Studies Dealing with the Intramolecular Ene Reaction of Cyclopropene Derivatives

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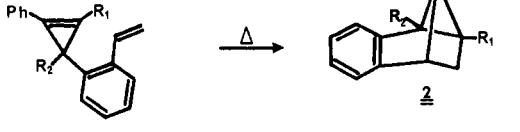
Abstract: The thermal and triplet-sensitized behavior of a series of 3-(*o*-alkenylphenyl)-substituted cyclopropenes has been studied. The results obtained indicate that the course of the thermolysis depends on the substituent groups present on the double bond. Thermolysis of the trans-substituted 3-(*o*-1-propenylphenyl)cyclopropene gives rise to a 2 + 2 cycloadduct. In marked contrast, heating a sample of the cis isomer results in a concerted ene reaction. The geometry for this type of reaction is easily achieved with the *Z* isomer. The triplet-sensitized reaction of these systems produced a 3:1 mixture of the 2 + 2 cycloadduct as well as the ene product. A related ene reaction was also observed with the 3-(*o*-(2-methyl-1-propenyl)-phenyl)-substituted cyclopropene. The primary deuterium isotope was determined (k_H/k_D = 3.5) and was found to be consistent with a concerted transition state where the hydrogen transfer is nonlinear. No significant isotope effect was encountered in the sensitized irradiation. The regiospecificity associated with the thermal and triplet-sensitized ene reaction of an unsymmetrically substituted cyclopropene was also studied. The regiochemistry encountered in the sensitized irradiation is attributed to π-π bridging to give the most stable diradical intermediate. Frontier MO theory provides a nice rationalization for the regiochemistry in the thermal reaction.

The thermal addition of an alkene to another olefin possessing an allylic hydrogen, the so-called "ene" reaction, is one of the most simple and versatile reactions of organic chemistry.[1-3] The reaction involves a multicentric addition with migration of the ene double bond and a 1,5-hydrogen shift. Early mechanistic proposals for the reaction of "enes" with various "enophiles" involved radical or ionic intermediates.[4-6] However, as the ubiquity of the allylic shift became established, proposals involving concerted mechanisms gained favor.[7-13] Recently, interest in synthetic applications of the ene reaction has increased substantially with the demonstration by several groups that Lewis acid catalysis can be dramatic.[14-17] Intramolecular ene reactions have been used as key steps in the synthesis of several natural products.[18] Like Diels-Alder reactions, thermal ene reactions are particularly facile with electron-donor (ene) and electron-deficient (enophile) components that maximize the HOMO (ene)-LUMO (enophile) interaction.[19,20] Olefins with strained double bonds are also prone to enter into ene reactions. For example, several cyclopropenes are known to undergo ready dimerization via the ene process.[21,22] Systematic probing into the cycloaddition behavior of a number of cyclopropene derivatives[23] led us to the discovery that (*Z*)-3-(*o*-alkenylphenyl)-substituted cyclopropenes undergo a smooth intramolecular ene reaction.[24] In this paper we wish to describe some of the salient features associted with this novel ene reaction.

Results

We have previously reported that the thermolysis of 3-(*o*-vinylphenyl)-substituted cyclopropenes (**1**) results in an intramolecular [2 + 2]-cycloaddition.[25] The question of possible stereochemical preference in the cycloaddition is of obvious interest, especially since the thermolysis of labeled 3-allyl-substituted cyclopropenes has been shown to occur with complete inversion of stereochemistry about the double bond.[26] The effect of substituents on the stereochemical course of the cycloaddition was probed by using (*E*)-**3** and (*Z*)-1,2-diphenyl-3-methyl-3-(*o*-1-propenylphenyl)cyclopropene (**4**). These compounds were prepared by treating diphenylmethylcyclopropenyl perchlorate with the Grignard reagents derived from (*E*)- and (*Z*)-1-(*o*-bromophenyl)-1-propene. Heating cyclopropene **3** at 175 °C gave a quantitative yield of two isomeric products in a ratio of 4.6:1 whose structures were identified as *exo*-**5** and *endo*-benzotricycloheptene (**6**). The stereochemistry of the cycloadducts was easily assigned



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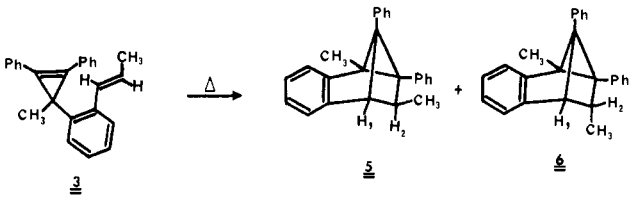

3 **5** **6**

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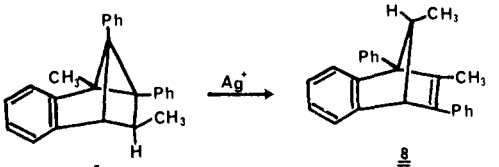
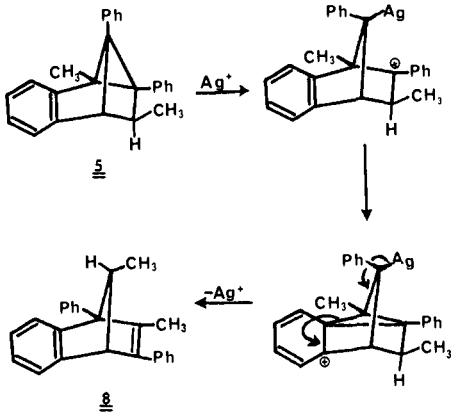
on the basis of their characteristic 100-MHz NMR spectra. The absence of coupling between H_1 and H_2 with *exo*-benzotricyclic **5** fixes the C_2-methyl group in the exo position. This is to be expected since molecular models show that the dihedral angle for this set of protons is ca. 90°. Appropriate control experiments established that no cis–trans isomerization of either the starting materials or the products was operative under the reaction conditions.

During our studies with benzotricycloheptenes **5** and **6**, we found that these substrates rearranged when chromatographed on a 10% silver nitrate silica gel column. Thus, treatment of **5** with silver perchlorate in benzene gave benzonorbornadiene **8** in 85% yield. This transformation formally corresponds to a silver-induced di-π-methane retrorearrangement.[27] Interestingly, Paquette and



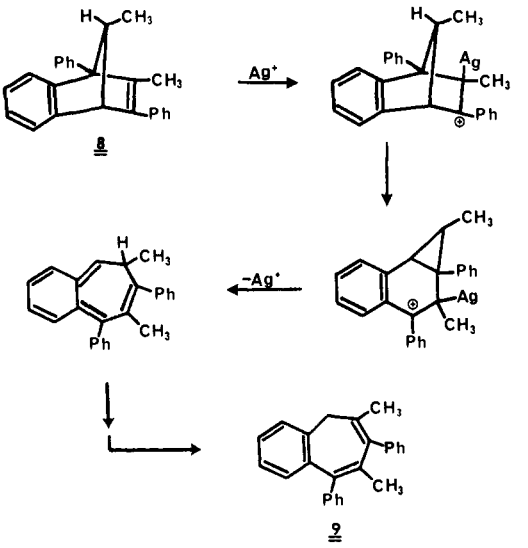
Zon have reported that the parent benzotricycloheptane ring is unreactive toward catalytic amounts of silver perchlorate in benzene.[28] The rearrangement of **5** to **8** probably involves addition of silver ion across the 1,7-σ bond.[29] This generates a stable carbonium ion which can be attacked by the π electrons of the neighboring aromatic ring. A subsequent reductive elimination of the metal ion would yield the observed product. The ready reactivity of **5** and the inertness of the parent benzotricycloheptane system is readily understandable in terms of relative carbonium ion stabilities.

The reaction of the *endo*-benzotricycloheptene **6** with silver perchlorate was much slower and required extended heating. The major product isolated was assigned as 6,8-diphenyl-7,9-dimethyl-5*H*-benzocycloheptene (**9**). Control experiments showed that structure **9** was formed by a silver-induced rearrangement of the initially formed benzonorbornadiene system. This reaction

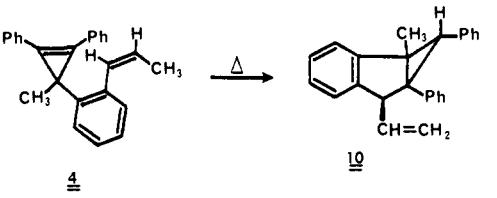


probably proceeds via a silver ion catalyzed 1,3-sigmatropic shift of the methano bridge followed by ring opening and a subsequent 1,5-hydrogen shift. Attempts to induce the rearrangement of benzotricycloheptenes **5** and **6** with other transition-metal catalysts such as bis(benzonitrile)palladium chloride and dicarbonylrhodium chloride dimer failed.

