

Reactions of Aldehydes and Ketones and their Derivatives

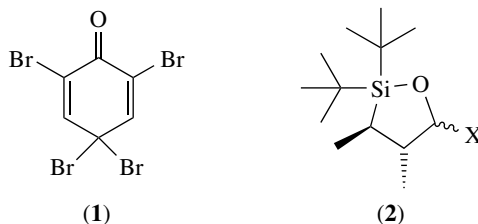
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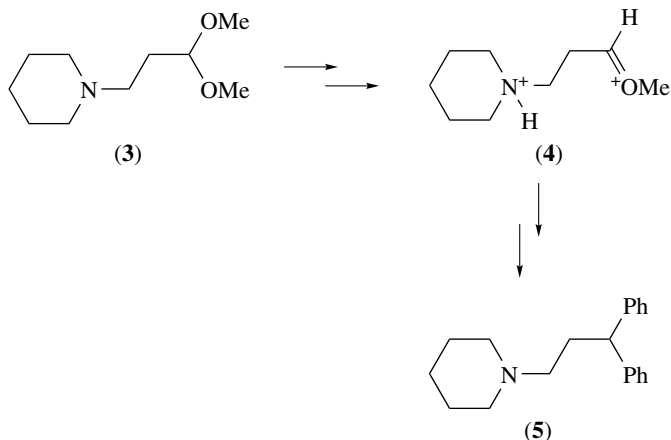
Formation and Reactions of Acetals and Related Species

2,4,4,6-Tetrabromo-2,5-cyclohexadienone (**1**, TABCO) is an efficient and chemoselective catalyst for the acetalization (and transacetalization) of carbonyl compounds and for the preparation of acetonides from epoxides and acylals from aldehydes.¹ TABCO, formed in the bromination of phenol, appears to act through its equilibrium with the corresponding bromonium phenolate, a ‘non-traditional’ Lewis acid.



Results for diastereoselective nucleophilic substitution reactions of oxasilacyclopentane acetals (**2**, X = OMe, OAc, NR₂) have been explained in terms of the ‘inside attack’ model for reactions of five-membered ring oxocarbenium ions.²

Both α - and β -aminoacetals (e.g. **3**) form dicationic electrophiles (**4**, *cis-trans* mixture) in superacids, as observed by low-temperature NMR. These electrophiles can react with benzene to give *gem*-diphenylamines (**5**).³



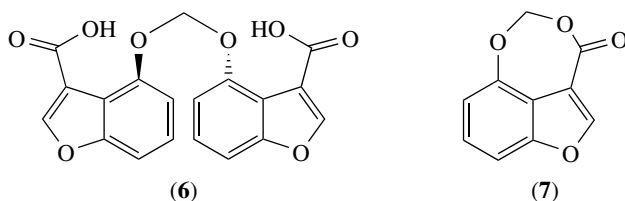
α -Propargyl ethers have been prepared by two related methods: (i) reaction of acetals with allenylsilanes and (ii) a three-component reaction of an aldehyde, alkoxy-silane, and an allenylsilane.⁴ Both reactions are catalysed by Lewis acids.

Two mixtures, 1 : 2 Me₃SiNEt₂-MeI and 1 : 1 Et₃SiH-MeI, act as iodossilane equivalents and can bring about ring-opening reactions on cyclic acetals and 1,3-oxazolidines.⁵ For aromatic ketone ethylene acetals, they act as mild deprotection agents.

Hydrogenation and alkylation of cyclic acetals have been reviewed, examining variations in acetal structure and the influence of catalyst type on the rate and direction of the process.⁶

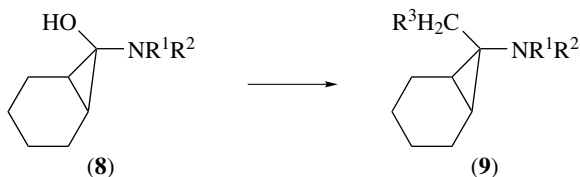
Compound (**6**) is a symmetrical formaldehyde acetal of 4-hydroxybenzofuran-3-carboxylic acid.⁷ Hydrolysis gives two molecules of 4-hydroxybenzofuran-3-carboxylic acid, but this occurs in two steps. Initially, one acid product is formed, plus cyclic acylal (**7**). The latter is then hydrolysed to give the second mole of product

(plus formaldehyde). pH–rate profiles for the two steps indicate that the most reactive form of (6) is its monanion, and that the carboxylate anion acts as a nucleophile to assist the general acid-catalysed cleavage of the C–O bond to the leaving group, in a concerted fashion. The neighbouring nucleophile participation enhances the rate 100-fold, out of a total enhancement of 10^5 over the rate expected for specific acid catalysis. The implications for the mechanisms of lysozymes are discussed.

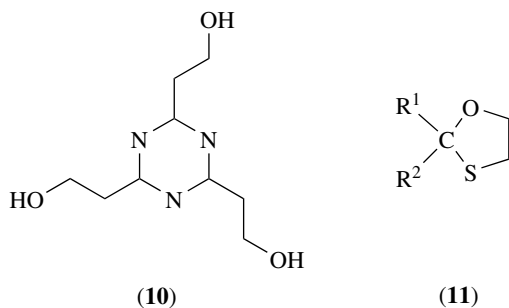


In a stereoselective investigation of ring opening of oxazolidines, the role of $n(\text{N}) \rightarrow \sigma^*(\text{C}-\text{O})$ electron delocalization (i.e. an *endo*-anomeric effect) in the cleavage of the intramolecular C–O bond has been explored, as has the reduction in reactivity – both hydrolytic and reductive ring opening – in *N*-acyloxazolidines.⁸

Bicyclo[4.1.0]heptan-7-one *N,O*-hemiacetals (8) undergo substitution by Wittig reagents, $\text{Ph}_3\text{P}=\text{CHR}^3$, to give 7-*exo*-amino-7-*endo*-substituted bicyclo[4.1.0]heptanes (9) stereoselectively.⁹ An iminium cation intermediate is proposed.



Rates of hydrolysis of 1,3,5-tris(2-hydroxyethyl)hexahydro-*s*-triazine (10) in aqueous solution are first order in hydronium ion, with a pH-independent term competing above pH 11.¹⁰ Reaction with hydrogen sulfide has also been characterized.



Ketones and aldehydes can be protected as their 1,3-oxathiolane derivatives (**11**; $R^1 = H, \text{alkyl, aryl}, R^2 = \text{alkyl, aryl}$).¹¹ A new deprotection method, $V_2O_5-H_2O_2$ -catalysed oxidation of NH_4Br in $CH_2Cl_2-H_2O$ at $0-5^\circ C$, regenerates the carbonyl very selectively. In particular, sensitive unsaturation in the R groups is not brominated. The mechanism presumably involves oxidation of bromide to Br^+ , which reacts with sulfur, then subsequent hydrolysis.

Indium(III) triflate catalyses thio- and transthiio-acetalization at ambient temperature.¹²

Lithium triflate catalyses dithioacetal formation from carbonyl derivatives in the absence of solvent, typically in minutes.¹³ Using thiols or dithiols, acyclic or cyclic products can be prepared, and the carbonyl reactant can be free ketones or aldehydes, or cyclic or acyclic acetals, or acylals. Significantly useful chemoselectivities are reported.

N-Bromosuccinimide catalyses oxathio-, thio-, and transthiio-acetalization of carbonyl compounds,¹⁴ while molten $Bu_4N^+Br^-$ catalyses transthiioacetalization of *O,O*-acetals to *S,S*-acetals.¹⁵

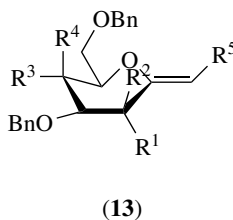
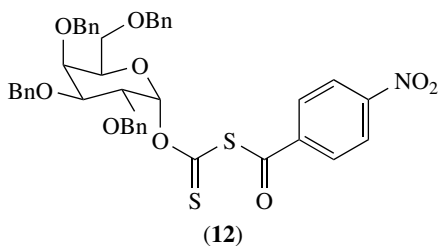
Titanocenes have been used to promote conversion of thioacetals to terminal alkenes with either a one- or two-carbon homologation, using ethylene as carbon source in both cases.¹⁶ The reaction mode, metathesis versus β -elimination, can be selected by adjusting the titanocene ligands.

Homoallylic thioethers have been prepared diastereoselectively via Lewis acid-promoted addition of chiral crotylsilanes to thioacetals of aldehydes, via thionium ions.¹⁷

(de)

Reactions of Glucosides and Nucleosides

α -Thiogalactoside derivatives have been prepared by rearrangement of 1-*O*-(thio-*p*-nitrobenzoyl) thiocarbonyl galactoside (**12**).¹⁸



Stereoselective syntheses and reactivities of a range of (*Z*)-*exo*-glycals (**13**) have been reported.¹⁹

(de)

A stereocontrolled synthesis of *C*-glycosides has been carried out using samarium diiodide mediation of a reductive coupling of epoxides of 1,2-anhydro sugars with carbonyl compounds; the stereoselectivity can be altered significantly by adding a source of protons.²⁰

(de)

TMS triflate mediates C(1') epimerization of β -thymidine to α -thymidine.²¹ A thermodynamic and kinetic study has examined neighbouring group participation effects for various 5'-hydroxy protecting groups. The equilibrium ratio, $K_{\alpha/\beta}$, is affected by steric hindrance from the protecting group, whereas rate constants k_{α} and k_{β} are mainly influenced by the stability of the oxonium ion intermediate.

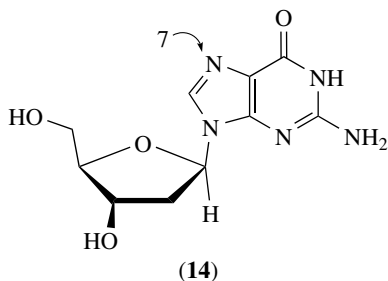
Bromobutyl mannopyranosides have been used successfully as both protected and unprotected glycosyl donors.²²

The stereoselectivity of transglucosidations of methyl and ethyl D-glucopyranosides has been studied in the presence of camphor-10-sulfonic acid, in methanol and ethanol solvents.²³ While the reaction proceeds via exocyclic C–O cleavage and formation of a glucopyranosilium ion, the eliminated alcohol exerts some steric hindrance. (ee)

O-Acetylation of alcohols, phenols, and sugars has been achieved cleanly at room temperature, using an ionic liquid, (*R*-yl)butylimidazolium dicyanamide (R = Et, Bu).²⁴ The solvent acts as a basic catalyst, but when bases are added as co-catalysts, significant variation in α/β product selectivity can be achieved in tests on α -D-glucose. (de)

Triflic acid is a useful reagent for solvolytic cleavage of glycosidic linkages.²⁵

A theoretical study of the depurination of deoxyguanosine (**14**) has been undertaken.²⁶ In accordance with experimental results, N(7) protonation lowers the barrier by ~ 10 kcal mol⁻¹. However, *platination* in this position – the first step in cisplatin binding to DNA – does not significantly alter the barrier. The factors explaining this difference are detailed, and may help to further our understanding of cisplatin's interactions with DNA.



The mechanism of decomposition of glucose in concentrated alkali at high temperature has been investigated by ¹³C NMR, using selectively labelled substrates and products.²⁷

O-Glycosylations under neutral or basic conditions have been reviewed (86 references).²⁸ While these conditions have historically been successful for the synthesis of *aryl* glycosides, recent results (presented in the review) suggest a growth in the preparation of *aliphatic* cases. (de)

Non-enzymatic mechanisms of glycopyranosyl and 5-thioglycopyranosyl transfers in solution have been reviewed.²⁹ The position of these reactions on the

dissociative/associative mechanistic borderline (i.e. S_N1/S_N2) is emphasized, together with five important factors determining the precise mechanism in aqueous solution: (i) charge on nucleophile; (ii) charge on leaving group; (iii) anomeric configuration; (iv) presence of acid or base catalysis; and (v) type of catalysis (general or specific).

The synthetic scope of the reaction of sulfur ylides and diazo compounds with monosaccharide derivatives³⁰ has been reviewed and the new journal *Glycoscience* contains several reviews, including rearrangement reactions in carbohydrates,³¹ oxidation, reduction, and deoxygenation reactions at the anomeric carbon of unprotected and protected glycosides and carbohydrates,³² the mechanism of *n*-pentenyl glycoside activation and glycosylation,³³ and the preparation, reactions, and bond cleavage of anomeric anhydro sugars.³⁴

The Maillard reaction – a complex series of processes initiated by condensation of an amine with a carbonyl group, typically of a reducing sugar – is of major importance in food science and also in the mechanisms of ageing.³⁵ Recent developments have been reviewed.

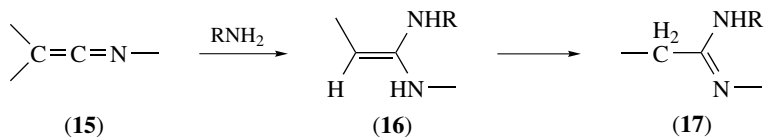
The use of TIBAL (triisobutylaluminium) in carbohydrate chemistry has been reviewed.³⁶ It promotes rearrangement of vinylacetals, such as hex-5-enopyranosides, to give highly functionalized and enantiomerically pure cyclohexanes. TIBAL, and also the more familiar DIBAL, promote regioselective de-*O*-benzylation of protected sugars.

For an asymmetric aldol used to prepare 1'-branched nucleosides, see the section *Aldols* below.

Reactions of Ketenes

Transition states have been calculated for the 2 + 2-addition of formaldehyde and ethylene across the C=C bond of ketene.³⁷

Amination of ketenimines (**15**) yields an amidine (**17**).³⁸ Computational and low-temperature NMR evidence that this can occur via addition to the C=N bond, i.e. via a vinylidenediamine (**16**), has been presented for the case of *N*-phenylphenylketenimine.



Enantioselective addition of amines to ketenes has also been reported.³⁹

Several reports focus on recent interest in the Staudinger 2 + 2-cycloaddition of ketenes to imines, to produce β -lactams, including penicillins. It is limited, however, by the tendency of methanimines to polymerize and the general instability of those derived from aliphatic aldehydes.^{40a} Building on an earlier report of the use of formaldehyde *N,N*-dialkylhydrazones as a more stable class of reactant,^{40b}

chiral hydrazones have now been employed. In particular, the use of a (2*R*,5*R*)-dimethylpyrrolidine substituent in the hydrazone stabilizes it, controls the stereochemical course of the reaction, and survives as a protecting group in the product β -lactam ring, but can nevertheless be readily removed therefrom. (de)
(ee)

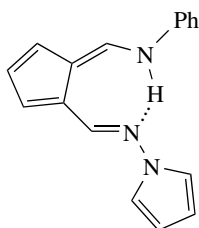
Direct Staudinger reactions of ketenes and imines have also been described, including an enantioselective Staudinger synthesis of β -lactams from ketenes and imine,⁴¹ reaction of unsymmetrical cyclic ketenes with imines as an entry point to spiro- β -lactams,⁴² and a catalytic, asymmetric synthesis from ketenes (or derived zwitterionic enolates) and electron-deficient imines has been reported, achieving induction through chiral amine catalysts.⁴³ A bifunctional catalyst consisting of a chiral nucleophile and an achiral Lewis acid [indium(III) triflate] promotes the diastereo- and enantio-selective coupling of phenylacetyl chloride (a ketene precursor) and an iminoester to give a β -lactam.⁴⁴ (ee)
(de)

Formation and Reactions of Nitrogen Derivatives

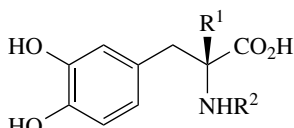
Imines

Iminopolyenes and their amino derivatives show considerable potential as neutral organic superbases; the conjugate acids of the latter show calculated pK_a values in the 30s in acetonitrile.⁴⁵ Calculations have been used to screen backbones to serve as carriers for bis(tetramethylguanidine) systems, with a particular focus on the role of intramolecular hydrogen bonding.⁴⁶

Complex tautomeric equilibria in 6-aminofulvene-1-aldimines (e.g. **18**), in both the solid state and solution, have been characterized by X-ray crystallography and NMR.⁴⁷ Examples of intramolecular proton transfer between nitrogens are described, and some systems exhibit proton transfer to a carbon of the carbocyclic five-membered ring.



(18)



(19)

A kinetic study has compared the reactivity of L-3,4-dihydroxyphenylalanine (L-DOPA; **19**: $R^1 = H = R^2$) with pyridoxal 5'-phosphate (to form a Schiff base) against that of the drug carbidopa (**19**: $R^1 = Me$, $R^2 = NH_2$), over the pH range 4–10.⁴⁸ Rates of hydrolysis of the Schiff bases are also reported, and the relative rates of the two processes for the two substrates are discussed in terms of the action of the latter in the brain. A similar study examined L-tryptophan and its methyl and *n*-butyl esters.⁴⁹

Theoretical modelling of a transimination reaction of a Schiff base derived from pyridoxal-5'-phosphate shows evidence for a *gem*-diamine intermediate.⁵⁰

Solvent effects on tautomerism of Schiff bases [*N*-(salicylidene)alkylamines] have been investigated by UV-visible spectroscopy and by measuring deuterium isotope effects on their ¹⁵N NMR spectra.⁵¹

The reaction kinetics of gas-phase condensation of propanal with ammonia, to give 2-ethyl-3,5-dimethylpyridine, have been studied in a fixed-bed reactor.⁵²

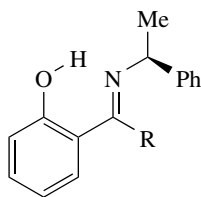
Many reports focus on the addition of organometallics to imines, especially asymmetrically. The mechanism of addition of ethyl-Grignards to imines catalysed by Cp₂ZrCl₂ has been probed by deuterium labelling experiments.⁵³ Two overlapping routes were found, leading to mono- and di-magnesiated products.

A copper-ruthenium system has been used to catalyse an efficient, Grignard-type addition of terminal alkynes to imines.⁵⁴ The reaction, generating the imine *in situ* from aldehyde and amine, can be conveniently carried out in water or without solvent.

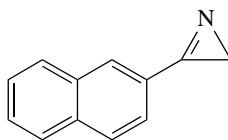
Stereochemical models explaining 1,3-asymmetric induction in addition of organometallic reagents to imines bearing stereogenic substituents have been reviewed.⁵⁵ (ee)

Diastereoselective addition of phenylmetallic reagents to chiral *N*-*t*-butanesulfinimines of aromatic aldehydes yields, after cleavage of the auxiliary, enantiomeric diarylmethylamines.⁵⁶ One enantiomer is obtained using phenylmagnesium bromide in toluene, and 'reagent switchover' to phenyllithium in THF gives the other enantiomer. (de)

Enantiopure 2-aminoalkylphenols have been prepared by stereoselective addition of Grignards to chiral imidoylphenols (**20**, R = H, Me, Et, Ph) derived from *o*-methylbenzylamine and an *o*-hydroxy-benzaldehyde or -phenyl ketone.⁵⁷ (ee)



(20)



(21)

Enantioselective addition of dialkylzincs to imines has been reported, using a paracyclophane-based *N,O*-ligand as catalyst,⁵⁸ and of diethylzinc using a readily available *N*-monosubstituted β -amino alcohol auxiliary.⁵⁹ (ee)

threo- β -Amino alcohols have been prepared in good *ee* by asymmetric lithiation of *O*-benzyl carbonates followed by reaction with benzaldimines.⁶⁰ (ee)

3-Aryl-2-propenyl-lithium and -zinc reagents have been added regio- and diastereoselectively to chiral diimines.⁶¹ Enantiomerically pure 1,3-imidazolidin-2-ones have been prepared by addition of *N*-Boc-pyrrolidin-2-yl lithium to optically active ketimines.⁶² (de)

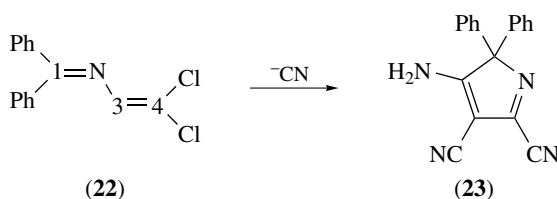
Methylolithium and other organometallics have been added to 3-(2-naphthyl)-2*H*-azirine (**21**) to give an aziridine.⁶³ Using chiral amine ligands, low enantioselectivities are observed. (ee)

Both *cis*- and *trans*-vinylaziridines have been prepared by stereocontrolled aziridination of imines using a sulfonium ylide route.⁶⁴ The reactivities of the imines and ylides employed is found to control the stereochemistry produced. (de)

N-Benzylideneaniline apparently yields *cis*-aziridine product on reaction with ethyl diazoacetate, in a reaction catalysed by Cp(CO)₂Fe(THF)⁺.⁶⁵ However, a more comprehensive investigation shows significant *trans*-product formation, but the latter isomer undergoes decomposition.

