
1

STRUCTURE AND REACTIVITY OF THE CYCLOPROPANE SPECIES

Numerous theoretical and experimental studies on cyclopropane compounds allow many of the specific properties of these substances to be elucidated, to synthesize a large number of their individual representatives, and to perform further conversion to other types of organic compounds. Consideration of the original publications on the studies of the structure and other physical and chemical properties of cyclopropane compounds and their reactive intermediates is beyond the scope of this chapter. However, references on the selected reviews of such publications together with a short synopsis from these reviews are provided instead.

1.1 GEOMETRY AND BONDING

Reviews: general [1–4]; theoretical models of bonding [3,5–8]; conjugative and substituent properties [7,9–13].

Synopsis. The C–C and C–H bonds in cyclopropane are shorter than in ethane (Figure 1).

The Coulson-Moffitt and Walsh theoretical models are usually used to describe the bonding in cyclopropane molecules. The Coulson-Moffitt model suggests the change in hybridization of the carbon orbitals toward increasing p-character of the C–C bonds resulted in a minimization of the difference between the conventional interorbital angles and the cyclopropane bond angles. This leads to the concept of bent C–C bonds and the formation of C–H orbitals which are relatively rich in s-character of the carbon atom. X-ray crystallographic data of cyclopropane derivatives agree with the deformation density of the C–C bond outside the triangle which includes the three carbons of the cyclopropane ring (Figure 2).

The Walsh model for cyclopropane also suggests the increased s-character of the C–H bonds are formed by sp^2 orbitals of the carbon atoms. The remaining carbon sp^2 orbitals are directed towards the center of the ring to form one bonding and two antibonding molecular orbitals. In turn, the overlap of p orbitals, which are in the plane of the cyclopropane ring, results in the formation of two C–C bonding and one antibonding bent interactions (Figure 2). The Walsh

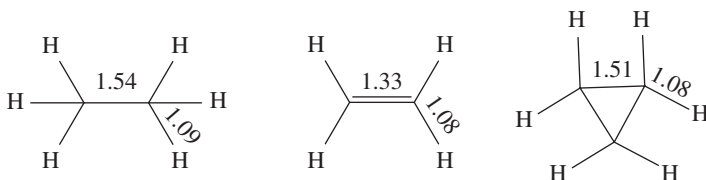


FIGURE 1. The bond lengths in ethane, ethylene, and cyclopropane (Å) (from left to right)

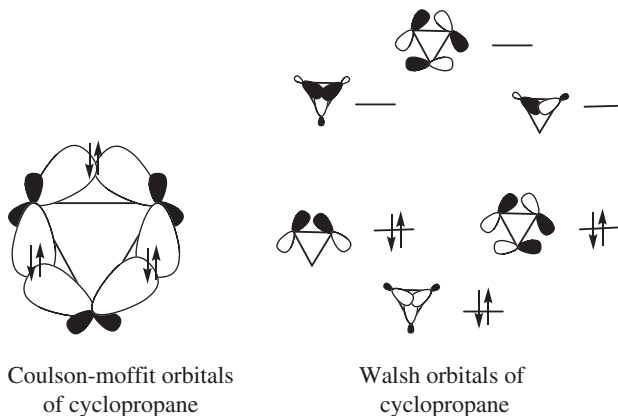


FIGURE 2. The Coulson-Moffit and Walsh theoretical models for a cyclopropane molecule

model more clearly describes the effect of substituents on the structure and conformational properties of functionally substituted cyclopropanes.

The conjugation of the cyclopropyl group with a carbonyl and other π -acceptor substituents in the preferred bisected conformation results in a lengthening of the adjacent bonds and in a shortening of the distal cyclopropane C—C bond. The influence of p-donating heteroatom substituents on the geometry of the cyclopropane ring is not so definite and it is likely that inductive effects of the heteroatom interfere with p-conjugation in these cases. For cyclopropanes bearing p-donor and π -acceptor substituents in vicinal positions, a lengthening of the C—C bond adjacent to both substituents takes place.

1.2 ENERGY

Reviews: general [3,7,14–17]; effect of the strain upon reactivity [5,6,18].

