Photochemistry of Cyclopropene Derivatives. 20. Deuterium Isotope Effects in the Triplet-Induced Photochemistry of Tetrasubstituted Cyclopropenes[1]

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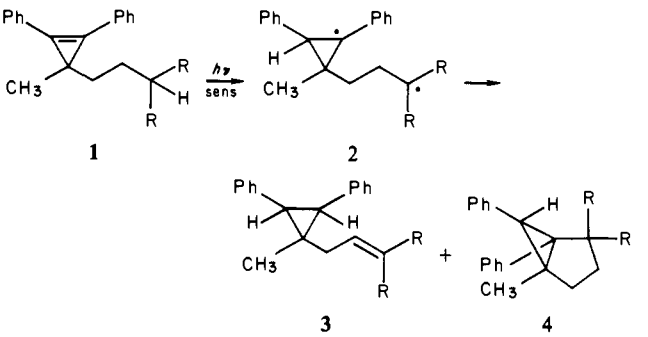
Abstract: The photochemical behavior of a number of 3-(*o*-alkylphenyl)-substituted cyclopropenes which contain a benzylic hydrogen in the γ-position of the side chain has been studied in mechanistic detail. The results obtained indicate that the products of the direct and triplet-sensitized photolysis are completely different. The singlet states of these systems react by σ-bond cleavage of the ring to give products which are explicable in terms of the chemistry of vinyl carbenes. The triplet state, generated by sensitization techniques, undergoes hydrogen atom abstraction by a mechanism analogous to the well-known Norrish type II process of carbonyl compounds. Rate constants for hydrogen abstraction were obtained by plotting Φ_o/Φ_q vs. *trans*-stilbene at a constant quencher to cyclopropene ratio. In contrast to the symmetrically substituted 1,2-diphenylcyclopropenes, the quantum efficiency of hydrogen abstraction of the 1,3 isomers was found to depend on the concentration of starting material. The primary deuterium isotope effect encountered with the symmetrical 1,2-diphenylcyclopropene systems is significantly larger than any previously reported value for hydrogen transfer to an excited state (k_H/k_D ca. 20/1). A substantial tunnel effect is proposed to rationalize the results. In contrast to the results obtained with the symmetrical cyclopropenes, a much smaller effect on the quantum efficiency was observed with the unsymmetrical systems (k_H/k_D = 3.3/1).

Of known photochemical processes, hydrogen abstraction has been surely one of the most intensively investigated reactions. Most studies have centered on the photochemistry of the carbonyl group. These include the photoreduction[2] of ketones in solvents with abstractable hydrogens and the type II reaction of ketones possessing γ-hydrogens.[3] The reactivity of the carbonyl group with respect to hydrogen abstraction depends dramatically on the configuration of the lowest lying triplet state.[4] The reactivity of n,π* triplets approximates that of alkoxy radicals,[5,6] whereas hydrogen abstraction by π,π* triplets is not observed or occurs at significantly lower rates.[7-9] The higher unpaired electron density on oxygen appears responsible for the greater reactivity in the former state.

In contrast to carbonyl compounds, examples of hydrogen abstraction in the direct and sensitized photolysis of olefins are less common. Nevertheless, a number of reports have appeared in the literature which show that the excited π,π* state of certain olefins have the ability to abstract hydrogen.[10-27] Thus, both intermolecular photoreduction and intramolecular hydrogen-transfer reactions have been reported for alkenes. Intramolecular hydrogen abstractions by carbon have also been observed in the photochemistry of α,β-unsaturated enones.[28] As part of a study designed to provide further information about the reactivity of excited olefins toward hydrogen abstraction, the triplet-induced photochemistry of a number of tetrasubstituted cyclopropenes has been investigated. In our previous studies we observed that the triplet-sensitized irradiation of tetrasubstituted cyclopropenes which possess γ-hydrogens leads to products involving intramolecular transfer of hydrogen from the side chain to the π–π* excited state of the alkene.[29,30] The products obtained were explained as resulting from disproportionation and/or collapse of a biradical intermediate. An example leading to both types of products is shown (Scheme I). The rate constants for hydrogen abstraction were found to be 2 orders of magnitude less than that

Scheme I



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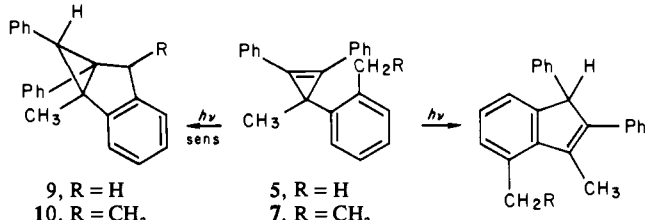
for related phenyl alkyl ketones and increased as the strength of the C–H bond in the γ-position decreased. The entropy of activation is typical of a reaction proceeding via a strain free six-center transition state and the activation energy associated with hydrogen abstraction was found to be dependent on the γ-C–H bond strength. The large value of the activation energy was attributed to the weak C–H bond that is being formed in the hydrogen abstraction reaction.[30] In order to provide more detailed information concerning the nature of the hydrogen abstraction reaction, we have investigated the photochemical behavior of a series of 3-*o*-alkylphenyl-substituted cyclopropenes. The effects of multiplicity, temperature, concentration, and deuteration upon the rate constants for intramolecular hydrogen abstraction have also been studied. As will be seen, the results indicate several, and important, differences from the now reasonably well-understood behavior of aromatic ketones. Our results also have important implications for understanding the triplet reactivity of olefins and for the more general question of rate enhancements in intramolecular hydrogen abstraction reactions.

Results

3-(*o*-Alkylphenyl)-substituted cyclopropenes were prepared by treating variously substituted cyclopropenyl cations with Grignard reagents according to the general procedure of Breslow and coworkers.[31] The mixture of isomeric cyclopropenes were readily separated by silica gel chromatography.

Direct irradiation of 1,2-diphenyl-3-methyl-3-*o*-tolylcyclopropene (**5**) in benzene with Pyrex-filtered light afforded 1,2-



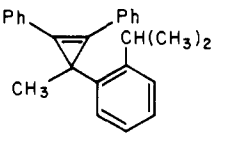
9, R = H
10, R = CH_3

5, R = H
7, R = CH_3

6, R = H
8, R = CH_3

diphenyl-3,4-dimethylindene (**6**) in 80% isolated yield. Similarly, the direct irradiation of the closely related (*o*-ethylphenyl)-cyclopropene system **7** afforded indene **8** in high yield. The structures of the photoproducts were deduced from their characteristic spectral data (see Experimental Section). In contrast to the direct photolysis, the sensitized irradiation of **5** in benzene (thioxanthone) produced 1-methyl-5,6-diphenyl-2,3-benzobicyclo[3.1.0]hexane **9** as the exclusive photoproduct. The identity of **9** was based on its characteristic NMR spectrum which showed a set of singlets at τ 8.48 (3 H) and 8.08 (1 H), a set of doublets at 6.86 (1 H, J = 16.0 Hz) and 6.56 (1 H, J = 16.0 Hz), and a multiplet at 2.8–3.6 (14 H). The sensitized photolysis of **7** also followed a different course from that encountered on direct irradiation and produced a mixture of *exo*- (**10a**) (80%) and *endo*-1,4-dimethyl-5,6-diphenyl-2,3-benzobicyclo[3.1.0]hexane (**10b**) (20%).

Further examples which would support the generality of the triplet-induced intramolecular hydrogen abstraction reaction of tetrasubstituted cyclopropenes were sought. With this in mind, we investigated the triplet-sensitized behavior of a number of 3-(*o*-alkylphenyl)-substituted cyclopropenes which contain a benzylic hydrogen atom. In each case, products arising from intramolecular hydrogen atom transfer were observed. The triplet-sensitized irradiation of 1,2-diphenyl-3-methyl-3-(*o*-isopropylphenyl)cyclopropene (**11**) in benzene resulted in a 3:2 mixture of 1,4,4-trimethyl-2,3-diphenyl-3,4-dihydronaphthalene (**12**) and benzobicyclohexane **13**. The NMR spectrum of **12** showed a set of singlets at τ 8.87 (3 H), 8.57 (3 H), 8.02 (3 H), and 6.78 (1 H) and a multiplet at 2.28–3.36 (14 H). Appropriate control experiments established that no interconversion of either



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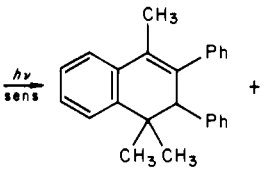

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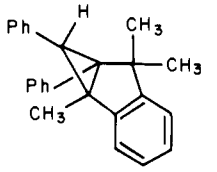

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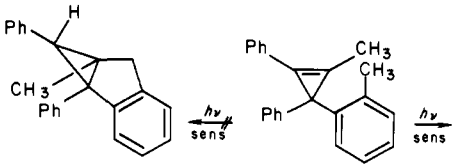
the photoproducts was operative under the reaction conditions. When the sensitized irradiation of an unsymmetrical cyclopropene such as 1,3-diphenyl-2-methyl-3-(*o*-tolyl)cyclopropene (**14**) was



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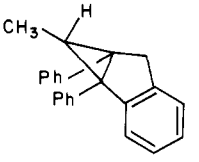

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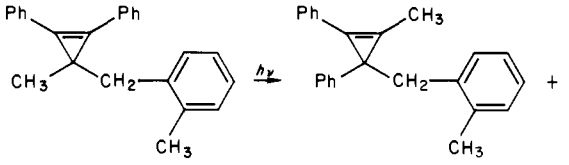
carried out in benzene, 1,5-diphenyl-6-methyl-2,3-benzobicyclo-[3.1.0]hexane (**15**) was isolated as the exclusive photoproduct. No signs of the isomeric 1,6-diphenyl-5-methyl-2,3-benzobicyclo[3.1.0]hexane (**16**) system could be detected in the crude photolysate.