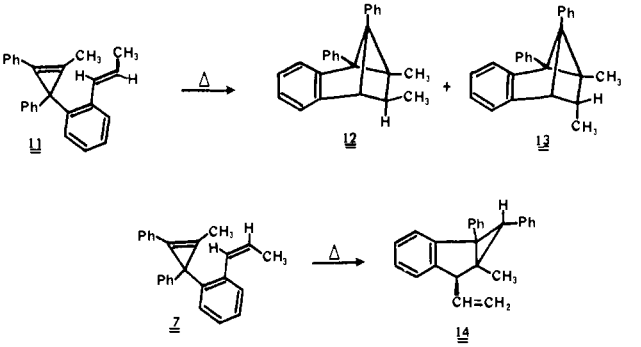
In marked contrast to the results obtained with the (*E*)-substituted cyclopropene **3**, thermolysis of the isomeric (*Z*)-cyclopropene **4** gave rise to 1-methyl-5,6-diphenyl-4-*endo*-vinyl-2,3-benzobicyclo[3.1.0]hexene (**10**) in quantitative yield. We suggest that **10** most reasonably arises from **4** by a concerted ene reaction. The geometry necessary for this type of reaction is easily achieved



with the (*Z*)-substituted cyclopropene **4**. Although bimolecular ene reactions of cyclopropenes are known,[30] the above case constitutes the first example of an intramolecular version of this reaction.



We have also investigated the thermal chemistry of several unsymmetrically substituted cyclopropenes. Heating a sample of the (*E*)-substituted cyclopropene **11** produced a 3:1 mixture of *exo*- and *endo*-benzotricycloheptenes (**12** and **13**). In contrast to this result, thermolysis of a sample of the (*Z*)-isomer **7** gave rise to benzobicyclohexane **14** in 98% yield. This reaction is completely regiospecific and involves hydrogen transfer to the carbon bearing the phenyl group.



The photosensitized reaction of these 3-(*o*-alkenylphenyl)-substituted cyclopropenes was also studied in order to assess the triplet-induced behavior of this system. We have previously shown that the triplet-sensitized irradiation of tetrasubstituted cyclopropenes containing π unsaturation is a particularly attractive route for the synthesis of some unusual tricyclic ring compounds.[31] In contrast to the thermal results, we found that the thioxanthone-sensitized irradiation of **3** gave rise to a mixture of benzotricycloheptenes (**5** and **6**) (1:1 ratio, 75%) as well as a benzobicyclohexene **10** (25%). Similar results were obtained with cyclopropenes **4**, **7**, and **11**. Partial isomerization about the π bond occurred when the photolysis of these systems was carried out for

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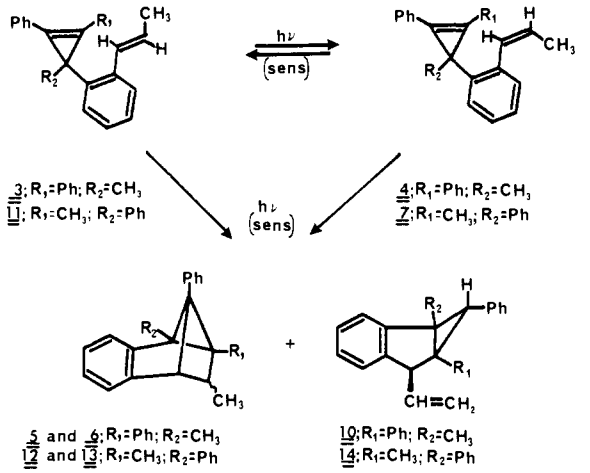
Table I. First-Order Rate Consants and Arrhenius Parameters for the Intramolecular Ene Reaction[a-g]

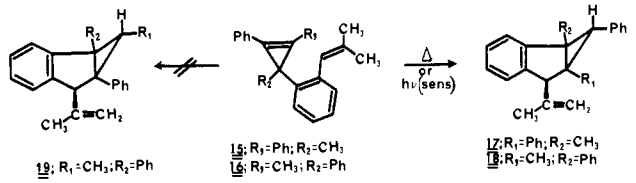
cyclopropene	k, $\times 10^5$ s^{-1}	E_a	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
4	4.25	30.8	30.2	33.3	−10.5
7	0.32	31.4	30.8	35.0	−14.0
15	21.0	29.5	28.9	32.1	−10.8
16	2.91	26.2	25.6	32.7	−23.8
20	19.9	30.0	29.4	31.2	−9.2
21	3.8	22.3	21.7	31.8	−34.0
22	6.0	29.0	28.4	32.7	−14.6
23	0.81	25.6	25.0	33.5	−28.5

[a] Temperature, 94 °C. [b] Energy units are kcal/mol. [c] Error limits in the reported rate constants are generally ±3%. [d] Arrhenius parameters were determined by plotting log K vs. $1/T$; the slope of the line is $-E_a/2.303R$. [e] $\Delta S^{\ddagger} = 4.576(\log A - 13.23)$ at 25 °C. [f] $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$. [g] $\Delta H^{\ddagger} = E_a - R$.

short periods. It is particularly important to note that the sensitized irradiation of **7** and **11** afforded benzobicyclohexene **14** as the major product (80%) together with lesser quantities of benzotricycloheptenes **12** and **13**. No signs of the other regioisomer benzobicyclohexene could be detected in the crude photolysate.

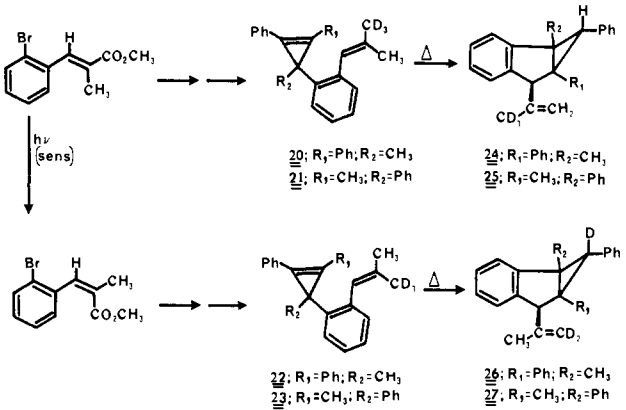


We have also studied the thermal- and triplet-sensitized behavior of the closely related 3-(*o*-2-methyl-1-propenyl)-substituted cyclopropene systems **15** and **16**. Both the thermolysis as well as the sensitized photolysis gave rise to the intramolecular ene product (i.e., **17** and/or **18**) in quantitative yield. No signs of the isomeric benzobicyclohexene **19** could be detected in the crude reaction mixture. As was the case with cyclopropene **7**, the intramolecular



ene reaction of the unsymmetrically substituted cyclopropene **16** is highly regiospecific and involves transfer of hydrogen to the carbon bearing the phenyl group.

Kinetic isotope effects provide a powerful diagnostic tool for the investigation of reaction mechanisms.[32] Studies dealing with deuterium isotope effects of the ene reaction have enforced the conclusion that the reaction is a synchronous process with a large (product-like) transition state.[33-36] In this commonly held view, the H-transfer step takes place in a somewhat nonlinear fashion in accompaniment to nonsymmetrical breaking and formation of the C–H bond. In order to provide more detailed information concerning the hydrogen-transfer step we have examined the effect of deuteration upon the rate constant for the ene reaction. Synthesis of the 1,2- and 1,3-diphenyl-substituted (2-methyl-d_3-1-propenyl)cyclopropenes **20–23** involved the reaction of diphenylmethylcyclopropenyl cation with trideuterio labeled *o*-bromoalkenyl Grignard reagent followed by chromatographic separation of the isomeric cyclopropenes. Heating the deuterio-labeled cyclopropenes at 160 °C produced the expected benzobicyclohexenes in quantitative yield. The NMR spectra of **26** and **27** show the complete absence of the cyclopropyl hydrogen signal and the mass spectra show them to be >98% d_3 labeled (i.e., m/e 339).