Several aldol-type transformations of imines have been described. A catalytic asymmetric synthesis of β-hydroxy-α-amino acid esters has been developed using direct aldol reaction of glycinate Schiff bases with aldehydes.⁶⁶ β-Aryl-β-amino acid derivatives have been prepared by stereoselective nucleophilic addition of chiral lithium enolates to (*N*-tosyl)aldimines.⁶⁷ Chiral tetrahydroquinoline derivatives have been prepared by stereocontrolled addition of allyltin reagents to chiral α-imino esters.⁶⁸ High pressure has been used to achieve reasonable yields in the Michael addition of chiral imines to alkyl and aryl crotonates, with regio-, diastereo-, and enantio-selectivity.⁶⁹ (ee)

Addition of cyanide to 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene (**22**) yields a 2*H*-pyrrole product (**23**), representing the incorporation of three cyanides into the structure.⁷⁰ The mechanism involves cyanide attack at C(3), loss of the two chlorides in succession, the second being replaced by cyanide [at C(4)], then the third attacks C(1), followed by C(4) intramolecularly attacking C(1) to close the ring. The anionic intermediate preceding this ring formation step has been trapped with methyl iodide. (de)



α-Deprotonation of aldimines by lithium diisopropylamide and subsequent trapping of the carbanion with *N*-tosylimines set up two useful product classes: hydrolysis gives β-aminoaldehydes whereas reduction gives 1,3-diamines.⁷¹

Stereoselective addition of the anion of 1,3-benzoxathiole 3-oxide to imines has been reported.⁷²

Hydrolyses of several series of *N*-benzylideneaniline derivatives, Ar¹CH=NAr², have been studied kinetically over a range of pH.⁷³ In one series, Ar¹ bears a 3- or 4-substituent to vary electron supply/demand, whereas Ar² bears a 3-boronic acid. A second series has the substituents reversed, while two more series without boronic acids act as controls. Substantial accelerations of hydrolysis are seen for

the boronic acid-bearing substrates (both sides) on addition of saccharides such as fructose, but only below the pK_a of the boronic acid, i.e. when it is in the neutral state. Intramolecular general acid catalysis has been inferred from results obtained when the type or concentration of saccharide was changed.

In hydrolyses of imine systems, carbodiimide ($\text{HN}=\text{C}=\text{NH}$) and methyleneimine ($\text{HN}=\text{CH}_2$) have been modelled theoretically, exploring the role of additional water molecules placed in the transition state.⁷⁴ Rates of addition of carboxylic acids to arylcarbodiimides, to yield a transient *O*-acylisourea, have been measured as a function of pH.⁷⁵ The mechanism appears to involve addition of carboxylate anion to a mono- or di-protonated carbodiimide.

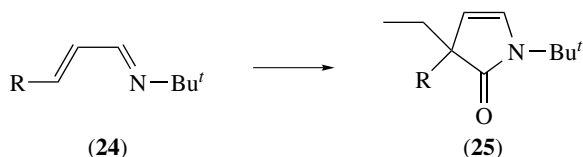
BF_3 -promoted hydrostannation of *N*-heteroatom-substituted imines (i.e. oximes and oxime ethers, nitrones, and *N*-sulfonylimines) derived from aromatic and aliphatic aldehydes and ketones gives $\text{C}=\text{N}$ bond reduction.⁷⁶

Moving to radical species, the reaction of CN radical with methanimine – a postulated interstellar reaction – has been explored computationally.⁷⁷ EPR spectroscopy has been used to investigate the reactivity of *N*-arylimines with *t*-butoxyl radicals.⁷⁸ Hydrogen abstraction, to give imidoyl radicals, competes with addition to the $\text{C}=\text{N}$ double bond to give aminyl radicals.

The mechanism of the rearrangement of *N*-(1-arylkylidene)cyanomethylamines, $\text{ArC}(\text{=NCH}_2\text{CN})\text{R}$, to the corresponding nitriles, $\text{ArCH}(\text{CN})\text{R}$, has been investigated in DMF at 150°C , for potassium carbonate catalyst.⁷⁹ A possible aziridine intermediate has been ruled out, as an authentic sample does not react. Rather, after an initial deprotonation, an intramolecular ring closure and CN elimination give a *2H*-azirine, which isomerizes to product. The mechanism has been confirmed via labelling studies.

The kinetics of the reversible chain reaction of a quinone-monoimine with a hydroquinone have been studied in chlorobenzene.⁸⁰

Ruthenium catalyses a three-component coupling reaction between α,β -unsaturated imines (**24**), CO, and ethylene to give α,α -disubstituted β,δ -unsaturated δ -butyrolactams (**25**).⁸¹ The first step, formation of a ketone by carbonylation of the β -olefinic C–H bond of the imine, is catalysed by $\text{Ru}_3(\text{CO})_{12}$. The imine nitrogen then attacks the new carbonyl group intramolecularly.

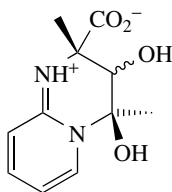


Fused amino γ -lactone products have been prepared diastereoselectively by electrophilic cyclization of unsaturated imines derived from glyoxylate, using catalysis by ytterbium(III) triflate.⁸²

For a reaction of methyl vinyl ketone with an *N*-arylidene tosylate, see the section *The Baylis–Hillman Reaction* below.

Iminium Ions

Methylglyoxal, MeCOCHO, is toxic and mutagenic. It is involved in complications of diabetes and in apoptosis.⁸³ A stereoselective reaction with 2-aminopyridine in water has now been reported, yielding (**26**; 60:40 ratio of isomers). Comparable products are reported for reaction with adenine, adenosine, and 2'-deoxyadenosine. The latter products may be implicated in *in vivo* reactions of methylglyoxal.



(26)

Reaction of iminium salts (derived from aromatic aldehydes) with α -chlorocarbanions of chloromethyl sulfones follows the Knoevenagel route, while the products of tertiary α -chlorocarbanions are those arising from vicarious nucleophilic substitution of hydrogen in the parent aldehydes.⁸⁴

Oximes

pH-rate profiles and Brønsted plots have been reported for the dehydration step of the reaction of furfural (and 5-nitrofurfural) with hydroxylamine and with its *N*- and *O*-methyl derivatives.⁸⁵ Evidence for a spontaneous mechanism of dehydration is presented.

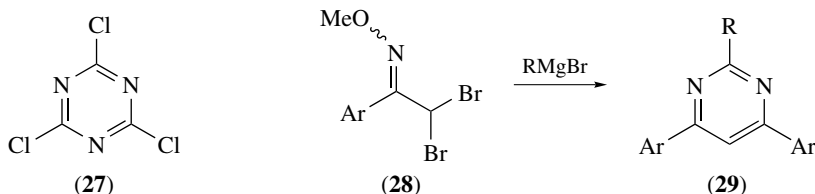
Rate and equilibrium constants have been measured for the formation of the oxime of methyl pyruvate, MeC(=NOH)CO₂Me, from pH 0 to 7 at 30 °C.⁸⁶ Carbinolamine dehydration is rate determining over the entire range. Below pH 5, the formation of carbinolamine is specific acid catalysed, whereas above pH 5, a water-catalysed reaction is observed and the dehydration of the carbinolamine has a large pH-independent component.

A photosensitized electron-transfer method for deprotecting oximes back to their carbonyl compounds appears to involve an iminoxyl radical.⁸⁷

2-Furaldoxime and the dioxime of α -fural (the corresponding α -dione) have been reduced by titanium(III) in aqueous sulfuric acid-ethanol, yielding a Schiff base of salicylaldehyde in each case.⁸⁸

Oximes are reduced to imines by tributylphosphine-phenyldisulfide reagent, via phenylthioimino intermediates.⁸⁹ The latter are then reduced to imines by the phosphine in combination with a source of protons.

Reports of Beckmann rearrangements include clean conversion of ketoximes to amides/lactams using ytterbium(III) triflate catalysis,⁹⁰ and 2,4,6-trichloro[1,3,5]triazine (**27**) forms a complex with DMF at room temperature which smoothly converts ketoximes to amides; aldioximes are similarly converted to nitriles.⁹¹



α,α -Dibromo oxime ethers (e.g. **28**, easily prepared from the dibromo ketone) react with Grignard reagents to give pyrimidines (**29**), with some evidence for an azirine intermediate.⁹²

3,4-Dihydro-2*H*-pyrroles have been prepared from γ,δ -unsaturated ketone *O*-acetyloximes; either oxime isomer can be used, as they isomerize under the reaction conditions.⁹³

Hydrazones

Magnesium iodide promotes an asymmetric Michael addition of prochiral alkylidene malonates to enantiopure formaldehyde *N,N*-dialkylhydrazones, the latter being derived from proline.⁹⁴ (de)

Kinetics of the hydrolyses of hydrazones of nitropyridine- and thiazole-aldehydes have been studied over a range of pH, temperature, and water:DMF solvent ratio.⁹⁵

Sodium salts of phenylhydrazones have been reacted with aldehydes to give epoxides: using triphenylarsine as catalyst, all reactant combinations give exclusively *trans*-product, and under mild conditions.⁹⁶ (de)

Alkylmercury(II) hydrides are a new reagent for radical rearrangement of cyclopropyl ketones, via their hydrazones.⁹⁷

C–C Bond Formation and Fission: Aldol and Related Reactions

Regio-, Enantio-, and Diastereo-selective Aldol and Related Reactions

A wide range of reviews describe the aldol and related reactions. Significant themes covered in the reviews, and in the experimental papers below, include asymmetric autocatalysis and (positive) non-linear effects, catalysis by L-proline, and aldols in water solvent. There is also a major emphasis on *direct* aldols, and especially on their most useful form: direct catalytic asymmetric.

Stoichiometric asymmetric processes have been reviewed (486 references), with major sections on α -alkylation, aldols, and additions to C=O and C=N bonds.⁹⁸ (de)

New water-compatible Lewis acids have been developed for catalytic asymmetric aldol reactions, including surfactant combinations not requiring organic co-solvents.⁹⁹ (ee)

Asymmetric two-centre catalyses have been reviewed, focusing on two catalyst combinations, Lewis acid–Brønsted base and Lewis acid–Lewis base, and on two important reaction types, direct catalytic enantioselective aldol and catalytic enantioselective cyanosilylation of aldehydes and ketones.¹⁰⁰ (ee)

Stereoselective organic reactions in aqueous solution have been reviewed (214 references), with sections dealing with strategies for enhancing solubility, the main types of catalysis, how stereocontrol is achieved, followed by several major reaction types.¹⁰¹ (de)

Stereo- and enantio-selective reactions of thio-aldehydes, -ketones, and -ketenes and thionolactones, mediated by ruthenium complexes, have been reviewed.¹⁰² (ee)

Other reviews include the state of the art of aldol additions,¹⁰³ asymmetric auto-catalysis (51 references),¹⁰⁴ and asymmetric reactions catalysed by proline (75 references).¹⁰⁵ (ee)

Electrophilic (electron-pair accepting) and oxidizing (one-electron accepting) properties of the central carbonyl of 1,2,3-triones in their reactions with electron-rich C=C bonds has been investigated, including ene-1,2-dials and -diamines and 2-alkoxyen-1-ols.¹⁰⁶

The proline-catalysed direct aldol reaction between acetone and acetaldehyde has been modelled using density functional theory.¹⁰⁷

L-Proline is an efficient and reusable catalyst for direct asymmetric aldol reactions in imidazolium-based ionic liquids.¹⁰⁸ (ee)

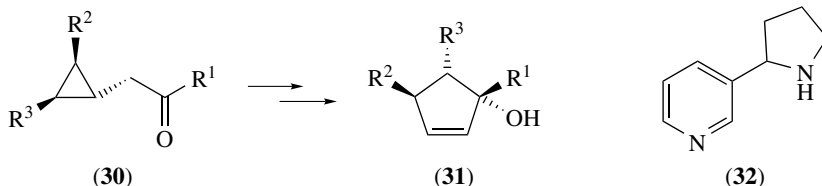
anti-1,2-Diols have been prepared in a diastereo- and enantio-selective direct catalytic aldol reaction of *o*-hydroxyacetophenones.¹⁰⁹ (de)

An ambifunctional titanium(IV) isopropoxide-(*R*)-mandelic acid complex has been characterized by X-ray crystallography and variable-temperature NMR.¹¹⁰ It acts as a direct aldol catalyst for aldehydes reacting with unactivated ketones. (ee)

Direct catalytic asymmetric aldol reactions of aldehydes are described,¹¹¹ and have been reviewed (19 references).¹¹²

In an intramolecular aldol, bifunctional catalysis of L-proline has been used to synthesize optically active cyclic ketols in good to excellent yield and *ee*.¹¹³ The results have been rationalized by conformational analysis. (ee)

In another intramolecular case, base treatment of β -ketocyclopropanes (**30**) causes ring opening to give either *cis*- or *trans*- α,β -unsaturated ketones.¹¹⁴ The *cis*-product, with appropriate choice of base, undergoes an intramolecular aldol to give allylic cyclopentenols (**31**) in high yields and diastereoselectivity. (de)



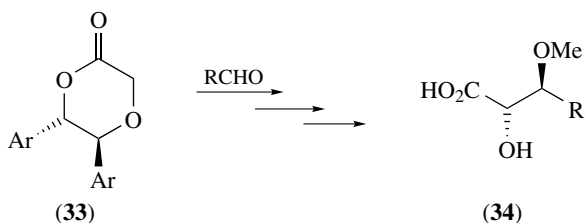
An aldolase antibody has been used for regioselective aldol reactions, catalysing the formation of otherwise disfavoured products.¹¹⁵ The chemical strategies employed by typical epimerase and racemase enzymes have been reviewed, including those of L-ribulose phosphate 4-epimerase, which uses a non-stereospecific retroaldol-aldol mechanism.¹¹⁶ (ee)

Nornicotine (**32**), the only psychoactive metabolite of nicotine and longer-lasting *in vivo* than nicotine itself, is an effective catalyst for aldol reactions in water, apparently via an enamine intermediate.¹¹⁷

Examples of diastereoselective aldols reported are *anti*-aldol reactions of chiral *N*-acyloxazolidinones with aldehydes (catalysed by magnesium halides),¹¹⁸ a stereoselective aldol promoted by samarium(II) iodide that has been used to prepare 1'-branched nucleosides,¹¹⁹ chiral auxiliaries for aldol, based on (1*R*,2*S*)-ephedrine,¹²⁰ and an acetate aldol reaction with aldehydes, using an oxazolidinethione derived from valine as auxiliary.¹²¹

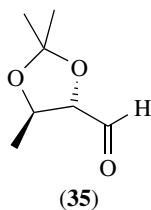
A chiral oxazaborolidine derived from *D*-phenylglycine catalyses a model aldol reaction in high *ee*.¹²² Boron enolates, generated by reaction of 9-borabicyclononane (9-BBN-H) with α -iodo ketones, react in high yield and with high *syn*-diastereoselectivity with a wide range of aldehydes.¹²³ In boron aldol additions to *L*-erythrose derivatives, both *syn*- and *anti*-selectivity can be selected by appropriate choice of protecting group.¹²⁴ Asymmetric 1,4-addition of potassium organotrifluoroborates to enones has been reported.¹²⁵

The boron enolate of 5*S*,6*S*-bis-5,6-(4-methoxyphenyl)-2-dioxanone (**33**) reacts with saturated and unsaturated aliphatic aldehydes to give *anti*-glycolate aldol products (**34**) (after deprotection).¹²⁶



Among new developments, a regioselective 'aldol' protocol for synthesis of β -ketols and α,β -unsaturated ketones has been reported,¹²⁷ and a simple NMR method has been developed to assign relative stereochemistry to β -hydroxy ketones derived from aldol reactions of methyl ketones.¹²⁸

The origins of *syn,anti*-selective aldol additions of a lithiated bis-lactim ether to 1,3-dioxolane-4-carboxaldehydes (**35**) have been explored computationally.¹²⁹ The most stable transition-state structures possess a non-Anh conformation in the aldehyde.



α -Halo ketones have been cross-coupled with organotin enolates, catalysed by zinc halides, to give δ - (i.e. 1,4-) diketones.¹³⁰ The initial aldol-type course of the reaction is followed by a rearrangement directed by zinc.

In a tandem radical addition–aldol condensation, diethylzinc–oxygen has been used to mediate the addition of alkyl radicals to chiral *N*-enoyloxazolidinones, via a zinc enolate.¹³¹ The mechanism of the double aldol reaction has been investigated, with spectroscopic characterization of a carbon-bound boron enolate, proposed to be a key intermediate.¹³² A new tandem 1,4-addition-aldol reaction involving an α,β -unsaturated ketone, an aldehyde, and 9-borabicyclononane with an aryl substituent on boron yields α -(arylmethyl)- β -hydroxy ketones.¹³³ Both steps are catalysed by rhodium(I), via an (oxa- π -allyl)rhodium intermediate.

Carbonyl-carbon kinetic isotope effects have been used to probe the mechanism of reaction of magnesium pinacolone enolate, $\text{H}_2\text{C}=\text{C}(\text{OMgBr})\text{Bu}^t$ with benzaldehyde.¹³⁴ The results, together with Hammett substituent effects and chemical probe experiments, suggest the polar mechanism (also seen for the *lithium* enolate), in contrast to the electron-transfer process seen with many organometallic counterparts.

A diastereoselective Henry (nitro-aldol) reaction has been reported, using a strategy of high pressure but no catalyst.¹³⁵ Although the *de* values are as yet only modest, the *ees* are good, and the procedure is very simple, avoiding the need to quench a catalyst. It is intended to extend the approach to similar cases (Michael, Mannich, Baylis–Hillman) that are accelerated by pressure. (de)

Diastereoselective Henry reactions of *N,N*-dibenzyl- α -aminoaldehydes and nitromethane have been effected using enantiopure guanidine catalysts.¹³⁶ (ee)

A new catalytic asymmetric nitron–aldol reaction yields functionalized β -hydroxynitrones.¹³⁷ The process, which is found to involve an enamine intermediate, is an example of nitrones acting as nucleophiles. (ee)

In a tandem Michael–aldol reaction of a magnesium thiolate with a β -substituted- α,β -unsaturated ester and an aldehyde, NMR evidence suggests that the magnesium thiolate first attacks the aldehyde, rather than the ester.¹³⁸ The *anti* selectivity observed in the aldol is the reverse of the finding with the lithium analogue. (de)

The condensation of 3-pyridinecarbaldehyde with 3-cyano-4,5,5-trimethyl-2(5*H*)-furanone has been modelled quantum chemically.¹³⁹

Mannich-type reactions of a protected α -imino ethyl glyoxalate with ketones yield functionalized α -amino acids with high regio-, diastereo-, and enantio-selectivity.¹⁴⁰ In a similar approach, unmodified aldehydes have been used as donors in catalytic asymmetric Mannich-type reactions, leading to either enantiomer of both α - and β -amino acid derivatives.¹⁴¹ (de)

The Horner–Wadsworth–Emmons (HWE) reactions of 2-fluoro-2-diethylphosphonoacetic acid, $(\text{EtO})_2\text{P}(=\text{O})\text{CHFCO}_2\text{H}$, with aldehydes is promoted by magnesium(II) and gives predominantly (*Z*)- α -fluoro- α,β -unsaturated carboxylic acids, apparently under thermodynamic control.¹⁴² α -Fluoro- α,β -unsaturated esters have been prepared by an enantioselective HWE reaction of 2-fluoro-2-diethylphosphonoacetates.¹⁴³ Chiral tetrahydro-furans and -pyrans have been prepared by sequential asymmetric HWE and ring-closure reactions on *meso*-dialdehydes.¹⁴⁴ (ee)

(de)

Thiamine can react with benzaldehyde to produce benzoin, but the thiamin is destroyed in the process.¹⁴⁵ A kinetic study of thiamine derivatives has been undertaken to explore how enzymatic systems using thiamin as a co-factor avoid the fragmentation of the latter.