Synopsis. The ring cleavage reactions in cyclopropane compounds proceed in milder conditions than the corresponding cleavage reactions of ordinary C—C bonds in other carbocyclic compounds and this difference is attributed to lower strength of the bent bond and to some other electron factors, which collectively are reflected in strain energy. Its amount is calculated as the difference between the observed heat of formation of the cyclopropane and that estimated for a strain-free model. Taking the experimental heat of formation of cyclohexane as -29.4 kcal/mol and that of cyclopropane as $+12.7$ kcal/mol allow the strain energy of cyclopropane to be estimated as $(12.7 + 29.4:2)$ kcal/mol = 27.4 kcal/mol (Figure 3).

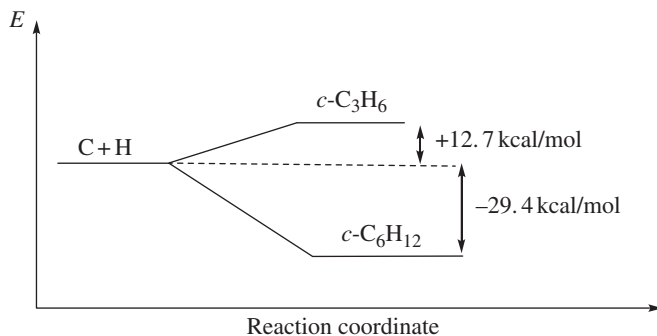


FIGURE 3. Strain energy of cyclopropane

1.3 SPECTRA

Reviews: NMR spectra [19,20]; vibrational and ultraviolet spectra [7,20]; photoelectron spectra [21–23]; chiroptical spectra [24].

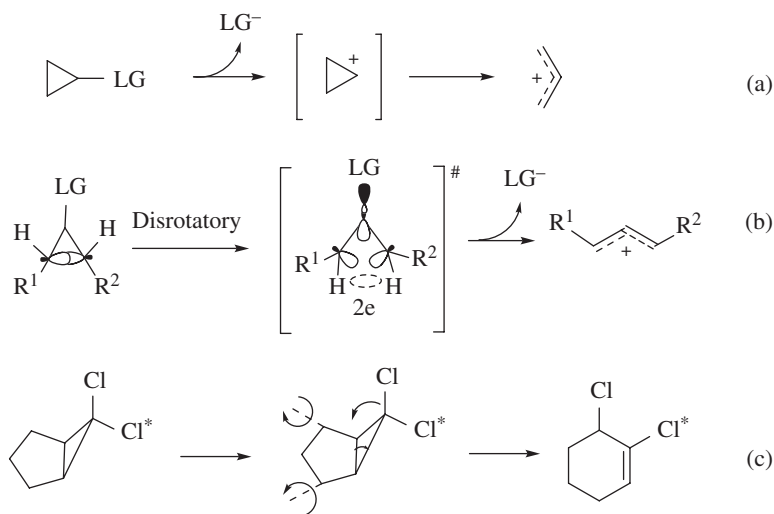
Synopsis. NMR spectra of cyclopropanes have remarkable upfield chemical shifts in comparison with homologues with larger ring size. Thus, the ¹H NMR chemical shift of cyclopropane (δ 0.22) is shifted upfield considerably with respect to cyclohexane (δ 1.43), and the ¹³C chemical shift for cyclopropane (δ -2.8) is also shifted upfield with respect to cyclohexane (δ 27.0) (Figure 4). The shielding of the protons is conventionally attributed to the magnetic induction of the aromatic-like ring current in cyclopropane, involving six electrons in the three C–C bonds. The opposite direction of the ¹H NMR shift for benzene to down field in comparison with the upper field cyclopropane shift is attributed to the different geometrical disposition of the hydrogens toward the rings. The lowered chemical shifts of the cyclopropane signals in ¹H NMR spectra considerably facilitates identification and structural determination of cyclopropane containing compounds.

Vibrational and electronic spectra of cyclopropanes are usually less informative for synthetic organic chemists than NMR spectra, however their use could be also valuable for experimental and theoretical studies. The absorptions in the region of 1020 and 865 cm⁻¹ are typical for the cyclopropane ring, and the first band is assigned to a symmetric vibration of the cyclopropane ring. The cyclopropane C–H stretching absorption lies in the range 3000–3100 cm⁻¹. The absorption bands in the ultraviolet spectra which correspond to the σ – σ^* transition from occupied and unoccupied orbitals in cyclopropane are observed in a non-characteristic area below 210 nm.