We have also studied the photochemistry of the closely related 3-(*o*-alkylbenzyl)-substituted cyclopropene system. Direct irradiation of 1,2-diphenyl-3-methyl-3-(*o*-methylbenzyl)cyclopropene (**17**) in benzene with Pyrex-filtered light afforded a mixture of



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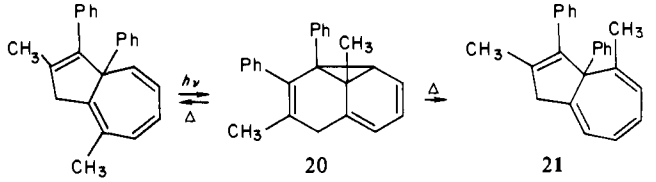

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1,3-diphenyl-2-methyl-3-(*o*-methylbenzyl)cyclopropene (**18**) (17%) and 2,8-dimethyl-3,4a-diphenyl-1,4a-dihydroazulene (**19**). The structure of dihydroazulene **19** was unequivocally established by an X-ray single-crystal structure analysis. The intensity data were measured on a Nicolet R_3 four-circle diffractometer using Cu Kα radiation. In the range of intensity measurements (0–100 in 2θ), 1836 unique reflections of the 2448 examined for the space group C2/c had peak counts significantly greater than background. The structure was derived by using direct methods and refined by least squares to give a R value of 0.0586 for all the data. The overall

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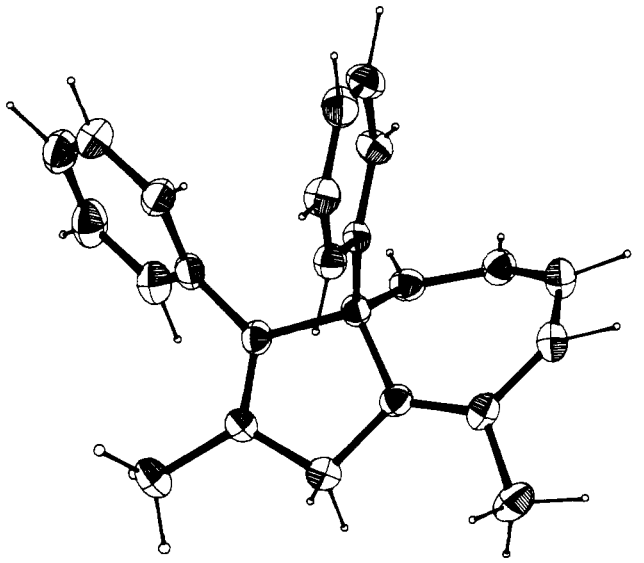
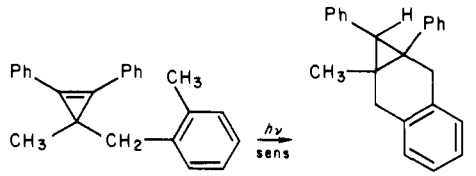


Figure 1. A general view of 2,8-dimethyl-3,4a-diphenyl-1,4a-dihydroazulene (**19**).

geometry of the molecule is shown in Figure 1.

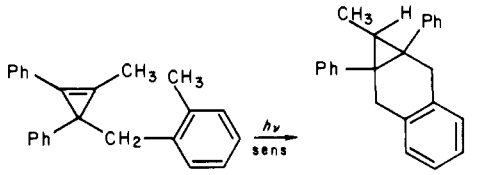
Dihydroazulene **19** was found to undergo a novel rearrangement on further irradiation. Thus, photolysis of a benzene solution of **19** through a Corex filter for 2 h produced 1,8-dimethyl-9,10-diphenyltricyclo[4.4.0.0^{2,10}]deca-3,5,8-triene (**20**) as the exclusive photoproduct. The structure of **20** was based on its characteristic spectral data. Further evidence supporting the structure of **20** was obtained by its thermal conversion to a 1:1 mixture of dihydroazulenes **19** and **21** on heating at 130 °C.

In contrast to the direct photolysis, the sensitized irradiation of **17** in benzene (thioxanthone) produced 1,7-diphenyl-6-



17 **22**

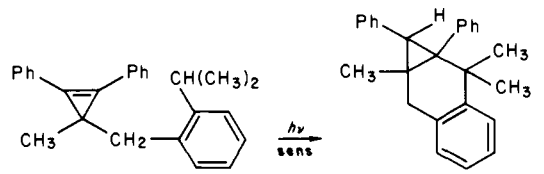
methyl-3,4-benzobicyclo[4.1.0]heptane (**22**) in 81% isolated yield. The structure of bicycloheptane **22** was assigned on the basis of its spectral properties (see Experimental Section). Subjection of the isomeric cyclopropene **18** to similar photolysis conditions gave



18 **23**

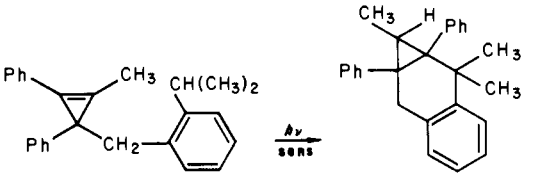
benzobicycloheptane **23** (86%). In this case only one of the two possible bicycloheptanes was produced.

Attention was next turned to the triplet-induced photobehavior of the 3-(*o*-isopropylbenzyl)-substituted cyclopropene system. The sensitized irradiation of cyclopropene **24** gave rise to 1,7-di-



24 **25**

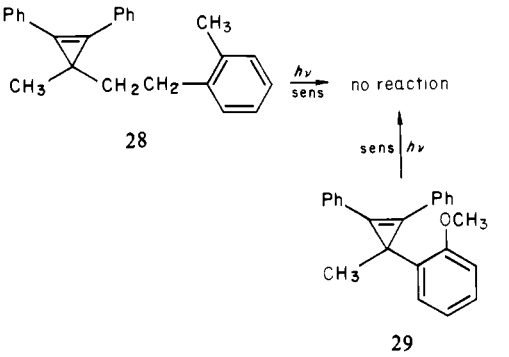
phenyl-2,2,6-trimethyl-3,4-benzobicyclo[4.1.0]heptane (**25**) in high yield. The identity of bicycloheptane **25** was determined by its straightforward spectral characteristics [NMR ($CDCl_3$, 100 MHz) τ 8.96 (s, 3 H), 8.69 (s, 3 H), 8.64 (s, 3 H), 7.76 (s, 1 H), 6.92 (d, 1 H, J = 16.0 Hz), 6.64 (d, 1 H, J = 16.0 Hz), 2.56–3.47 (m, 14 H)]. A similar result was obtained when the unsymmetrically substituted cyclopropene **26** was irradiated in the presence of a



26 **27**

triplet sensitizer. The structure of the photoproduct obtained (**27**) was deduced from its characteristic spectral data (see Experimental Section).

We also examined the triplet-induced photobehavior of cyclopropenes **28** and **29**. Both of these compounds were found



28 **29**

to be stable on irradiation in the presence of a triplet photosensitizer. The reluctance of cyclopropene **28** to undergo hydrogen atom transfer is undoubtedly a result of the absence of a hydrogen atom in the γ- or δ-position of the side chain. The lack of reactivity of cyclopropene **29**, on the other hand, is probably a result of the large activation energy associated with the transfer of a nonbenzylic hydrogen atom to the excited cyclopropene moiety.

Determination of Reaction Efficiency and Reaction Rates. For the derivation of additional mechanistic information concerning these intramolecular hydrogen-transfer reactions, a more quantitative investigation of these processes was undertaken. Quantum yields for product formation were determined by using benzophenone–benzhydrol as the chemical actinometer.[32] The triplet energy of 1,2-diphenyl-substituted cyclopropenes has been estimated as approximately 55 kcal/mol from the kinetics of reversible energy transfer to low-lying triplet sensitizers.[33-35] We suspect that the triplet state of the unsymmetrically substituted cyclopropene system (i.e., 1,3-diphenyl-2-methyl) is higher lying in energy. Since the chromophore is the same as 1-phenylpropene, we assume that the triplet energy of this system is about 65 kcal/mol.[36] The photosensitized reactions were reasonably efficient, with quantum yields varying from 0.13–0.9 at 40 °C.

Measurements of the quantum yield of reaction of the 1,2-diphenyl-substituted cyclopropenes in the presence of quenchers can be used to calculate the rate constant for hydrogen abstraction. Since the intersystem-crossing quantum yield for these systems is close to zero,[33,37] it is necessary to use a sensitizer to populate

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Scheme II

$$S_0 \xrightarrow{h\nu} S^{*1} \xrightarrow{k_{isc}} S^{*3}$$
$$S^{*3} + C_0 \xrightarrow{k_{SC}} C^{*3} + S_0$$
$$S^{*3} + Q_0 \xrightarrow{k_{SQ}} Q^{*3} + S_0$$
$$S^{*3} \xrightarrow{k_{SD}} S_0$$
$$C^{*3} \xrightarrow{k_r} B \rightarrow P_0$$
$$C^{*3} \xrightarrow{k_d} C_0$$
$$C^{*3} + Q_0 \xrightarrow{k_{CQ}} C_0 + Q^{*3}$$

Table I. Quantum Yield and Kinetic Data for the Triplet-Sensitized Hydrogen Abstraction Reaction[a,b]

cyclopropene	Φ[c,d]	$k_{CQ}\tau^3 C$, M[e]	$10^7\tau$, s^{-1}	$10^5 k_r$, s^{-1}
5	0.19	4850	9.7	1.96
30-d_3	0.0098	5730	11.5	0.085
7	0.68	4200	8.13	8.36
17	0.13	4760	9.52	1.37
32-d_3	0.008	5050	10.1	0.079
24	0.91	4620	9.24	9.83
14	0.56[f]			
31-d_3	0.165[f]			
18	0.30[f]			
33-d_3	0.091[f]			
26	0.24[f]			

[a] Concentration of cyclopropene ca. 1×10^{-2} M. [b] 40 °C. [c] Sum of all products. [d] ±10%. [e] ±20%. [f] 1.5×10^{-2} M.

the triplet state. We found that *trans*-stilbene (E_T = 50 kcal/mol)[38] can act as a quencher for the triplet-sensitized hydrogen-transfer reaction of the cyclopropenes. In these experiments, *trans*-stilbene intercepts both the sensitizer triplet (thioxanthone) and the cyclopropene triplet. It was assumed that both triplets (thioxanthone (E_T = 65.6 kcal/mol)[38] and cyclopropene (E_T = ≈ 55 kcal/mol)) were quenched at the same diffusion-controlled rate. In order to minimize the amount of energy transfer from the sensitizer to the quencher, it is important to keep the ratio of [cyclopropene]/[stilbene] as high as possible.

