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(12) Typical reaction quantities: 35.0 mmol of **17**; 1.36 mmol of Fe; 0.173 mmol of products, which were separated by preparative GLC. **19** is a known compound[13] and was identified by comparison to an authentic sample; the 200-MHz $^1$H NMR and 50.32-MHz $^{13}$C NMR spectra of **18**, which is a new compound, were virtual superpositions of those of **19** and 1,1′-dibutylferrocene.[11b] The latter could not be detected in the reaction mixture, either before or after hydrogenation.[10]

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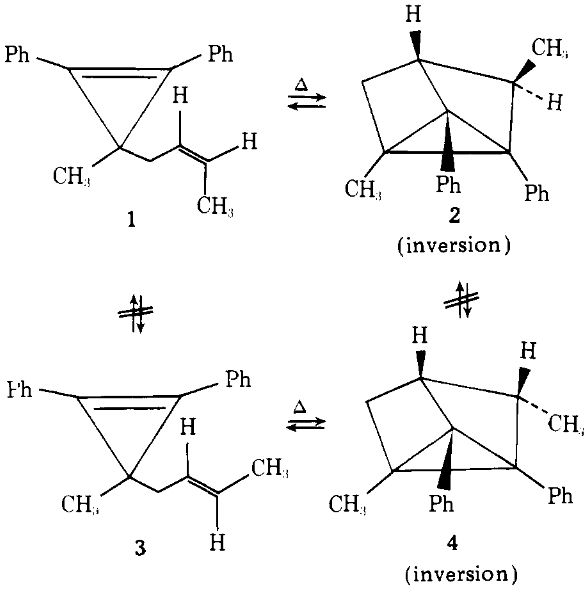
## On the Stereochemical Course of the Thermal and Photosensitized Intramolecular [2 + 2] Cycloaddition Reaction of Allyl-Substituted Cyclopropenes[1]

*Sir:*

Cycloaddition of two olefins and its reverse, cycloreversion or the cleavage of cyclobutane, have been the object of extensive theoretical[2] and experimental studies.[3] Thermal [2 + 2] cycloaddition reactions of olefins can be symmetry allowed and therefore concerted if the $[_\pi2_s + _\pi2_a]$ combination mode is followed. To our knowledge, no authenticated examples of this phenomenon have been reported to date with simple $\pi$ systems.[4,5] Presumably this is because steric hindrance and angle strain factors generally develop to rather prohibitive levels as the two $\pi$ bonds attempt to attain the requisite orthogonality. Related studies dealing with the pyrolysis of stereochemically labeled alkylcyclobutanes have disclosed that antarafacial motion by at least one of the developing olefinic moieties is not readily achieved.[6] As a result, little stereoselectivity has been observed. In this communication we wish to describe the stereochemical course of the thermal and photosensitized intramolecular [2 + 2] cycloaddition reactions of a number of allyl-substituted cyclopropenes. Although the results obtained are compatible with orbital symmetry predictions,[2] the cycloaddition reactions actually proceed via a diradical intermediate.

Thermolysis of (*Z*)-1,2-diphenyl-3-methyl-3-(2-butenyl)-cyclopropene (**1**) at 190 °C for 48 h produced an equilibrium mixture of recovered starting material (55%) and *exo*-3,6-dimethyl-1,2-diphenyltricyclo[2.2.0.0$^{2,6}$]hexane (**2**) (45%). The same distribution of products was obtained by heating tricyclohexane **2** at 190 °C for 48 h. The thermal cycloaddition reaction of the isomeric *E*-substituted cyclopropene **3** was also investigated.[7] Heating a sample of cyclopropene **3** under similar conditions afforded an equilibrium mixture of recovered starting material (80%) and *endo*-tricyclohexane **4** (20%). Appropriate control experiments established that no cis–trans isomerization of either the starting materials or the products was operative under the reaction conditions.



The thermal chemistry of the closely related (*Z*)- (**5**) and (*E*)-1,3-diphenyl-2-methyl-3-(2-butenyl)cyclopropenes (**6**) were also studied so as to provide additional documentation for the stereochemical course of the cycloaddition reaction. Thermolysis of cyclopropene **5** at 175 °C for 12 h afforded a mixture of *exo*-tricyclohexane **7** (16%) and cyclopropene **8** (11%).[8] Subjection of **6** to similar thermolysis conditions produced a 2:1 mixture of *endo*-tricyclohexane **9** and cyclopropene **8**. The structures of the *endo*- and *exo*-methyl-substituted tricyclohexanes were easily assigned on the basis of their characteristic 270-MHz NMR spectra. The absence of coupling between $H_3$ and $H_4$ with tricyclohexanes **2** and **7** fixes the $C_3$-methyl group in the exo position. This is to be expected since molecular models show that the dihedral angle for this set of protons is ~90°. Spin-decoupling experiments indicate that protons $H_3$ and $H_4$ in the endo-substituted series (**4** and **9**) are coupled by 4.5 Hz.[9]

