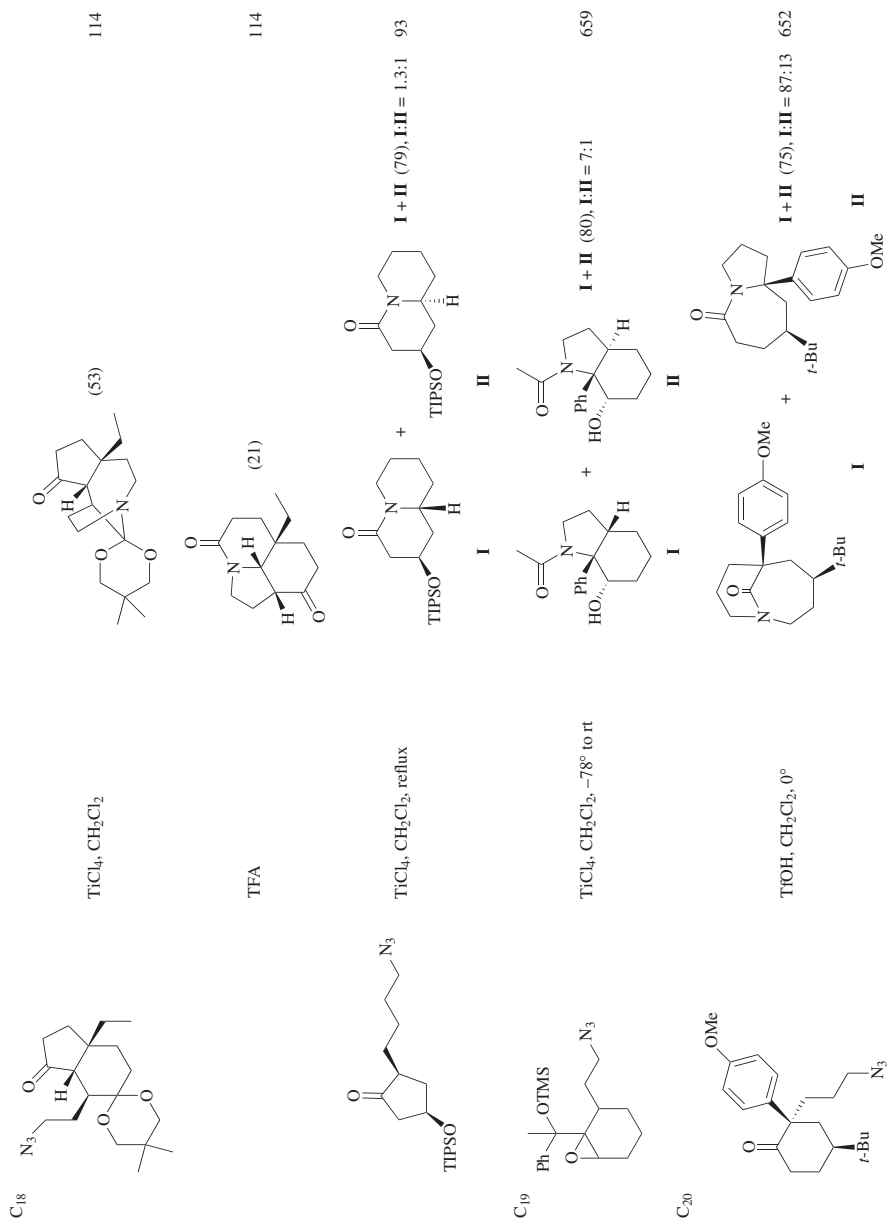
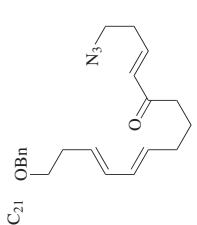
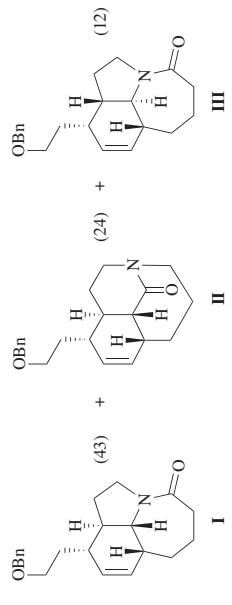
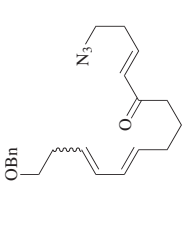
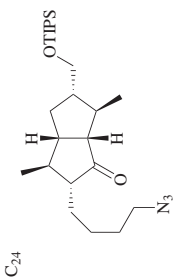
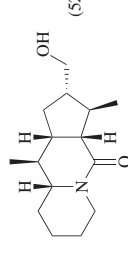
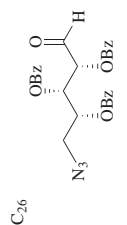
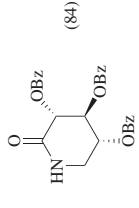


TABLE 1.1. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																														
 C ₂₁	Et ₂ AlCl, CH ₂ Cl ₂ , reflux, 18 h	 I (43) + II (24) + III (12) 92	663																														
 C ₂₄	Promoter CH ₂ Cl ₂ , 45°	<table border="1" data-bbox="493 468 665 815"> <thead> <tr> <th>Promoter</th> <th>x</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>InCl₃</td> <td>2.0^a</td> <td>(20)</td> <td>(22)</td> <td>(18)</td> </tr> <tr> <td>AlMe₃</td> <td>1.0</td> <td>(0)</td> <td>(0)</td> <td>(0)</td> </tr> <tr> <td>Et₂AlCl</td> <td>1.3^a</td> <td>(28)</td> <td>(20)</td> <td>(12)</td> </tr> <tr> <td>Et₂AlCl</td> <td>1.0</td> <td>(41)</td> <td>(28)</td> <td>(9)</td> </tr> <tr> <td>Me₂AlCl₂</td> <td>1.0</td> <td>(43)</td> <td>(24)</td> <td>(12)</td> </tr> </tbody> </table> I + II + III	Promoter	x	I	II	III	InCl ₃	2.0 ^a	(20)	(22)	(18)	AlMe ₃	1.0	(0)	(0)	(0)	Et ₂ AlCl	1.3 ^a	(28)	(20)	(12)	Et ₂ AlCl	1.0	(41)	(28)	(9)	Me ₂ AlCl ₂	1.0	(43)	(24)	(12)	663
Promoter	x	I	II	III																													
InCl ₃	2.0 ^a	(20)	(22)	(18)																													
AlMe ₃	1.0	(0)	(0)	(0)																													
Et ₂ AlCl	1.3 ^a	(28)	(20)	(12)																													
Et ₂ AlCl	1.0	(41)	(28)	(9)																													
Me ₂ AlCl ₂	1.0	(43)	(24)	(12)																													
 C ₂₄	TfOH, CH ₂ Cl ₂ , 0°, 30 min	 (52)	660																														
 C ₂₆	TiCl ₄ , CH ₂ Cl ₂ , 0° to rt, 18 h	 (84)	664																														

^a The Promoter was added in two equal portions.

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