We have used Cristol's method[39] to approximate the rate of hydrogen transfer of the triplet state of the symmetrically 1,2-diphenyl-substituted cyclopropene system. The kinetic expression for the triplet-photosensitized reaction, involving sensitizer S_0, cyclopropene C_0, and quencher Q_0 to give bicyclo[3.1.0]pentane *P*, was derived from Scheme II. The extent of conversion of triplet cyclopropene to product in benzene was studied as a function of the concentration of *trans*-stilbene as quencher. Plots of Φ_0/Φ_q at varying quencher concentration but with constant [Q]/[C] ratios ([Q]/[C] = 1/50) give lines whose intercepts afford k_{SQ}/k_{SC} ratios whose slopes divided by the intercepts give $k_{CQ}{}^3$ values (eq 1). The modified Stern–Volmer plots obtained were linear with

$$\Phi_0/\Phi_q = \left[1 + \frac{k_{SQ}[Q]}{k_{SC}[C]}\right] + \left[1 + \frac{k_{SQ}[Q]}{k_{SC}[C]}\right] k_{CQ}\tau^3 C[Q] \quad (1)$$

the slopes listed in Table I as $k_{CQ}\tau^3$ *C* values. The value of k_{CQ} in benzene is taken to be 5×10^9 L mol^{-1}.[40] Quantum yields and k_r values are given in Table I for the cyclopropenes studied. The data clearly show that the symmetrically 1,2-diphenyl-substituted cyclopropenes all accept excitation from triplet thioxanthone with a reaction rate constant k_{SC} which is essentially diffusion controlled to give excited π–π^* states which have lifetimes, as measured by *trans*-stilbene quenching, of a few microseconds before trans-

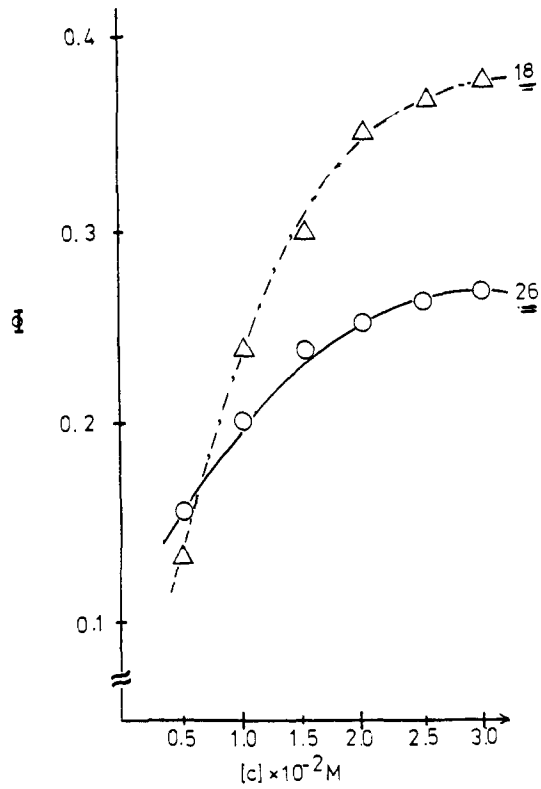
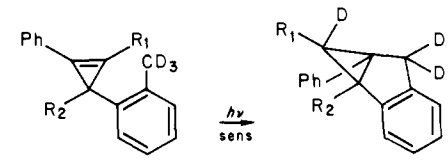


Figure 2. Quantum yield of reaction of cyclopropenes **18** and **26** vs. concentration of starting material.

formation to product or to some biradical species (B) leading to product. If the biradical intermediate B, formed by hydrogen transfer, reverts to cyclopropene, then the mechanism shown in Scheme I would have to be modified and the expression for Φ_0 would include a factor representing the fraction of biradicals that go on to product. This latter fraction is not known, though a minimum value for it is given by the reaction quantum yield.

We have also carried out similar experiments with the unsymmetrically substituted cyclopropenes **14**, **18**, and **26**. With these systems, however, the quantum yield for reaction was found to depend on the concentration of starting material. As a result of this dependence it was not possible to determine the rate of hydrogen abstraction by Cristol's method.[39] This unusual concentration effect was only observed with the unsymmetrically substituted cyclopropenes. The quantum yield of reaction of the symmetrical 1,2-diphenyl-substituted cyclopropene system was found to be independent of the concentration of starting material. At low concentrations of starting material, the quantum yield for reaction of unsymmetrical cyclopropene **18** is 0.13. At higher concentrations it levels off to a value of 0.38. With cyclopropene **26**, a concentration dependence of the quantum yield is also observed with values ranging from 0.16 to 0.27 (see Figure 2).

Deuterium Isotope Effects. In order to provide more detailed information concerning the hydrogen transfer reaction, we have examined the effect of deuteration upon the rate constant for hydrogen abstraction. Synthesis of the 1,2- and 1,3-diphenyl-substituted (*o*-methyl-d_3-phenyl)cyclopropenes **30** and **31** involved



30, R_1 = Ph, R_2 = CH_3
31, R_1 = CH_3, R_2 = Ph

the reaction of diphenylmethylcyclopropenyl cation with trideuterio-labeled *o*-bromotoluene Grignard reagent followed by chromatographic separation of the isomeric cyclopropenes. For

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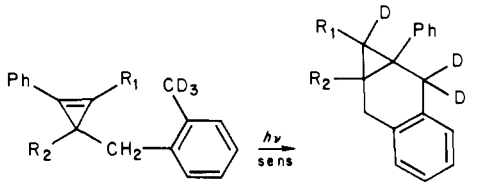
the deuterated (*o*-methylbenzyl)-substituted cyclopropenes **32** and **33**, the labeled Grignard reagent was prepared from (*o*-methyl-



32, $R_1 = Ph$, $R_2 = CH_3$
33, $R_1 = CH_3$, $R_2 = Ph$

d_3-benzyl) chloride, obtained from the reduction of ethyl *o*-methyl-d_3-benzoate followed by treatment with hydrochloric acid. The NMR spectra of **32** and **33** show the complete absence of the benzylic methyl signal and the mass spectra show them to be >98% d_3 labeled (i.e., m/e 313). The triplet-sensitized photolysis of the deuterated cyclopropenes was much slower than the undeuterated compounds. Comparative NMR spectra of deuterated and authentic undeuterated photoproduct indicate that one deuterium was present in the expected endo position of the benzobicycloalkane ring.

Quantitative runs were carried out with the four deuterated cyclopropenes in benzene by using thioxanthone as the sensitizer. The progress of reaction and the quantum yield of product formation were followed by quantitative high-pressure liquid chromatography. The results of the Stern–Volmer plots obtained with the symmetrical cyclopropenes **30** and **32**, using a ratio of [Q]/[C] = 1/50 and *trans*-stilbene as quencher, are given in Table I. As may be noted, the data lead to similar $k_{CQ}\tau^3 C$ values of 5730 and 5050 for cyclopropenes **30** and **32**. The quantum yields for the sensitized hydrogen atom transfer reaction of the four deuterated cyclopropenes are also given in Table I. It was not possible to determine the triplet lifetimes of the unsymmetrically substituted 1,3-diphenyl-deuterated cyclopropenes, since the quantum efficiency of the reaction was markedly dependent on the concentration of starting material. The quantum yields for the triplet state hydrogen-transfer reaction of the symmetrical systems (i.e., **30** and **32**) decreased substantially with deuterium substitution. For example, the quantum yield decreases from 0.19 for cyclopropene **5** to 0.0098 for deuterated cyclopropene **30**. Similarly, the quantum efficiency for reaction of the homologous benzyl–*o*-tolyl system (**32**) drops from 0.13 to 0.008.

The relative lifetimes of the triplet states of the deuterated and nondeuterated cyclopropenes may be estimated from the relative ratios of the Stern–Volmer slopes. Our work shows that the triplet lifetimes are very similar (ca. within 10%) and consequently the ratio of quantum yields provides a good indication of the magnitude of the primary deuterium isotope effect.

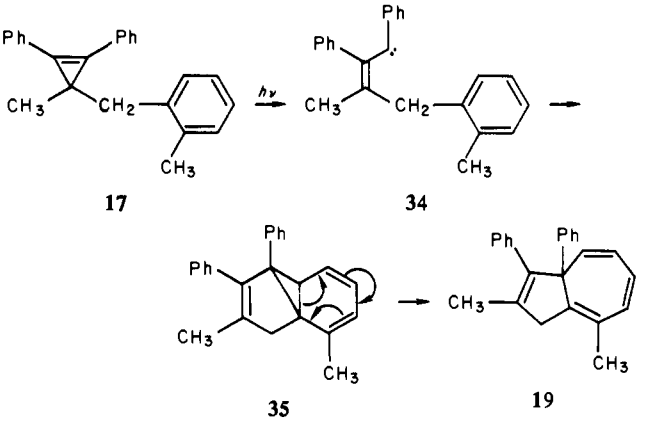
$$\Phi_H = k_{r_H}\tau_H \qquad \Phi_D = k_{r_D}\tau_D \qquad \frac{\Phi_H}{\tau_H}\frac{\tau_D}{\Phi_D} = k_H/k_D$$

The results obtained with the deuterated symmetrical cyclopropene systems indicate that the deuterium isotope effect on the γ-abstraction reaction is $k_H/k_D = 23$ for **30** and $k_H/k_D = 17$ for **32**. The primary isotope effects found for hydrogen transfer with cyclopropenes **30** and **32** are significantly larger than any previously reported values. We have searched for sources of gross error in these isotope effects, including those arising from effects of impurities, light intensity, concentration, product analysis, and uncertainties in temperature, extinction coefficient, and time errors, and we have not found any. The reproducibility of our measurements was found to be better than ±7% on the quantum yield determinations.

Whereas an extremely large isotope effect was encountered with cyclopropenes **30** and **32**, a much smaller effect on the quantum efficiency of product formation was observed with the unsymmetrical cyclopropenes **31** and **33**. With these two compounds, the deuterium isotope effect (k_H/k_D ca. 3) is much smaller than the previously determined values for **30** ($k_H/k_D = 23$) and **32** ($k_H/k_D = 17$). As was pointed out earlier, the ratio of quantum yields provides for a good approximation of the deuterium isotope effect. A possible explanation to account for the lower value of the isotope effect in the unsymmetrical systems will be described in the Discussion.

Discussion

The photochemistry of cyclopropene derivatives has attracted considerable interest over the past several years.[41] The photochemical behavior of this highly strained ring system has been shown to be remarkably dependent on the multiplicity of the excited state involved.[33,41] Singlet states generally react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinyl carbenes.[42] Thus, the formation of indenes **6** and **8** can readily be accounted for in terms of a transient vinyl carbene which cyclizes to an isoindene intermediate which subsequently undergoes a 1,5-sigmatropic shift to give the aromatic indene system.[43,44] Yet another reaction undoubtedly resulting from a vinyl carbene intermediate is the formation of dihydroazulene **19** from the irradiation of cyclopropene **17**. The formation of **19** is perfectly consistent with a vinyl carbene intermediate (i.e., **34**) which attacks the π-electrons of the adjacent aromatic ring to give **35** as a transient species. This reactive norcaradiene is rapidly converted to **19** via an electrocyclic ring opening reaction. The formation of dihydroazulene **19** from the addition of the vinyl carbene onto the neighboring aromatic ring has precedent in the literature.[45,46] In fact, this reaction has been used as the key step in a general azulene synthesis.[47]



17 **34** **35** **19**

We consider that the most economical explanation for the formation of the tricyclo[4.4.0.0^{2,10}]decatriene system from the irradiation of dihydroazulene **19** is that illustrated in Scheme III. Photolysis of **19** results in ring closure to regenerate norcaradiene **35**. The observed product can then be derived from this intermediate by a series of bond scission and recombination steps as outlined in Scheme III. The mechanism of Scheme III also serves to rationalize the formation of a mixture of dihydroazulenes **19** and **21** on thermolysis of tricyclodecatriene **20**.