Examination of the reaction kinetics of the thermolysis of the above systems was carried out in order to determine the kinetic isotope effect. Rates of reaction were effected in ampules sealed under vacuum. A trace of pyridine was added to inhibit any acid-catalyzed reaction. The ene reaction was followed by HPLC and good first-order dependence of the rate data was obtained, indicating that the reaction is a true unimolecular process. Rate constants for conversion of the cyclopropene to the benzobicyclohexene were measured at three temperatures over a 20-day range. The activation parameters were determined by least-squares analysis and are given in Table I. A comparison of the rates at the three temperatures employed in this study for cyclopropenes **20** and **22** gives an average kinetic isotope effect of $k_H/k_D = 3.5 \pm 0.5$.

We also studied the triplet-sensitized reaction of cyclopropenes **20–23** so as to contrast the behavior with that encountered on thermolysis. The sensitized irradiation of either cyclopropene **20** or **22** produced the same 3:2 mixture of benzobicyclohexanes **24** and **26**. Control experiments showed that the two alkenes did not equilibrate under the reaction conditions. Similarly, thioxanthone-sensitized irradiation of cyclopropenes **21** and **23** also afforded a 3:2 mixture of bicyclohexanes **25** and **27**. Again, no equilibration of **21** and **23** occurred during the course of the irradiation. These results clearly indicate that there is a major difference in the mechanism of the thermal- and triplet-induced ene reaction of these *o*-alkenyl-substituted cyclopropenes.

Discussion

The results obtained on thermolysis of the (*E*)-3-(*o*-1-propenylphenyl)-substituted cyclopropene ring systems (i.e., **3** and **11**) may be most simply interpreted on the basis of an unusually easy bond formation between the double bond and the cyclopropene ring to produce a diradical intermediate which collapses to the observed cycloadduct. The driving force for the thermal reaction is undoubtedly associated with the considerable relief of bond angle strain of the cyclopropene ring. It would seem as though the strain energy present in the benzotricycloheptene skeleton is less than that present in the cyclopropene ring.[37] The most significant finding here is that the thermal [2 + 2]-cycloaddition of the (*E*)-isomer proceeds with predominant (82%)

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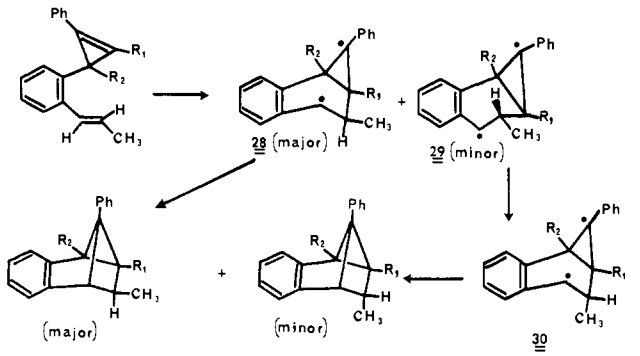
(37) Schleyer, P. V. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

Scheme I

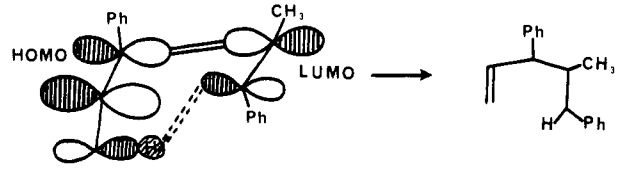


retention of stereochemistry about the π bond. This result indicates that although stereochemistry is partly lost during the cycloaddition reaction, complete randomization of the label is not occurring. Different stereochemistries in the benzotricycloheptene formed would occur from the two biradical configurations **28** and **29** as shown in Scheme I. Ring inversion of diradical **29** to **30** followed by radical coupling gives rise to the endo-substituted benzotricycloheptene (**6** or **13**). The preferential formation of diradical **28** is probably related to the fact that the nonbonded interactions between the methyl and R_1 groups are minimized in the initial bonding step. It should also be pointed out that in the case of the unsymmetrically substituted cyclopropene system **11** (i.e., $R_1 = CH_3$; $R_2 = Ph$), there is a distinct preference for that product arising from bonding between the terminal olefinic carbon and the cyclopropene carbon bearing the methyl group. This is undoubtedly related to the fact that π-π bridging will give the most stable biradical and thus lead to the preferential formation of benzotricycloheptenes **12** and **13**.

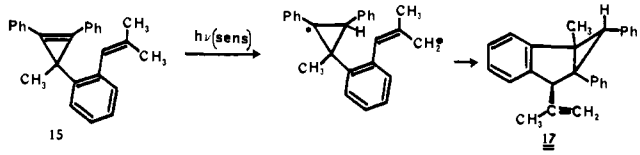
The formation of bicyclohexenes **10** and **14** from the thermolysis of the (*Z*)-substituted cyclopropenes **4** and **7** can be interpreted in terms of an intramolecular ene reaction.[18] The ene reaction is usually considered to proceed in a symmetry-allowed concerted manner[3] by means of a six-membered cyclic transition state, unless prohibited by steric factors.[38] The conclusion deduced by several groups studying deuterium isotope effects on the ene reaction[39-41] can be summarized in terms of two generalizations: viz., (1) a primary isotope effect $k_H/k_D \neq 1.0$ supports a concerted reaction mechanism and (2) values that are clearly short[3] of the theoretical maximum ($k_H/k_D = 7$) are indicative of a nonsymmetrical transition state. The results that we have encountered with cyclopropenes **20–23** compare favorably with previous determinations of an isotope effect in an ene reaction of 2.8–4.1.[36,39] A primary isotope effect such as 3.5 might be expected for a reaction where the hydrogen transfer does not take place through a linear transition state. O'Ferrall has found that primary isotope effects depend smoothly upon the β angles in the transition state, with a maximum being obtained where $\beta = 180°$.[42] By using this method of calculation, a hydrogen angle of 100° for β is obtained for our transition state,[43] a value which certainly would be consistent with expectations.

An important point worth noting is that in the case of the unsymmetrical substituted cyclopropene system (i.e., **7**, **16**, **21**, and **23**), the ene reaction is completely regiospecific and involves hydrogen transfer to the carbon bearing the phenyl group. Frontier orbital theory nicely rationalizes the observed regiochemistry. The thermal "ene" reaction has been described in terms of a three-orbital interaction among the HOMO of the π bond in the alkyl olefin, the LUMO of the π bond of the enophile, and the LUMO

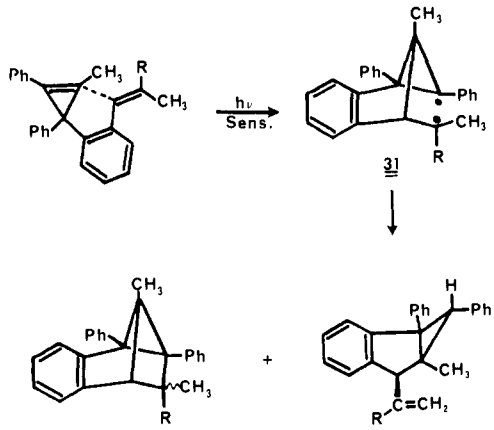
Scheme II



Scheme III. Mechanism A



Scheme IV. Mechanism B



of the C–H bond of the olefin.[13] Recent MO calculations concerning the ene process suggest that C–C bond formation is much more developed in the transition state than C–H bond formation. According to perturbation theory, the regioselectivity associated with the ene reaction is the result of best orbital overlap,[20] i.e., the atoms with the largest orbital coefficients combine preferentially. The orbital coefficients of the HOMO and LUMO of 1-phenylpropene are presented in generalized form by the size of the orbital lobes in Scheme II.[44] The large coefficient is found at the methyl-substituted carbon atom in both the HOMO and LUMO.[20] The coefficient on the carbon end of the ene component is much larger than that on the hydrogen atom.[13] Consequently, the MO perturbation treatment of the frontier orbital interaction of 1-phenylpropene with itself predicts that hydrogen transfer will occur on the carbon atom bearing the phenyl group. This is exactly what happens in the thermal ene reaction of the unsymmetrically substituted system.

In our previous studies we observed that the triplet-sensitized irradiation of tetrasubstituted cyclopropenes which possess γ hydrogens lead to products involving intramolecular transfer of hydrogen from the side chain to the π–π^* excited state of the alkene.[45] Thus, a reasonable mechanism which can rationalize formation of the benzobicyclohexane ring system assumes that the reaction proceeds via an internal hydrogen transfer followed by diradical coupling (Scheme III, mechanism A). The mechanism, however, is not compatible with some of the data. The primary deuterium isotope effect encountered in the sensitized irradiation of the symmetrical 1,2-diphenylcyclopropene system is significantly larger than any previously reported value for hy-

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(41) Schaefer, J. P.; Horvath, B.; Klein, H. P. *J. Org. Chem.* **1968**, *33*, 2647.
(42) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 785.
(43) The β angle is defined as the angle made by the ene terminus (i.e, the cyclopropene π system) with the hydrogen being transferred and the carbon from which the hydrogen is removed.