The striking feature of these results is that the intramolecular thermal cycloaddition reaction proceeds with total inversion of stereochemistry about the olefinic $\pi$ bond. A mechanism which is consonant with all the available data is

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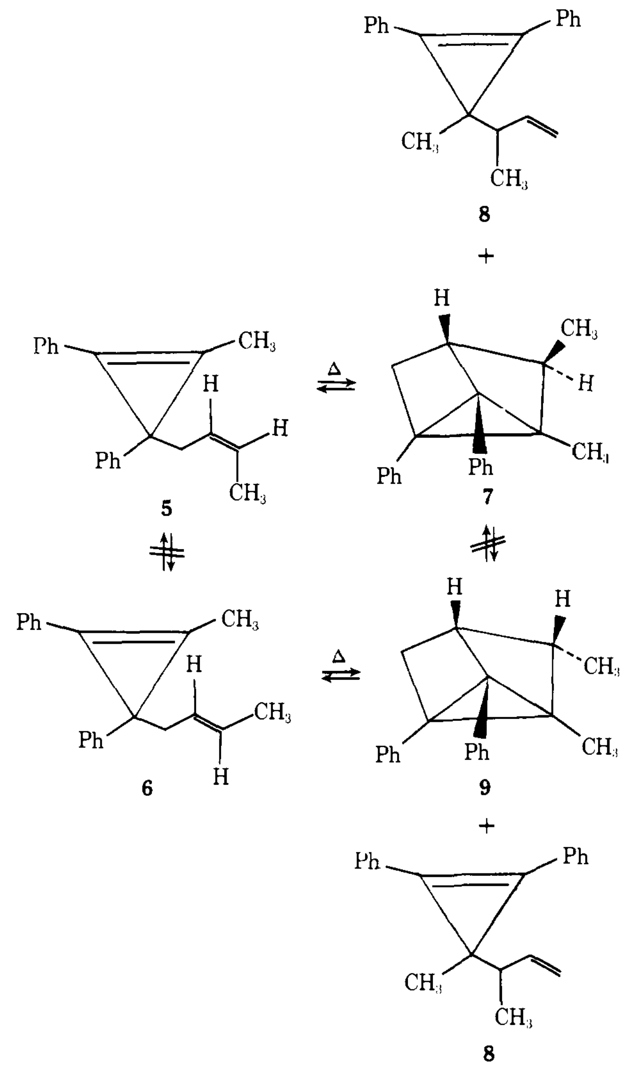
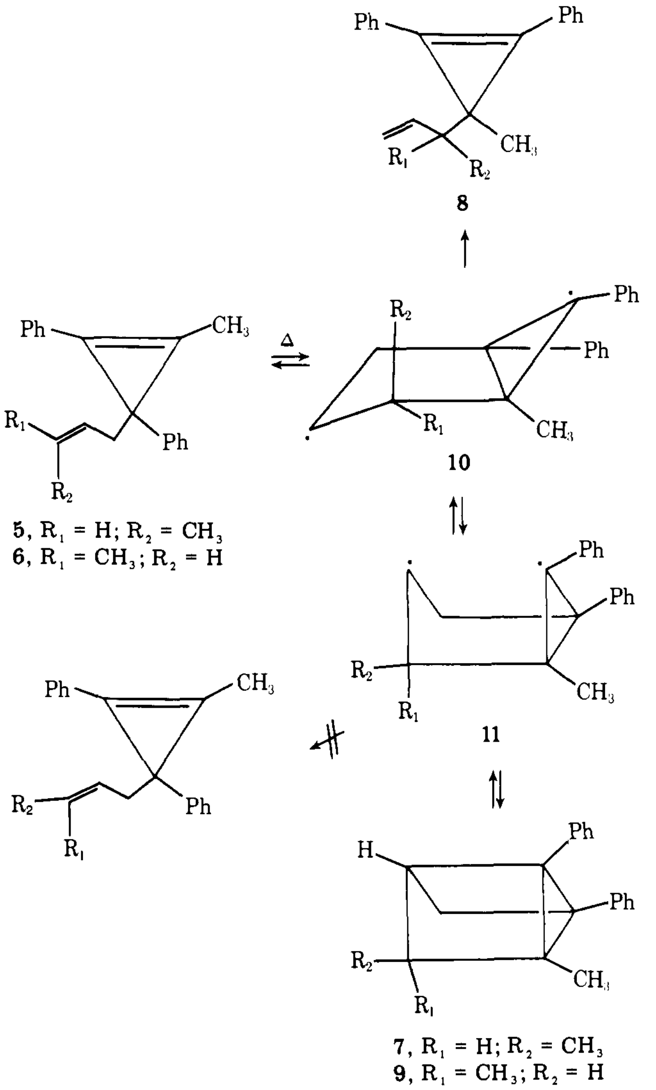