New imidazolium catalyts have been reported for the benzoin condensation.¹⁴⁶

The Mukaiyama Aldol and Related Reactions

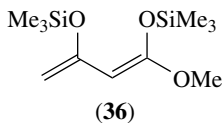
A chemoselective Mukaiyama-type aldol coupling of silyl enolates with vinyl and aryl aldehydes and acetals is catalysed by magnesium iodide etherate, $\text{MgI}_2 \cdot (\text{OEt}_2)_n$.¹⁴⁷

A new BINOL–zirconate catalyst for highly *anti*-selective aldol reactions depends on water for its formation and requires an alcohol additive for efficient turnover.¹⁴⁸

Diastereoselective aldol reactions have been carried out in water using a catalytic amount of a diarylborinic acid, apparently via boron enolates generated from the boron source.¹⁴⁹

An aldol polymer has been made from a bis(trimethylsilyl enol ether) and a dialdehyde in a highly stereoselective manner by a repeated asymmetric Mukaiyama aldol reaction.¹⁵⁰

Diene (**36**), a masked acetoacetate ester, undergoes an enantioselective aldol condensation with benzaldehyde, showing auto-induction and positive non-linear effects, in a process catalysed by titanium(IV) and a chiral BINOL.¹⁵¹



Lithium diphenylamide catalyses an aldol reaction between a variety of aldehyde types and trimethylsilyl enol ethers under mild conditions.¹⁵²

Fast enantioselective addition of silyl ketene acetals to aldehydes has been achieved using a BINAP-dimer catalyst at -78°C ; high *des* are also observed, and aliphatic aldehydes do not present a problem.¹⁵³

In other reports, diastereoselective aldol condensation of acylsilane silyl enol ethers with dimethyl acetals of aromatic aldehydes is described,¹⁵⁴ calcium chloride acts as a Lewis base in the aldol reaction of dimethylsilylenolates with a range of aldehydes in aqueous DMF,¹⁵⁵ and diastereoselective aldol additions of chiral β -hydroxy ethyl ketone trichlorosilyl enolates are catalysed by Lewis bases.^{156,157}

Silyl enol ethers have been prepared from aldehydes in a regioselective and highly stereoselective fashion, using TMS–diazomethane.¹⁵⁸ Labelling studies have yielded usefully labelled products, and also mechanistic information: of the two hydrogens of the terminal silyl enol ether, one originates from the aldehyde and the other from the reaction quench. If the methanolic quench is changed to one with methyl iodide, a methyl-substituted product is obtained.

The Baylis–Hillman Reaction

Investigation of the Baylis–Hillman (BH) reaction has mushroomed in recent years, driven by catalytic advances which have brought dramatically shorter reaction times.

Focus on the catalysts continues: in a useful sulfur version of the BH reaction, ethyl thioacrylate has been combined with benzaldehydes to give α -methylene- β -hydroxy thioesters.¹⁵⁹ Carried out at 0 °C in dichloromethane, the reaction is promoted by diethylaluminium iodide and requires no Lewis base, with irreversible loss of ethane providing driving force. The method has been extended to reaction of benzaldehyde with α,β -unsaturated cycloketones.¹⁶⁰

BH reactions of *N*-arylidenediphenylphosphinamides, $\text{ArCH}=\text{NP}(=\text{O})\text{Ph}_2$, with methyl vinyl ketone, methyl acrylate, and acrylonitrile have been optimized with different Lewis bases for each.¹⁶¹

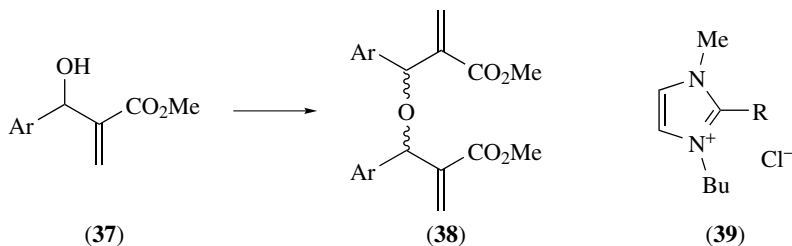
The standard BH reaction of arylaldehydes and methyl vinyl ketone can be effected with even weak bases such as imidazole or triethylamine, if proline is added.¹⁶²

BH reactions of aryl aldehydes have been catalysed by Lewis acid–base combinations.¹⁶³ Using titanium(IV), boron(III), or zirconium(IV) chloride as acid, and an amine as base, chlorinated alcohol [$\text{ArCH}(\text{OH})\text{CH}(\text{CH}_2\text{Cl})\text{COMe}$] is produced in high yield at –20 °C or below, whereas the corresponding elimination product [$\text{ArCH}=\text{C}(\text{CH}_2\text{Cl})\text{COMe}$] is formed at room temperature.

The medium of the BH reaction is also important: it can be substantially accelerated in water, apparently owing to favourable hydrogen-bonding effects, rather than a hydrophobic influence.¹⁶⁴ Unhindered acrylate esters are, however, readily hydrolysed under the basic conditions employed, but in this case the accelerations found in formamide solution prove useful, especially when supplemented with Yb(III) triflate catalysis. From the position of a few years ago when the BH reaction was seen as limited and slow, the possibility of convenient reactivity for hindered or deactivated aldehydes, and possibly even ketones, has opened up.

Imidazole catalyses BH reactions of cyclopent-2-enone with aromatic and aliphatic aldehydes in aqueous media, and the presence of water appears essential for achieving reasonable reaction times and yields.¹⁶⁵

The BH reaction has been carried out efficiently in supercritical CO_2 , at modest temperature and pressure.¹⁶⁶ Investigating the model reaction of *p*-nitrobenzaldehyde with methyl acrylate, the product (**37**) is found to dimerize (with loss of water) to a highly functionalized ether (**38**), in the low-pressure range. Highly functionalized



unsymmetrical ethers can also be prepared using a novel one-pot coupling with three components, viz. the two BH reactants plus a benzyl alcohol.

While employing a common ionic liquid (**39a**, R = H, butylmethylimidazolium chloride) as solvent for a model BH reaction of benzaldehyde, low yields and an unexpected product [**39b**, R = CH(OH)Ph] were obtained.¹⁶⁷ Even though the bases employed are relatively mild (DABCO, quinuclidine), imidazoliums are clearly deprotonable at C(2) under these conditions, an implication which may limit their use as 'green' solvents.

Using pressures of ca 200 MPa induced by water freezing enhances the rate of the BH reaction: using 3-hydroxyquinuclidine as base, arylaldehydes react with methyl acrylate in less than 1 day, at -20°C , using sealed autoclaves.¹⁶⁸

Selective BH reactions have also been developed. Catalytic, asymmetric reactions of aromatic imines (ArCH=NTs) have been carried out with methyl vinyl ketone, the simplest acceptor, in fair to good yield, and up to 96% *ee*, using a chiral Lewis base.¹⁶⁹ The reaction is also successful for methyl acrylate. The Lewis base includes a pendant hydroxyquinoline moiety: its hydroxyl may hydrogen bond to the imine adduct as part of the reaction mechanism. (ee)

Chiral *N*-sulfinimines, *p*-TolS(=O)N=CHR, undergo diastereoselective BH-type reactions with cyclopent-2-en-1-one, using a phosphine as Lewis base.¹⁷⁰ (de)

In a BH reaction mediated by a sulfide and boron trifluoride etherate, the sulfide directly participates via a Michael addition to the alkene, analogous to amine catalysis.¹⁷¹ Modest *ees* were obtained with a chiral sulfide. (ee)

Unexpected BH outcomes include *phenyl* vinyl ketone giving a dimeric adduct with aromatic aldehydes, in contrast to the normal products of methyl vinyl ketone with such substrates.¹⁷² Also, arylaldehydes undergo a variety of reactions with 3-butyne-2-one, methyl propiolate, and propynenitrile in the presence of TiBr₄ or BBr₃, with dramatic variations in product balance with temperature.¹⁷³ BH reactions and α - and β -brominations are among the possibilities encountered. The BH reaction of an *N*-arylidene tosylate with methyl vinyl ketone proceeds normally with Lewis bases such as DMAP, PPh₃, or DABCO, but pyrrole derivatives are obtained when PBu₃ is employed.¹⁷⁴

Several BH variants have been examined. α,β -Unsaturated thioesters with a pendant aldehyde moiety (even an enolizable one) undergo intramolecular reactions using DMAP–DMAP.HCl in ethanol or trimethylphosphine in dichloromethane.¹⁷⁵

α -Trifluoromethylaldehydes and ketones undergo BH reactions with a variety of enones and ene-nitriles, using DABCO as base.¹⁷⁶ Reactants, however, need to be matched for reactivity: otherwise, very reactive alkenes react with themselves in the presence of the base, while highly reactive electrophiles like fluoral also self-react if the alkene is not sufficiently reactive.

An aza-Baylis–Hillman reaction gives α -methylene- β -amino acid derivatives from arylaldehydes, sulfonamides, and α,β -unsaturated carbonyl compounds in a one-pot procedure.¹⁷⁷

Allylations

The mechanism of the $B(C_6F_5)_3$ -catalysed allylstannation of aromatic aldehydes has been investigated by NMR, using signals from 1H , ^{11}B , ^{19}F , and ^{119}Sn to help characterize intermediates.¹⁷⁸ Of particular interest were *ortho*-donor substituents, which are substantially more reactive than their *para*-isomers. However, this effect does not appear to arise from a chelation control mechanism in the classic sense.

Both normal and inverse secondary deuterium kinetic isotope effects have been observed in the irreversible addition of allyl reagents of various types to benzaldehyde-*h* and -*d*, allowing distinction of mechanisms.¹⁷⁹

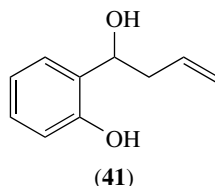
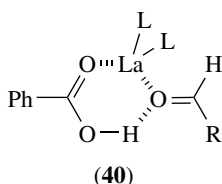
Aldehydes, including sterically hindered aliphatic cases, have been allylated with allylTMS using iron(III) chloride catalysis, at low temperatures.¹⁸⁰

Indium(III) chloride enhances the Lewis acidity of chlorosilanes in allylation, hydrosilylation, and Friedel–Crafts alkylation.¹⁸¹

$SnCl_2$ -mediated coupling of allyl halides with aldehydes or ketones is catalysed by copper metal in water.¹⁸²

Hydrates of α -keto aldehydes and glyoxylates have been allylated with allyltrimethylsilane, using sulfonic acids as catalysts.¹⁸³

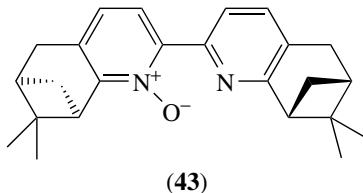
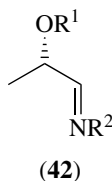
In a simple and robust synthetic protocol, a range of aldehydes have been allylated (using tributylallyl tin) with catalysis by lanthanum triflate and benzoic acid.¹⁸⁴ Evidence for a Brønsted-assisted Lewis acid process, via an intermediate such as (40), is reported.



o-(*O*-Allyl)benzaldehyde undergoes an intramolecular allyl transfer to yield an allyl alcohol, (41), in an electrochemical reaction catalysed by Ni^0 complexes, via a η^3 -allylnickel(II) species.¹⁸⁵ This observation has led to replacement of the nickel(0) catalysts with more stable nickel(II) compounds.

Several stereoselective allylations have been recorded, including diastereoselective allylation of a series of (2*S*)-lactalimines (42) with allylmagnesium chloride, which shows cases of both *anti* and *syn* selectivity.¹⁸⁶ However, substituent effects alone are insufficient to explain the behaviours observed. Significant changes in entropic effects give rise to inversion temperatures (for the stereoselectivities), apparently due to changes in dynamic solvation properties. (de)

A chiral 2,2'-bipyridine-type *N*-monoxide (43) has been used as a catalyst for the Sakurai–Hosomi allylation of aromatic aldehydes by allyltrichlorosilane, in up to 98% *ee*.¹⁸⁷ Compound (43) is heterobidentate in nature, with one strong and one (ee)



weak donor. It is suggested that the high *ees* depend on this characteristic and on a separation of roles, with the NO group activating the allylsilanes and the other nitrogen stabilizing an intermediate by chelation.

Other reports include: the use of Lewis acids in allylboration of aldehydes, helping to bring about catalytic, regio- and diastereo-specific, enantioselective synthesis of homoallyl alcohols;¹⁸⁸ diastereoselective addition of δ -substituted allylic nucleophiles to ketones, yielding tertiary homoallylic alcohols, with catalysis by SnCl₂ or BF₃-etherate;¹⁸⁹ nickel(II)-catalysed homoallylation of aldehydes with 1,3-dienes in the presence of diethylzinc, giving γ,δ -alkenyl alcohols in good yields and *des*;¹⁹⁰ diastereoselective additions of ester enolates and allyl Grignards to optically active *N*-sulfinimines;¹⁹¹ and diastereoselective addition of (*E*)-cinnamyl(tributyl)tin to α -keto esters.¹⁹²

The effects of various Lewis acid catalysts on the diastereoselectivity of the addition of allyltrimethylsilane to L-alaninals and L-serinals have been described.¹⁹³

3-Deuterioallyl-tin and -silicon agents were reacted with aldehydes in the presence of boron trifluoride etherate.¹⁹⁴ Results support a *syn*-synclinal transition state.

The low diastereoselectivity of the S_E2' reaction of aldehydes with the propargylsilane, Me₃SiCHMe-C \equiv CSiMe₃, has been investigated and compared with the more selective reactions of the allyl- and allenyl-silanes.¹⁹⁵ Enantioselective alkynylation of aldehydes has also been studied.¹⁹⁶ A C₂-symmetric diamine-diol auxiliary gives up to 99% *ee* in alkynylation of ketones.¹⁹⁷

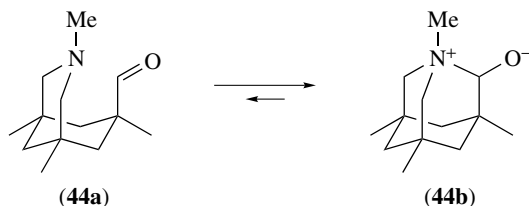
Addition of vinylalanes to α -chiral aldehydes gave the vinyl alcoholic products in higher *de* than the more familiar vinylolithium or vinyl Grignard reagents.¹⁹⁸

Other Addition Reactions

General and Theoretical

Conformationally restricted aminoaldehyde (**44a**) exists predominantly as zwitterionic tetrahedral addition product (**44b**) in polar solvents and in the monohydrate crystal.¹⁹⁹ The crystal structure indicates that the stereochemistry at the central carbon is only slightly distorted from tetrahedral, and C–N bond formation is well advanced. In solution, the conjugate acid of (**44b**) has a p*K*_a of 10.09, not very different from the parent acyclic Me₃N⁺CH₂OH (9.33). Compound (**44b**) is atypical as a zwitterion, being resistant to oxidation, reduction, and *O*-alkylation.

Protonation equilibria of 5-substituted 2-furaldehydes have been studied in aqueous sulfuric acid, seeking evidence for π -polarization in such systems.²⁰⁰

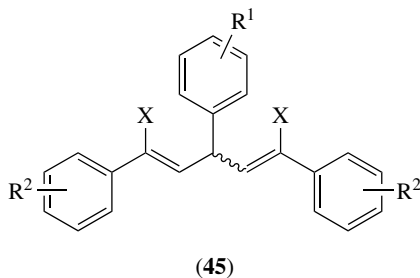


The basicity of 21 carbonyl compounds has been measured in carbon tetrachloride, using 4-fluorophenol as a reference.^{201a} Two theoretical descriptors, the global energy of protonation and the charge variation on the oxygen atom, have been used to interpret the results. Values of these parameters have been calculated by density functional theory methods. Such a combination of a global and local descriptor had previously been reported (by the same group) for carbon acids in water.^{201b}

Based on further calculations on the course of nucleophilic attack on α -chiral carbonyl compounds, together with literature experimental data, a revision of the Felkin–Anh model is proposed.²⁰²

Reviews covering topics related to addition include: the syntheses and reactivities of azetidine-3-, oxetan-3-, and thietan-3-ones (254 references),²⁰³ the structure and reactivity of β -enaminones,²⁰⁴ and new procedures for including quantum mechanical effects in calculations of the kinetic processes of enzymes, including examples such as dehydrogenases, and enolase.²⁰⁵

Aryl aldehydes react with BX_3 and 2 equiv. of an aryl acetylene to give a 1,3,5-triaryl-1,5-dihalopenta-1,4-diene (**45**).²⁰⁶ The dichloro product obtained with boron trichloride is (*E,Z*)-, whereas the tribromide gives a (*Z,Z*)-dibromo product.



N-Protected α -silyloxy pyrroles have been added to electron-deficient *p*-quinones to give a variety of interesting substituted and polycyclic products.²⁰⁷

Aldehyde and ketone azines have been reacted with dimethyl acetylenedicarboxylate, to give pentalene and tetraene azine derivatives, some of which underwent further rearrangements.²⁰⁸

The relative reactivities of dimethoxycarbene with carbonyl and thiocarbonyl groups have been explored,²⁰⁹ and an enantioselective Reformatsky reaction of ketones using cinchona alkaloids has been described.²¹⁰

Addition of Organozincs

Most reports concern dialkylzincs, and in particular the enantioselectivity of addition. (ee)

Anomalous non-linear effects in the enantioselective alkylation of substituted benzaldehydes^{211a} have been rationalized in terms of a more detailed analysis of the thermodynamic and kinetic factors that give rise to such effects.^{211b}

The achievement of chiral discrimination via asymmetric autocatalysis has been reviewed.²¹² For the example of enantioselective addition of diisopropylzinc to a range of heterocyclic aldehydes, the corresponding heterocyclic alkanols are catalytic, with examples quoted of catalysts with *ee* < 1% auto-multiplying their effects up to 99.5%.