The formation of the unsymmetrical cyclopropene **18** from the irradiation of **17** merits some comment. This reaction corresponds to a rare example of a singlet state reaction of a cyclopropene in which the three-membered ring has been retained.[48] A mechanism analogous to that accepted for the type I reaction of ketones[49]

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(43) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N. *J. Am. Chem. Soc.* **1977**, *99*, 2344. Padwa, A.; Loza, R.; Getman, D. *Tetrahedron Lett.* **1977**, 2847. Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481.
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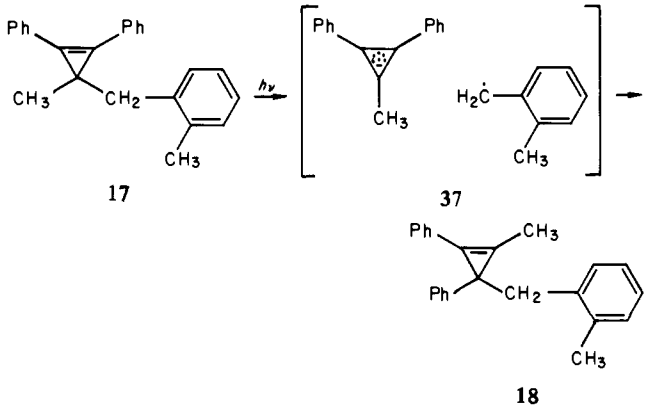
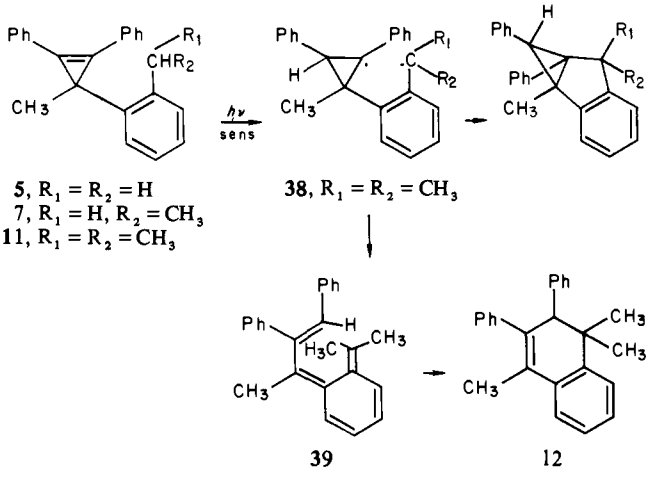
(49) Turro, N. J. "Modern Molecular Photochemistry"; The Benjamin-Cummings Publishing Co.; Menlo Park, CA, 1978.



17 37 18

can readily account for the formation of the rearranged cyclopropene. Introduction of a (*o*-methoxybenzyl) group on the 3-position of the cyclopropene ring apparently stabilizes the radical pair intermediate **37** enough to allow fragmentation to compete with ring cleavage. Cyclopropenes **5** and **7**, without this stabilization, yield only ring-opened products. It should be pointed out that the formation of the unsymmetrical cyclopropene from the radical pair **37** is to be expected since the transition state prefers to localize the odd electron on the phenylated carbon of the cyclopropene ring.[50]

In contrast to the photobehavior exhibited by the electronically excited singlet state, triplet states of tetrasubstituted cyclopropenes which possess γ-hydrogens have been found to undergo an intramolecular hydrogen-transfer reaction[30] by a mechanism analogous to the well-known Norrish type II photoreaction of carbonyl compounds.[3] Thus, the triplet state of cyclopropene **5** (or **7**) readily abstracts a hydrogen from the neighboring benzylic



5, $R_1 = R_2 = H$
7, $R_1 = H$, $R_2 = CH_3$
11, $R_1 = R_2 = CH_3$

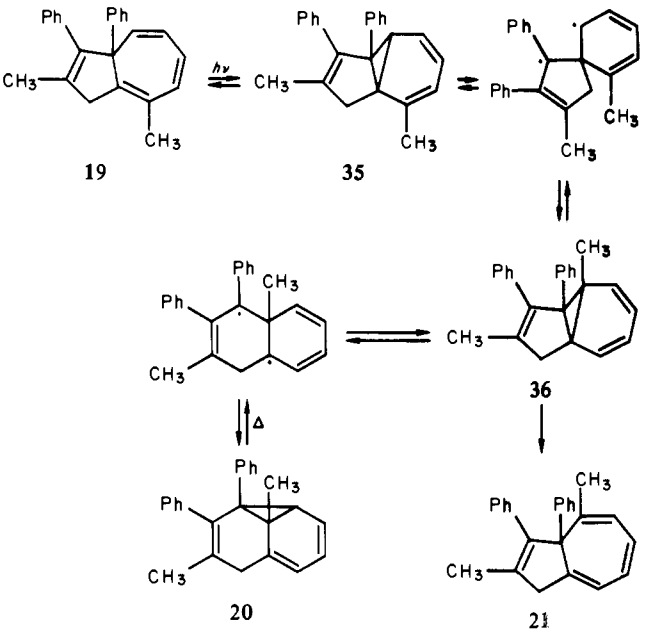
38, $R_1 = R_2 = CH_3$

39 12

methyl group to produce a biradical intermediate **38** which collapses to give the benzobicyclo[3.1.0]hexane ring system. Similar hydrogen abstraction with the triplet state of cyclopropene **11** would be expected to lead to a related biradical intermediate (**38**). Simple collapse of **38** with carbon–carbon bond formation would furnish benzobicyclohexane **13** directly. In addition, the biradical intermediate generated from **11** is long enough lived to undergo cyclopropyl ring opening in competition with coupling. Opening of the cyclopropyl ring produces hexatriene **39** which subsequently cyclizes to give **12**. Cyclopropenes **5** and **7**, without the added methyl group stabilization, generates a more reactive diradical which rapidly couples before it has a chance to undergo ring opening.

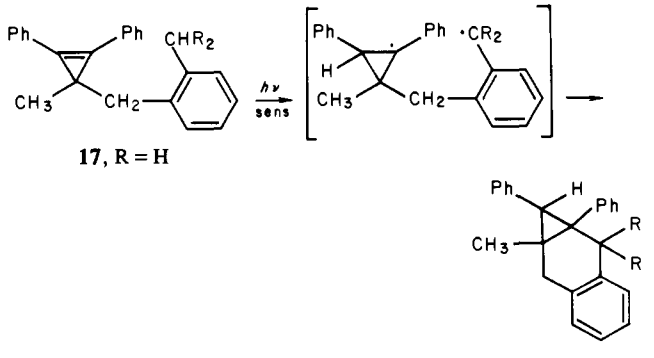
The relative rate constants for the triplet states of cyclopropenes **5** and **7** in benzene are easily rationalized on the basis of structural considerations. Abstraction of the secondary hydrogen of **7** occurs 4 times more readily than primary hydrogen removal (i.e., k_7/k_5 = 4/1). Moreover, the quantum efficiency of abstraction for these two cyclopropenes is directly related to the triplet state reactivity. With these systems, the initially produced biradical intermediate does not undergo reverse hydrogen transfer as was observed in the phenyl alkyl ketone system.[51] This is to be expected since it is highly unlikely that the 1,5-biradical will regenerate the highly strained (53 kcal/mol)[52] cyclopropene ring when it can easily undergo coupling. The high quantum efficiency associated with these reactions is fully compatible with the suggestion that the 1,5-biradical intermediate does not revert to starting material by reverse hydrogen transfer. It is also of interest to note that the triplet lifetimes (see Table I) of the cyclopropenes are several hundred times greater than those for the related phenyl alkyl ketones.[3,4] The longer lifetime of the cyclopropenes may very well reflect the weaker C–H bond being formed in the abstraction reaction. In addition, the rate of hydrogen abstraction is significantly less than that for the phenyl ketone system. The much lower rate constant for hydrogen abstraction is probably related to radical delocalization of the triplet state by the attached phenyl groups and perhaps also to a lower reactivity of the planar π–π^* state.

Scheme III



19 35 36 20 21

The formation of benzobicyclo[4.1.0]heptane **21** in quantitative



17, R = H

21

yield from the triplet-sensitized irradiation of **17** clearly indicates that δ-hydrogen abstraction can also occur. It is worthy to note that δ-hydrogen abstraction with cyclopropene **24** (R = CH_3) proceeds with a quantum efficiency approaching unity (i.e., Φ_{24} = 0.91). The extremely high quantum yield is consistent with

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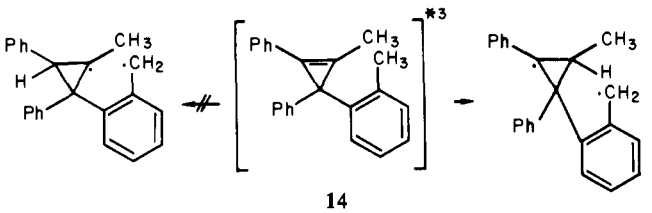
very efficient biradical formation. The presence of two methyl groups on the benzylic carbon atom was found to increase both the quantum yield and rate constant for reaction by a factor of 7. The reluctance of the homologous cyclopropene **28** to undergo ϵ-hydrogen transfer is undoubtedly a result of unfavorable entropy requirements. The lack of reactivity of cyclopropene **29**, on the other hand, is probably related to the much greater bond dissociation energy of the C–H bond of the methyl ether functionality. This would tend to suggest that the rate of hydrogen transfer in the cyclopropene series is much more sensitive to the strength of the γ-C–H bond than that observed with the corresponding phenyl alkyl ketone system. This is quite reasonable since a benzylic type radical should be much more selective than an alkoxy radical toward hydrogen abstraction as a consequence of the greater endothermicity of the reaction.

We have found that the sensitized irradiation of an unsymmetrically substituted cyclopropene such as **14**, **18**, or **26** proceeds



14

via hydrogen transfer to the carbon bearing the methyl group. The complete regiospecificity of the reaction is undoubtedly related to the fact that the diradical produced on hydrogen transfer to the methyl-bearing carbon allows maximum delocalization of the radical centers in the resulting diradical intermediate.

Another point worth mentioning is that the quantum yield for hydrogen transfer from cyclopropene **26** ($\Phi = 0.24$) is actually less than that observed with cyclopropene **18** ($\Phi = 0.3$). This is most unusual since a tertiary benzylic C–H bond is weaker than a primary benzylic C–H bond. We had previously noted in the symmetrical diphenyl series that the quantum efficiency associated with the hydrogen-transfer reaction decreases as the strength of the C–H bond increases.[30] The quantum yield for hydrogen transfer in the unsymmetrical series, however, depends on the concentration of starting material, and, consequently, it was not possible to determine the rate of hydrogen transfer by Cristol's method.[39] As may be noted from Figure 2, the quantum yield of reaction with cyclopropene **18** is much more sensitive to concentration effects than that noted with **26**. In fact, at low concentrations of starting material, we find that the quantum yield for reaction of **26** is actually larger than that for **18**. One possible rationale which could account for the unusual concentration effect in the unsymmetrical series is that the hydrogen-transfer reaction proceeds by both an intramolecular and bimolecular component. The bimolecular portion may involve an electron-transfer reaction which proceeds via a short radical chain.[30] Further work is necessary in order to establish this point.