**8** + **5** ⇌ **7**; **6** ⇌ **9** + **8**



**5**, $R_1$ = H; $R_2$ = $CH_3$
**6**, $R_1$ = $CH_3$; $R_2$ = H

**8**

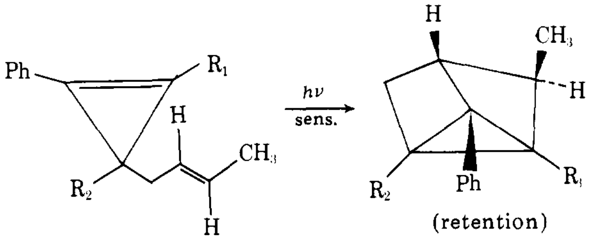
**10**

**11**

**7**, $R_1$ = H; $R_2$ = $CH_3$
**9**, $R_1$ = $CH_3$; $R_2$ = H

outlined below. This process involves the initial formation of a biradical in a conformation which is analogous to the chair conformation of cyclohexane. Ring inversion of the initially formed chair intermediate **10** generates the boat biradical **11** which cyclizes to the tricyclo[2.2.0.0$^{2,6}$]hexane ring system at a faster rate than bond fragmentation.[10] The ring flip of the initially formed chair intermediate **10** to the boat diradical **11** is the major factor responsible for the overall inversion of stereochemistry in the thermal cycloaddition. It is interesting to note that the thermolysis of **5** and **6** produces both the tricyclohexane ring and the Cope rearranged product **8**. Cyclopropenes **1** and **3**, on the other hand, give only [2 + 2] cycloadducts. This difference in behavior is probably a consequence of the restoration of conjugation between the phenyl substituents which can take place with **5** and **6** but not with **1** and **3**. Also noteworthy is the fact that there is a distinct regiochemical preference in the intramolecular cycloaddition reaction of cyclopropenes **5** and **6**. The observed regioselectivity can be rationalized in terms of the formation of the most stable biradical intermediate (i.e., **10**). The facility with which these systems undergo internal cycloaddition relative to other 1,5-dienes merits some comment. Undoubtedly, the high degree of strain present in the cyclopropene ring (54 kcal/mol)[11] makes the tricyclo[2.2.0.0$^{2,6}$]hexane skeleton thermodynamically more stable. The strain relieved in bond-making results in a lower energy pathway for cycloaddition than bond-breaking to an allyl and cyclopropenyl radical.

In marked contrast to the thermal results, the photosensitized (thioxanthone) cycloaddition reaction of cyclopropenes **3** and **12** gave rise to tricyclohexanes **2** and **13** where complete retention of stereochemistry about the $\pi$ bond has occurred. A similar result was noted with cyclopropene **6**.[12]