Investigations of enantioselective addition, by agent and substrate, include the following:

1. *Diethylzinc to benzaldehyde* (typically as a model reaction to test an asymmetric reagent): chiral sulfonamide ligands (derived from chiral aziridines) have been applied to titanium-mediated addition;²¹³ enantioselective addition has been achieved using (*S*)-diphenyl-BINOL together with achiral or *meso* ligands which adopt chiral conformations during the catalytic cycle;²¹⁴ bi- and tri-dentate chiral pyridine catalysts have been compared: tridentation adds little to the *ee*;²¹⁵ chiral α -hydroxycarboxylic acids catalyse titanium-mediated addition in up to 86% *ee*;²¹⁶ norbornene-derived β -amino alcohols²¹⁷ and β -amino alcohols derived from limonene oxide act as catalysts.²¹⁸ (ee)

2. *Diethylzinc to substituted benzaldehydes*: a chiral organometallic triangle containing three BINOL units complexing titanium(IV) catalyses high-yielding additions, with 90% *ee* typical;²¹⁹ BINAP- β -hydroxyamines have been used as catalysts,²²⁰ as have norbornane-derived β -amino alcohols;²²¹ chiral ligands based on the Betti base [1-(α -aminobenzyl)-2-naphthol] give high yields and *ees*;²²² chiral 1,3-diols have been used as catalysts;²²³ *N*-hydroxyalkyl-L-menthopyrazoles catalyse in up to 70% *ee*.²²⁴ (ee)

3. *Diethylzinc to aldehydes (typically both aromatic and aliphatic)*: planar and centrally chiral [2.2]paracyclophane-based salen-type ligands²²⁵ and [(*R*)-thiolan-2-yl]diphenylmethanol, together with a metal alkoxide²²⁶ have been employed as catalysts; a chiral β -amino alcohol catalyses with *ees* typically in the high 90%;²²⁷ BINAP-aminophenols have been used to catalyse Et₂Zn (and Ph₂Zn) additions;²²⁸ α -hydroxysulfonamides derived from D-glucosamine act as enantioselective titanium ligands,²²⁹ as do *trans*-2-aminoindan-1-ol catalysts, derived from L-phenylalanine;²³⁰ (*S*)-BINOL derivatives with conformationally defined aryl substituents in the 3- and 3'-positions show excellent catalysis and enantioselectivity.²³¹ (ee)

4. *Dialkylzincs to aldehydes*: chiral allenes have been used in an autocatalytic asymmetric addition of diisopropylzinc to pyrimidone-5-carbaldehyde;²³² an atropisomeric hydrocarbon, (*R*)-1,1'-binaphthyl, acts as a chiral initiator of asymmetric autocatalysis of pyrimidyl alcohol in the enantioselective addition of diisopropylzinc to the same aldehyde;²³³ and dendrimers bearing either four or 12 chiral β -amino alcohols catalyse addition of dialkylzincs to a range of aldehydes.²³⁴ (ee)

5. *Dialkylzincs to ketones*: the well-known addition of diethylzinc to aldehydes typically fails for the less reactive ketones, but a bis(sulfonamide)diol, derived from *trans*-1,2-diaminocyclohexane and two camphors, catalyses asymmetric addition to a wide range of ketones in 70 to >99% *ee*, in hydrocarbon solvents at room temperature, using a 2 mol% loading;²³⁵ and tertiary alcohols have been prepared in sometimes >99% *ee* by addition of alkylzincs to aryl alkyl ketones in the presence of bis(camphorsulfonamides) of *trans*-1,2-diaminocyclohexane.²³⁶

Asymmetric alkynylations have also been carried out: an (*S*)-BINOL–Ti(O^{*i*}Pr)₄ combination catalyses diethylzinc-mediated alkynylation of a very wide range of aldehyde types, in up to 99% *ee*;²³⁷ propargyl alcohols have been prepared enantioselectively by addition of alkynylzinc to aromatic aldehydes, with titanium(IV)–BINOL auxiliaries;²³⁸ and an asymmetric alkynylzinc addition to aromatic aldehydes has been reported.²³⁹

Other enantioselective reactions include the use of cinchona alkaloids as auxiliaries in addition of diethylzinc to a phosphinoylimine²⁴⁰ and catalytic addition of organozincs to α -keto esters has been achieved using a bis(salen)–titanium auxiliary containing both Lewis acid and Lewis base activating groups.²⁴¹

Diastereoselective examples include addition of organozincs to chiral α -imino esters, pre-complexed with zinc bromide, which proceeds with complete regioselectivity for the imine carbon, giving useful functionalized amino esters as products;²⁴² and a highly diastereoselective addition of unsaturated organozincs to a series of cyclohexenyl carbaldehydes depends on the chelating effect of a β -(*N,N*-dialkylamino) substituent.²⁴³

The kinetics of the reaction of Et₃ZnLi with di-*t*-butyl ketone have been measured in toluene.²⁴⁴ Dramatic variation in the observed rate behaviour is seen as the organometallic concentration is varied from excess to deficiency. Also, the rate of addition with Et₃ZnK is over 10 000 times slower.

Addition of Other Organometallics

⁶Li and ¹³C NMR have been used to study solvation, dimerization, and addition processes in reactions of *n*-Buli and PhLi with aldehydes and imines, in the presence of complexing amines such as *N,N,N',N'*-tetramethylethylenediamine (TMEDA).²⁴⁵ Assumptions that strongly coordinating solvents necessarily promote deaggregation, or that simple structure–reactivity relationships are accessible in such systems, are challenged.

Addition of methyllithium to substituted benzophenones in diethyl ether at 0 °C exhibits a Hammett ρ value of 0.94,^{246a} substantially higher than the value of 0.27 reported previously.^{246b}

Deuterium isotope effects have been exploited synthetically.²⁴⁷ In the reductive cyclization of an alkenyllithium on to a ketone in which an organolithium intermediate could abstract an α -proton and thus divert the reaction, the decreased kinetic acidity of the α -deuterio isotopomer allowed suppression of the unwanted reaction.

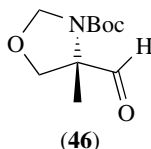
An experimental and computational study of the enantioselective butylation of benzaldehyde and isobutyraldehyde by *n*-butyllithium in the presence of chiral

amino ethers considers ligand, solvent, aggregation, and thermodynamic factors affecting *ee*.²⁴⁸ Diastereoselective additions of unsaturated organolithiums to oxazolidines give highly functionalized β -amino alcohols.²⁴⁹

The Iotsich reagent, $\text{HC}\equiv\text{CMgBr}$, reacts with aldehydes, RCHO , to give the magnesium alcoholate, $\text{RCH}(\text{C}\equiv\text{CH})\text{OMgBr}$.²⁵⁰ The potential energy surface for the subsequent hydride transfer to give acetylenic ketone, $\text{RCOC}\equiv\text{CH}$, and alcohol, RCH_2OH , has been examined and the calculated results are compared with experimental data in the literature.

Chiral organomagnesium amides alkylate aldehydes to form secondary alcohols in high *ee*.²⁵¹ Copper salts have a 1,4-directing effect on addition of organometallic reagents to enones.²⁵² A 5 mol% concentration of indium(III) chloride has now been reported to direct Grignards 1,2-, giving α,β -unsaturated alcohols.

Diastereoselective addition of unsaturated organotitaniums to Garner's aldehyde (**46**) gives *anti*-1,2-amino alcohol products; allylic, allenylic, homoallylic, and homo-propargylic alcohol examples are demonstrated.²⁵³



The use of bifunctional catalysts for enantioselective cyanation reactions has been reviewed, covering Strecker- and Reissert-type reactions and cyanosilylation of aldehydes and ketones.²⁵⁴ The latter reactions, catalysed by a metallic Lewis acid and phosphine oxide base combined on a BINOL or carbohydrate scaffold, involve dual activation of substrate and trimethylsilyl cyanide by the bifunctional catalyst.

The indium(III) bromide catalysis of the addition of TMS cyanide to ketones apparently involves a dimeric indium species, based on kinetic and spectroscopic observations,²⁵⁵ and enantioselective trimethylsilylcyanation of aldehydes has also been reported.²⁵⁶

O-Acetylcyanohydrins, $\text{RCH}(\text{CN})\text{OAc}$, have been prepared asymmetrically from aldehydes using KCN and acetic anhydride, with catalysis by chiral titanium(IV)- and vanadium(V)-salen complexes.²⁵⁷

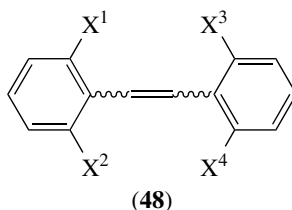
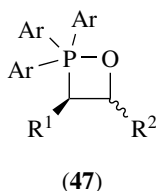
Trimethylsilyl-derived iodohydrins, $\text{R}_2\text{CHCH}(\text{I})\text{OTMS}$, can be prepared *in situ* from aldehydes, R_2CHCHO , and trimethylsilyl iodide.²⁵⁸ They react with electron-rich alkenes to give condensation products.

Regiospecific syntheses of alkylarylpyrimidines have been achieved in reactions of aliphatic ketones with aromatic aldehydes.²⁵⁹

The Wittig Reaction and Variants

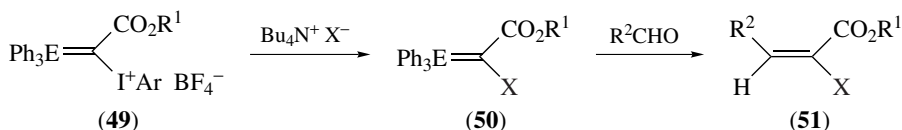
Theoretical studies suggest that variation of substituents at phosphorus in the Wittig reaction gives a reactivity order $\text{F} < \text{H} < \text{Ph} < \text{Me}$.²⁶⁰

2-Furyl substituents on phosphorus markedly increase (*Z*)-alkene selectivities in Wittig reactions.²⁶¹ In a series of reactions of $\text{EtAr}_3\text{P}^+\text{I}^-$ with benzaldehyde, the *Z*:*E* ratio, starting at 70:30 for $\text{Ar} = \text{Ph}$, rises sharply as 2-furyls are incorporated, reaching 98:2 for three such groups on phosphorus. 2-Furyl stabilizes the $1,2\lambda^5$ -oxaphosphetane intermediate (**47**; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$) to the extent that it was actually isolated (and a crystal structure obtained) for the tris(2-furyl) case.



o-Halo-substituted stilbenes (**48**) have been formed by Wittig reaction of the corresponding benzyltriphenylphosphonium salts and benzaldehyde.²⁶² Cooperative effects have been observed: one halide on each reactant increases *Z*-selectivity, whereas two halides on each favours *E*-product.

α -Hypervalent iodo-functionalized phosphonium and arsonium ylides (**49**; $\text{E} = \text{P}$, As) react as umpolung reagents with nucleophiles to give substituted ylides (**50**).²⁶³ Wittig reaction then gives (*Z*)- α -halo- α,β -unsaturated esters (**51**).



An arsonium ylide derivative of (*S*)-BINAP olefinates 4-substituted cyclohexanones enantioselectively.²⁶⁴ Chiral BINAP-phosphonates of 1,3-diketones undergo an intramolecular asymmetric Wittig-type olefination.²⁶⁵

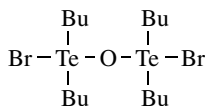
A ditelluride (**52**) catalyses two reactions of α -bromocarbonyl compounds: (i) Wittig-type reaction with aromatic aldehydes to yield α,β -unsaturated carbonyls (with *Z*-selectivity); and (ii) reductive debromination, under mild conditions.²⁶⁶

Tellurides catalyse Wittig-type olefinations, but high loadings are often required.²⁶⁷ A 10-fold lowering of telluride salt has been achieved by the use of PEG (polyethylene glycol) to solubilize it.

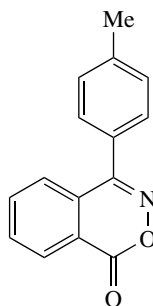
Isoquinolones have been prepared by insertion of alkylidene phosphoranes into 4-(4-methylphenyl)-2,3-benzoxazin-1-one (**53**).²⁶⁸

Mechanisms have been proposed for new products formed through reaction of 1,2,3-indantrione with Wittig–Horner reagents.²⁶⁹

A theoretical study of the aza-Wittig reaction of iminophosphoranes, $\text{H}_3\text{P}=\text{NH}$ and $\text{Cl}_3\text{P}=\text{NH}$, with formaldehyde indicates that the former reaction is more favourable,



(52)



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both in the gas phase and in water.²⁷⁰ A four-membered ring intermediate is found in all cases.

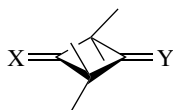
The Peterson olefination, a silicon variant of the Wittig, has been reviewed (42 references), with evidence presented for both concerted and stepwise mechanisms.²⁷¹ Given oxygen's affinity for silicon, the reaction takes preference over the related Julia and Wittig processes in the presence of *S*- and *P*-stabilized silyl carbanions.

(*Z*)-Selective syntheses of α,β -unsaturated amides have been achieved with Peterson reaction of (triphenylsilyl)acetamides, $\text{Ph}_3\text{SiCH}_2\text{CONR}_2$ ($\text{R} = \text{Me}, \text{Bn}$), with a wide range of aldehydes.²⁷²

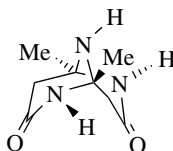
Miscellaneous Additions

The regioselectivity (1,2- versus 1,4-) of the addition to α,β -unsaturated carbonyl compounds of titanium(IV) enolates derived from α -diazo- β -ketocarboxyls has been controlled with Lewis acids.²⁷³

Trimethyl(trifluoromethyl)silane, F_3CSiMe_3 , has been reacted with cyclobutane-1,3-dione systems (**54**; $\text{X}/\text{Y} = \text{O}/\text{S}$) with fluoride catalysis.²⁷⁴ Most processes appear to start with attack of trifluoromethyl anion on the carbonyl or thiocarbonyl carbon. For ketones, it typically then gives the formal product of reagent addition, by silylation of the alcoholate. With thioketone functionality, further reaction is seen, leading to dithianes, sulfides, and other materials.



(54)



(55)

The ammonolysis of alkyl acetoacetates, $\text{MeCOCH}_2\text{CO}_2\text{R}$, in 15% aqueous ammonia does not give the acetoacetamide product as expected.²⁷⁵ Rather, alkyl β -amino crotonates, $\text{MeC}(\text{NH}_2)=\text{CHCO}_2\text{R}$, are formed. This is followed by slow conversion

to heterocyclic products, mainly 1,5-dimethyl-2,6,9-triaza-bicyclo[3.3.1]nonane-3,7-dione (**55**).

A direct catalytic asymmetric α -amination of aldehydes has been reported; proline is used as catalyst.²⁷⁶

Chiral diarylmethanols have been accessed by means of an aryl-transfer reaction using a boronic acid as aryl source and a chiral ferrocene auxiliary.²⁷⁷

Nucleophilic perfluoroalkylations have been carried out on an acetylenic aldehyde and ketone, $\text{PhC}\equiv\text{CCOR}$ ($\text{R} = \text{H}, \text{Me}$), using Me_3SiR_f with CsF catalysis, to yield the corresponding alkanols, $\text{PhC}\equiv\text{CCR}(\text{OH})\text{R}_f$ ($\text{R}_f = \text{perfluoro-C}_{1/6/7/8}$).²⁷⁸

A diastereoselective synthesis of α -aminophosphonic acids has been achieved by addition of a lithiated bis(diethylamino) phosphine borane complex, $(\text{Et}_2\text{N})_2\text{-P}(\text{BH}_3)\text{Li}$, to enantiopure sulfinimines derived from aldehydes.²⁷⁹

New enantiopure aziridine-sulfinimines have been synthesized from the corresponding aziridine-carboxaldehyde.²⁸⁰ They react diastereoselectively with phosphate anions.

Reactions of α -dicarbonyl systems – diketones and *o*-quinones – with phosphorus compounds have been reviewed (469 references).²⁸¹

In sodium hydride solutions in THF, DMSO reacts with arylaldehydes to give three products, a sulfide ($\text{ArCH}=\text{CHSMe}$), a sulfoxide ($\text{ArCH}=\text{CHSOMe}$), and a 'dimeric' oxystyrene ($\text{ArCH}=\text{CHOCH}_2\text{Ar}$).²⁸² Benzophenone gives the two sulfur products (i.e. $\text{Ph}_2\text{C}=\text{CHSMe}$ and $\text{Ph}_2\text{C}=\text{CHSOMe}$) plus 1,1-diphenylethene ($\text{Ph}_2\text{C}=\text{CH}_2$). Although full mechanisms have not been established, most of the products are readily derivable from a first step in which DMSyl anion attacks the carbonyl carbon.

Dialkylboron chlorides react with aromatic aldehydes in the presence of oxygen to give arylalkylmethanols, whereas alkylboron dichlorides give arylalkyl chlorides.²⁸³

Pentafluorobenzylidene chloride ($\text{F}_5\text{C}_6\text{CHCl}_2$) is formed from the corresponding benzaldehydes, in reaction with a range of chlorine donors, RCCl_3 ($\text{R} = \text{Cl}, \text{Ph}, \text{C}_6\text{F}_5$), with AlCl_3 catalysis.²⁸⁴

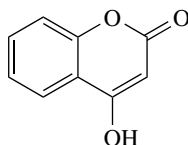
The origin of the enantioselectivity in the formation of epoxides from the reaction of sulfur ylides, $(\text{R}^1)_2\text{S}^+\text{C}^-\text{HR}^2$, and aldehydes has been explored using density functional theory.²⁸⁵ In the *anti* pathway (leading to the *trans*-epoxide), the initial addition is rate determining, whereas in the *syn* (i.e. *cis*) case, a torsional rotation step is unusually and unexpectedly the slowest.

Aldehydes, and some cyclohexanones, have been converted to glycidic esters (α,β -epoxy esters) using ethyl diazoacetate, and lanthanide triflate catalysis, without solvent.²⁸⁶ The lanthanide is a 'weak' and selective catalyst which, although it complexes the carbonyl carbon, allows it to retain sufficient nucleophilicity.

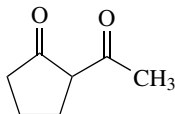
The syntheses and mechanisms of the reaction of 1,3-dicarbonyls with hexamethyltetramine, to yield 1,4-dihydropyridines (and pyridines by aerial oxidation), has been investigated in aqueous solution at ambient temperature.²⁸⁷

Enolization and Related Reactions

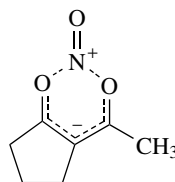
The results of a series of base-catalysed reactions between 4-hydroxycoumarin (**56**) and α,β -unsaturated carbonyls and 1,3-dicarbonyls provide evidence for the



(56)



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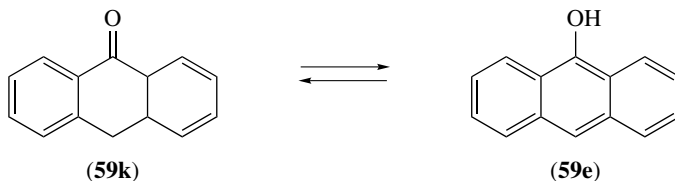
intermediacy of two less stable tautomers of (56), the 2,4-dione and the 2-hydroxy-en-4-one.²⁸⁸

Keto–enol rate and equilibrium measurements have been carried out on 2-acetylcyclopentanone (57).²⁸⁹ Interconversion of tautomers is much more rapid than its cyclohexyl analogue, and K_{enol} is 0.38 (i.e. >25% enol at equilibrium). Both tautomers are fairly acidic: the $\text{p}K_{\text{a}}$ s are 8.12 and 7.74. The rate of nitrosation, which proceeds via the enol, has also been studied, and is very different from those of other β -dicarbonyls. The dependence on $[\text{H}^+]$ is not first order, but rather it is fractional (between 0 and 1). A chelate–nitrosyl complex (58) has been invoked to explain the kinetic results.

The kinetics of enolization of two acetylisoxazoles and an acetylpyrazole have been measured by halogen trapping in water at 25 °C.²⁹⁰ Catalysis by OH^- , H_3O^+ , water, and metal ions have all been studied, and the results have been compared extensively with those for acetyl heterocyclics in the literature. Differences between compounds have been separated into heteroatom electron-withdrawing effects, heteroatom basicity effects, and the ability of some substances to chelate with metal atoms using the carbonyl oxygen and an appropriately placed heteroatom. The analysis is supported by *ab initio* calculations.

The first and second $\text{p}K_{\text{a}}$ s and the keto–enol equilibrium of 5-hydroxy-6-methyluracil have been measured over a range of temperatures in water.²⁹¹

10*H*-Anthr-9-one (59k) is the stable ketone tautomer of 9-anthrol (59e).²⁹² Thermodynamic and kinetic parameters for these structures and their related conjugate acid and base have been obtained from rates of equilibration over the pH range 1–13. The keto–enol (or ‘keto–phenol’) equilibrium constant is $10^{-2.17}$ and the phenol has a $\text{p}K_{\text{a}}$ of 7.84.



(59k)

(59e)

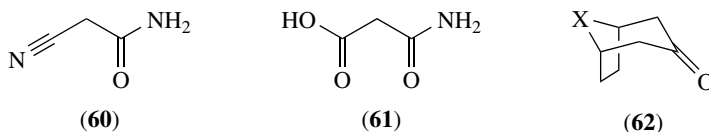
The ketone–phenol tautomerization of anthrone (59k) has been studied kinetically in aqueous solution, together with the hydrolysis of the methyl ether of the phenol tautomer.²⁹³ $\text{p}K_{\text{enol}}$ was obtained as 2.10 from ratios of ketonization and

phenolization and the pK_a for the ionization of anthrone was measured spectrophotometrically as 10.0, giving a value of 7.9 for the phenol pK_a . H_3O^+ catalysis of hydrolysis of the methyl ether is 3000 times slower than that for the ketonization of 9-anthrol.