Perhaps the most striking result that we have uncovered in the course of our studies is the extremely large kinetic isotope effect encountered with cyclopropenes **30** and **32**. Substitution of hydrogen with deuterium in organic compounds may exert a marked effect on certain properties of their excited states.[53-56] The deuterium isotope effect on the physical behavior of excited states may be attributed, in part, to the differences in the magnitude of the vibrational overlap integral between the ground and the excited states.[57,58] In addition, the usual isotope effect involved in the breaking of a C–D bond may cause a modification in the photochemical behavior of an organic compound. The extent of these isotope effects may depend on how extensively the C–D bond interacts with the excited states. Deuterium labeling has been widely used in mechanistic studies of the type II photoelimination of ketones.[59-64] Primary kinetic isotope effects have been reported for several ketones with values of k_H/k_D ranging from 1.7 to 5.5.[13-15] It should also be noted that negative deuterium isotope effects on the quantum yield of the type II photoelimination of carbonyl compounds have occasionally been observed.[59,68,69] The explanation that has been offered to account for the increased quantum yield of the deuterated ketones is that reversion of the biradical to the ketone is slower when deuterium rather than hydrogen is being transferred.[59]

Secondary as well as primary deuterium isotope effects will influence the rate constant for the hydrogen abstraction reaction. A secondary α-isotope effect on the order of 1.10–1.15 per deuterium has been reported for several homolytic reactions.[70] Consequently, the secondary deuterium isotope effect associated with the hydrogen-transfer reaction of cyclopropenes **30** and **32** should be approximately 1.30, which is the maximum value predicted by Streitweiser for a change from sp^3 to sp^2 hybridization.[71] The primary deuterium isotope effect for the hydrogen-transfer reaction of **30** is still extremely large ($k_H/k_D \approx 18$). In fact, the deuterium isotope effect encountered with the symmetrical cyclopropene system is larger than any previously reported value for hydrogen transfer in the excited state.

The magnitude of the primary isotope effect in a hydrogen-transfer reaction varies with the symmetry of the transition state and is a maximum when the hydrogen is symmetrically bonded to the atoms between which it is being transferred.[72-76] Calculations of isotope effects for simplified models of hydrogen-transfer reactions are consistent with the conclusion that the isotope effect should pass through a maximum for a symmetrical transition state.[77] It is evident from Table I that the largest isotope effects occur with the symmetrical 1,2-diphenyl-substituted cyclopropenes in which hydrogen transfer is approximately half complete at the transition state. The transition state for the abstraction reaction is very nearly symmetrical, and the isotope effect should be near

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(77) Calculations supporting this postulate are given by: O'Ferrall, R. A. M.; Kouba, J. *J. Chem. Soc. B* **1967**, 985.

the maximum. In fact, the primary isotope effect encountered with cyclopropenes **30** and **32** is even larger than that calculated as the upper limit on the basis of ordinary absolute reaction rate theory. Melander[72c] calculated for a breakage of a normal C–H bond a maximum $k_H/k_D = 17$ at room temperature, and various other estimates are about the same or lower. The transition states required to give these values, however, are highly unrealistic for a proton transfer. A substantial tunnel correction is necessary to reconcile these results with absolute reaction rate theory. The criterium for tunneling was proposed and originally found by Bell.[75,78] Thus, a plausible explanation to account for the large isotope effect is that the barrier for hydrogen transfer with cyclopropenes **30** and **32** is high and thin, which is the ideal situation for tunneling.[79]

Hammond's postulate suggests that the most symmetrical transition state should occur for that case in which the heat of reaction is most nearly zero.[80,81] Exothermic or endothermic reactions, on the other hand, would be predicted to have relatively unsymmetrical transition states resembling either reactants or products, respectively. Biradical formation from the symmetrical cyclopropene involves the making and breaking of bonds with similar dissociation energies.[82] With the 1,3-diphenyl-substituted systems, hydrogen abstraction occurs on the methyl-bearing carbon atom and therefore the heat of reaction would be expected to be considerably more exothermic. The primary isotope effects noted with cyclopropenes **31** and **33** indicate an early transition state according to Hammond's postulate. The values obtained (i.e., k_H/k_D ca. 3.3) correlate well with related results in the literature.[83] The greater exothermicity of biradical formation from cyclopropenes **31** and **33** is thus in accord with the smaller kinetic isotope effect for hydrogen abstraction.

An additional line of evidence for an early transition state with these unsymmetrical systems is the absence of a significant difference in the quantum efficiency for product formation with cyclopropenes **22** and **26**. As was mentioned earlier, the quantum yield for the hydrogen abstraction reaction of these tetrasubstituted cyclopropenes is directly related to triplet state reactivity. With cyclopropenes **5** and **7**, the relative rate constants for transfer of the primary and tertiary benzylic hydrogens closely parallels the relative quantum yields. With the unsymmetrical cyclopropenes **22** and **26**, however, we find essentially no difference in the quantum yield for product formation. This indicates the absence of a significant rate enhancement by substituents which traditionally stabilize benzylic radicals. Such behavior is common in exothermic homolytic reactions[84] and has been noted for both intramolecular[67] and intermolecular hydrogen abstraction reactions of aromatic ketones.[85,86]

In conclusion, the results obtained from this investigation indicate that triplet states of tetrasubstituted cyclopropenes possessing γ-hydrogens undergo ready intramolecular hydrogen transfer. The magnitude of the primary isotope effect in the hydrogen-transfer reaction was found to be markedly dependent on the nature of the substituent groups attached to the double bond. The primary isotope effect found with 1,2-diphenyl-substituted cyclopropenes is significantly larger than any previously reported value for hydrogen transfer to an excited state. We are continuing to examine the hydrogen-transfer reaction and will report additional findings at a later date.

Experimental Section[87]

Preparation of 1,2-Diphenyl-3-methyl-3-(*o*-tolyl)cyclopropene (5) and 1,3-Diphenyl-2-methyl-3-(*o*-tolyl)cyclopropene (14). To a suspension containing 5.0 g of 3-methyl-1,2-diphenylcyclopropenyl perchlorate[30] in 200 mL of tetrahydrofuran at −78 °C was added 100 mL of a 0.67 M solution of *o*-tolylmagnesium bromide in ether. The mixture was stirred at −78 °C for 4 h and was then allowed to warm to room temperature. The solution was quenched with a saturated ammonium chloride solution, and the organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the resulting yellow oil was subjected to silica gel chromatography with use of hexane as the eluant. The major component isolated from the column contained 1.5 g (30%) of a crystalline solid (mp 72–73 °C) whose structure was assigned as 1,2-diphenyl-3-methyl-3-(*o*-tolyl)-cyclopropene (**5**) on the basis of its spectroscopic properties: IR (KBr) 3.32, 3.45, 5.53, 6.25, 6.70, 6.93, 7.30, 7.75, 7.83, 9.30, 9.60, 10.95, 13.25, 13.70, 14.55 μm; UV (95% ethanol) 316 nm (ε 18 500); NMR ($CDCl_3$, 100 MHz) τ 8.16 (s, 3 H), 7.44 (s, 3 H), 2.2–2.96 (m, 14 H); *m/e* 296 (M^+, base), 281, 265, 219, 203, 202, 105, 91, 77.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 92.93; H, 6.87.

The second component isolated from the column contained 0.98 g (20%) of a crystalline solid, mp 118–119 °C, whose structure was assigned as 1,3-diphenyl-2-methyl-3-(*o*-tolyl)cyclopropene (**14**) on the basis of its spectral data: IR (KBr) 3.25, 3.48, 5.33, 6.15, 6.66, 6.88, 7.18, 8.77, 9.26, 10.83, 11.01, 11.41, 12.47, 13.10, 13.35, 13.68, 14.05, 14.26, 14.40 μm; UV (95% ethanol) 262 nm (ε 16 800); NMR ($CDCl_3$, 100 MHz) τ 7.76 (s, 3 H), 7.55 (s, 3 H), 2.2–2.98 (m, 14 H); *m/e* 296 (M^+, base), 282, 281, 205, 203, 202, 91, 77.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.51; H, 6.88.

Direct Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-tolyl)cyclopropene (5). A solution containing 100 mg of **5** in 100 mL of benzene under an argon atmosphere was irradiated with a 450-W Hanovia lamp through a Pyrex filter sleeve for 2.5 h. Removal of the solvent under reduced pressure left a pale yellow oil which was chromatographed on a thick-layer plate with use of hexane as the eluant. The major band contained 80 mg (80%) of a clear oil whose structure is assigned as 1,2-diphenyl-3,4-dimethylindene (**6**) on the basis of its spectroscopic properties: IR (neat) 3.25, 3.35, 6.20, 6.65, 6.85, 7.20, 9.35, 9.45, 9.70, 9.95, 10.95, 12.45, 13.10, 13.45, 13.60, 14.43 μm; UV (95% ethanol) 290 nm (ε 11 100); NMR ($CDCl_3$, 100 MHz) τ 7.60 (d, 3 H, J = 2. 0 Hz), 7.36 (s, 3 H), 5.20 (q, 1 H, J = 2.0 Hz), 2.6–3.1 (m, 13 H); *m/e* 296 (M^+, base), 281, 266, 265, 219, 205, 203, 202, 91, 84, 77.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.06; H, 6.72.

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-tolyl)-cyclopropene (5). A mixture containing 100 mg of **5** and 10 mg of thioxanthone in 100 mL of benzene was irradiated through a Uranium filter sleeve with use of a 450-W Hanovia mercury lamp for 2.5 h. The solvent was removed under reduced pressure, and the resulting yellow oil was subjected to thick-layer chromatography with use of hexane as the eluant. The major component isolated contained 83 mg (83%) of a white solid (mp 106–107 °C) whose structure was assigned as 1-methyl-5,6-diphenyl-2,3-benzobicyclo[3.1.0]hexane (**9**) on the basis of its spectroscopic properties: IR (KBr) 3.30, 3.45, 6.26, 6.60, 6.90, 7.22, 8.15, 8.30, 8.60, 9.20, 9.70, 10.72, 11.71, 12.20, 13.0, 13.62, 14.30 μm; UV (95% ethanol) end absorption; NMR ($CDCl_3$, 100 MHz) τ 8.48 (s, 3 H), 8.08 (s, 1 H), 6.86 (d, 1 H, J = 16.0 Hz), 6.56 (d, 1 H, J = 16.0 Hz), 2.8–3.6 (*m*, 14 H); *m/e* 296 (M^+, base), 281, 219, 205, 167, 86, 84.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.16; H, 6.64.