1.4 CYCLOPROPYL CATIONS

Reviews: general [10,25]; cyclopropyl cations [26]; cyclopropyl to allyl rearrangements [27–29]; protonated cyclopropanes [30,31]; cyclopropyl cation radicals [32–36].

Synopsis. The generation of cyclopropyl cations is usually accompanied by cleavage of the opposite C–C bond affording allyl cations (Scheme 1a). This cationic cyclopropyl–allyl rearrangement proceeds in a concerted disrotatory fashion in agreement with the Woodward–Hoffman principle of the conservation of orbital symmetry. Of the two possible directions of disrotatory rotation, one of them is more favorable, namely if ionization and ring opening occur synchronously. The reason for this can be best understood by the better overlap of the bonding orbital of the breaking C–C bond with the antibonding orbital of the breaking orbital of the leaving group through a two-electron cyclic aromatic transition state (Scheme 1b).



SCHEME 1. Disrotatory isomerization of cyclopropyl cations to allyl cations




| |  |  |  |
|-------------------------------------|---|---|---|
| $^1\text{H NMR}$ (δ ppm) | 0.22 | 1.43 | 7.36 |
| $^{13}\text{C NMR}$ (δ ppm) | -2.8 | 27.0 | 128.5 |
| IR (ν cm^{-1}) | 3000–3100 | 2600–2700 | 3100–3200 |
| UV (λ nm) | <210 | <210 | <250 |

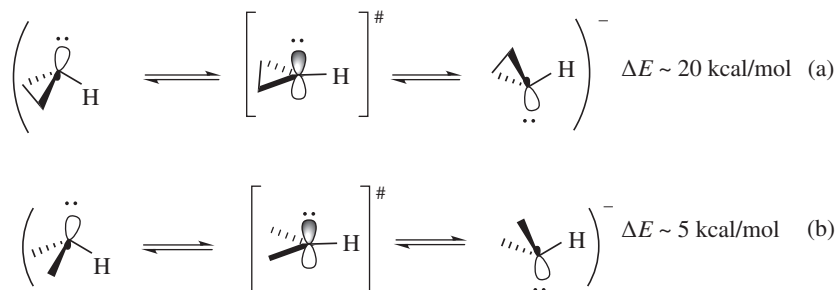
FIGURE 4. Characteristic spectral bands of cyclopropane, cyclohexane, and benzene (from left to right)

If two leaving groups are present in the molecule, for example at cyclopropyl–allyl isomerization of gem-dihalocyclopropanes, the ionization is usually initiated by the leaving group which leads to the formation of the less hindered allylic cation (Scheme 1c). The cationic cyclopropyl–allyl isomerization may be prevented by the presence in the cyclopropane ring in α -position to the leaving group of a strong p-electron donor substituent, for example an alkoxide group.

1.5 CYCLOPROPYL ANIONS

Reviews: general [10,25]; basicity [30]; organometallic derivatives [37–41]; anion radicals [32,35].

Synopsis. Cyclopropane is relatively more acidic than other saturated cycloalkanes with larger ring size and is estimated to have a pK_a of about 50. At the same time cyclopropanes bearing π -acceptor substituents appear to have diminished acidity relative to the corresponding



SCHEME 2. Inversion configuration of (a) the cyclopropyl anion and (b) the 2-isopropyl anion

isopropyl analogs because planarization of the carbanionic center increases bond angle distortion thus resulting in greater internal strain (I-strain). Theoretical calculations predict essentially the same geometry for cyclopropane and the cyclopropyl anion. For the same reason, the barrier for inversion of the cyclopropyl anion estimated to be near 20 kcal/mol is much higher than the barrier for inversion of open chain carbanions (~5 kcal/mol) (Scheme 2). The higher configurational stability of the cyclopropyl anion system allows a configurationally stable cyclopropyl carbanionic species to be generated at lowered or ordinary temperatures. Such species also have a low reactivity to isomerization to the corresponding allyl anions, with the exception of those products which are strongly stabilized by π -acceptor substituents.