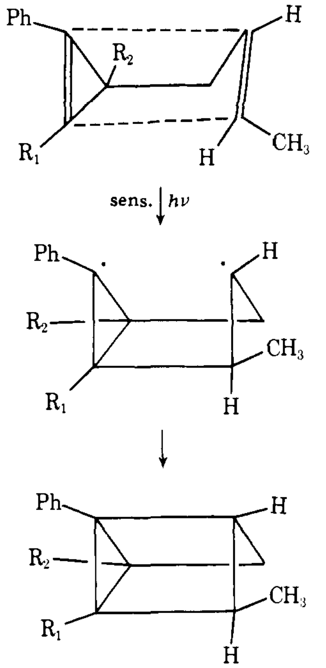


**3**, $R_1$ = Ph; $R_2$ = $CH_3$
**6**, $R_1$ = $CH_3$; $R_2$ = Ph
**12**, $R_1$ = $R_2$ = Ph

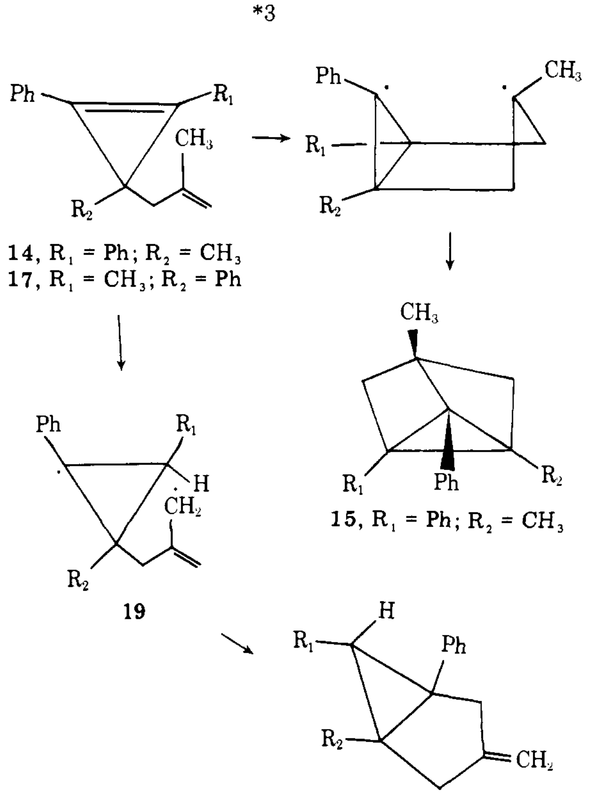
**2**, $R_1$ = Ph; $R_2$ = $CH_3$
**7**, $R_1$ = $CH_3$; $R_2$ = Ph
**13**, $R_1$ = $R_2$ = Ph

The above results indicate that there is a major difference in the stereochemical course of the thermal and triplet induced [2 + 2] cycloaddition reactions of these allyl-substituted cyclopropenes. Reasonable mechanistic options for the sensitized cycloaddition reaction include a concerted pathway or a stepwise process involving a diradical intermediate. It is tempting to suggest that the triplet-induced reaction proceeds through a boatlike conformation. Overlap of the frontier orbitals involved in the [2 + 2] cycloaddition reaction should favor the boatlike arrangement in the excited state and disfavor it in the ground state.[13]

Finally, it should be noted that the triplet-sensitized reaction of cyclopropene **14** gave rise to a [2 + 2] cycloadduct **15** (80%) and a 3-methylene-substituted bicyclo[3.1.0]hexane **16** (20%).



Similar results were encountered with cyclopropene **17**, although, in this case, only one of the two possible bicyclohexanes was produced (ratio of **15**:**18** = 5:3). The formation of the bicyclohexane ring proceeds via an intramolecular hydrogen atom transfer reaction.[14] Both products were equally quenched with added triplet quenchers, thereby indicating that they are both derived from a common triplet state. The regioselectivity exhibited by cyclopropene **17** is undoubtedly related to the fact that hydrogen transfer to the methyl bearing carbon allows maximum delocalization of the radical centers in the resulting diradical intermediate (i.e., **19**).



**14**, $R_1$ = Ph; $R_2$ = $CH_3$
**17**, $R_1$ = $CH_3$; $R_2$ = Ph

**19**

**15**, $R_1$ = Ph; $R_2$ = $CH_3$

**16**, $R_1$ = Ph; $R_2$ = $CH_3$
**18**, $R_1$ = $CH_3$; $R_2$ = Ph

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(7) Cyclopropenes **1**, **3**, **5**, and **6** were prepared from the reaction of diphenylmethylcyclopropenyl cation with lithio-*tert*-butyl acetate followed by chromatographic separation of the isomeric acetates. Subsequent Dibal reduction, reaction with ethylenetriphenylphosphorane, and chromatographic separation on a silver nitrate column afforded pure samples of the cis and trans olefins. Complete spectroscopic details will be provided in a later publication. Satisfactory spectral and analytical data were obtained for each new compound.

(8) The thermal cycloaddition reactions of cyclopropenes **5** and **6** were carried out to ca. 30% conversion since further thermolysis of **8** resulted in a mixture of **5** (9%), **6** (36%), **7** (14%), and **9** (21%).

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## Reaction of $[Fe(SC_6H_5)_4]^{2-}$ with Organic Trisulfides and Implications Concerning the Biosynthesis of Ferredoxins. Synthesis and Structure of the $[(C_6H_5)_4P]_2Fe_2S_{12}$ Complex

*Sir:*

The synthesis,[1] structural characterization,[2] and the Mössbauer spectral properties[3] of the tetrahedral $[Fe(SC_6H_5)_4]^{2-}$ complex anion (I) have been reported. The electronic spectra, magnetic properties, and fine and hyperfine parameters as derived from an analysis of the Mössbauer