Novel *o*-carborane-based ketonitriles have been prepared by two routes and appear to exist in enol form.²⁹⁴

The tendency for enols to be protonated at carbon on the less hindered face during acid-catalysed ketonization can be counteracted by designing an intramolecular transfer to the more hindered face.²⁹⁵

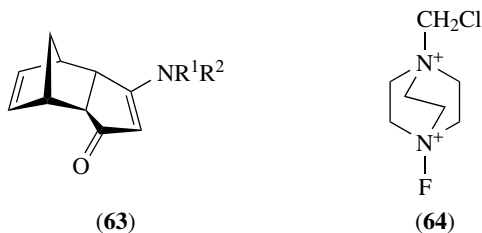
Bromination and iodination kinetics have been reported for 2-cyanoacetamide (**60**) and malonic acid (**61**) in aqueous acid.²⁹⁶ For the cyano compound, the behaviour is consistent with rate-limiting halogenation of the enol tautomer, and K_{enol} was determined as 6×10^{-10} . The position is less clear with malonic acid, both because it can spontaneously decarboxylate and because its mode of enolization (amide or acid group?) is uncertain, although the authors favour the amide mode. It does, however, brominate, and with acid catalysis.



Results of a kinetic study of the enolization of cyclobutanone in basic solution, when compared with related non-cyclic compounds, suggest that ring strain has little effect on the energy barrier to deprotonation at carbon.²⁹⁷

Enantioselective deprotonation of tropinone (**62**; X = NMe) and its sulfur analogue by chiral lithium amides such as lithium *N*-benzyl- α -methylbenzylamide, followed by addition of the resulting enolates to benzaldehyde, gives higher *ee* as the concentration of lithium amide is lowered.²⁹⁸ The possible role of dimeric and oligomeric lithium species is discussed. (ee)

Among α -substitutions mentioned, *N*-halosuccinimides have been used to halogenate 5-amino-*endo*-tricyclodecenylenaminones (**63**) regioselectively.²⁹⁹ Exclusive α, N - or α, δ -dihalogenation can be achieved by tuning the reaction conditions, and two different halogens can be placed α, δ - by sequential use of 1 mol each of the respective succinimides.



1-Fluoro-4-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane (**64**), as its tetrafluoroborate salt (Selectfluoro™), iodates aryl alkyl ketones in the presence of elemental iodine.³⁰⁰ By suitable choice of solvent, a useful regioselectivity can be achieved: α -iodo (methanol) versus iodoaryl (acetonitrile).

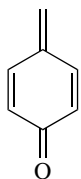
Two methods of α -tosyloxylation of ketones are recorded: (i) *n*-butylpyridinium tetrafluoroborate, an ionic liquid, is a serviceable 'green' solvent alternative for α -tosyloxylation of enolizable ketones, allowing most transformations to be carried out in 1 h at 90 °C, and recycling of the solvent causes no diminution in yield,³⁰¹ and (ii) new hypervalent iodine reagents have been reported for α -tosyloxylation and α -phosphoryloxylation of ketones.³⁰²

Quinone Methides

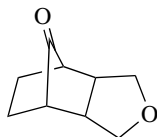
o-Quinone methides have been reviewed (147 references), with a major emphasis on their potential as intermediates in organic synthesis.³⁰³

The conformations of hindered and unhindered benzoquinone methides have been calculated by density functional theory.³⁰⁴

Flash photolysis of *p*-hydroxybenzyl acetate in aqueous solution yields *p*-quinone methide (**65**).³⁰⁵ Hydration (back to the precursor) has been followed kinetically, and also nucleophilic addition reactions with chloride, bromide, and thiocyanate ions and with thiourea. The data with bromide allowed the estimation of the equilibrium constant and forward and reverse rate constants for the combination of *p*-hydroxybenzyl cation with bromide anion.



(65)



(66)



(67)

Oxidation and Reduction of Carbonyl Compounds

Regio-, Enantio-, Diastereo-selective, and Other Reductions

π -Selectivities of hydride addition to 4-oxatricyclo[5.2.1.0^{2,6}]decan-10-one (**66**) and the corresponding 8-alkene have been measured and calculated.³⁰⁶ The results do not support arguments based on electrostatic interactions or electron donation from the ring oxygen. The study has been extended to more heteroatoms, with computations.³⁰⁷

The rates of axial and equatorial attack on *trans*-4-X-decal-1-ones (**67**) in reduction reactions have been measured.³⁰⁸ Axial reactivity is found to be independent of the substituent's conformation, but this is not so for equatorial reactivity. In reactions on the equatorial side of the molecule, axial substituents display much lower electronegativity than their equatorial counterparts. The authors suggest that the idea

that questions of π -facial diastereoselection can be answered simply by measuring k_{ax}/k_{eq} ratios should be abandoned.

A mechanistic investigation of the enantioselective hydrogenation of a chiral ketone, using an Ru–BINAP catalyst, has yielded a complete identification of a diastereomeric catalyst–substrate (alkoxide) species for this reaction.³⁰⁹

The role of the heteroatom in the stereoselectivity of complex metal hydride reduction of methyl-substituted and hetero-cyclohexanones has been reviewed.³¹⁰

An *ab initio* molecular orbital study of the mechanism of enantioselective reduction of prochiral ketones by borane, catalysed by oxazaborolidines, shows the transfer of hydride from the borane moiety to the carbonyl carbon to be the controlling step.³¹¹

Biphenyl alkyl ketones have been enantio- and diastereo-selectively reduced by a chiral oxazaborolidine–borane system.³¹²

A variety of ketone structures have been reduced to the corresponding alcohols in up to 89% *ee* by borane, mediated by a range of common (*S*)-amino acids.³¹³

The presence of sodium borohydride as a stabilizer in borane–THF reagent can lower enantioselectivities in the reduction of ketones catalysed by chiral oxazaborolidines; a variety of strategies to counteract this effect are described.³¹⁴

Enantioselective hydrogenations of acetophenone and of phenylglyoxylate methyl ester (PhCOCO₂Me) have been carried in aqueous media using as catalyst iridium(I) liganded with a C₂-symmetric chiral diamine.³¹⁵

A ruthenium complex of the Schiff base derived from aminohydroxy-BINAP and pyridine-2-carbaldehyde gave a 97% *ee* in the transfer hydrogenation of acetophenone with propan-2-ol.³¹⁶ Aryl ketones have been transfer-hydrogenated with propan-2-ol in high *ee*, using ruthenium(I) complexed with a chiral oxazoline ligand.³¹⁷

Aromatic 1,3-diketones, typically ArCOCH₂COMe, have been reduced by sodium borohydride to *anti*-1,3-diols in up to 96% *de*, through the use of a 1 : 1 complex with albumin.³¹⁸

Appropriate choice of an *N*-protecting group for α -amino ketones allows for either diastereoselection to be achieved in reduction with LiAlH(OBu^{*t*})₃ to give 1,2-amino alcohols: carbamate sets up the *anti*-product, whereas trityl favours *syn*-.³¹⁹

Whereas tributyltin hydride will not reduce ketones even with catalysis by a tetraphosphinopalladium(0) species, Bu₃SnH₂ does, with some diastereoselectivity in the case of cyclic ketones.³²⁰

syn-Selective reduction of 2-alkyl-1,3-diketones has been achieved, mediated by chiral ruthenium catalysts.³²¹

Rate constants have been measured for the reduction of a series of ketones by samarium(II) iodide in dry THF.³²² Results over a range of temperatures yielded activation parameters. (One point) coordination and chelation mechanisms are considered, with the evidence favouring the latter, especially the enhanced rates for *ortho*-F/NH₂/MeO-acetophenones, relative to their *para*-isomers. Comparable β -substituent effects are observed in aliphatic ketones.

The effect of HMPA on SmI₂-promoted reductions has been examined.³²³ Such reductions in the case of ketones in alcohol take minutes rather than days.³²⁴ However, an alternative is desirable, as HMPA is carcinogenic. Both water and amines

give some acceleration, but their *combined* use has now been reported to effect reduction in seconds, in solution in THF.

In 1964, an unusual case of base-catalysed ketone hydrogenation not requiring a transition metal catalyst was reported: benzophenone was reduced to benzhydrol by H_2 (100 atm)– $Bu'OK$ at $200^\circ C$.^{325a} In an effort to widen the scope of this reaction and achieve milder conditions, kinetic studies of non-enolizable ketones have been undertaken, including isotope exchange and equilibration with HD and D_2 .^{325b} The evidence points towards a six-membered cyclic transition state involving H_2 and an aggregate of the base, cation, and ketone. Analogies exist with Noyori's ruthenium catalysts. H_2 fission is apparently not rate limiting. Rather, the reactive conformation is poorly populated, indicating that better preorganization of substrate and base is required.

A wide variety of carbonyl types – aromatic aldehydes, ketones, oxoaldehydes, and diketones – have been reduced to alcohols using $TiCl_3-NH_3$ in aqueous methanol.³²⁶ The method has been adjusted to bring about reduction of aromatic ketones in the presence of aromatic aldehydes, a reversal of the normal chemoselectivity facilitated by *in situ* protection of the aldehyde as its dimethyl acetal.

Oxidation Reactions

Benzylic alcohols have been converted to benzaldehydes by aerobic free-radical oxidation at room temperature, using *N*-hydroxyphthalimide as catalyst.³²⁷ The factors that favour aldehyde product over acid have been explained.

In reports on Baeyer–Villiger oxidation, cyclic and acyclic ketones react at room temperature using oxygen as oxidant, and aldehyde as a co-reductant, with compressed CO_2 as a green solvent/diluent.³²⁸ Enantioselective oxidation of ketones has been achieved using a zirconium–salen complex.³²⁹ Conversion of sterically congested cyclic and acyclic ketones, to give lactones and esters, respectively, is accelerated when performed solvent free on the surface of crystals of sodium hydrogencarbonate.³³⁰

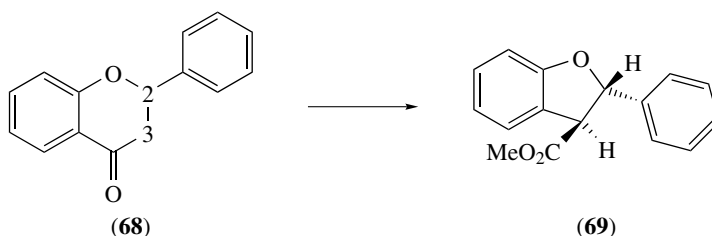
Kinetics of the ruthenium(III)-catalysed oxidation of propanone and butanone by periodate in perchloric acid have been reported.³³¹

The rate of oxidation of pyruvic acid by quinolinium dichromate has been measured and correlated with the hydration equilibrium of the ketone carbonyl group.³³² Heterocyclic aldehydes (2-fur-, 2-pyrrolicarb-, and 2-thiophenecarb-aldehyde) have been oxidized to their acids using quinolinium dichromate in aqueous sulfuric/acetic acids.³³³ Again, the comparison of the kinetics with the hydration equilibria for the aldehydes suggest that oxidative decomposition of the chromate ester of the hydrate is rate determining. Similar studies of the oxidation of 2-furaldehyde have been reported using quinolinium di-³³⁴ and chloro-chromate³³⁵ and chromic acid.³³⁶

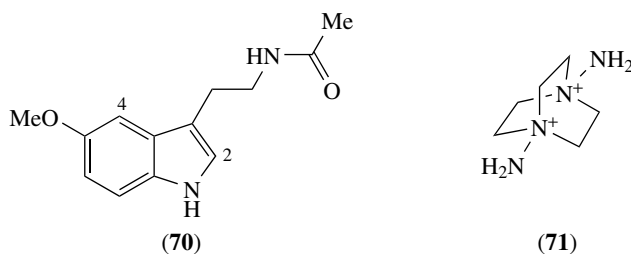
The kinetics of the oxidation of a series of *ortho*-, *meta*-, and *para*-substituted benzaldehydes by benzyltrimethylammonium tribromide have been measured in aqueous acetic acid.³³⁷ Other kinetic studies examined *para*-substituted benzaldehydes with hypochlorite,³³⁸ benzaldehyde with cerium(IV) in sulfuric acid,³³⁹ and benzaldehydes with nicotinium dichromate.³⁴⁰

ee

Flavanone (**68**) is oxidized by iodobenzene diacetate, $\text{PhI}(\text{OAc})_2$, in sulfuric acid–trimethyl orthoformate, undergoing a stereospecific ring contraction involving an aryl shift.³⁴¹ The major product is *trans*-methyl 2-phenyl-2,3-dihydrobenzo[*b*]-furan-3-carboxylate (**69**). Using a single enantiomer of (**68**), the mechanism has been investigated by NMR, circular dichroism, and chiral HPLC. The evidence suggests that, after initial formation of methyl enol ether *in situ*, electrophilic attack of the hypervalent iodine reagent at C(3) is followed by aryl migration and loss of iodide to give an exocyclic carbocation which rearranges to (**69**). (de)



In a study of the products and mechanisms of the reactions of hydroxyl radical with melatonin (**70**), keto–enol tautomerism of the 2-hydroxy product and keto–phenol tautomerism of the 4-hydroxy product have been invoked to explain the production of the final metabolites.³⁴²



N,N'-Diamino-1,4-diazoniabicyclo[2.2.2]octane (**71**), as its dinitrate, is a nitrogen–nitrogen ylide precursor.³⁴³ In a one-pot reaction in the presence of sodium hydride, it converts α,β -unsaturated ketones into the corresponding aziridine ketones.

In Simmons–Smith-mediated epoxidation, diethylzinc, chloriodomethane, and a sulfide are used to convert an aldehyde to a terminal epoxide.³⁴⁴ In an aza analogue, terminal aziridines can be prepared from aldimines. Efforts to develop enantioselective methods via chiral liganding of zinc are described. (ee)

The kinetics of the oxidative decarboxylation of α -keto acids, RCOCO_2H ($\text{R} = \text{Me}, \text{Ph}$), by peroxomonophosphoric acid in aqueous media are first order in both reactants (at constant pH); the activation energy and thermodynamic parameters have been measured and a mechanism proposed.³⁴⁵

A 'green' aerobic oxidation of aryl methyl ketones to give benzoic acids shows evidence of two independent reaction paths: base-catalysed autoxidation and a single electron-transfer process.³⁴⁶

In a C–C bond cleavage under mild, neutral conditions, electron-deficient aryl alkyl ketones, EWG-ArCOCH₂R (R = H, Me, Bn), are converted to aryl carboxylic esters, EWG-ArCO₂Me, by refluxing with the dimethyl acetal of DMF in methanol.³⁴⁷ The proposed mechanism involves the cleaved moiety emerging as an aldehyde (RCH₂CHO), which has indeed been isolated from some reactions.

Active pentafluorophenyl thioesters, PhCH₂CH₂C(=O)SC₆F₅, have been prepared from 3-phenylpropanal and dipentafluorophenyl disulfide in aqueous micellar systems, using a water-soluble radical initiator.³⁴⁸

Density functional theory has been used to calculate the stabilities of carbonyl oxides (R₂COO; R = H, F, Me) and their cyclizations to dioxiranes,³⁴⁹ and the kinetics of reaction of acids with diphenylcarbonyl oxide have been reported.³⁵⁰

Redox reactions at the anomeric carbon of glycosides have been reviewed.³²

Atmospheric Reactions

Further investigation of the reaction of OH radicals with acetone suggests no evidence for direct formation of acetic acids³⁵¹ (despite reports to the contrary). The dominant reaction for both substrates at 290 K is reported as hydrogen abstraction: this finding is backed up by theoretical calculations, which put the barrier for OH addition at 6.0 ± 0.5 kcal mol⁻¹, at least 2.5 kcal mol⁻¹ higher than for H abstraction. Another study of OH radicals with acetone and acetaldehyde comes to the same conclusion, suggesting no evidence for substantial direct formation of formic or acetic acids:³⁵² the dominant reaction for both substrates at 251 and 296 K is reported to be hydrogen abstraction, i.e. the α -H of acetone and the aldehydic H of acetaldehyde. And the upper limits for formation of formic and acetic acids from reaction of hydroxyl radicals with acetaldehyde at 296 K have been measured as 3 and 2%, respectively.³⁵³

Rate constants for reaction of hydroxyl radical with ketones in the gas phase have been measured and used to calculate their atmospheric lifetimes.³⁵⁴ The results are compared with those for chlorine radicals and for the reactions of the precursor alkanes with both radicals.

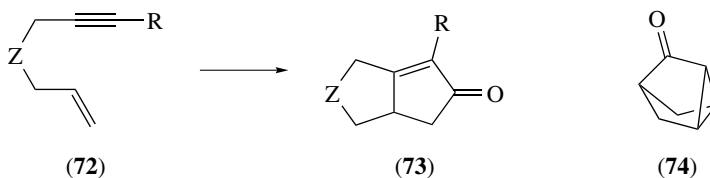
Rate constants for reaction of OH and Cl radicals with benzaldehyde and the three tolualdehydes at 298 K and 1 atm are reported.³⁵⁵

The kinetics of H abstraction from a series of aldehydes, RCHO (R = H, Me, F, Cl), by NO₃ have been studied computationally.³⁵⁶

Alkyl radicals in the gas phase can add to carbonyl compounds or abstract hydrogen from them.³⁵⁷ For methyl radical addition to formaldehyde, acetaldehyde, and acetone, the barriers have been calculated as 28, 29 and 40 kJ mol⁻¹, respectively, allowing H abstraction to compete. The barriers fall significantly for primary alkyl radicals, are almost negligible for secondary (ca 5 kJ mol⁻¹), and unidentifiably small for tertiary, so H abstraction is minor compared with primary radical addition and effectively squeezed out with more substituted radicals.

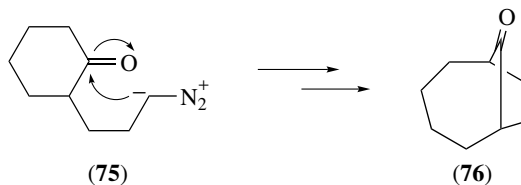
Other Reactions

Aldehydes have been employed as a CO source in a Pauson–Khand-type carbonylative alkene–alkyne coupling (**72**) of to produce a bicyclopentenone (**73**).³⁵⁸ The reaction is catalysed by rhodium, the aldehyde doubles as solvent (cinnamaldehyde was the best of those tried), and an enantioselective trial with added BINAP gave 83% *ee* (R = Ph, Z = O).



A variety of regioselective oxy (–O–) and imino (–NH–) group insertions into the strained ketone 3-nortricyclanone (**74**) have been described.³⁵⁹

Intramolecular insertion of diazo ketones (e.g. **75**) has been employed to produce bridged-bicyclic ring systems (e.g. **76**).³⁶⁰



1,2-Diketones react with bis(iodozincio)methane, $\text{CH}_2(\text{ZnI})_2$, in a 2 + 1-cycloaddition with high diastereoselectivity, to give a *cis*-cyclopropane-1,2-diol.³⁶¹

Rhodium(I) activates a C–H bond in large 2-cycloalkenones (7–15-membered) to give a ring-opened dicarbonyl product or a product of ring contraction.³⁶²

Cyclizations of α,β -unsaturated ketones with aminoguanidine which were expected to give 1,2,4-triazines as products, gave pyrazole derivatives instead.³⁶³

o-Hydroxybenzaldehydes undergo unusual cyclizations with 2,3-dihydrofurans, 3,4-dihydro-2*H*-1-benzopyrans, and acetophenones to give 3,4-dihydro-2*H*-1-benzopyran derivatives with high diastereoselectivity, using ytterbium(III) triflate as catalyst.³⁶⁴

Benzil, PhCOCOPh , reacts with phenol at 180 °C in the presence of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ to give a benzofuran, a benzofuranol, a benzodifuran, and a benzofuranone.³⁶⁵ Under anhydrous conditions, a benzofuranofuranone is also formed.

Whereas benzyl nitriles bearing electron-donating groups react with ketones in the presence of triflic anhydride to give naphthalenamines, switching to electron-withdrawing substituents gives 2,4-dibenzyl-substituted pyrimidines as products.³⁶⁶ Mechanisms to explain this divergence are proposed.