1.6 CYCLOPROPYL RADICALS

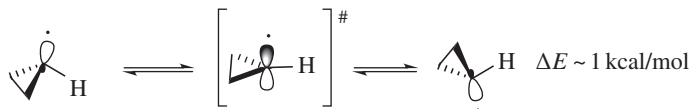
Reviews: general [10,25]; special [42]; ion radicals [32–35].

Synopsis. The cyclopropyl radical, as well as the cyclopropyl anion, exists as a pyramidal species, however its configuration inversion proceeds considerably faster. For unconstrained cyclopropyl radicals the inversion proceeds rapidly ($k_1 \sim 10^8 \text{ s}^{-1}$, $\Delta E^\ddagger \sim 1 \text{ kcal/mol}$) through a plane p-centered radical transition state configuration that creates difficulties for performing radical substitution reactions (e.g., Hunsdiecker reaction) at the cyclopropane ring with maintaining or inversion configuration of a chiral center (Scheme 3). Electronegative heteroatom substituents (F, Cl, alkoxy group) at the α -position of the radical center sufficiently increase the configurational stability of the cyclopropyl radicals. The rearrangement of the cyclopropyl radicals to the corresponding allyl radicals occurs when a highly delocalized radical intermediate is formed and these reactions, as well as in the anionic cyclopropyl–allyl rearrangements, have no high synthetic importance. Notably, the gas-phase chemistry of the cyclopropyl cation radicals generated in a mass spectrometer, by radiolysis or other methods, sufficiently differs from the chemistry of cyclopropyl cations and cyclopropyl radicals.

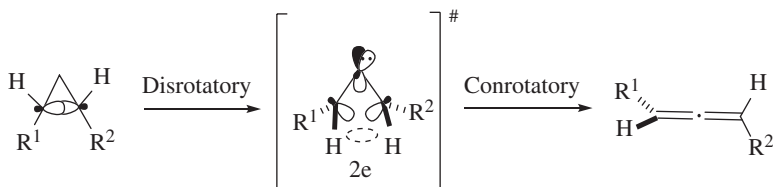
1.7 CYCLOPROPYLIDENES

Reviews: general [10–25]; special [43].

Synopsis. Cyclopropyl carbene, or cyclopropylidene transforms to allene at low temperatures spontaneously via cleavage of the C–C bond distal to the carbenic center. *Ab initio* calculations provide evidence for cyclopropylidene in a singlet ground state, and various mechanisms were proposed for cyclopropylidene–allene isomerization. It is conventional that in the initial stages the



SCHEME 3. Inversion configuration of the cyclopropyl radical



SCHEME 4. Disrotatory–conrotatory isomerization of cyclopropylidenes to allenes

disrotatory cleavage of the C–C bond takes place, probably due to operation of the driving forces which promote a disrotatory ring cleavage in the isoelectronic cyclopropyl cation in accordance with the Woodward–Hoffmann rules (Scheme 4). At the same time the ring opening of cyclopropylidene involves four electrons and the disrotatory motion to be interrupted to afford the overall conrotatory motion affording allenes in a stereoselective or nonstereoselective manner. Thus, the rearrangement of *cis*-2,3-dimethylcyclopropylidene is nonstereoselective whereas that for the *trans* isomer is highly stereoselective. Steric effects and other factors can play an important role in determining the stereochemical result.

1.8 CYCLOPROPYLCARBINYL CATIONS

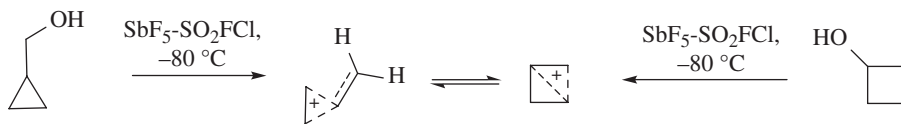
Reviews: general [10,25,28]; special [44–48]; cation radicals [35].