Triplet-Sensitized Irradiation of 1,3-Diphenyl-2-methyl-3-(*o*-tolyl)-cyclopropene (14). A solution containing 200 mg of **14** and 20 mg of thioxanthone in 150 mL of benzene was irradiated with a 450-W Ha-

(78) Bell, R. P.; Fendley, T. A.; Hulett, J. R. *Proc. R. Soc. London, Ser. A* **1956**, *A235*, 453.
(79) Bell, R. P. "The Proton in Chemistry"; Cornell University Press: Ithaca, NY, 1959.
(80) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.
(81) For the application to free radical reactions, see: Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; p 156.
(82) A simple analysis of energetics for the conversion of **5** to diradical **38** suggests that the overall process is exothermic by ca. 25 kcal/mol. This is primarily due to the change in strain energy on going from a planar cyclopropene triplet to a cyclopropyl radical. Nevertheless, biradical formation with the 1,2-diphenyl-substituted system involves the making and breaking of C–H bonds which are much closer in energy than the related 1,3-diphenyl isomer.
(83) Bergman, N. A.; Saunders, W. H.; Melander, L. *Acta Chem. Scand.* **1972**, *26*, 1130. Pryor, W. A.; Kneipp, K. G. *J. Am. Chem. Soc.* **1971**, *93*, 5584.
(84) Ruchardt, C. *Proc. Int. Cong. Pure Appl. Chem.* **1971**, *4*, 223.
(85) Giering, L.; Berger, M.; Steel, C. *J. Am. Chem. Soc.* **1974**, *96*, 953.
(86) Previtali, C. M.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1667; *Ibid.* **1972**, 1672.

(87) 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 Model 137 infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer by using 1-cm matched cells. The proton magnetic resonance spectra were determined at 90 MHz by using a Varian EM-390 spectrometer and at 100 MHz with a Varian XL-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All irradiations were carried out by using a 450-W Hanovia medium-pressure mercury arc lamp.

novia lamp equipped with a Uranium glass filter sleeve for 2 h under an argon atmosphere. The solvent was removed under reduced pressure, and the resulting residue was passed through a Florisil column to remove the thioxanthone. The yellow oil obtained was subjected to thick-layer chromatography with use of hexane as the eluant. The major component isolated contained 142 mg (71%) of a white solid (mp 76–77 °C) whose structure was assigned as 1,5-diphenyl-6-methyl-2,3-benzobicyclo-[3.1.0]hexane (**15**) on the basis of its spectroscopic properties: IR (KBr) 3.32, 3.48, 6.29, 6.72, 6.91, 6.98, 8.65, 9.16, 9.31, 9.67, 9.77, 10.36, 13.23, 13.41, 14.26 μm; NMR ($CDCl_3$, 100 MHz) τ 8.82 (br s, 4 H), 6.38 (s, 2 H), 2.32–3.44 (m, 14 H); (benzene-d_6, 100 MHz) τ 8.91 (br s, 4 H), 6.57 (AB quartet, 2 H, J_{ab} = 17.5 Hz), 2.44–3.30 (m, 14 H); UV (95% ethanol) 230 nm (shoulder, ε 15000); *m/e* 296 (M^+), 282, 281 (base), 265, 219, 205, 203, 202, 191, 105, 91, 77.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.08; H, 6.92.

Preparation of 1,2-Diphenyl-3-methyl-3-(*o*-ethylphenyl)cyclopropene (7). To a suspension containing 6.0 g of diphenylmethylcyclopropenyl perchlorate in 200 mL of tetrahydrofuran at −78 °C was added 100 mL of a 0.67 M solution of (*o*-ethylphenyl)magnesium bromide in ether. The mixture was stirred at −78 °C for 6 h and was then allowed to warm to room temperature. The excess Grignard reagent was destroyed by the addition of a saturated ammonium chloride solution, and the organic layer was taken up in ether. The ethereal layer was washed with water and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was subjected to silica gel chromatography with use of hexane as the eluant. The major component isolated from the column contained 1.43 g (23%) of 1,2-diphenyl-3-methyl-3-(*o*-ethylphenyl)cyclopropene (**7**) as a crystalline solid: mp 68–69 °C; IR (KBr) 3.30, 3.40, 3.51, 5.50, 6.25, 6.75, 6.95, 7.30, 7.90, 9.30, 9.45, 9.70, 10.95, 13.25, 13.50, 14.50 μm; UV (95% ethanol) 317 nm (ε 21600); NMR ($CDCl_3$, 100 MHz) τ 8.76 (t, 3 H, *J* = 8.0 Hz), 8.16 (s, 3 H), 6.98 (q, 2 H, *J* = 8.0 Hz), 2.2–3.2 (m, 14 H); *m/e* 310 (M^+, base), 295, 281, 265, 185, 105.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.84; H, 6.93.

Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-ethylphenyl)cyclopropene (7). A solution containing 100 mg of **7** in 100 mL of benzene was irradiated with use of a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 2.5 h. Removal of the solvent under reduced pressure left a yellow oil which was subjected to thick-layer chromatography with use of hexane as the eluant. The major band isolated contained 75 mg (75%) of a colorless oil whose structure was assigned as 1,2-diphenyl-3-methyl-4-ethylindene (**8**) on the basis of its spectroscopic properties: IR (neat) 3.30, 3.40, 3.48, 6.24, 6.71, 6.80, 6.92, 7.31, 7.85, 8.50, 9.30, 9.40, 9.65, 9.85, 10.02, 10.90, 11.67, 12.40, 12.70, 13.05, 13.55, 14.35 μm; UV (95% ethanol) 288 nm (ε 10300); NMR ($CDCl_3$, 100 MHz) τ 8.68 (t, 3 H, *J* = 8.0 Hz), 7.60 (d, 3 H, *J* = 1.5 Hz), 6.96 (q, 2 H, *J* = 8.0 Hz), 5.20 (q, 1 H, *J* = 1.5 Hz), 2.6–3.2 (*m*, 14 H); *m/e* 310 (M^+, base), 295, 281, 265, 203, 202, 194, 166, 139, 105, 84.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.78; H, 7.24.

Triplet Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-ethylphenyl)cyclopropene (7). A mixture containing 100 mg of **7** and 10 mg of thioxanthone in 100 mL of benzene was irradiated through a Uranium filter sleeve with use of a 450-W Hanovia mercury lamp for 2.5 h. The solvent was removed under reduced pressure, and the resulting yellow oil was chromatographed on a thick layer plate with use of hexane as the eluant. The major band contained 75 mg (75%) of an inseparable mixture of the exo (80%) and endo (20%) isomers of 1,4-dimethyl-5,6-diphenyl-2,3-benzobicyclo[3.1.0]hexane (**10**) as a colorless oil: IR (neat) 3.30, 3.40, 3.50, 6.24, 6.65, 6.75, 6.90, 7.25, 8.15, 8.30, 8.62, 9.30, 9.72, 9.85, 11.60, 12.51, 13.09, 13.52, 14.3 μm; *m/e* 310 (M^+, base), 295, 280, 233, 219, 205, 194, 167, 166, 105, 91, 84, 77; NMR ($CDCl_3$, 100 MHz) exo isomer τ 8.62 (d, 3 H, *J* = 8.0 Hz), 8.48 (s, 3 H), 7.96 (s, 1 H), 6.48 (q, 1 H, *J* = 8.0 Hz), 2.2–3.4 (m, 14 H), endo isomer τ 9.08 (d, 3 H, *J* = 8.0 Hz), 8.48 (s, 3 H), 8.12 (s, 1 H), 6.48 (q, 1 H, *J* = 8.0 Hz), 2.2–3.4 (m, 14 H).

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.82; H, 7.03.

Preparation of 1,2-Diphenyl-3-methyl-3-(*o*-isopropylphenyl)cyclopropene (11). To a suspension containing 6.0 g of diphenylmethylcyclopropenyl perchlorate in 100 mL of tetrahydrofuran at −78 °C was added 100 mL of a 0.67 M solution of (*o*-isopropylphenyl)magnesium chloride in ether. The mixture was stirred at −78 °C for 4 h and was then allowed to warm to room temperature. The excess Grignard reagent was destroyed with a saturated ammonium chloride solution, and the organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the resulting yellow oil was subjected to thick-layer chromatography. The major component isolated from the thick-layer plate contained 450 mg of 1,2-diphenyl-3-methyl-3-(*o*-isopropylphenyl)cyclopropene (**11**) as a crystalline solid: mp 75–76 °C; IR (KBr) 3.30, 3.40, 3.50, 5.51, 6.24, 6.72, 6.93, 7.10, 7.92, 9.05, 9.28, 9.48, 9.70, 10.70, 10.92, 13.21, 13.50, 14.50 μm; UV (95% ethanol) 318 nm (ε 19600); NMR ($CDCl_3$, 100 MHz) τ 8.84 (d, 6 H, *J* = 7.0 Hz), 8.16 (s, 3 H), 6.24 (sept, 1 H, *J* = 7.0 Hz), 2.36–3.2 (m, 14 H); *m/e* 324 (M^+), 309, 281 (base), 229, 203, 202, 131, 130, 105, 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.51; H, 7.28.

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-isopropylphenyl)cyclopropene (11). A solution containing 120 mg of **11** and 12 mg of thioxanthone in 125 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium glass filter sleeve for 90 min under an argon atmosphere. The solvent was removed under reduced pressure, and the residue was passed through a Florisil column with hexane to remove the thioxanthone. The pale yellow oil obtained (92 mg, 77%) was shown to contain two components in a 3:2 ratio by NMR analysis. The mixture of components was separated by preparative gas chromatography with use of 10 ft 20% carbowax 20M column on chromosorb W at 260 °C. The first component isolated from the column contained a clear oil whose structure was assigned as 1,4,4-trimethyl-2,3-diphenyl-3,4-dihydronaphthalene (**12**) (60%) on the basis of its spectral data: IR (neat) 3.60, 3.63, 5.13, 6.22, 6.73, 6.92, 7.23, 7.36, 7.74, 8.63, 9.02, 9.27, 9.53, 9.65, 10.94, 12.51, 13.19, 13.61, 14.32 μm; NMR ($CDCl_3$, 100 MHz) τ 8.87 (s, 3 H), 8.57 (s, 3 H), 8.02 (s, 3 H), 6.78 (s, 1 H), 2.28–3.36 (m, 14 H); UV (95% ethanol) 281 nm (ε 14900), 226 (20000); *m/e* 324 (M^+, base), 310, 309, 294, 91, 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.11; H, 7.46.

The second component isolated from the gas chromatograph was a crystalline solid, mp 148–149 °C, whose structure was assigned as 1,4,4-trimethyl-5,6-diphenyl-2,3-benzobicyclo[3.1.0]hexane (**13**) on the basis of its spectral data: IR (KBr) 3.64, 6.17, 6.70, 6.84, 7.18, 9.39, 9.72, 10.57, 10.85, 12.74, 13.18, 13.60, 14.14, 14.25 μm; NMR ($CDCl_3$, 100 MHz) τ 9.13 (s, 3 H), 8.54 (s, 3 H), 8.39 (s, 3 H), 8.08 (s, 1 H), 2.45–2.68 (m, 14 H); UV (95% ethanol) 243 nm (ε 17400), 271 (8100), 278 (6800); *m/e* 324 (M^+), 309 (base), 294, 219, 215, 167, 115, 91, 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.27; H, 7.67.