Trapping experiments have been used to study the reaction of alkyl isocyanides with ethynyl phenyl ketone.³⁶⁷

A Fries rearrangement of aryl formates has been used to prepare a range of aromatic hydroxyaldehydes; Lewis acids such as BBr_3 and BCl_3 are effective catalysts, whereas the use of triflic acid opens up the possibility of regioisomeric products, through rearrangements.³⁶⁸

A selectivity effect in the hydrosilylation of an alkynylketone, not seen in a control, has been explained in terms of $\sigma-\pi$ chelation of silicon: σ - by the lone pair of the carbonyl and π - by the alkyne moiety.³⁶⁹

Condensations of thiophene with ketones have been reported.³⁷⁰

(de)

References

- 1 Firouzabadi, H., Iranpoor, N., and Shaterian, H. R., *Bull. Chem. Soc. Jpn*, **75**, 2195 (2002).
- 2 Bear, T. J., Shaw, J. T., and Woerpel, K. A., *J. Org. Chem.*, **67**, 2056 (2002).
- 3 Klumpp, D. A., Sanchez, G. V., Aguirre, S. L., Zhang, Y., and de Leon, S., *J. Org. Chem.*, **67**, 5028 (2002).
- 4 Niimi, L., Hiraoka, S., and Yokozawa, T., *Tetrahedron*, **58**, 245 (2002).
- 5 Iwata, A., Tang, H., and Kunai, A., *J. Org. Chem.*, **67**, 5170 (2002).
- 6 Vostrikova, O. S., Gafarova, J. T., Dokichev, V. A., and Zlotisky, S. S., *Bashkirskii Khim. Zh.*, **7**, 3 (2000); *Chem. Abs.*, **136**, 69752 (2002).
- 7 Dean, K. E. S. and Kirby, A. J., *J. Chem. Soc., Perkin Trans. 2*, **2002**, 428.
- 8 Selambarom, J., Monge, S., Carre, F., Roque, J. P., and Pavia, A. A., *Tetrahedron*, **58**, 9559 (2002).
- 9 Mitome, H., Nagasawa, T., Miyaoka, H., Yamada, Y., and van Soest, R. W. M., *Tetrahedron*, **58**, 1673 (2002).
- 10 Bakke, J. M., Buhaug J., and Riha, J., *Ind. Eng. Chem. Res.*, **40**, 6051 (2001); *Chem. Abs.*, **136**, 118115 (2002).
- 11 Mondal, E., Sabu, P. R., Bose, G., and Khan, A. T., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1026.
- 12 Muthusamy, S., Babu, S. A., and Gunanathan, C., *Tetrahedron*, **58**, 7897 (2002).
- 13 Firouzabadi, H., Eslami, S., and Karimi, B., *Bull. Chem. Soc. Jpn*, **74**, 2401 (2001).
- 14 Kamal, A., Chouhan, G., and Ahmed, K., *Tetrahedron Lett.*, **43**, 6947 (2002).
- 15 Ranu, B. C., Das, A., and Samanta, S., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1520.
- 16 Tsubouchi, A., Nishio, E., Kato, Y., Fujiwara, T., and Takeda, T., *Tetrahedron Lett.*, **43**, 5755 (2002).
- 17 Liu, P., Binnun, E. D., Schaus, J. V., Valentino, N. M., and Panek, J. S., *J. Org. Chem.*, **67**, 1705 (2002).
- 18 Josse, S., Le Gal, J., Pipelier, M., Cleophax, J., Olesker, A., Pradere, J.-P., and Deubreuil, D., *Tetrahedron Lett.*, **43**, 237 (2002).
- 19 Yang, W.-B., Yang, Y.-Y., Gu, Y.-F., Wang, S.-H., Chang, C.-C., and Lin, C.-H., *J. Org. Chem.*, **67**, 3773 (2002).
- 20 Chiara, J. L. and Sesmilo, E., *Angew. Chem. Int. Ed.*, **41**, 3242 (2002).
- 21 Sato, Y., Tateno, G., Seio, K., and Sekine, M., *Eur. J. Org. Chem.*, **2002**, 87.
- 22 Davis, B. G., Wood, S. D., and Maughan, M. A. T., *Can. J. Chem.*, **80**, 555 (1999).
- 23 Garegg, P. J., Johannsson K.-J., Konradsson, P., Lindberg, B., and Trumpakaj, Z., *Carbohydr. Res.*, **337**, 517 (2001); *Chem. Abs.*, **136**, 386305 (2002).
- 24 Forsyth, S. A., MacFarlane, D. R., Thomson, R. J., and von Itzstein, M., *Chem. Commun. (Cambridge)*, **2002**, 714.
- 25 Knirel, Y. A. and Perebolov, A. V., *Aust. J. Chem.*, **55**, 69 (2002).
- 26 Baik, M.-H., Friesner, R. A., and Lippard, S. J., *J. Am. Chem. Soc.*, **124**, 4495 (2002).
- 27 Ellis, A. V. and Wilson, M. A., *J. Org. Chem.*, **67**, 8469 (2002).
- 28 Jensen, K. J., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 2219.
- 29 Bennet, A. J. and Kitos, T. E., *J. Chem. Soc., Perkin Trans. 2*, **2002**, 1207.
- 30 Herrera, F. J. L., Garcia, F. R. S., and Gonzalez, M. S. P., *Recent Res. Dev. Org. Chem.*, **4**, 465 (2000); *Chem. Abs.*, **137**, 311091 (2002).
- 31 Koto, S., *Glycoscience*, **1**, 417 (2001); *Chem. Abs.*, **137**, 325563 (2002).
- 32 Lundt, I., *Glycoscience*, **1**, 501 (2001); *Chem. Abs.*, **137**, 325564 (2002).
- 33 Konradsson, P., *Glycoscience*, **1**, 535 (2001); *Chem. Abs.*, **137**, 325565 (2002).

- ³⁴ Stick, R. V. and Williams, S. J., *Glycoscience*, **1**, 627 (2001); *Chem. Abs.*, **137**, 325568 (2002).
- ³⁵ Gerrard, J. A., *Aust. J. Chem.*, **55**, 299 (2002).
- ³⁶ Pearce, A. J. and Sinay, P., *Trends Org. Chem.*, **8**, 129 (2000); *Chem. Abs.*, **136**, 167572 (2002).
- ³⁷ Deubel, D. V., *J. Phys. Chem. A*, **106**, 431 (2002).
- ³⁸ Sung, K., Wu, S.-H., Wu, R.-R., and Sun, S.-Y., *J. Org. Chem.*, **67**, 4298 (2002).
- ³⁹ Hodous, B. L. and Fu, G. C., *J. Am. Chem. Soc.*, **124**, 10006 (2002).
- ⁴⁰ (a) Fernandez, R., Ferrete, A., Lassaletta, J. M., Llera, J. M., Martin-Zamora, E., and Monge, A., *Angew. Chem.*, **112**, 3015 (2000); *Angew. Chem. Int. Ed.*, **39**, 2893 (2000); (b) Fernandez, R., Ferrete, A., Lassaletta, J. M., Llera, J. M., and Martin-Zamora, E., *Angew. Chem. Int. Ed.*, **41**, 831 (2002).
- ⁴¹ Hodous, B. L. and Fu, G. C., *J. Am. Chem. Soc.*, **124**, 1578 (2002).
- ⁴² Alonso, E., del Pozo, C., and Gonzalez, J., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 571.
- ⁴³ Taggi, A. E., Hafez, A. M., Wack, H., Young, B., Ferraris, D., and Lectka, T., *J. Am. Chem. Soc.*, **124**, 6626 (2002).
- ⁴⁴ Shibata, T., Toshida, N., and Takagi, K., *Org. Lett.*, **4**, 1603 (2002).
- ⁴⁵ Vianello, R., Kovacevic, B., and Maksie, Z. B., *New J. Chem.*, **26**, 1324 (2002).
- ⁴⁶ Kovacevic, B., Maksie, Z. B., Vianello, R., and Primorac, M., *New J. Chem.*, **26**, 1329 (2002).
- ⁴⁷ Sanz, D., Perez-Torralla, M., Alarcon, S. H., Claramunt, R. M., Foces-Foces, C., and Elguero, J., *J. Org. Chem.*, **67**, 1462 (2002).
- ⁴⁸ Gorostidi, G. R. E., and Santos, J. G., Figueroa, J., and Blanco, F. G., *Bull. Chem. Soc. Jpn.*, **75**, 545 (2002).
- ⁴⁹ Gorostidi, G. R. E., Santos, J. G., Basagoitia, A., and Blanco, F. G., *Bull. Chem. Soc. Jpn.*, **75**, 2471 (2002).
- ⁵⁰ Salva, A., Donosa, J., Frau, J., and Munoz, F., *Int. J. Quantum Chem.*, **89**, 48 (2002); *Chem. Abs.*, **137**, 294808 (2002).
- ⁵¹ Dziembowska, T., Jagodzinska, E., Rozwadowski, Z., and Kotfica, M., *J. Mol. Struct.*, **598**, 229 (2001); *Chem. Abs.*, **136**, 232031 (2002).
- ⁵² Xiao, G. and Zhang, J., *Dongnan Daxue Zuebao, Ziran Kexueban*, **31**, 80 (2001); *Chem. Abs.*, **136**, 199846 (2002).
- ⁵³ Gandon, V., Bertus, P., and Szymoniak, J., *C. R. Acad. Sci., Ser. 2*, **5**, 127 (2002).
- ⁵⁴ Li, C.-J. and Wei, C., *Chem. Commun. (Cambridge)*, **2002**, 268.
- ⁵⁵ Alvaro, G. and Savoia, D., *Synlett*, 651 (2002); *Chem. Abs.*, **137**, 169065 (2002).
- ⁵⁶ Plobeck, N. and Powell, D., *Tetrahedron: Asymmetry*, **13**, 303 (2002).
- ⁵⁷ Cimarelli, C., Palmieri, G., and Volpini, E., *Tetrahedron: Asymmetry*, **13**, 2011 (2002).
- ⁵⁸ Dahmen, S. and Brase, S., *J. Am. Chem. Soc.*, **124**, 5940 (2002).
- ⁵⁹ Kabalka, G. W., Wu, Z., and Ju, W., *Org. Lett.*, **4**, 1399 (2002).
- ⁶⁰ Arrasate, S., Lete, E., and Sotomayor, N., *Tetrahedron: Asymmetry*, **13**, 311 (2002).
- ⁶¹ Fiorelli, C., Lucia, M., Martelli, G., Savoia, D., and Zazzetta, C., *Tetrahedron*, **58**, 8679 (2002).
- ⁶² von Keyserlingk, N. G. and Martens, J., *Eur. J. Org. Chem.*, **2002**, 301.
- ⁶³ Risberg, E. and Somfai, P., *Tetrahedron: Asymmetry*, **13**, 1957 (2002).
- ⁶⁴ Yang, X.-F., Zhang, M.-J., Hou, X.-L., and Dai, L.-X., *J. Org. Chem.*, **67**, 8097 (2002).
- ⁶⁵ Mayer, M. F., Wang, Q., and Hossain, M. M., *J. Organomet. Chem.*, **630**, 78 (2001); *Chem. Abs.*, **135**, 371305 (2001).
- ⁶⁶ Yoshikawa, N. and Shibasaki, M., *Tetrahedron*, **58**, 8289 (2002).
- ⁶⁷ Ma, Z., Zhao, Y., Jiang, N., Jin, X., and Wang, J., *Tetrahedron Lett.*, **43**, 3209 (2002).
- ⁶⁸ Di Fabio, R., Alvaro, G., Bertani, B., Donati, D., Giacobbe, S., Marchioro, C., Palma, C., and Lynn, S. M., *J. Org. Chem.*, **67**, 7319 (2002).
- ⁶⁹ Camera, C., Joseph, D., Dumas, F., d'Angelo, J., and Chiaroni, A., *Tetrahedron Lett.*, **43**, 1445 (2002).
- ⁷⁰ Jacquot-Rousseau, S., Schmitt, G., Laude, B., Kubicki, M. M., and Blacque, O., *J. Chem. Res. (S)*, **2002**, 151.
- ⁷¹ Hou, X.-L., Luo, Y.-M., Yuan, K., and Dai, L.-X., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1487.
- ⁷² Cabiddu, S., Cadoni, E., Ianni, A., Gelli, G., Melis, S., Bernard, A. M., Cabiddu, M. G., De Montis, S., and Fattuoni, C., *Eur. J. Org. Chem.*, **2002**, 3393.
- ⁷³ Hartley, J. H., Phillips, M. D., and James, T. D., *New J. Chem.*, **26**, 1228 (2002).
- ⁷⁴ Lewis, M. and Glaser, R., *Chem. Eur. J.*, **8**, 1934 (2002).
- ⁷⁵ Mock, W. L. and Ochwat, K. J., *J. Chem. Soc., Perkin Trans. 2*, **2002**, 843.
- ⁷⁶ Ueda, M., Miyabe, H., Namba, M., Nakabayashi, T., and Naito, T., *Tetrahedron Lett.*, **43**, 4369 (2002).

- ⁷⁷ Basiuk, V. A., Crevenna, E., Alvaro, H., Montiel, M., and Hector, M., *Int. J. Quantum Chem.*, **87**, 101 (2002); *Chem. Abs.*, **136**, 401320 (2002).
- ⁷⁸ Nanni, D., Pareschi, P., and Walton, J. C., *J. Chem. Soc., Perkin Trans. 2*, **2002**, 1098.
- ⁷⁹ Perosa, A., and Selva, M., and Tundo, P., *J. Chem. Soc., Perkin Trans. 2*, **2002**, 1033.
- ⁸⁰ Varlamov, V. T., *Kinet. Catal. (translation of Kinet. Katal.)*, **42**, 759 (2001); *Chem. Abs.*, **136**, 279003 (2002).
- ⁸¹ Chatani, N., Kamitani, A., and Murai, S., *J. Org. Chem.*, **67**, 7014 (2002).
- ⁸² Jia, Q., Xie, W., Zhang, W., Janczuk, A., Luo, S., Zhang, B., Cheng, J. P., Ksebati, M. B., and Wang, P. G., *Tetrahedron Lett.*, **43**, 2339 (2002).
- ⁸³ Routaboul, C., Dumas, L., Gautier-Luneau, I., Vergne, J., Maurel, M.-C., and Decout, J.-L., *Chem. Commun. (Cambridge)*, **2002**, 1114.
- ⁸⁴ Makosza, M. and Kozhevnikov, D. N., *Russ. Chem. Bull. (translation of Izv. Akad. Nauk, Ser. Khim.)*, **50**, 2236 (2001); *Chem. Abs.*, **137**, 247229 (2002).
- ⁸⁵ Travala, S. A., Brighente, I. M. C., and Yunes, R. A., *Int. J. Chem. Kinet.*, **34**, 685 (2002).
- ⁸⁶ Cordova, T., Peraza, A. J., and Malpica, A., *J. Phys. Org. Chem.*, **15**, 48 (2002).
- ⁸⁷ Cantlin, R. J., Drake, J., and Nagorski, R. W., *Org. Lett.*, **4**, 2325 (2002).
- ⁸⁸ Yashoda, M. P., Sherigara, B. S., and Vaidya, V. P., *J. Saudi Chem. Soc.*, **5**, 255 (2001); *Chem. Abs.*, **136**, 53439 (2002).
- ⁸⁹ Lukin, K. A. and Narayanan, B. A., *Tetrahedron*, **58**, 215 (2002).
- ⁹⁰ Yadav, J. S., Reddy, B. V. S., Madhavi, A. V., and Ganesh, Y. S. S., *J. Chem. Res. (S)*, **2002**, 236.
- ⁹¹ De Luca, L., Giacomelli, G., and Porcheddu, A., *J. Org. Chem.*, **67**, 6272 (2002).
- ⁹² Kakiya, H., Yagi, K., Shinokubo, H., and Oshima, K., *J. Am. Chem. Soc.*, **124**, 9032 (2002).
- ⁹³ Yoshida, M., Kitamura, M., and Narasaka, K., *Chem. Lett.*, **2002**, 144.
- ⁹⁴ Vazquez, J., Prieto, A., Fernandez, R., Enders, D., and Lassaletta, J. M., *Chem. Commun. (Cambridge)*, **2002**, 498.
- ⁹⁵ El-Nady, A. M., *J. Chin. Chem. Soc.*, **48**, 1081 (2001); *Chem. Abs.*, **137**, 46840 (2002).
- ⁹⁶ Aggarwal, V. K., Patel, M., and Studley, J., *Chem. Commun. (Cambridge)*, **2002**, 1514.
- ⁹⁷ Di Chenna, P. H., Ferrara, A., Ghini, A. A., and Burton, G., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 227.
- ⁹⁸ Jones, S., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1.
- ⁹⁹ Kobayashi, S. and Manabe, K., *Acc. Chem. Res.*, **35**, 209 (2002).
- ¹⁰⁰ Shibasaki, M., Kanai, M., and Funabashi, K., *Chem. Commun. (Cambridge)*, **2002**, 1989.
- ¹⁰¹ Lindstrom, U. M., *Chem. Rev.*, **102**, 2751 (2002).
- ¹⁰² Schenk, W. A., Beucke, T., Kummel, J., Servatius, F., Sonnhalter, N., Bringmann, G., and Wuzik, A., *Selected Reactions of Metal-activated Molecules, Proceedings of the Symposium, 3rd, Würzburg, Germany, 17–19, September 1997*, 1998, p. 247; (publ.1998), eds. Werner, H. and Schreier, P., Friedrich Vieweg and Sohn Verlagsgesellschaft, Wiesbaden; *Chem. Abs.*, **136**, 151203 (2002).
- ¹⁰³ Palomo, C., Oiarbide, M., and Garcia, J. M., *Chem. Eur. J.*, **8**, 36 (2002).
- ¹⁰⁴ Todd, M. H., *Chem. Soc. Rev.*, **31**, 211 (2002).
- ¹⁰⁵ List, B., *Tetrahedron*, **58**, 5573 (2002).
- ¹⁰⁶ Schank, K., Bouillon, G., Funfrocken, M., Lick, C., and Lieder, R., *Helv. Chim. Acta*, **85**, 1295 (2002).
- ¹⁰⁷ Rankin, K. N., Gauld, J. W., and Boyd, R. J., *J. Phys. Chem. A*, **106**, 5155 (2002).
- ¹⁰⁸ Loh, T.-P., Feng, L.-C., Yang, H.-Y., and Yang, J.-Y., *Tetrahedron Lett.*, **43**, 8741 (2002).
- ¹⁰⁹ Yoshikawa, N., Suzuki, T., and Shibasaki, M., *J. Org. Chem.*, **67**, 2556 (2002).
- ¹¹⁰ Mahrwald, R. and Ziemer, B., *Tetrahedron Lett.*, **43**, 4459 (2002).
- ¹¹¹ Bøgevig, A., Kumaragurabaran, N., and Jørgensen, K. A., *Chem. Commun. (Cambridge)*, **2002**, 620.
- ¹¹² Alcaide, B. and Almendros, P., *Eur. J. Org. Chem.*, **2002**, 1595.
- ¹¹³ Ye, X.-L., *Huaxue Xuebao*, **59**, 1680 (2001); *Chem. Abs.*, **136**, 262746 (2002).
- ¹¹⁴ Gatrex, B. W., Taylor, D. K., and Tiekink, E. R. T., *Org. Lett.*, **4**, 221 (2002).
- ¹¹⁵ Maggioni, V., Resmini, M., and Gouverneur, V., *Angew. Chem. Int. Ed.*, **41**, 1012 (2002).
- ¹¹⁶ Tanner, M. E. *Acc. Chem. Res.*, **35**, 237 (2002).
- ¹¹⁷ Dickerson, T. J. and Janda, K. D., *J. Am. Chem. Soc.*, **124**, 3220 (2002).
- ¹¹⁸ Evans, D. A., Tedrow, J. S., Shaw, J. T., and Downey, C. W., *J. Am. Chem. Soc.*, **124**, 392 (2002).
- ¹¹⁹ Kodama, T., Shuto, S., Ichikawa, S., and Matsuda, A., *J. Org. Chem.*, **67**, 7706 (2002).
- ¹²⁰ Casper, D. M., Burgeson, J. R., Esken, J. M., Ferrence, G. M., and Hitchcock, S. R., *Org. Lett.*, **4**, 3739 (2002).
- ¹²¹ de Lijser, H. J. P., Fardoun, F. H., Sawyer, J. R., and Quant, M., *Org. Lett.*, **4**, 2253 (2002).