(44) The HOMO of 1-phenylpropene is isoconjugate with 1-phenylbutadiene with the σ bond having the same nodal characteristics as the terminal π bond. Simple Hückel calculations suggest the hydrogen and the orbital holding it to have the same sign in the HOMO. The next two p orbitals are negative.
(45) Padwa, A.; Chiacchio, U.; Hatanaka, N. *J. Am. Chem. Soc.* **1978**, *100*, 3928. Padwa, A.; Blacklock, T. J.; Chou, C. S.; Hatanaka, N. *J. Am. Chem. Soc.* **1979**, *100*, 5743.

drogen transfer to an excited state (k_H/k_D ca. 20/1).[46] A substantial tunnel effect was proposed to account for the large deuterium isotope effect.[47] Accordingly, mechanism A demands the existence of a large deuterium isotope effect for the sensitized irradiation of cyclopropene **22**. In fact, the results obtained with this system indicate that there is no significant primary isotope effect on the formation of the benzobicyclohexane ring system (i.e., $\Phi_{22} = \Phi_{20} = \Phi_{15} = 0.18$). Moreover, mechanism A cannot rationalize the regiochemistry obtained in the sensitized irradiation of cyclopropene **16**. This process would be expected to give rise to benzobicyclohexene **19**. We had previously demonstrated that unsymmetrically substituted cyclopropenes transfer hydrogen exclusively to the carbon bearing the methyl group.[44-46] The regiospecificity associated with the hydrogen-transfer reaction was attributed to formation of the most stable diradical intermediate. The exclusive formation of bicyclohexene **18** in the sensitized irradiation is best explained by an alternate mechanism which involves $\pi-\pi$ bridging to give the most stable diradical which undergoes a subsequent disproportionation (i.e., Scheme IV, mechanism B). This mechanism nicely rationalizes the fact that a mixture of bicyclohexanes (i.e., **24** and **26**) is formed from the sensitized irradiation of **20**. In this case the initially produced diradical (**31**, R = CD_3) is long lived enough to allow for rotation about the C–C bond to compete with the internal disproportionation.[49] Mechanism B also accounts for the formation of both the benzotricycloheptene (**5**, **6**) and benzobicyclohexane (**10**) ring systems from the sensitized irradiation of cyclopropene **3**. In simple cases, the activation energies for recombination and disproportionation of radicals have been found to be equal.[48] The exclusive formation of the benzobicyclohexane ring system from the sensitized irradiation of **15** reflects the greater steric hindrance to recombination of a tertiary site compared with a secondary site.[50] Cyclization of the triplet state of these *o*-alkenylphenyl-substituted cyclopropenes proceeds according to the "Rule of Five".[51,52]

One final point worth noting is that thermolysis of the (*E*)-substituted cyclopropene system (i.e., **3** and **11**) affords only the [2 + 2]-cycloaddition products. This observation established that six-ring cyclization is the preferred thermal path, perhaps as a consequence of radical stability. In the excited state, however, a kinetic preference for the formation of the five-membered ring diradical (i.e., **30**) seems to be the controlling factor.

Experimental Section

All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. The infrared absorption spectra were determined on a Perkin-Elmer 467 infrared spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer, using 1-cm matched cells. The proton magnetic resonance spectra were determined at 90 MHz by using a Varian EM-390 spectrometer. Mass spectra were determined with a Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV. All thermolyses were carried out in a 20% pyridine–benzene mixture in a sealed Carius tube. The crude reaction mixtures were chromatographed on silica gel with hexane as the eluent.

Preparation of (*E*)-1-(Propen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)benzene (3). To a stirred suspension containing 5.3 g of magnesium in 20 mL of anhydrous ether under a nitrogen atmosphere was added 26.3 g of ethyl bromide in 120 mL of anhydrous ether so as to maintain a gentle reflux. The mixture was allowed to stir for an additional 2 h. To the above Grignard solution was added 25.36 g of *o*-bromobenzaldehyde in 200 mL of anhydrous ether over a 1-h, period. The reaction mixture was allowed to stir for 12 h at room temperature before being quenched by the addition of a saturated ammonium chloride solution. The ethereal layer was washed three times with water and a saturated sodium chloride solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave 30.10 g (99%) of 1-(*o*-bromophenyl)propanol: NMR ($CDCl_3$, 100 MHz) δ 0.93 (t, 3 H, J = 7.8 Hz), 1.45–1.95 (m, 2 H), 3.25–3.38 (m, 1 H), 4.90–5.12 (m, 1 H), 7.00–7.60 (m, 4 H).

To a mixture of 2.8 g of fused potassium hydrogen sulfate, 1.2 g of phosphorus pentoxide, and 10 mg of 4-*tert*-butylcatechol at 230 °C (100 mm) was added 28.93 g of 1-(*o*-bromophenyl)propanol at a rate which maintained a slow constant distillation of water. After the addition was completed, the pressure was decreased to 20 mm until no more distillate could be collected. The distillate was taken up in ether, washed with water, and dried over magnesium sulfate and the solvent was removed under reduced pressure. The resulting residue was chromatographed on a 30 × 1.5 cm silica gel column with hexane as the eluent. The first component isolated from the column contained 23.06 g (87%) of (*E*)-1-(*o*-bromophenyl)propene: NMR ($CDCl_3$, 100 MHz) δ 1.87 (dd, 3 H, J = 6.5, 1.8 Hz), 6.10 (dq, 1 H, J = 15.5, 6.5 Hz), 6.77 (dq, 1 H, J = 15.5, 1.8 Hz), 6.85–7.52 (m, 4 H). Analysis by gas chromatography indicated that the (*Z*)-isomer was present in less than 5% yield.

To a stirred suspension of activated magnesium, prepared according to the method of Rieke,[53] in 150 mL of anhydrous tetrahydrofuran at 60 °C was added 6.33 g of (*E*)-1-(*o*-bromophenyl)propene. The mixture was allowed to stir for 40 min, and the Grignard solution was then added to a stirred suspension containing 1.75 g of 1-methyl-2,3-diphenylcyclopropenylium perchlorate in 150 mL of anhydrous ether at −78 °C under a nitrogen atmosphere. The mixture was allowed to warm to 5 °C overnight. After the mixture was quenched with a saturated ammonium chloride solution, the organic layer was taken up in ether, washed five times with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure to give a light yellow oil which was chromatographed on a 100 × 1.5 cm silica gel column with hexane as the eluent. The first component isolated contained a small amount of β-methylstyrene. The second component isolated from the column contained 1.66 g (90%) of a white crystalline solid whose structure was assigned as (*E*)-1-(propen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)benzene (**3**) on the basis of its spectral properties: mp 70–71 °C; IR (KBr) 3010, 2855, 1790, 1585, 1485, 1435, 1375, 1065, 1035, 970, 905, 770, 755, 730, 690 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.85 (s, 3 H), 1.86 (dd, 3 H, J = 6.5, 1.8 Hz), 5.99 (dq, 1 H, J = 15.2, 6.5 Hz), 6.94–7.81 (*m*, 15 H); UV (95% ethanol) 317, shoulder 248, 228 nm (ϵ 22 000, 19 300, 31 100); *m/e* 322 (M^+, base), 308, 307, 291, 278, 230, 229, 228, 216, 215, 202.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.09; H, 6.90.

Preparation of (*Z*)-1-(Propen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)benzene (4) and (*Z*)-1-(Propen-1-yl)-2-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)benzene (7). A solution containing 23.06 g of (*E*)-1-(*o*-bromophenyl)propene and 500 mg of thioxanthen-9-one in 1.25 L of anhydrous benzene was irradiated for 14.5 h under an argon atmosphere with a 450-W Hanovia mercury arc lamp equipped with a uranium filter sleeve. The solvent was removed under reduced pressure, and the resulting liquid was chromatographed on a 15 × 1.5 cm silica gel column with hexane as the eluent. The major fraction collected contained 21.85 g (95%) of a 3:2 mixture of (*Z*)- and (*E*)-1-(*o*-bromophenyl)propene which was fractionally distilled through a 30-cm Nester Faust spinning band column at a pressure of 90 nm. The lower boiling fraction (bp 117–120 °C) contained a pure sample of (*Z*)-1-(*o*-bromophenyl)propene.