Synopsis. The study of cyclopropylcarbinyl cations using various techniques, including highly informative low-temperature NMR spectroscopy, has a rich history which about 50 years ago led to proposals for the existence of these species as an equilibrated mixture of the delocalized bisected cyclopropylcarbinyl cation and nonclassical bicyclobutonium ion. This model still remains a topic for discussion and development, centered on the structure and relative energies of the rapidly equilibrating carbenium ions. The most important features of the cyclopropylcarbinyl cations for synthetic organic chemists are their easy generation due to a high internal stabilization, as well as their ability for selective conversion in reactions with nucleophiles to synthetically valued homoallyl and cyclobutane derivatives. Notably, comparative NMR studies of the protonated cyclopropyl carbinols and cyclopropyl ketones show in the latter species much smaller delocalization of the cationic charge at the cyclopropane ring, as indicated by the mainly double bond character of the carbonyl group (Scheme 5).

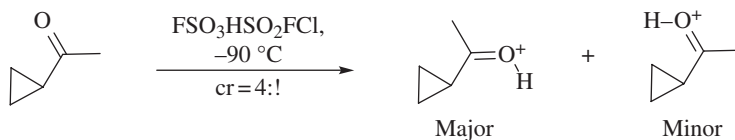
1.9 CYCLOPROPYLCARBINYL ANIONS

Reviews: general [10,25]; organometallic derivatives [37]; homoenolate anions [49–51]; anion radicals [35].

Synopsis. Cyclopropylcarbinyl anions have a tendency to undergo cyclopropane ring opening giving the but-3-enyl anions (Scheme 6a). In contrast to the easy formation of cyclopropylcarbinyl

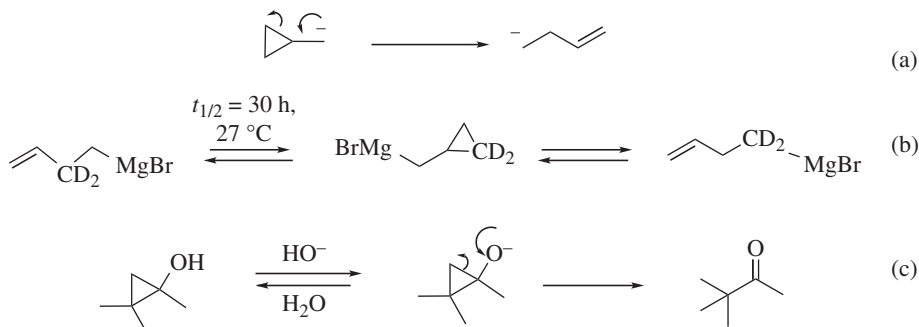


^{13}C NMR (δ ppm): 55.2, 108.4



^{13}C NMR (δ ppm) major conformer: 29.75, 30.75

SCHEME 5. Structure and NMR data of cyclopropylmethyl cations



SCHEME 6. Anionic cyclopropylcarbinyl-homoallyl rearrangement

cations in solvolytic conditions, the generation of cyclopropylcarbinyl anions by deprotonation does not exhibit large kinetic effects of the cyclopropyl group. Rate data for base-catalyzed hydrogen exchange in benzylcyclopropane and related compounds suggest that cyclopropyl exerts only a weak stabilizing effect on an adjacent carbanion, much smaller than the effects of vinyl or phenyl groups. At the same time the cyclopropylmethyl anion is 5–15 kcal/mol more stable than primary and secondary alkyl anions. Anionic cyclopropylcarbinyl-homoallyl rearrangement impedes the preparation and synthetic applications of cyclopropylcarbinyl organometallic compounds which are usually transformed in the reaction conditions to the corresponding homoallyl derivatives. In turn, isotopic labeling experiments demonstrate that the α - and β -carbon atoms of 3-butenyl magnesium bromide interchange their positions presumably via reverse formation of the cyclopropylmethyl magnesium bromide (Scheme 6b). Heteroatom substituted cyclopropanes are also involved in isoelectronic cyclopropylcarbinyl-homoallyl rearrangement. For example, the base-catalyzed cyclopropane ring cleavage in cyclopropanols leading to the corresponding carbonyl compounds proceeds at a rate several orders faster than for the cleavage of cyclobutanols (Scheme 6c).