- ¹²² Zhang, J., Yuan, Y., and Xie, R., *Huaxue Yanji Yu Yingyong*, **13**, 499 (2001); *Chem. Abs.*, **137**, 216909 (2002).
- ¹²³ Mukaiyama, T., Imachi, S., Yamane, K., and Mizuta, M., *Chem. Lett.*, **2002**, 698.
- ¹²⁴ Murga, J., Falomir, E., Gonzalez, F., Carda, M., and Marco, J. A., *Tetrahedron*, **58**, 9697 (2002).
- ¹²⁵ Pucheault, M., Darses, S., and Genet, J.-P., *Eur. J. Org. Chem.*, **2002**, 3552.
- ¹²⁶ Andrus, M. B., Mendenhall, K. G., Meredith, E. L., and Sekhar, B. B. V. S., *Tetrahedron Lett.*, **43**, 1789 (2002).
- ¹²⁷ Kourouli, T., Kefalas, P., Ragoussis, N., and Ragoussis, V., *J. Org. Chem.*, **67**, 4615 (2002).
- ¹²⁸ Roush, W. R., Bannister, T. D., Wendt, M. D., VanNieuwenhze, M. S., Gustin, D. J., Dilley, G. J., Lane, G. C., Scheidt, K. A., and Smith, W. J., *J. Org. Chem.*, **67**, 4284 (2002).
- ¹²⁹ Ruiz, M., Ojea, V., and Quintela, J. M., *Tetrahedron: Asymmetry*, **13**, 1863 (2002).
- ¹³⁰ Yasuda, M., Tsuji, S., Shigeyoshi, Y., and Baba, A., *J. Am. Chem. Soc.*, **124**, 7440 (2002).
- ¹³¹ Bazin, S., Feray, L., Siri, D., Naubron, J.-V., and Bertrand, M. P., *Chem. Commun. (Cambridge)*, **2002**, 2506.
- ¹³² Abiko, A., Inoue, T., and Masamune, S., *J. Am. Chem. Soc.*, **124**, 10759 (2002).
- ¹³³ Yoshida, K., Ogasawara, M., and Hayashi, T., *J. Am. Chem. Soc.*, **124**, 10984 (2002).
- ¹³⁴ Yamataka, H., Shimizu, M., and Mishima, M., *Bull. Chem. Soc. Jpn.*, **75**, 127 (2002).
- ¹³⁵ Misumi, Y. and Matsumoto, K., *Angew. Chem. Int. Ed.*, **41**, 1031 (2002).
- ¹³⁶ Ma, D., Pan, Q., and Han, F., *Tetrahedron Lett.*, **43**, 9401 (2002).
- ¹³⁷ Bøgevig, A., Gothelf, K. V., and Jørgensen, K. A., *Chem. Eur. J.*, **8**, 5652 (2002).
- ¹³⁸ Kamimura, A., Mitsudera, H., Omata, Y., Matsuura, K., Shirau, M., and Kakehi, A., *Tetrahedron*, **58**, 9817 (2002).
- ¹³⁹ Fleisher, M., Jansone, D., Andreeva, G., Leite, L., and Lukevics, E., *Chem. Heterocycl. Compd. (translation of Khim. Geterotsikli. Soedin.)*, **37**, 688 (2001); *Chem. Abs.*, **136**, 231976 (2002).
- ¹⁴⁰ Cordova, A., Notz, W., Zhong, G., Betancort, J. M., and Barbas, C. F., *J. Am. Chem. Soc.*, **124**, 1842 (2002).
- ¹⁴¹ Cordova, A., Watanabe, S.-i., Tanaka, F., Notz, W., and Barbas, C. F., *J. Am. Chem. Soc.*, **124**, 1866 (2002).
- ¹⁴² Sano, S., Teranishi, R., and Nagao, Y., *Tetrahedron Lett.*, **43**, 9183 (2002).
- ¹⁴³ Sano, S., Yokoyama, K., Teranishi, R., Shiro, M., and Nagao, Y., *Tetrahedron Lett.*, **43**, 281 (2002).
- ¹⁴⁴ Vares, L. and Rein, T., *J. Org. Chem.*, **67**, 7226 (2002).
- ¹⁴⁵ Moore, I. F. and Kluger, R., *J. Am. Chem. Soc.*, **124**, 1669 (2002).
- ¹⁴⁶ Gao, G., Xiao, R., Yuan, Y., Zhou, C.-H., You, J., and Xie, R.-G., *J. Chem. Res. (S)*, **2002**, 262.
- ¹⁴⁷ Li, W.-D. Z. and Zhang, X.-X., *Org. Lett.*, **4**, 3485 (2002).
- ¹⁴⁸ Yamashita, Y., Ishitani, H., Shimizu, H., and Kobayashi, S., *J. Am. Chem. Soc.*, **124**, 3292 (2002).
- ¹⁴⁹ Mori, Y., Kobayashi, J., Manabe, K., and Kobayashi, S., *Tetrahedron*, **58**, 8263 (2002).
- ¹⁵⁰ Itsuno, S. and Komura, K., *Tetrahedron*, **58**, 8237 (2002).
- ¹⁵¹ Villano, R., De Rosa, M., Salerno, C., Soriente, A., and Scettri, A., *Tetrahedron: Asymmetry*, **13**, 1949 (2002).
- ¹⁵² Fujisawa, H. and Mukaiyama, T., *Chem. Lett.*, **2002**, 182.
- ¹⁵³ Denmark, S. E., Wynn, T., and Beutner, G. L., *J. Am. Chem. Soc.*, **124**, 13405 (2002).
- ¹⁵⁴ Honda, M., Oguchi, W., Segi, M., and Nakajima, T., *Tetrahedron*, **58**, 6815 (2002).
- ¹⁵⁵ Miura, K., Nakagawa, T., and Hosomi, A., *J. Am. Chem. Soc.*, **124**, 536 (2002).
- ¹⁵⁶ Denmark, S. E. and Fujimori, S., *Org. Lett.*, **4**, 3473 (2002).
- ¹⁵⁷ Denmark, S. E. and Fujimori, S., *Org. Lett.*, **4**, 3477 (2002).
- ¹⁵⁸ Aggarwal, V. K., Sheldon, C. G., Macdonald, G. J., and Martin, W. P., *J. Am. Chem. Soc.*, **124**, 10300 (2002).
- ¹⁵⁹ Pei, W., Wei, H.-X., and Li, G., *Chem. Commun. (Cambridge)*, **2002**, 1856.
- ¹⁶⁰ Pei, W., Wei, H.-X., and Li, G., *Chem. Commun. (Cambridge)*, **2002**, 2412.
- ¹⁶¹ Shi, M. and Zhao, G.-L., *Tetrahedron Lett.*, **43**, 4499 (2002).
- ¹⁶² Shi, M., Jiang, J.-K., and Li, C.-Q., *Tetrahedron Lett.*, **43**, 127 (2002).
- ¹⁶³ Shi, M., Jiang, J.-K., and Cui, S.-K., *Molecules*, **6**, 852 (2001); *Chem. Abs.*, **136**, 166976 (2002).
- ¹⁶⁴ Aggarwal, V. A., Dean, D. K., Mereu, A., and Williams, R., *J. Org. Chem.*, **67**, 510 (2002).
- ¹⁶⁵ Luo, S., Zhang, B., He, J., Janczuk, A., Wang, P. G., and Cheng, J.-P., *Tetrahedron Lett.*, **43**, 7369 (2002).
- ¹⁶⁶ Rose, P. M., Clifford, A. A., and Rayner, C. M., *Chem. Commun. (Cambridge)*, **2002**, 968.
- ¹⁶⁷ Aggarwal, V. K., Emme, I., and Mereu, A., *Chem. Commun. (Cambridge)*, **2002**, 1612.
- ¹⁶⁸ Hayashi, Y., Okado, K., Ashimine, I., and Shoji, M., *Tetrahedron Lett.*, **43**, 8683 (2002).
- ¹⁶⁹ Shi, M. and Xu, Y.-M., *Angew. Chem. Int. Ed.*, **41**, 4507 (2002).

- 170 Shi, M. and Xu, Y.-M., *Tetrahedron: Asymmetry*, **13**, 1195 (2002).
- 171 Walsh, L. M., Winn, C. L., and Goodman, J. M., *Tetrahedron Lett.*, **43**, 8219 (2002).
- 172 Shi, M., Li, C.-Q., and Jiang, J.-K., *Helv. Chim. Acta*, **85**, 1051 (2002).
- 173 Shi, M. and Wang, C.-J., *Tetrahedron*, **58**, 9063 (2002).
- 174 Shi, M. and Xu, Y.-M., *Eur. J. Org. Chem.*, **2002**, 696.
- 175 Heck, G. E. and Welch, D. S., *Org. Lett.*, **4**, 3687 (2002).
- 176 Reddy, M. V. R., Rudd, M. T., and Ramachandran, P. V., *J. Org. Chem.*, **67**, 5382 (2002).
- 177 Balan, D. and Adolffson, H., *J. Org. Chem.*, **67**, 2329 (2002).
- 178 Blackwell, J. M., Piers, W. E., and McDonald, R., *J. Am. Chem. Soc.*, **124**, 1295 (2002).
- 179 Gajewski, J. J., Bocian, W., Brichford, N. L., and Henderson, J. I., *J. Org. Chem.*, **67**, 4236 (2002).
- 180 Watahiki, T. and Oriyama, T., *Tetrahedron Lett.*, **43**, 8959 (2002).
- 181 Onishi, Y., Ito, T., Yasuda, M., and Baba, A., *Tetrahedron*, **58**, 8227 (2002).
- 182 Tan, X.-H., Shen, B., Liu, L., and Guo, Q.-X., *Tetrahedron Lett.*, **43**, 9373 (2002).
- 183 Wang, M. W., Chen, Y. J., and Wang, D., *Heteroat. Chem.*, **12**, 534 (2001); *Chem. Abs.*, **136**, 85449 (2002).
- 184 Aspinall, H. C., Bissett, J. S., Greeves, N., and Levin, D., *Tetrahedron Lett.*, **43**, 319 (2002).
- 185 Franco, D., Wenger, K., Antonczak, S., Cabrol-Bass, D., Dunach, E., Rocamora, M., Gomez, M., and Muller, G., *Chem. Eur. J.*, **8**, 664 (2002).
- 186 Cainelli, G., Giacomini, D., Galletti, P., and Quintavalla, A., *Eur. J. Org. Chem.*, **2002**, 3153.
- 187 Malkov, A. V., Orsini, M., Pernazza, D., Muir, K. W., Langer, V., Meghani, P., and Kocovsky, P., *Org. Lett.*, **4**, 1047 (2002).
- 188 Ishiyama, T., Ahiko, T.-a., and Miyaura, N., *J. Am. Chem. Soc.*, **124**, 12414 (2002).
- 189 Yasuda, M., Hirata, K., Nishino, M., Yamamoto, A., and Baba, A., *J. Am. Chem. Soc.*, **124**, 13442 (2002).
- 190 Loh, T.-P., Song, H.-Y., and Zhou, Y., *Org. Lett.*, **4**, 2715 (2002).
- 191 Koriyama, Y., Nozawa, A., Hayakawa, R., and Shimizu, M., *Tetrahedron*, **58**, 9621 (2002).
- 192 Basavaiah, D. and Sreenivasulu, B., *Tetrahedron Lett.*, **43**, 2989 (2002).
- 193 Gryko, D., Prokopowicz, P., and Jurczak, J., *Tetrahedron: Asymmetry*, **13**, 1103 (2002).
- 194 Nishigaichi, Y. and Takuwa, A., *Tetrahedron Lett.*, **43**, 3045 (2002).
- 195 Fleming, I. and Pang, K. L. C., *Tetrahedron Lett.*, **43**, 5985 (2002).
- 196 Jiang, B., Chen, Z., and Xiong, W., *Chem. Commun. (Cambridge)*, **2002**, 1524.
- 197 Jiang, B. and Feng, Y., *Tetrahedron Lett.*, **43**, 2975 (2002).
- 198 Spino, C., Granger, M.-C., Boisvert, L., and Beaulieu, C., *Tetrahedron Lett.*, **43**, 4183 (2002).
- 199 Kirby, A. J., Komarov, I. V., Bilenko, V. A., Davies, J. E., and Rawson, J. M., *Chem. Commun. (Cambridge)*, **2002**, 2106.
- 200 Lee, I., Uhm, T. S., Ryu, Z. H., Koo, I. S., and Lee, J. P., *Bull. Korean Chem. Soc.*, **23**, 758 (2002); *Chem. Abs.*, **137**, 232339 (2002).
- 201 (a) Carrasco, N., Gonzalez-Nilo, F., and Rezende, M. C., *Tetrahedron*, **58**, 5141 (2002); (b) Rezende, M. C., *Tetrahedron*, **57**, 5923 (2001);
- 202 Smith, R. J., Trzoss, M., Buhl, M., and Bienz, S., *Eur. J. Org. Chem.*, **2002**, 2770.
- 203 Dejaegher, Y., Kuz'menok, N. M., Zvonok, A. M., and De Kimpe, N., *Chem. Rev.*, **102**, 29 (2002).
- 204 Simunek, P., *Sci. Pap. Univ. Pardubice, Seri. A Fac. Chem. Technol.*, **7**, 101, (2001); *Chem. Abs.*, **137**, 154561 (2002).
- 205 Truhlar, D. G., Gao, J., Alhambra, C., Garcia-Viloca, M., Corchado, J., Sanchez, M. L., and Villa J., *Acc. Chem. Res.*, **35**, 341 (2002).
- 206 Jun, C.-H., Moon, C. W., Lim, S.-G., and Lee, H., *Org. Lett.*, **4**, 1491 (2002).
- 207 Brimble, M. A., Halim, R., and Petersson, M., *Tetrahedron Lett.*, **43**, 4777 (2002).
- 208 El-Alali, A. and Al-Kamali, A. S., *Can. J. Chem.*, **80**, 1293 (2002).
- 209 Dawid, M., Mloston, G., and Warkentin, J., *Chem. Eur. J.*, **8**, 2184 (2002).
- 210 Ojida, A., Yamano, T., Taya, N., and Tasaka, A., *Org. Lett.*, **4**, 3051 (2002).
- 211 (a) Chen, Y. K., Costa, A. M., and Walsh, P. J., *J. Am. Chem. Soc.*, **123**, 5378 (2001); (b) Buono, F., Walsh, P. J., and Blackmond, D. G., *J. Am. Chem. Soc.*, **124**, 13652 (2002).
- 212 Soai, K. and Sato, I., *Chirality*, **14**, 548 (2002); *Chem. Abs.*, **137**, 278769 (2002).
- 213 Lake, F. and Moberg, C., *Eur. J. Org. Chem.*, **2002**, 3179.
- 214 Costa, A. M., Jimeno, C., Gavenonis, J., Carroll, P. J., and Walsh, P. J., *J. Am. Chem. Soc.*, **124**, 6929 (2002).
- 215 Le Goanvic, D., Holler, M., and Pale, P., *Tetrahedron: Asymmetry*, **13**, 119 (2002).
- 216 Bauer, T. and Tarasiuk, J., *Tetrahedron Lett.*, **43**, 687 (2002).

- 217 Martinez, A. G., Vilar, E. T., Fraile, A. G., de la Moya Cerero, S., Martinez-Ruiz, P., and Vilas, P. C., *Tetrahedron: Asymmetry*, **13**, 1 (2002).
- 218 Steiner, D., Sethofer, S. G., Goralski, C. T., and Singaram, B., *Tetrahedron: Asymmetry*, **13**, 1477 (2002).
- 219 Lee, S. J., Hu, A., and Lin, W., *J. Am. Chem. Soc.*, **124**, 12948 (2002).
- 220 Superchi, S., Giorgio, E., Scafato, P., and Rosini, C., *Tetrahedron: Asymmetry*, **13**, 1385 (2002).
- 221 Martinez, A. G., Vilar, E. T., Fraile, A. G., Cerero, S. d. I. M., and Martinez-Ruiz, P., *Tetrahedron: Asymmetry*, **13**, 1457 (2002).
- 222 Lu, J., Xu, X., Wang, C., He, J., Hu, Y., and Hu, H., *Tetrahedron Lett.*, **43**, 8367 (2002).
- 223 Sarvary, I., Wan, Y., and Frejd, T., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 645.
- 224 Kashima, C., Higashide, K., Miwa, K., and Tsukamoto, Y., *J. Heterocycl. Chem.*, **39**, 917 (2002).
- 225 Dahmen, S. and Bräse, S., *Chem. Commun. (Cambridge)*, **2002**, 26.
- 226 Shiina, I., Konishi, K., and Kuramoto, Y.-s., *Chem. Lett.*, **2002**, 164.
- 227 Guz, N. R. and Phillips, A. J., *Org. Lett.*, **4**, 2133 (2002).
- 228 Ko, D.-H., Kim, K. H., and Ha, D.-C., *Org. Lett.*, **4**, 3759 (2002).
- 229 Bauer, T., Tarasiuk, J., and Pasniczek, K., *Tetrahedron: Asymmetry*, **13**, 77 (2002).
- 230 Xu, Q., Yang, H., Pan, X., and Chan, A. S. C., *Tetrahedron: Asymmetry*, **13**, 945 (2002).
- 231 Simonson, D. L., Kingsbury, K., Xu, M.-H., Hu, Q.-S., Sabat, M., and Pu, L., *Tetrahedron*, **58**, 8189 (2002).
- 232 Sato, I., Matsueda, Y., Kadowaki, K., Yonebuko, S., Shibata, T., and Soai, K., *Helv. Chim. Acta*, **85**, 3383 (2002).
- 233 Sato, I., Osanai, S., Kadowaki, K., Sugiyama, T., Shibata, T., and Soai, K., *Chem. Lett.*, **2002**, 168.
- 234 Sato, I., Kodaka, R., Hosoi, K., and Soai, K., *Tetrahedron: Asymmetry*, **13**, 805 (2002).
- 235 Garcia, C., LaRochelle, L. K., and Walsh, P. J., *J. Am. Chem. Soc.*, **124**, 10970 (2002).
- 236 Yus, M., Ramon, D. J., and Prieto, O., *Tetrahedron: Asymmetry*, **13**, 2291 (2002).
- 237 Gao, G., Moore, D., Xie, R.-G., and Pu, L., *Org. Lett.*, **4**, 4143 (2002).
- 238 Li, X., Lu, G., Kwok, W. H., and Chan, A. S. C., *J. Am. Chem. Soc.*, **124**, 12636 (2002).
- 239 Moore, D., Huang, W.-S., Xu, M.-H., and Pu, L., *Tetrahedron Lett.*, **43**, 8831 (2002).
- 240 Beresford, K. J. M., *Tetrahedron Lett.*, **43**, 7175 (2002).
- 241 DiMauro, E. F. and Kozlowski, M. C., *Org. Lett.*, **4**, 3781 (2002).
- 242 Chiev, K. P., Roland, S., and Mangeney, P., *Tetrahedron: Asymmetry*, **13**, 2205 (2002).
- 243 Soucy, R. L., Kozhinov, D., and Behar, V., *J. Org. Chem.*, **67**, 1947 (2002).
- 244 Maclin, K. M. and Richey, H. G., *J. Org. Chem.*, **67**, 4602 (2002).
- 245 Rutherford, J. L., Hoffmann, D., and Collum, D. B., *J. Am. Chem. Soc.*, **124**, 264 (2002).
- 246 (a) Maclin, K. M. and Richey, H. G., *J. Org. Chem.*, **67**, 4370 (2002); (b) Yamataka, H., Fujimura, N., Kawafuji, Y., and Hanafusa, T., *J. Am. Chem. Soc.*, **109**, 4305 (1987).
- 247 Dudley, G. B., Danishefsky, S. J., and Sukenick, G., *Tetrahedron Lett.*, **43**, 5605 (2002).
- 248 Granander, J., Sott, R., and Hilmersson, G., *Tetrahedron*, **58**, 4717 (2002).
- 249 Agami, C., Comesse, S., and Kadouri-Puchot, C., *J. Org. Chem.*, **67**, 1496 (2002).
- 250 Ivanova, N. M., Markus, V. A., and Muldakhmetov, Z. M., *Izv. Minist. Obrazov. Nauki Respub. Kazakh. Nats. Akad. Nauk Respub. Kazakh.*, **2001**, 63; *Chem. Abs.*, **136**, 216381 (2002).
- 251 Yong, K. H., Taylor, N. J., and Chong, J. M., *Org. Lett.*, **4**, 3553 (2002).
- 252 Kelly, B. G. and Gilheany, D. G., *Tetrahedron Lett.*, **43**, 887 (2002).
- 253 Delas, C., Okamoto, S., and Sato, F., *Tetrahedron Lett.*, **43**, 4373 (2002).
- 254 Kanai, M., *Yakugaku Zasshi*, **121**, 949 (2001); *Chem. Abs.*, **136**, 216291 (2002).
- 255 Bandini, M., Cozzi, P. G., Garelli, A., Melchiorre, P., and Umani-Ronchi, A., *Eur. J. Org. Chem.*, **2002**, 3243.
- 256 Liang, S. and Bu, X. R., *J. Org. Chem.*, **67**, 2702 (2002).
- 257 Belokon, Y. N., Carta, P., Gutnov, A. V., Maleev, V., Moskalenko, M. A., Yashkina, L. V., Ikonnikov, N. S., Voskoboev, N. V., Khrustalev, V. N., and North, M., *Helv. Chim. Acta*, **85**, 3301 (2002).
- 258 Ishai, E., Shamaï, S., and Feit, B.-A., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 434.
- 259 Herrera, A., Martinez-Alvarez, R., Chioua, M., Chioua, R., and Sanchez, A., *Tetrahedron*, **58**, 10053 (2002).
- 260 Lu, W. C., Wong, N. B., and Zhang, R. Q., *Theor. Chem. Acc.*, **107**, 206 (2002); *Chem. Abs.*, **137**, 232220 (2002).
- 261 Appel, M., Blaurock, S., and Berger, S., *Eur. J. Org. Chem.*, **2002**, 1143.
- 262 Dunne, E. C., Coyne, E. J., Crowley, P. B., and Gilheany, D. G., *Tetrahedron Lett.*, **43**, 2449 (2002).
- 263 Huang, Z.-Z., Yu, X.-C., and Huang, X., *Tetrahedron Lett.*, **43**, 6823 (2002).