To a stirred suspension of activated magnesium, prepared according to the method of Rieke,[53] in 100 mL of tetrahydrofuran at 60 °C was added 1.70 g of (*Z*)-1-(*o*-bromophenyl)propene. The mixture was allowed to stir for 40 min, and the Grignard solution was then added to a stirred suspension containing 1.84 g of 1-methyl-2,3-diphenylcyclopropenylium perchlorate in 150 mL of anhydrous ether at −78 °C under a nitrogen atmosphere. The mixture was allowed to warm to 5 °C overnight. After the mixture was quenched with a saturated ammonium chloride solution, the organic layer was taken up in ether, washed five times with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure to give a light yellow oil which was chromatographed on a 60 × 2.5 cm silica gel column with hexane as the eluent. The first component isolated contained a small amount of β-methylstyrene. The second component isolated from the column contained 1.07 g (55%) of a clear colorless oil whose structure was assigned as (*Z*)-1-(propen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-benzene (**4**) on the basis of its spectral properties: IR (neat) 2995, 2905, 1800, 1595, 1495, 1475, 1445, 1360, 1075, 1040, 1025, 925, 910, 820, 765, 710, 690 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.64 (dd, 3 H, J = 6.8, 1.8 Hz), 1.84 (s, 3 H), 5.71 (dq, 1 H, J = 11.5, 6.8 Hz), 6.88 (dq, 1 H,

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(48) Kraus, J.; Calvert, J. *J. Am. Chem. Soc.* **1957**, *79*, 5921.
(49) It should be pointed out that the starting cyclopropene **20** does not isomerize under the photolytic conditions employed.
(50) Engle, P. S.; Bishop, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 2148.
(51) Srinivason, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932.
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J = 11.5, 1.8 Hz), 6.99–7.78 (m, 14 H); UV (95% ethanol) shoulder 332, 317, shoulder 227 nm (ε 12 000, 15 700, 24 500); *m/e* 322 (M^+, base), 307, 292, 291, 229, 228, 215, 165, 11k, 77.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.99; H, 6.94.

The third component isolated from the column contained 80 mg (4%) of a white crystalline solid whose structure was identified as (*E*)-1-(propen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)benzene (**3**). The fourth component isolated from the column contained 125 mg (6%) of a white crystalline solid whose structure was assigned as (*Z*)-1-(propen-1-yl)-2-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)benzene (**7**) on the basis of its spectral properties: mp 129–130 °C; IR (KBr) 3020, 2910, 1845, 1590, 1480, 1465, 1435, 1065, 1030, 910, 790, 780, 750, 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.70 (dd, 3 H, J = 6.8, 1.7 Hz), 2.38 (s, 3 H), 5.59 (dq, 1 H, J = 11.7, 6.8 Hz), 6.47 (dq, 1 H, J = 11.7, 1.7 Hz), 6.93–7.63 (m, 14 H); UV (95% ethanol) 257 nm (ε 21 800); *m/e* 322 (M^+), 307, 293, 278, 229 (base), 215, 202, 91, 77.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.02; H, 6.90.

Thermolysis of (*E*)-1-(Propen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)benzene (3). A solution containing 109 mg of **3** in 0.5 mL of a 20% pyridine–benzene mixture was heated at 156° in a sealed tube for 4 h. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on a 2 × 0.5 cm silica gel column with hexane as the eluent. The white crystalline solid obtained contained 106 mg (97%) of a 82:18 mixture of *exo*- (**5**) and *endo*- (**6**) (1α,1aβ,6α,6aβ)-1,1a-6,6a-tetrahydro-*exo*-1a,7-dimethyl-1,6a-diphenyl-1,6-methanocycloprop[*a*]indene. Fractional crystallization of this material from ethanol provided a pure sample of the exo-isomer **5**: mp 160–161 °C; IR (KBr) 3005, 2890, 2835, 1590, 1490, 1450, 1435, 1375, 1360. 1175, 1145, 1100, 1095, 1070, 1030, 1010, 770, 750, 700 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.32 (s, 3 H), 1.33 (d, 3 H, J = 6.0 Hz), 1.63 (q, 1 H, J = 6.0 Hz), 3.09 (s, 1 H), 7.01–7.38 (m, 4 H); UV (95% ethanol) shoulder 222 nm (ε 24 000); *m/e* 322 (M^+, base), 308, 307, 292, 229, 217, 215. 205, 91.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.07; H, 6.88.

The residue from the above recrystallization was chromatographed on a silica gel column and the endo isomer was recrystallized from ethanol to give a pure sample of **6**: mp 100–101 °C; IR (KBr) 3060, 2980, 2950, 2920, 1595, 1495, 1490, 1455, 1440, 1380, 1365, 1170, 1145, 1070, 1060, 1025, 1010, 760, 755, 745, 725, 690 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 0.12 (d, 3 H, J = 6.0 Hz), 1.32 (s, 3 H), 3.12 (dq, 1 H, J = 8.0, 6.0 Hz), 3.80 (d, 1 H, J = 8.0 Hz), 7.05–7.40 (m, 14 H); UV (95% ethanol) shoulder 224 nm (ε 22 400); *m/e* 322 (M^+), 307 (base), 292, 229, 215, 205, 203, 202, 117, 115, 105. 91, 77.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.01; H, 6.93.

Silver(I)-Induced Rearrangement of *exo*- (5) and *endo*-Benzotricycloheptene 6. During an attempt to separate the exo- (**5**) and *endo*-benzotricycloheptenes (**6**) derived from the thermolysis of **3** we subjected the mixture of a silica gel column impregnated with a 10% silver nitrate solution. This caused a rearrangement to occur. In order to elucidate the details of the rearrangement we studied the silver-catalyzed isomerization directly. Thus, a solution containing 110 mg of **5** and 300 mg of silver perchlorate in 25 mL of benzene was heated at reflux for 7 h. The reaction mixture was taken up in hexane, washed with water, and dried over magnesium sulfate. Removal of the solvent followed by chromatography of the residue on silica gel gave a crystalline solid, mp 117–118 °C, whose structure was assigned as 1,4-dihydro-*exo*-2,9-dimethyl-1,3-diphenyl-1,4-methanonaphthalene (**8**) on the basis of its spectroscopic properties; IR (KBr) 3060, 3030, 3010, 2985, 2960, 2940, 2920, 2880, 1600, 1505, 1495, 1480, 1460, 1450, 1385, 1050, 965, 880, 825, 800, 790, 775, 765, 745, 740 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.94 (d, 3 H, J = 6.0 Hz), 1.90 (s, 3 H), 2.78 (qd, 1 H, J = 6.0, 1.4 Hz), 3.90 (d, 1 H, J = 1.4 Hz), 6.88–7.62 (m, 14 H); UV (95% ethanol) 248 nm (ε 11 700); *m/e* 322 (M^+, base) 307, 293, 292, 245, 244, 229, 228. 215. 154, 115, 91, 77.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.97; H, 6.92.

When a sample of **8** or the endo-isomer **6** was subjected to silver perchlorate in refluxing benzene for 270 h a single compound was formed, mp 138–139 °C, whose structure was assigned as 6,8-diphenyl-7,9-dimethyl-5*H*-benzocycloheptene (**9**) on the basis of its characteristic spectra: IR (KBr) 3080, 3070, 3040, 2960, 2880, 1600, 1500, 1460, 1450, 1395, 1390, 1100, 1055. 1030. 1020. 790, 760. 755, 740. 730 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.05 (s, 3 H), 2.36 (s, 3 H), 4.53 (s, 2 H), 7.03–7.59 (m, 12 H), 7.90–8.18 (m, 2 H); UV (95% ethanol) 294, 283, 236 nm (ε 7 490. 6 750, 63 700); *m/e* 322 (M^+, base), 307. 292, 229, 228, 216, 215. 105, 91.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.95; H, 6.93.