Preparation of 1,2-Diphenyl-3-methyl-3-(*o*-methylbenzyl)cyclopropene (17) and 1,3-Diphenyl-2-methyl-3-(*o*-methylbenzyl)cyclopropene (18). To a suspension containing 3.0 g of 1,2-diphenyl-3-methylcyclopropenyl perchlorate in 200 mL of tetrahydrofuran at −78 °C was added 20 mL of a 0.67 M solution of (*o*-methylbenzyl)magnesium chloride in ether. The mixture was stirred at −78 °C for 4 h and was then allowed to warm to room temperature. The excess Grignard reagent was destroyed with a saturated ammonium chloride solution, and the organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the resulting oil was subjected to silica gel chromatography with use of hexane as the eluant. The first component isolated from the column contained 1.02 g (33%) of a crystalline solid (mp 81–82 °C) whose structure was assigned as 1,2-diphenyl-3-methyl-3-(*o*-methylbenzyl)cyclopropene (**17**) on the basis of the following data: IR (KBr) 3.45, 5.52, 6.26, 6.70, 6.94, 7.23, 8.95, 9.35, 9.73, 10.87, 12.97, 13.23, 14.48, 14.50 μm; NMR ($CDCl_3$, 100 MHz) τ 8.51 (s, 3 H), 7.90 (s, 3 H), 6.90 (s, 2 H), 2.36–3.33 (m, 14 H); UV (95% ethanol) 344 nm (shoulder, ε 16100), 322 (22800), 238 (shoulder, 15300), 229 (18800); *m/e* 310 (M^+), 295, 219, 206, 205 (base), 203, 77.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.75; H, 7.21.

The second component isolated from the column gave a clear oil which solidifed on standing. Recrystallization of this material from methanol gave 1.47 g (48%) of 1,3-diphenyl-2-methyl-3-(*o*-methylbenzyl)cyclopropene (**18**): mp 64–65 °C: IR (KBr) 3.30, 3.41, 5.42, 6.23, 6.69, 6.91, 7.23, 8.52, 8.61, 9.33, 9.63, 10.58, 10.90, 12.91, 13.12, 13.38, 13.80, 14.42 μm; NMR ($CDCl_3$, 100 MHz) τ 7.93 (s, 3 H), 7.85 (s, 3 H), 6.56 (AB quartet, 2 H, J_{ab} = 14.0 Hz), 2.59–3.48 (m, 14 H); UV (95% ethanol) 266 nm (ε 21100); *m/e* 310 (M^+, base), 295, 215, 206, 205, 203, 202, 105, 91, 77.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.54; H, 7.23.

Direct Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-methylbenzyl)cyclopropene (17). A solution containing 302 mg of **17** in 300 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 90 min under an argon atmosphere. The solvent was removed under reduced pressure, and the residual oil was subjected to silica gel chromatography with use of hexane as the eluant. The first component isolated from the column contained 212 mg (70%) of a crystalline solid, mp 105–106 °C, whose structure is assigned as 2,8-dimethyl-3,4a-di-

phenyl-1,4a-dihydroazulene (**19**) on the basis of the following data: IR (KBr) 3.36, 3.45, 6.23, 6.70, 6.91, 7.24, 8.48, 9.38, 9.64, 9.91, 11.15, 11.43, 12.72, 13.35, 13.69, 14.40 μm; NMR ($CDCl_3$, 100 MHz) τ 8.05 (s, 3 H), 8.30 (s, 3 H), 6.68 (d, 1 H, J = 18.0 Hz), 6.40 (d, 1 H, J = 18.0 Hz), 4.50 (m, 1 H), 3.88 (m, 3 H), 3.52 (m, 1 H), 2.76–3.16 (m, 8 H); m/e 310 (M^+), 296, 295 (base), 280, 262, 233, 218, 91, 77.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.69; H, 7.16.

The second component isolated from the column contained 52 mg (17%) of 1,3-diphenyl-2-methyl-3-(*o*-methylbenzyl)cyclopropene (**18**) which was in every detail identical with an authentic sample.

When the irradiation of cyclopropene **17** was carried out for 3 h, a new compound was formed (20%) in addition to dihydroazulene **19** and cyclopropene **18**. This same compound was produced when a 100-mg sample of dihydroazulene **19** was irradiated in 100 mL of benzene for 2 h. The structure of this material is assigned as 1,8-dimethyl-9,10-diphenyltricyclo[4.4.0.0^{2,10}]deca-3,5,8-triene (**20**) on the basis of its spectral data: IR (neat) 3.35, 3.48, 6.23, 6.70, 6.95, 7.31, 9.35, 9.72, 10.45, 12.05, 13.30, 14.30 μm; NMR ($CDCl_3$, 270 MHz) τ 8.27 (s, 3 H), 8.19 (s, 3 H), 7.20 (d, 1 H, J = 18 Hz), 6.94 (d, 1 H, J = 18 Hz), 6.55 (br s, 1 H), 4.79 (br s, 1 H), 4.33 (br s, 1 H), 3.93 (br s, 1 H), 2.6–3.04 (m, 10 H); m/e 310 (M^+), 296, 295 (base), 280, 233, 219, 218, 217.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.81; H, 7.08.

Thermolysis of a 50-mg sample of **20** in benzene at 130 °C in a sealed tube for 5 h followed by silica gel chromatography with use of hexane as the eluant gave 26 mg (52%) of a clear oil whose structure is assigned as 2,4-dimethyl-3,4a-diphenyl-1,4a-dihydroazulene (**21**) on the basis of its spectral data: IR (neat) 3.41, 3.52, 6.31, 6.76, 7.02, 7.35, 8.26, 8.71, 9.26, 9.65, 9.95, 13.41, 13.72, 14.30 μm; NMR ($CDCl_3$, 100 MHz) τ 8.20 (s, 3 H), 7.78 (s, 3 H), 7.32 (d, 1 H, J = 18 Hz), 6.42 (d, 1 H, J = 18 Hz), 4.00 (m, 3 H), 3.71 (m, 1 H), 3.02–2.46 (m, 10 H); m/e 310 (M^+), 295 (base), 280, 233.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.73; H, 7.02.

The second component isolated from the chromatography column (24 mg, 48%) was identified as dihydroazulene **19**. This material was identical with a sample of **19** isolated from the photolysis of cyclopropene **17**.

X-ray Crystal Structure Analysis of 2,8-Dimethyl-3,4a-diphenyl-1,4a-dihydroazulene (19). The molecular structure of dihydroazulene **19** was unequivocally determined by an X-ray crystal-structure analysis. A pale yellow crystal with approximate dimensions 0.5 × 0.3 × 0.1 mm, obtained from isopropyl alcohol, was mounted on a glass fiber by using epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis. Unit-cell parameters and the orientation matrix were determined on a Nicolet R3 four-circle diffractometer using Cu Kα radiation at a takeoff angle of 60°. Fifteen reflections whose 2θ values ranged from 4 to 100° were machine centered and used in least-squares refinement of the lattice parameters and orientation matrix. Unit-cell parameters obtained were a = 21.913 (4) Å,[88] b = 9.102 (3) Å, c = 18.27 (4) Å, β = 107.73 (2)°, and γ = 3595 (2) Å^3. The calculated density of 1.14 g cm^{-3} for 8 formula units per cell agrees with the experimental density of 1.12 g cm^{-3} measured by the flotation method using a mixture of water and sodium iodide. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.2°, indicating a satisfactory mosaic spread for the crystal. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined for systematic absences. The absence of $h + k = 2n$ for h,k,l and $l = 2n$ for h,o,l reflections is consistent with only space group $C2/c$.[89]

Intensity data were collected by using θ–2θ scans with the X-ray source identical with that used for the determination of the unit cell parameters. A variable scan rate of from 4.88 to 29.3°/min was used, and a scan width of 2° was sufficient to collect all the peak intensity. Stationary background counts were measured at the beginning (B_1) and at the end (B_2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (002, 040, 600) monitored every 97 reflections. Intensities were calculated from the total scan count (CT) and background counts by the relationship of eq 2.

$$I = \mathrm{CT} - \mathrm{TR}(B_1 + B_2) \tag{2}$$

The intensities were assigned standard deviations according to the formula in eq 3 for a total of 2448 reflections collected in half of the complete hemisphere (±h,±l) of data out to 2θ = 100°; 2448 were accepted as statistically above background on the basis that F was greater than 3σ(F). Lorentz and polarization corrections were made in the usual way.

$$\sigma(I) = [\mathrm{CT} + (\mathrm{TR})^2(B_1 + B_2)]^{1/2} \tag{3}$$

Computations were performed by using standard programs;[90] all computations were carried out on the UNIVAC 90/80 computer. For structure factor calculations the scattering factors were taken from Cromer and Waber's tabulation.[91] The scattering factor(s) for all atoms except hydrogen were corrected for the real and imaginary anomalous dispersion components.[91] The agreement factors are defined in the usual way as in eq 4 and 5. In all least-squares refinements, the quantity

$$R = (\sum||F_o| - |F_c||)/\sum|F_o| \tag{4}$$

$$R_w = (\sum(|F_o| - |F_c|)w^{0.5}/\sum(|F_o|)w^{0.5} \tag{5}$$

minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics $w = 1/\sigma F^2 + F^2$ was employed for calculating R_w and in the least-squares refinement.

The structure was solved by using direct methods. Parameters varied included anisotropic thermal parameters for all atoms other than hydrogen atoms, and an overall isotropic temperature factor was applied to the hydrogen atoms. The least-squares refinement for the 1836 unique reflections, converged at R = 0.0586 and R_w = 0.0623. The final positional and thermal parameters are given in Table II of the supplementary material.

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-methylbenzyl)cyclopropene (17). A solution containing 324 mg of **17** and 33 mg of thioxanthone in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium glass filter sleeve for 2 h under an argon atmosphere. The solvent was removed under reduced pressure, and the residue was passed through a Florisil column to remove the thioxanthone. The resulting residue was subjected to thick-layer chromatography with use of hexane as the eluant. The major component isolated from the thick-layer plate contained 266 mg (81%) of a crystalline solid, mp 152–153 °C, whose structure is assigned as 1,7-diphenyl-6-methyl-3,4-benzobicyclo[4.1.0]heptane (**22**) on the basis of the following data: IR (KBr) 3.27, 3.40, 6.19, 6.67, 6.86, 7.18, 8.09, 8.34, 8.89, 9.47, 9.60, 10.14, 10.69, 12.66, 13.02, 13.12, 13.27, 14.13 μm; NMR ($CDCl_3$, 100 MHz) τ 8.72 (s, 3 H), 7.78 (s, 1 H), 6.86 (br s, 4 H), 2.34–3.58 (m, 14 H); UV (95% ethanol) 271 nm (shoulder, ε 6500), 266 (6800); m/e 310 (M^+), 295, 232, 219, 205 (base), 204, 192, 178, 115, 91, 77.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.54; H, 7.28.