1.10 CYCLOPROPYLCARBINYL RADICALS

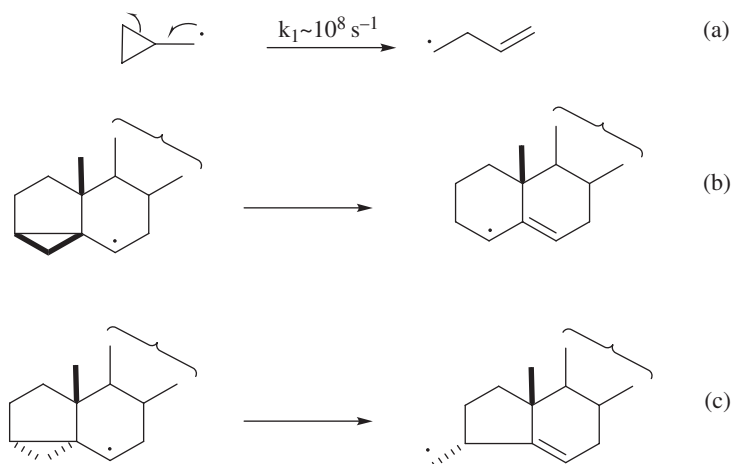
Reviews: general [10,25,36]; special [52–56]; ion radicals [33,34].

Synopsis. The cyclopropylmethyl radical rapidly rearranges at ordinary temperature to the but-3-enyl radical with a rate constant $\sim 10^8 \text{ s}^{-1}$ (Scheme 7a). A strong dependence of the rate constants on the substituents in easily available cyclopropylcarbinyl radical precursor substituents led to widespread use of these compounds as “radical clocks” for studies of organic and bioorganic reaction mechanisms. Spectral data evidence shows that the preferred conformation of the cyclopropylmethyl radicals is bisected, however in contrast to the rearrangements of cyclopropylcarbinyl cations, cyclopropylmethyl radicals have no tendency to rearrange in the cyclobutane derivatives. The regioselectivity of the ring opening of conformationally labile systems usually corresponds to the formation of the more stabilized butenyl radicals, or depends on kinetic effects connected to the reversibility of the rearrangement. For bicyclic cyclopropylcarbinyl radicals regioselectivity of the ring opening may also be determined by stereoelectronic factors or relief of internal strain (Scheme 7b and c). Cyclopropylcarbinyl radicals generated by one-electron reduction of the cyclopropylcarbinyl compounds, or the related isoelectronic species by one-electron oxidation of hetero-substituted cyclopropanes, are also readily involved in the rearrangement affording synthetically value functionalized olefins.

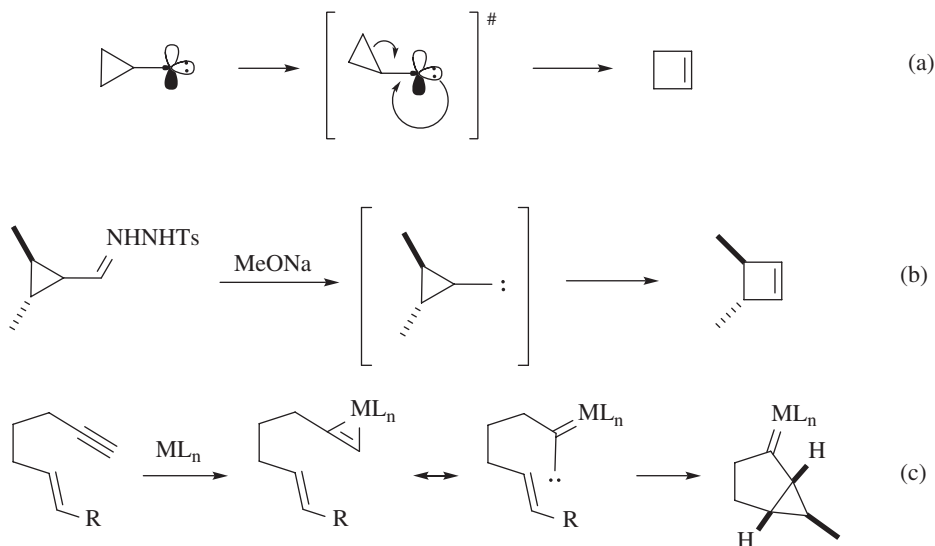
1.11 CYCLOPROPYLCARBENES

Reviews: general [10,25,37]; complexes with transition metals [57–59].