Thermolysis of (*Z*)-1-(Propen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)benzene (4). A solution containing 89 mg of **4** in 0.5 mL of a 20% pyridine–benzene mixture was heated at 160 °C in a sealed tube for 30 min. The solvent was removed under reduced pressure to give a light yellow solid which was chromatographed on a 2 × 0.5 cm silica gel column with hexane as the eluent. The white crystalline solid that was obtained (87 mg, 97%) was assigned as 1,1a,6,6a-tetrahydro-1a-methyl-*exo*-1,6a-diphenyl-*endo*-6-ethylcycloprop[*a*]indene (**10**) on the basis of its spectral properties: mp 125–126 °C; IR (KBr 3010, 2950, 2795, 1590, 1490, 1470, 1435, 1375, 1065, 990, 920, 770, 760, 755, 740, 725, 700 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.56 (s, 3 H), 2.02 (s, 1 H), 4.07 (d, 1 H, J = 7.0 Hz), 4.96 (1 H, dd, J = 16.7 and 1.5 Hz), 5.12 (1 H, dd, J = 10.0 and 1.5 Hz), 6.03 (ddd, 1 H, J = 16.7, 10.0, 7.0 Hz), 6.51–7.28 (m, 14 H); UV (95% ethanol) 241 nm (ε 18 400); *m/e* 322 (M^+, base), 307, 251, 249, 218, 217, 216, 215, 205, 203, 202, 167, 143, 91.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.06; H, 6.90.

Thermolysis of (*Z*)-1-(Propen-1-yl)-2-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)benzene (7). A solution containing 48 mg of **7** in 0.5 mL of a 20% pyridine–benzene mixture was heated at 175 °C in a sealed tube for 15 min. The solvent was removed under reduced pressure to give a light yellow oil which was chromatographed on a 2 × 0.5 cm silica gel column with hexane as the eluent. The resulting colorless oil that was obtained (47 mg, 98%) was assigned as 1,1a,6,6a-tetrahydro-6a-methyl-*exo*-1,1a-diphenyl-*endo*-6-ethenylcycloprop[*a*]indene (**14**) on the basis of its spectral properties: IR (neat) 3070, 3040, 2955, 2935, 2880, 2870, 1600, 1500, 1480, 1460, 1450, 1390, 1085, 1040, 1000, 930, 775, 765, 715 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.39 (s, 3 H), 2.07 (s, 1 H), 4.18 (br d, 1 H, J = 7.9 Hz), 5.10–5.48 (m, 2 H), 6.08 (ddd, 1 H, J = 17.3, 9.7, 7.9 Hz), 6.60–7.47 (m, 14 H); UV (95% ethanol) shoulder 235 nm (ε 16 700); *m/e* 322 (M^+), 307, 293, 292, 245, 229 (bas), 202, 142, 91, 77.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.05; H, 6.90.

Preparation of (*E*)-1-(Propen-1-yl)-2-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)benzene (11). A solution containing 120 mg of (*Z*)-1-(propen-1-yl)-2-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)benzene (**7**) and **13** mg of thioxanthen-9-one in 200 mL of benzene was irradiated for 7 min under an argon atmosphere with a 450-W Hanovia mercury arc lamp equipped with a Uranium filter sleeve. The solvent was removed under reduced pressure, and the resulting residue was subjected to silica gel chromatography with hexane as the eluent. The first fraction contained 52 mg of recovered starting material. The second fraction contained 60 mg of a white solid, mp 110–111 °C, whose structure was assigned as the (*E*)-isomer **11** on the basis of its spectral data: IR (KBr) 3080, 3060, 3030, 2930, 2860, 1845, 1595, 1495, 1475, 1440, 1000, 990, 820, 780, 720, 685 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.70 (dd, 3 H, J = 6.0 and 1.5 Hz), 2.42 (s, 3 H), 6.03 (dq, 1 H, J = 16.0 and 6.0 Hz), 6.68 (dq, 1 H, J = 16.0 and 15 Hz), 6.91–7.62 (m, 14 H); UV (95% ethanol) 258 nm (ε 25 200); *m/e* 322 (M^+), 307, 293, 278, 230, 229 (base), 216, 215, 202, 91.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.05; H, 6.90.

Thermolysis of (*E*)-1-(Propen-1-yl)-2-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)benzene (11). A solution containing 270 mg of **11** in 1.5 mL of a 20% pyridine–benzene mixture was heated at 175 °C for 2.5 h. The solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column with hexane as the eluent. The first component isolated from the column (76%) was a crystalline solid, mp 160–161 °C, whose structure was assigned as (1α,1aβ,6α,6aβ)-1,1a,6,6a-tetrahydro-*exo*-1,7-dimethyl-1a,6a-diphenyl-1,6-methanocycloprop[*a*]indene (**12**) on the basis of its spectral properties: IR (KBr) 3060, 3030, 3010, 2985, 2960, 2940, 2920, 2880, 1600, 1505, 1495, 1480, 1460, 1385, 1050, 965, 880, 825, 800, 790, 775, 765, 745, 740 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.32–1.59 (m, 4 H), 1.45 (s, 3 H), 3.20 (s, 1 H), 6.60–7.37 (m, 14 H); UV (95% ethanol) 248 nm (ε 11 700); *m/e* 322 (M^+), 307, 292, 291, 265, 230, 229 (base), 215, 91.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.24; H, 6.71.

The second fraction isolated from the column was a clear oil (24%) whose structure was assigned as (1α,1aβ,6α,6aβ)-1,1a,6,6a-tetrahydro-*endo*-1,7-dimethyl-1a,6a-diphenyl-1,6-methanocycloprop[*a*]indene (**13**): IR (neat) 3090, 3070, 3030, 2980, 2960, 2940, 2880, 1600, 1505, 1500, 1490, 1475, 1460, 1390, 1095, 790, 760, 730 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.21 (d, 3 H, J = 6.0 Hz), 1.54 (s, 3 H), 2.91 (dq, 1 H, J = 8.0 and 6.0 Hz), 3.89 (d, 1 H, J = 8.0 Hz), and 6.53–7.48 (m, 14 H); *m/e* 322 (M^+, base), 307, 292, 229, 199, 171, 158, 112, 91.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.02; H, 6.71.

Triplet-Sensitized Irradiation of (*E*)- (3) and (*Z*)-1-(Propen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)benzene (4) in Benzene. A solution containing 111 mg of **3** and 11 mg of thioxanthen-9-one in 200 mL of anhydrous benzene was irradiated for 20 min under an argon atmosphere with a 200-W Hanovia mercury arc lamp equipped with a uranium filter sleeve. The solvent was removed under reduced pressure, and the resulting yellow oil was chromatographed on a 1.5 × 5 cm silica gel column with hexane as the eluent. The resulting colorless oil (110 mg, 99%) was shown to contain a 37:37:25 mixture of *exo*- (**5**) and **endo**- (**6**) (1α,1aβ,6α,6aβ)-1,1a,6,6a-tetrahydro-1a,7-dimethyl-1,6a-diphenyl-1,6-methanocycloprop[*a*]indene as well as 1,1a,6,6a-tetrahydro-1a-methyl-*exo*-1,6a-diphenyl-*endo*-6-ethenylcycloprop[*a*]indene (**10**) was judged by NMR spectroscopy. The same distribution of products was obtained from the photolysis of the (*Z*)-isomer **4** when the irradiation was carried out under identical experimental conditions.

Triplet-Sensitized Irradiation of (*Z*)-1-(Propen-1-yl)-2-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)benzene (7) in Benzene. A solution containing 106 mg of **7** and 10.0 mg of thioxanthen-9-one in 200 mL of anhydrous benzene was irradiated for 3 h under an argon atmosphere with a 450-W Hanovia mercury arc lamp equipped with a uranium filter sleeve. The solvent was removed under reduced pressure, and the resulting yellow oil was chromatographed on a 5 × 1.5 cm silica gel column with hexane as the eluent. The resulting colorless oil was rechromatographed on a 100 × 1.5 cm silica gel column with hexane as the eluent. The three components isolated from the column were identified as benzobicyclohexane **14** (80%) and *exo*- (**12**) and *endo*- (**13**) benzotricycloheptenes.

Preparation of 1-(2-Methylpropen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)benzene (15) and 1-(2-Methylpropen-1-yl)-2-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)benzene (16). To a stirred suspension of activated magnesium in 150 mL of refluxing tetrahydrofuran was added 3.57 g of 1-(*o*-bromophenyl)-2-methyl-1-propene.[54] The mixture was heated at reflux for 45 min, and the Grignard solution was then added to a stirred slurry containing 2.0 g of diphenylmethylcyclopropenylium perchlorate in 100 mL of ether at −78 °C. Standard workup procedures followed by silica gel chromatography with hexane as the eluent gave 990 mg (44%) of **15** as a clear oil: IR (neat) 3055, 3015, 2965, 2925, 2880, 1805, 1595, 1495, 1480, 1450, 1375, 1075, 1040, 910, 835, 760, 735, 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.50 (d, 3 H, *J* = 1.5 Hz), 1.69 (d, 3 H, *J* = 1.5 Hz), 1.81 (s, 3 H), 6.59 (m, 1 H), 6.92–7.88 (m, 14 H); UV (95% ethanol) 317 and 227 nm (ε 19 500 and 26 000); *m/e* 336 (M^+), 321, 281 (base), 229, 215, 205, 115, 91.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.67; H, 7.24.