- 264 Dai, W.-M., Xu, A., and Wu, H., *Tetrahedron: Asymmetry*, **13**, 2187(2002).
- 265 Bedekar, A. V., Watanabe, T., Tanaka, K., and Fuji, K., *Tetrahedron: Asymmetry*, **13**, 721 (2002).
- 266 Huang, Z.-Z. and Tang, Y., *J. Org. Chem.*, **67**, 5320 (2002).
- 267 Huang, Z.-Z., Ye, S., Xia, W., Yu, Y.-H., and Tang, Y., *J. Org. Chem.*, **67**, 3096 (2002).
- 268 Abdou, W. M., Fahmy, A. M. H., and Kamel, A. A. A., *Eur. J. Org. Chem.*, **2002**, 1696.
- 269 Abd, E.-R. N. M. and Boulos, L. S., *Molecules*, **7**, 81 (2002); *Chem. Abs.*, **137**, 216996 (2002).
- 270 Xue, Y., Xie, D., and Yan, G., *J. Phys. Chem. A*, **106**, 9053 (2002).
- 271 van Staden, L. F., Gravestock, D., and Ager, D. J., *Chem. Soc. Rev.*, **31**, 195 (2002).
- 272 Kojima, S., Inai, H., Hidaka, T., Fukuzaki, T., and Ohkata, K., *J. Org. Chem.*, **67**, 4093 (2002).
- 273 Deng, G., Tian, X., Qu, Z., and Wang, J., *Angew. Chem. Int. Ed.*, **41**, 2773 (2002).
- 274 Mloston, G., Prakash, G. K. P., Olah, G. A., and Heimgartner, H., *Helv. Chim. Acta*, **85**, 1644 (2002).
- 275 Paredes, R., Abonia, R., Cadavid, J., Moreno-F., R., Jaramillo, A., Hormaza, A., Ramirez, A., and Kennedy, A., *Tetrahedron*, **58**, 55 (2002).
- 276 List, B., *J. Am. Chem. Soc.*, **124**, 5656 (2002).
- 277 Bolm, C. and Rudolph, J., *J. Am. Chem. Soc.*, **124**, 14850 (2002).
- 278 Manandhar, S., Singh, R. P., and Shreeve, J. M., *Collect. Czech. Chem. Commun.*, **67**, 1296 (2002).
- 279 Mikolajczyk, M., Lyzwa, P., and Drabowicz, J., *Tetrahedron: Asymmetry*, **13**, 2571 (2002).
- 280 Li, B.-F., Zhang, M.-J., Hou, X.-L., and Dai, L.-X., *J. Org. Chem.*, **67**, 2902 (2002).
- 281 Osman, F. H. and El-Samahy, F. A., *Chem. Rev.*, **102**, 629 (2002).
- 282 Shi, M. and Shen, Y.-M., *J. Chem. Res. (S)*, **2002**, 422.
- 283 Kabalka, G. W., Wu, Z., and Ju, W., *Tetrahedron*, **58**, 3243 (2002).
- 284 Petrova, T. D., Platonov, V. E., and Pokrovskii, L. M., *Russ. Chem. Bull. (translation of Izv. Akad. Nauk, Ser. Khim.)*, **51**, 544, (2002); *Chem. Abs.*, **137**, 294581 (2002).
- 285 Aggarwal, V. K., Harvey, J. N., and Richardson, J., *J. Am. Chem. Soc.*, **124**, 5747 (2002).
- 286 Curini, M., Epifano, F., Marcotullio, M. C., and Rosati, O., *Eur. J. Org. Chem.*, **2002**, 1562.
- 287 Nomura, M., Nakata, S., and Hamada, F., *Nippon Kagaku Kaishi*, **45**, 141 (2002); *Chem. Abs.*, **137**, 125065 (2002).
- 288 Talapatra, B., Mandal, S. K., Biswas, K., Chakrabarti, R., and Talapatra, S. K., *J. Indian Chem. Soc.*, **78**, 765 (2001); *Chem. Abs.*, **137**, 201245 (2002).
- 289 Iglesias, E., *New J. Chem.*, **26**, 1352 (2002).
- 290 Fontana, A., De Maria, P., Pierini, M., Siani, G., Cerritelli, S., and Macaluso, G., *J. Phys. Org. Chem.*, **15**, 247 (2002).
- 291 Ivanov, S. P., Konkina, I. G., Gaifutdinova, R. K., and Murinov, Y. I., *Bashkirskii Khim. Zh.*, **7**, 30 (2000); *Chem. Abs.*, **136**, 69513 (2002).
- 292 Friermuth, B., Hellrung, B., Peterli, S., Schultz, M.-F., Wintgens, D., and Wirz, J., *Helv. Chim. Acta*, **84**, 3796 (2001).
- 293 McCann, G. M., and McDonnell, C. M., Magris, L., and More O'Ferrall, R. A., *J. Chem. Soc., Perkin Trans. 2*, **2002**, 784.
- 294 Semioshkin, A. A., Inyushin, S. G., Petrovskii, P. V., and Bregadze, V. I., *Collect. Czech. Chem. Commun.*, **67**, 831 (2002).
- 295 Zimmerman, H. E. and Wang, P., *Org. Lett.*, **4**, 2593 (2002).
- 296 Eberlin, A. and Williams, D. L. H., *J. Chem. Soc., Perkin Trans. 2*, **2002**, 1316.
- 297 Dalton, A. M., Zhang, Y., Davie, C. P., and Danheiser, R. L., *Org. Lett.*, **4**, 2433 (2002).
- 298 Majewski, M. and Wang, F., *Tetrahedron*, **58**, 4567 (2002).
- 299 Ramesh, N. G., Heijne, E. H., Klunder, A. J. H., and Zwanenburg, B., *Tetrahedron*, **58**, 1361 (2002).
- 300 Stavber, S., Jereb, M., and Zupan, M., *Chem. Commun. (Cambridge)*, **2002**, 488.
- 301 Xie, Y. Y., Chen, Z. C., and Zheng, Q. G., *J. Chem. Res. (S)*, **2002**, 618.
- 302 Nabana, T. and Togo, H., *J. Org. Chem.*, **67**, 4362 (2002).
- 303 Van De Water, R. W. and Pettus, T. R. R., *Tetrahedron*, **58**, 5367 (2002).
- 304 Baik, W., Kim, S. J., Hurh, E.-Y., Koo, S., and Kim, B. H., *Bull. Korean Chem. Soc.*, **22**, 1127 (2001); *Chem. Abs.*, **136**, 150805 (2002).
- 305 Chiang, Y., Kresge, A. J., and Zhu, Y., *J. Am. Chem. Soc.*, **124**, 6349 (2002).
- 306 Yadav, V. K. and Balamurugan, R., *J. Org. Chem.*, **67**, 587 (2002).
- 307 Mehta, G., Gagliardini, V., Priyakumar, U. D., and Sastry, G. N., *Tetrahedron Lett.*, **43**, 2487 (2002).
- 308 Di Maio, G., Mascia, M. G., and Vecchi, E., *Tetrahedron*, **58**, 3313 (2002).
- 309 Daley, C. J. A. and Bergens, S. H., *J. Am. Chem. Soc.*, **124**, 3680 (2002).
- 310 Senda, Y., *Chirality*, **14**, 110 (2002); *Chem. Abs.*, **136**, 325065 (2002).

- ³¹¹ Li, M., Xie, R., and Tian A., *Sci. China, Ser. B: Chem.*, **44**, 616 (2001); *Chem. Abs.*, **136**, 278941 (2002).
- ³¹² Delogum G., Fabbri, D., de Candia, C., Patti, A., and Pedotti, S., *Tetrahedron: Asymmetry*, **13**, 891 (2002).
- ³¹³ Teodorovic, A. V., Joksovic, M. D., Gutman, I., and Tomovic, Z., *Monatsh. Chem.*, **133**, 23 (2002).
- ³¹⁴ Nettles, S. M., Matos, K., Burkhardt, E. R., Rouda, D. R., and Corella, J. A., *J. Org. Chem.*, **67**, 2970 (2002).
- ³¹⁵ Ferrand, A., Bruno, M., Tommasino, M. L., and Lemaire, M., *Tetrahedron: Asymmetry*, **13**, 1379 (2002).
- ³¹⁶ Brunner, H., Henning, F., and Weber, M., *Tetrahedron: Asymmetry*, **13**, 37 (2002).
- ³¹⁷ Zhou, Y.-B., Tang, F.-Y., Xu, H.-D., Wu, X.-Y., Ma, J.-A., and Zhou, Q.-L., *Tetrahedron: Asymmetry*, **13**, 469 (2002).
- ³¹⁸ Benedetti, F., Berti, F., Donati, I., and Fregonese, M., *Chem. Commun. (Cambridge)*, **2002**, 828.
- ³¹⁹ Hoffman, R. V., Maslouh, N., and Cervantes-Lee, F., *J. Org. Chem.*, **67**, 1045 (2002).
- ³²⁰ Kamiya, I. and Ogawa, A., *Tetrahedron Lett.*, **43**, 1701 (2002).
- ³²¹ Zhang, H.-L., Zhang, X.-M., Gong, L.-Z., Mi, A.-Q., Cui, X., Jiang, Y.-Z., Choi, M. C. K., and Chan, A. S. C., *Org. Lett.*, **4**, 1263 (2002).
- ³²² Prasad, E. and Flowers, R. A., *J. Am. Chem. Soc.*, **124**, 6357 (2002).
- ³²³ Prasad, E. and Flowers, R. A., *J. Am. Chem. Soc.*, **124**, 6895 (2002).
- ³²⁴ Dahlen, A. and Hilmersson, G., *Tetrahedron Lett.*, **43**, 7197 (2002).
- ³²⁵ (a) Walling, C. and Bollyky, L., *J. Am. Chem. Soc.*, **83**, 2968 (1961); **86**, 3750 (1964); (b) Berkessel, A., Schubert, T. J. S., and Muller, T. M., *J. Am. Chem. Soc.*, **124**, 8693 (2002).
- ³²⁶ Clerici, A., Pastori, N., and Porta, O., *Eur. J. Org. Chem.*, **2002**, 3326.
- ³²⁷ Minisci, F., Punta, C., Recupero, F., Fontana, F., and Pedulli, G. F., *Chem. Commun. (Cambridge)*, **2002**, 688.
- ³²⁸ Bolm, C., Palazzi, C., Francio and Leitner, W., *Chem. Commun. (Cambridge)*, **2002**, 1588.
- ³²⁹ Watanabe, A., Uchida, T., Ito, K., and Katsuki, T., *Tetrahedron Lett.*, **43**, 4481 (2002).
- ³³⁰ Yakura, T., Kitano, T., Ikeda, M., and Uenishi, J., *Tetrahedron Lett.*, **43**, 6925 (2002).
- ³³¹ Singh, K., Tripathi, H., Awasthi, A., and Srivastava, Sh., *Oxid. Commun.*, **24**, 388 (2001); *Chem. Abs.*, **136**, 69531 (2002).
- ³³² Lyngdoh, C. B., Das, S., and Mahanti, M. K., *Oxid. Commun.*, **24**, 382 (2001); *Chem. Abs.*, **136**, 69530 (2002).
- ³³³ Chaubey, G. S., Das, S., and Mahanti, M. K., *Bull. Chem. Soc. Jpn.*, **75**, 2215 (2002).
- ³³⁴ Kharnaor, G. G., Chaubey, G. S., and Mahanti, M. K., *Oxid. Commun.*, **21**, 377 (2001); *Chem. Abs.*, **136**, 37217 (2002).
- ³³⁵ Sekar, K. G. and Ravinashar, M., *Oxid. Commun.*, **24**, 368 (2001); *Chem. Abs.*, **136**, 37215 (2002).
- ³³⁶ Sekar, K. G., Ramkumar, B., and Rajaji, R., *Oxid. Commun.*, **24**, 364 (2001); *Chem. Abs.*, **136**, 37214 (2002).
- ³³⁷ Mehla, S. K., Kothari, S., and Banerji, K. K., *Indian J. Chem., Sect. B*, **41**, 832 (2002); *Chem. Abs.*, **137**, 169143 (2002).
- ³³⁸ Rahiman, K. K. A. and Nair, T. D. K., *Asian J. Chem.* **14**, 898 (2002); *Chem. Abs.*, **137**, 154620 (2002).
- ³³⁹ Muresanu, C., Baldea, I., and Budusan, A.-M., *Stud. Univ. Babeş-Bolyai, Chem.*, **43**, 161 (1998); *Chem. Abs.*, **136**, 294434 (2002).
- ³⁴⁰ Sekar, K. G., *J. Chem. Res. (S)*, **2002**, 626.
- ³⁴¹ Juhasz, L., Szilagy, L., Antus, S., Visy, J., Zsila, K., and Simonyi, M., *Tetrahedron*, **58**, 4261 (2002).
- ³⁴² Horstman, J. A., Wrona, M. Z., and Dryhurst, G., *Bioorg. Chem.*, **30**, 371 (2002).
- ³⁴³ Xu, J. and Jiao, P., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1491.
- ³⁴⁴ Aggarwal, V. K., Coogan, M. P., Stenson, R. A., Jones, R. V. H., Fieldhouse, R., and Blacker, J., *Eur. J. Org. Chem.*, **2002**, 319.
- ³⁴⁵ Radhasyam, P. and Chakrapani, P., *Bull. Korean Chem. Soc.*, **22**, 909 (2001); *Chem. Abs.*, **136**, 5640 (2002).
- ³⁴⁶ Bjorsvik, H.-R., Liguori, L., Gonzalez, R. R., and Merinero, J. A. V., *Tetrahedron Lett.*, **43**, 4985 (2002).
- ³⁴⁷ Zhang, N. and Vozzolo, J., *J. Org. Chem.*, **67**, 1703 (2002).
- ³⁴⁸ Nambu, H., Hata, K., Matsugi, M., and Kita, Y., *Chem. Commun. (Cambridge)*, **2002**, 1082.
- ³⁴⁹ Wang, Y.-c., Geng, Z.-y., and Chen, H.-s., *Wuli Huaxue Xuebao*, **18**, 45 (2002); *Chem. Abs.*, **136**, 309556 (2002).

- ³⁵⁰ Nazarov, A. M., Khursan, S. L., Chainikova, E. M., and Komissarov, V. D., *Russ. Chem. Bull.* (translation of *Izv. Akad. Nauk, Ser. Khim.*), **51**, 608 (2002); *Chem. Abs.*, **137**, 278885 (2002).
- ³⁵¹ Vandenberk, S., Vereecken, L., and Peeters, J., *Phys. Chem. Chem. Phys.*, **4**, 461 (2002).
- ³⁵² Tyndall, G. S., Orlando, J. J., Wallington, T. J., Hurley, M. D., Goto, M., and Kawasaki, M., *Phys. Chem. Chem. Phys.*, **4**, 2189 (2002).
- ³⁵³ Cameron, M., Sivakumaran, V., Dillon, T. J., and Crowley, J. N., *Phys. Chem. Chem. Phys.*, **4**, 3628 (2002).
- ³⁵⁴ Nolan, S., Treacy, J., and Sidebottom, H., *Transport and Chemical Transformation in the Troposphere, Proceedings of EUROTRAC Symposium, 6th, Garmisch-Partenkirchen, Germany, 27–31, March 2000*, 2001, 422; (publ. 2001), eds. Midgley, P., Reuther, M., and Williams, M., Springer-Verlag, Berlin, *Chem. Abs.*, **136**, 118156 (2002).
- ³⁵⁵ Thiault, G., Mellouki, A., and Le Bras, G., *Phys. Chem. Chem. Phys.*, **4**, 2194 (2002).
- ³⁵⁶ Mora-Diez, N. and Boyd, R. J., *J. Phys. Chem. A*, **106**, 384 (2002).
- ³⁵⁷ Hippler, H. and Viskolcz, B., *Phys. Chem. Chem. Phys.*, **4**, 4663 (2002).
- ³⁵⁸ Nugent, W. A., *Org. Lett.*, **4**, 1619 (2002).
- ³⁵⁹ Rosenberg, M. G., Haslinger, U., and Brinker, U. H., *J. Org. Chem.*, **67**, 450 (2002).
- ³⁶⁰ Chen, L., Zhang, X., and Schultz, A., *Tetrahedron Lett.*, **43**, 4711 (2002).
- ³⁶¹ Matsubara, S., Ukai, K., Fushimi, H., Yokota, Y., Yoshino, H., Oshima, K., Omoto, K., Ogawa, A., Hioki, Y., and Fujimoto, H., *Tetrahedron*, **58**, 8255 (2002).
- ³⁶² France, S., Wack, H., Hafez, A. M., Taggi, A. E., Witsil, D. R., and Lectka, T., *Org. Lett.*, **4**, 1595 (2002).
- ³⁶³ Svetlik, J. and Sallai, L., *J. Heterocycl. Chem.*, **39**, 363 (2002).
- ³⁶⁴ Yadav, J. S., Reddy, B. V. S., Aruna, M., Venugopal, C., Ramalingam, T., Kumar, S. K., and Kunwar, A. C., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 165.
- ³⁶⁵ Morrison, B. J. and Musgrave, O. C., *Tetrahedron*, **58**, 4255 (2002).
- ³⁶⁶ Herrera, A., Martinez-Alvarez, R., Ramiro, P., Chioua, M., and Torres, R., *Tetrahedron*, **58**, 3755 (2002).
- ³⁶⁷ Yavari, I., Anary-Abbasinejad, M., and Alizadeh, A., *Monatsh. Chem.*, **133**, 1221 (2002).
- ³⁶⁸ Ziegler, G., Haug, E., Frey, W., and Kantlehner, W., *Z. Naturforsch., Teil B* **56**, 1178 (2001); *Chem. Abs.*, **136**, 294606 (2002).
- ³⁶⁹ Asao, N., Ohishi, T., Sato, K., and Yamamoto, Y., *Tetrahedron*, **58**, 8195 (2002).
- ³⁷⁰ Morrison, B. J. and Musgrave, O. C., *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1944.