Synopsis. Singlet cyclopropylcarbene undergoes a ring enlargement reaction to cyclobutenes spontaneously (Scheme 8a) and disproportionates in a minor side reaction to ethylene and acetylene. The ring expansion reactions of substituted cyclopropylcarbenes often



SCHEME 7. Radical cyclopropylcarbinyl–homoallyl rearrangement



SCHEME 8. Rearrangement of cyclopropyl carbenes to cyclobutenes and intramolecular formation of metal cyclopropyl carbenes from enines


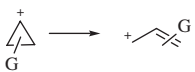

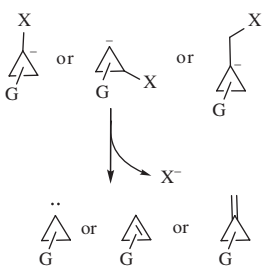

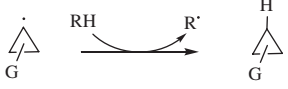

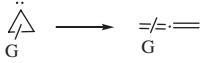

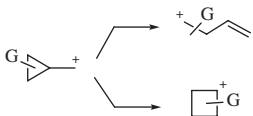

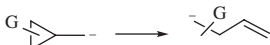

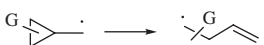

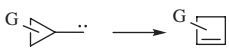
proceed with high regio- and stereoselectivity and are used for the synthesis of cyclobutenes (Scheme 8b). The theoretical calculations predict the preference of a bisected conformation for the ground singlet state, which changed on completion of the rearrangement via 1,2-sigmatropic shift of the proximal cyclopropane C—C bond to the carbene carbon. The reaction includes an electrophilic phase when the ordinary C—C bond is formed with participation of the empty p atomic orbital and a nucleophilic phase for the formation of the olefin bond.

Nowadays, considerable development has led to understanding the chemistry of easily available cyclopropylcarbene-metal complexes (Scheme 8c) which in addition to rearrangement into cyclobutane derivatives can be involved in various other synthetically useful reactions.

1.12 CONCLUSION

Specific properties of cyclopropane compounds, as well as cyclopropyl and cyclopropylcarbinyl reactive species, often determine the results of the transformations of functionally substituted cyclopropanes on treatment with various reagents. Table 1 summarizes the data on the stability of cyclopropyl and cyclopropylcarbinyl cations, anions, radicals, and carbenes in the temperature ranges commonly used in organic synthesis, as well as examples of their most synthetically useful transformations. The knowledge of the properties of these species greatly facilitates the understanding of the reaction mechanisms of functionally substituted cyclopropanes and facilitates the planning of the target-directed synthesis of organic compound by using the versatility of the regio- and stereoselective ring cleavage reactions of suitable cyclopropane synthetic intermediates.

TABLE 1. Properties of the Cyclopropane Reactive Intermediates

| Reactive intermediate | Stability at temperatures commonly used for synthetic transformations | Synthetically useful transformation |
|--|---|---|
|  Cyclopropyl cations | Usually unstable |  Disrotatory cyclopropyl–allyl isomerization |
|  Cyclopropyl anions | Usually stable |  α - and β -Elimination |
|  Cyclopropyl radicals | Stable (configurationally unstable) |  Abstraction of the hydrogen or halogen atom |
|  Cyclopropylidenes | Unstable |  Cyclopropylidene–allyne isomerization |
|  Cyclopropylmethyl cations | Usually unstable |  Cationic cyclopropylcarbinyl–homoallyl and cyclopropylcarbinyl–homoallyl isomerization |
|  Cyclopropylmethyl anions | Unstable |  Anionic cyclopropylcarbinyl–homoallyl isomerization |
|  Cyclopropylmethyl radicals | Very unstable |  Radical cyclopropylcarbinyl–homoallyl isomerization (radical clocks) |
|  Cyclopropyl carbenes | Unstable |  Cyclopropyl carbene–cyclobutene isomerization |

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