The second component isolated from the column contained 760 mg (30%) of **16** as a clear oil: IR (neat) 3030, 3015, 2965, 2940, 2860, 1855, 1600, 1495, 1450, 1360, 785, 760, 715, 695, 665, 625 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.58 (d, 3 H, *J* = 1.5 Hz), 1.64 (d, 3 H, *J* = 1.5 Hz), 2.32 (s, 3 H), 6.21 (m, 1 H), 6.6–7.6 (m, 14 H); UV (95% ethanol) 255 nm (ε 24 000); *m/e* 336 (M^+ and base), 321, 293, 281, 243, 229, 215, 205, 115, 91.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.70; H, 7.22.

Thermolysis of 1-(2-Methylpropen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)benzene (15). A solution containing 530 mg of **15** in 0.5 mL of a 20% pyridine–benzene mixture was heated at 160° for 6 min. The solvent was removed under reduced pressure, and the resulting residue was purified by thick-layer chromatography to give 510 mg (96') of a white solid, mp 151–152 °C, whose structure was assigned as 1,a,6,6a-tetrahydro-1a-methyl-*exo*-1,6a-diphenyl-*endo*-6-(2-propenyl)-cycloprop[*a*]indene (**17**) on the basis of its characteristic spectral properties: IR (KBr) 3150, 3100, 1630, 1620, 1500, 1460, 1400, 900, 770, 680 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.52 (s, 3 H), 1.75 (m, 3 H), 2.20 (br s, 1 H), 4.25 (br s, 1 H), 4.60–4.71 (m, 1 H), 4.90–5.01 (m, 1 H), 6.6–7.4 (m, 14 H); UV (95% ethanol) 238 nm (ε 17 500); *m/e* 336 (M^+ and base), 321, 245, 243, 218, 217, 216, 215.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.67 H, 7.22.

The triplet-sensitized irradiation of **15** with thioxanthone as the sensitizer also afforded benzobicyclohexane **17** as the exclusive photoproduct (94%).

Thermolysis of 1-(2-Methylpropen-1-yl)-2-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)benzene (16). A solution containing 490 mg of **16** in 0.5 mL of a 20% pyridine–benzene solution was heated at 160 °C for 22 min. Removal of the solvent under reduced pressure followed by purification of the residue by thick-layer chromatography afforded 460 mg of a white solid, mp 109–110 °C, whose structure was assigned as 1,1a,6,6a-tetrahydro-6a-methyl-*exo*-1,1a-diphenyl-*endo*-6-(2-propenyl)-cycloprop[*a*]indene (**18**) on the basis of its spectral properties: IR (KBr) 3120, 3000, 1620, 1510, 1460, 1380, 1270, 1080, 1030, 900, 750, 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.39 (s, 3 H), 1.75–1.94 (m, 3 H), 2.19 (s, 1 H), 4.29 (br s, 1 H), 4.89–4.99 (m, 1 H), 5.00–5.11 (m, 1 H), 6.59–7.52 (m, 14 H); UV (95% ethanol) 237 nm (ε 16 200); *m/e* 336 (M^+ and base), 321, 232, 215, 205, 131, 115, 105, 91, 77.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81 H, 7.19. Found: C, 92.70; H, 7.25.

The triplet-sensitized irradiation of **16** with thioxanthone as the sensitizer also afforded **18** as the exclusive photoproduct (96%).

Preparation and Thermolysis of 1-(2-Methyl-d_3-propen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)benzene (20) and 1-(2-Methyl-d_3-propen-1-yl)-2-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)benzene (21). A sample of (*E*)-(*o*-bromophenyl)-2-methyl-3,3,3-trideuterio-1-propene was prepared by starting from (*E*)-1-(*o*-bromophenyl)-2-carboethoxy-1-propene [NMR ($CDCl_3$, 90 MHz) δ 1.29 (t, 3 H, *J* = 7.2 Hz), 1.90 (d, 3 H, *J* = 1.5 Hz), 4.19 (q, 2 H, *J* = 7.2 Hz), 6.94–7.67 (m, 4 H), 7.72 (q, 1 H, *J* = 1.5 Hz)]. The latter material was prepared from a Wittig reaction of *o*-bromobenzaldehyde with carboethoxymethyltriphenylphosphorane. A 7.95-g sample of the above olefin was reduced with 0.7 g of lithium aluminum tetradeuteride to give 6.76 g of (*E*)-1-(*o*-bromophenyl)-2-methyl-3,3-dideuterio-1-propen-3-ol as a colorless oil [NMR ($CDCl_3$, 90 MHz) δ 1.70 (d, 3 H, *J* = 1.3 Hz), 2.98 (s, 1 H), 6.54 (q, 1 H, *J* = 1.3 Hz), 6.90–7.63 (m, 4 H)]. This material was converted to the corresponding mesylate in 94% yield [NMR ($CDCl_3$) δ 1.70 (d, 3 H, *J* = 1.5 Hz), 3.03 (s, 3 H), 6.62 (q, 1 H, *J* = 1.5 Hz), 7.0–7.7 (m, 4 H)]. Reduction of a 8.97-g sample of the mesylate with 0.42 g of lithium aluminum tetradeuteride gave 5.94 g of (*E*)-(*o*-bromophenyl)-2-methyl-3,3,3-trideuterio-1-propene [NMR ($CDCl_3$, 90 MHz) δ 1.65 (d, 3 H, *J* = 1.3 Hz), 6.22 (q, 1 H, *J* = 1.3 Hz), 6.85–7.61 (m, 4 H)]. This bromide was treated with activated magnesium metal, and the resulting Grignard reagent was condensed with diphenylmethylcyclopropenyl cation to give a mixture of **20** and **21** [NMR ($CDCl_3$, 90 MHz): **20**–δ 1.50 (*d*, 3 H, *J* = 1.3 Hz), 1.79 (s, 3 H), 6.54 (q, 1 H, *J* = 1.3 Hz), 6.87–7.89 (m, 14 H); *m/e* 339 (M^+ and base), 321, 205, 178, 105, 91, 77; **21**—δ 1.58 (d, 3 H, *J* = 1.3 Hz), 2.30 (s, 3 H), 6.21 (br q, 1 H, *J* = 1.3 Hz), 6.8–7.7 (m, 14 H); *m/e* 339, 281, 215, 205, 115, 91, 77].

The thermolysis of a sample of **20** in a 20% pyridine–benzene mixture at 160 °C for 12 min gave a 96% yield of the expected benzobicyclohexane **24** [NMR ($CDCl_3$, 90 MHz) δ 1.54 (s, 3 H), 2.20 (s, 1 H), 4.22 (br s, 1 H), 4.66 (br dd, 1 H, *J* = 2.4 and 2.3 Hz), 4.95 (br d, 1 H, *J* = 2.3 Hz), 6.6–7.4 (m, 12 H)].

The corresponding (*Z*)-deuterated system **22** was prepared from (*Z*)-1-(*o*-bromophenyl)-2-methyl propenate [NMR δ 2.07 (d, 3 H, *J* = 1.8 Hz), 3.52 (s, 3 H), 6.87 (q, 1 H, *J* = 1.8 Hz), 6.9–7.6 (m, 14 H)]. The above (*Z*) ester was prepared from the thioxanthone-sensitized irradiation of (*E*)-1-(*o*-bromophenyl)-2-carboethoxy-1-propene followed by separation of the mixture of isomers (3:2 steady-state ratio (*Z*:*E*)). Reduction of the (*Z*) ester with lithium aluminum deuteride gave the corresponding alcohol [NMR δ 1.98 (d, 3 H, *J* = 1.3 Hz), 3.94 (br s, 1 H), 6.29 (q, 1 H, *J* = 1.3 Hz), 6.8–7.6 (m, 4 H)]. This material was converted to the mesylate [NMR δ 1.86 (d, 3 H, *J* = 1.3 Hz), 3.03 (s, 3 H), 6.30 (q, 1 H, *J* = 1.3 Hz), 6.8–7.6 (m, 4 H)] which in turn was reduced to (*Z*)-(*o*-bromophenyl)-2-methyl-3,3,3-trideuterio-u-propene by lithium aluminum deuteride [NMR 1.81 (d, 3 H, *J* = 1.3 Hz), 6.21 (q, 1 H, *J* = 1.3 Hz), 6.83–7.52 (m, 4 H)]. This bromide was converted to the corresponding Grignard reagent which was allowed to react with diphenylmethylcyclopropenyl perchlorate to give a 38% yield of **22** [NMR δ 1.68 (d, 3 H, *J* = 1.3 Hz), 1.79 (s, 3 H), 6.56 (q, 1 H, *J* = 1.3 Hz), 6.9–7.9 (m, 14 H); *m/e* 339 (M^+ and base), 324, 205, 178, 105, 91, 77]. In addition of **22**, a 6% yield of the isomeric unsymmetrically substituted isomer **23** was also obtained [NMR δ 1.64 (d, 3 H, *J* = 1.3 Hz), 2.32 (s, 3 H), 6.21 (br q, 1 H, *J* = 1.3 Hz), 6.9–7.6 (m, 14 H); *m/e* 339 (M^+ and base), 324, 244, 205, 115, 105, 91, 77.

The thermolysis of a sample a sample of **22** in a 20% pyridine–benzene mixture at 160 °C for 10 min gave a 95% yield of **26**: mp 151–152 °C; NMR ($CDCl_3$, 90 MHz) δ 1.53 (s, 3 H), 1.75 (s, 3 H), 4.22 (br s, 1 H), 6.6–7.4 (m, 14 H); *m/e* 339, 329, 205, 168, 91, 77. Similarly, thermolysis of a sample of the unsymmetrical isomer **23** at 160 °C for 15 min produced the expected deuterium-labeled benzobicyclohexene **27** in 94% yield: mp 109–110 °C; NMR ($CDCl_3$, 90 MHz) δ 1.39 (s, 3 H), 1.75 (s, 3 H), 4.29 (br s, 1 H), 6.6–7.5 (m, 14 H).

Rate Studies. Stock solutions which were 10^{-3} M in the appropriate cyclopropene, 10^{-4} M in hexachlorobenzene (internal standard), containing 5.0 mL of anhydrous pyridine and 20 mL of anhydrous benzene were prepared. From each stock solution, 0.5-mL aliquots were withdrawn, degassed, and sealed under vacuum in 5-mm thick-walled glass ampules. The ampules were immersed in a thermostated (±0.1 °C) oil

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bath at the designated temperatures, and samples were periodically withdrawn for analysis. The product concentrations were determined by HPLC with a Waters Associates ALC 201 liquid chromatograph equipped with a Altex 4.6 mm × 250 mm Ultrasphere-ODS 5 μm column interface to a Hewlett-Packard 3380A integrator.

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Conformational Studies of Macrocyclic 1,2-Semidiones[1]

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Abstract: The rate of internal rotation in *trans*-tetracosane-1,2-semidione (**3**) has been measured: k(248 K) = 3.4 × 10^7 s^{-1}, $\Delta H^{\ddagger}$ = 5.7 kcal/mol. Similar rates were observed for the *trans*-1,2-semidiones derived from *p*-cyclophanes **4** and **5**, while the *p*-cyclophane derivative **6** has k(348 K) = 2.7 × 10^7 s^{-1}, $\Delta H^{\ddagger}$ = 10.8 kcal/mol. For **7**, the *trans*-1,2-semidione is locked in an asymmetric conformation at 353 K. The *cis*-1,2-semidiones in macrocyclic rings also have appreciable barriers to conformational motion which time-averages pairs of α-hydrogen atoms. For *cis*-**7** this process has $\Delta H^{\ddagger}$ = 16 kcal/mol while *cis*-**8** exists at 373 K in a locked conformation possessing two pairs of magnetically equivalent hydrogen atoms α to the dicarbonyl system.

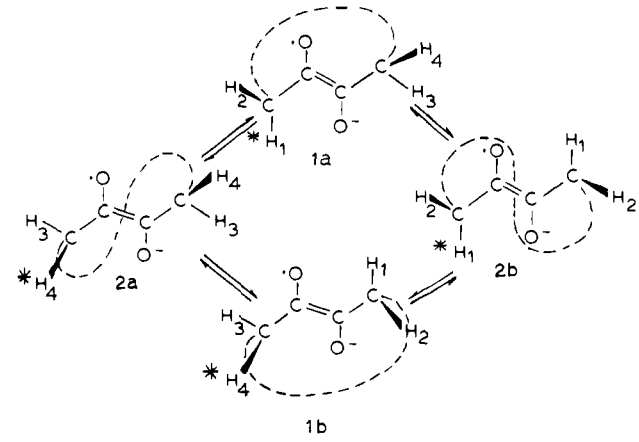
Cyclic 1,2-semidiones in rings of 11-15 atoms give complex ESR spectra in Me_2SO/K^+ because of the presence of trans and cis isomers both of which may display selective line broadening from conformational motion.[2] Ion pairing is more prominent for the cis isomer and leads to a lower g value.[3] In the presence of [2.2.2]-cryptand the trans isomer predominates for rings of more than 10 atoms.[2] Well-defined hyperfine splitting (hfs) by two pairs of α-hydrogen atoms has been observed in the trans isomers of cycloundecane-1,2-semidione at 170 °C,[2] 6,6-dimethyl-6-silacyclononane-1,2-semidione (25-110 °C),[4] 7,7-dimethyl-7-silacycloundecane-1,2-semidione (25-140 °C),[2] and cyclopentadecane-1,2-semidione (25-100 °C).[2] Heating the C_{15} semidione to 130 °C appeared to time average the pairs of α-hydrogen atoms, but the coalescence temperature was above the limit of thermal stability of the semidione.[2]

1,2-Semidiones give weak signals below 0 °C because of the disproportionation reaction 1 whose equilibrium is shifted to the right by complexing counterions, particularly in nonpolar solvents. However, in DMF at -20 °C a spectrum of *trans*-6,6-dimethyl-6-silacyclononane-1,2-semidione was obtained which was

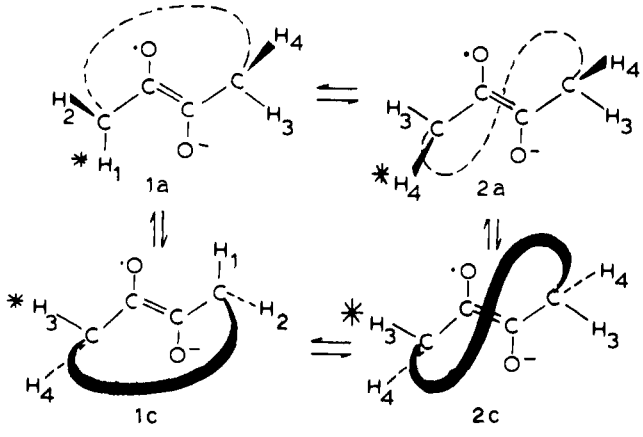
$$2RC(O\cdot)=C(O^-)R \rightleftharpoons RCOCOR + RC(O^-)=C(O^-)R \quad (1)$$

consistent with a selectively line broadened spectrum from a time-averaging process in which four magnetically different α-hydrogen atoms were being averaged to give two pairs of α-hydrogen atoms.[4] This observation led to the conclusion that in this case the preferred conformation of the *trans*-cyclic-1,2-semidione is asymmetric (**1a**,**b**) with different quasiaxial and quasiequatorial α-hydrogen atoms and with an appreciable energy barrier to the time-averaging process of Scheme I which produces pairs of hydrogen atoms ($H_1 \rightleftharpoons H_4$, $H_2 \rightleftharpoons H_3$). In conformation **1a** hydrogen atoms H(1) and H(3) are in the plane of the π-system (quasiequatorial) and their hyperconjugative interaction with the semidione spin should be much smaller than the interaction of the quasiaxial hydrogen atoms H(2) and H(4). The result of time averaging between **1a** and **1b** leads to two pairs of magnetically equivalent hydrogen atoms α to the dicarbonyl system (H(1)-H(4) and H(2)-H(3)) with nearly equivalent hfs. In the case of *trans*-6,6-dimethyl-6-silacyclononane-1,2-semidione, these hydrogens have a^H = 3.5 (2 H) and 2.5 (2 H) G at 25 °C.[4] *trans*-Cycloundecane-1,2-semidione at 170 °C also gave a time-averaged spectrum with a^H = 4.7 (2 H) and 3.1 (2 H) G.[2] On the other hand, the *trans*-1,2-semidiones of larger cycles, such as

Scheme I



Scheme II



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