Triplet-Sensitized Irradiation of 1,3-Diphenyl-2-methyl-3-(*o*-methylbenzyl)cyclopropene (18). A solution containing 240 mg of **18** and 25 mg of thioxanthone in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium glass filter sleeve for 2 h under an argon atmosphere. The solvent was removed under reduced pressure, and the residue was passed through a Florisil column with hexane to remove thioxanthone. The crystalline solid obtained (86%) on removal of the solvent (mp 151–152 °C) was assigned the structure of 1,6-diphenyl-7-methyl-3,4-benzobicyclo[4.1.0]heptane (**23**) on the basis of its spectroscopic properties: IR (KBr) 3.29, 3.40, 6.19, 6.67, 6.90, 7.20, 8.92, 9.18, 9.57, 10.30, 12.61, 13.22, 13.48, 14.12, 14.30 μm; NMR ($CDCl_3$, 100 MHz) τ 8.89 (d, 3 H, J = 6.0 Hz), 6.76 (AB quartet, 4 H, J_{ab} = 15.0 Hz), 2.20–3.36 (m, 14 H); UV (95% ethanol) 271 nm (ε 4200), 264 (4400), 259 (shoulder ε 4200); m/e 310 (M^+), 219, 205 (base), 204, 191, 115, 105, 91, 77.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.66; H, 7.21.

Preparation of 1,2-Diphenyl-3-methyl-3-(*o*-isopropylbenzyl)cyclopropene (24) and 1,3-Diphenyl-2-methyl-3-(*o*-isopropylbenzyl)cyclopropene (26). A sample of *o*-isopropylbenzyl chloride was prepared from *o*-toluic acid according to the following procedure. A 7.0 g sample of *o*-toluic acid in 100 mL of anhydrous tetrahydrofuran was added to an excess (6 mol) LDA solution at 0 °C, and the mixture was allowed to stir at 0 °C for an additional 45 min. At the end of this time excess methyl iodide in hexane was added to the solution until the color changed from black to yellow. The reaction mixture was stirred at room temperature for 30 min and was quenched with water. The organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 6.2 g (75%) of *o*-isopropylbenzoic acid: mp 64–65 °C (liq.[92] mp 64–65 °C); NMR

(88) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

(89) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1952; Vol. I.

(90) Programs utilized were Sheldrick's SHELX-76 program and Johnson's ORTEP program.

(91) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101, 149–150.

($CDCl_3$, 100 MHz) δ 1.26 (d, 6 H, J = 7.0 Hz) 3.93 (q, 1 H, J = 7.0 Hz), 7.06–8.08 (m, 4 H), 12.6 (s, 1 H).

To a suspension containing 2.0 g of lithium aluminum hydride in 100 mL of anhydrous ether was added a solution containing 6.2 g of *o*-isopropylbenzoic acid in 50 mL of ether. The mixture was heated at reflux for 4 h, quenched with water, and concentrated under reduced pressure to give 5.6 g (99%) of *o*-isopropylbenzyl alcohol: NMR ($CDCl_3$, 100 MHz) τ 8.80 (d, 6 H, J = 7.0 Hz), 7.45 (br s, 1 H), 6.87 (q, 1 H, J = 7.0 Hz), 5.48 (s, 2 H), 2.43–3.09 (m, 4 H). The above material was taken up in 20 mL of ether and was allowed to react with 30 mL of concentrated hydrochloric acid at reflux for 10 h. The organic layer was taken up in ether, washed with a 5% sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent followed by filtration of the residue through a plug of silica gel with hexane gave 5.5 g (87%) of *o*-isopropylbenzyl chloride: NMR ($CDCl_3$, 100 MHz) τ 8.76 (d, 6 H, J = 7.0 Hz), 6.78 (g, 1 H, J = 7.0 Hz), 5.47 (s, 2 H), 2.54–2.95 (m, 4 H). To a solution containing 2.33 g of *o*-isopropylbenzyl chloride in 30 mL of ether was added 1.5 g of magnesium turnings in 20 mL of ether. After the reaction started to reflux, an additional 4.67 g of the chloride in 60 mL of ether was added. After being stirred for 1 h at room temperature, the mixture was heated at reflux for 30 min. The Grignard reagent prepared in this fashion was approximately 0.8 M.

To a suspension containing 4.0 g of 1,2-diphenyl-3-methylcyclopropenyl perchlorate in 200 mL of anhydrous tetrahydrofuran at −78 °C was added 50 mL of a 0.8 M solution of (*o*-isopropylbenzyl)magnesium chloride in ether. The mixture was stirred at −78 °C for 4 h and was then allowed to warm to room temperature. The excess Grignard reagent was destroyed with a saturated ammonium chloride solution, and the organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the resulting oil was subjected to silica gel chromatography with use of hexane as the eluant. The first component isolated from the column contained 1.21 g (27%) of a clear oil whose structure was assigned as 1,2-diphenyl-3-methyl-3-(*o*-isopropylbenzyl)cyclopropene (**24**) on the basis of its spectral properties: IR (neat) 3.38, 3.47, 5.61, 6.32, 7.02, 7.23, 7.40, 9.40, 9.73, 11.04, 13.10, 13.35, 14.56 μm; UV (95% ethanol) 338 nm (shoulder, ϵ 16 100), 321 (22 700), 230 (20 000); NMR ($CDCl_3$, 100 MHz) τ 9.07 (d, 6 H, J = 7.0 Hz), 8.47 (s, 3 H), 6.94 (q, 1 H, J = 7.0 Hz), 6.85 (s, 2 H), 2.51–3.42 (m, 14 H); m/e 338 (M^+), 295, 205 (base).

Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.76.

The second component isolated from the column contained 2.25 g (51%) of a crystalline solid (mp 62–63 °C) whose structure was assigned as 1,3-diphenyl-2-methyl-3-(*o*-isopropylbenzyl)cyclopropene (**26**) on the basis of its spectral properties: IR (KBr) 3.38, 5.37, 6.21, 6.65, 6.92, 7.21, 8.42, 9.30, 9.63, 10.86, 11.90, 12.91, 13.08, 14.37 μm; UV (95% ethanol) 265 nm (ϵ 15 900); NMR ($CDCl_3$, 100 MHz) τ 9.05 (d, 3 H, J = 7.0 Hz), 8.87 (d, 3 H, J = 7.0 Hz), 7.92 (s, 3 H), 6.96 (q, 1 H, J = 7.0 Hz), 6.63 (d, 1 H, J = 16.0 Hz), 6.26 (d, 1 H, J = 16.0 Hz), 2.62–3.26 (m, 14 H); m/e 338 (M^+), 295, 206, 205 (base), 133.

Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.16; H, 7.78.

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-isopropylbenzyl)cyclopropene (24). A solution containing 250 mg of **24** and 30 mg of thioxanthone in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium filter sleeve for 2 h under an argon atmosphere. The solvent was removed under reduced pressure, and the residue was passed through a Florisil column with use of hexane as the eluant. The major fraction isolated contained 208 mg (83%) of a crystalline solid (mp 105–106 °C) whose structure was assigned as 1,7-diphenyl-2,2,6-trimethyl-3,4-benzobicyclo[4.1.0]heptane (**25**) on the basis of its spectral properties: IR (KBr) 3.50, 6.31, 6.79, 7.02, 7.33, 7.45, 8.53, 9.23, 9.47, 9.62, 10.28, 13.05, 13.62, 14.17 μm; UV (95% ethanol) 272 nm (ϵ 5400), 266 (6500), 260 (6500); NMR ($CDCl_3$, 100 MHz) τ 8.96 (s, 3 H), 8.69 (s, 3 H), 8.64 (s, 3 H), 7.76 (s, 1 H), 6.92 (d, 1 H, J = 16.0 Hz), 6.64 (d, 1 H, J = 16.0 Hz), 2.56–3.47 (m, 14 H); m/e 338 (M^+), 295, 105 (base).

Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.14; H, 7.79.

Triplet-Sensitized Irradiation of 1,3-Diphenyl-2-methyl-3-(*o*-isopropylbenzyl)cyclopropene (26). A solution containing 152 mg of **26** and 20 mg of thioxanthone in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium glass filter sleeve under an argon atmosphere for 90 min. The solvent was removed under reduced pressure, and the residue was passed through a Florisil column with use of hexane as the eluant. The major fraction obtained was a crystalline solid (134 mg, 88%) (mp 143–144 °C) whose structure was assigned as 1,6-diphenyl-2,2,7-trimethyl-3,4-benzobicyclo[4.1.0]heptane (**27**) on the basis of its spectral properties: IR (KBr) 3.40, 3.52, 6.26, 6.73, 7.28, 7.40, 8.21, 9.30, 9.58, 10.38, 12.95, 14.06, 14.25 μm; UV (95% ethanol) 265 nm, 268 (ϵ 6900, 5500); NMR ($CDCl_3$, 100 MHz) τ 8.76 (s, 3 H), 8.74 (s, 3 H), 8.37–8.96 (m, 4 H), 6.90 (d, 1 H, J = 16.0 Hz), 6.23 (d, 1 H, J = 16.0 Hz), 2.37–3.10 (m, 14 H); m/e 338 (M^+), 295, 268, 233, 229 (base), 205, 105.

Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.14; H, 7.77.

Preparation and Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(2-(*o*-tolyl)ethyl)cyclopropene (28). To a suspension containing 2.0 g of 3-methyl-1,2-diphenylcyclopropenyl perchlorate in 200 mL of tetrahydrofuran at −78 °C was added 100 mL of a 0.15 M solution of (2-(*o*-tolyl)ethyl)magnesium bromide in ether. The mixture was stirred at −78 °C for 2 h and was then allowed to warm to room temperature. After being stirred at 25 °C for 2 h, the excess Grignard reagent was quenched with a saturated ammonium chloride solution and the organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the resulting yellow oil was subjected to silica gel chromatography with use of hexane as the eluant. The first fraction isolated from the column contained 530 mg (27%) of a crystalline solid (mp 80–81 °C), whose structure was assigned as 1,2-diphenyl-3-methyl-3-(2-(*o*-tolyl)ethyl)-cyclopropene (**28**): IR (KBr) 3.48, 3.55, 5.57, 6.28, 6.95, 7.27, 7.33, 9.00, 9.35, 9.73, 10.98, 13.30, 14.60 μm; NMR ($CDCl_3$, 100 MHz) τ 8.49 (s, 3 H), 7.88 (s, 3 H), 7.67–8.0 (m, 2 H), 7.32–7.56 (m, 2 H), 2.24–3.31 (m, 14 H); UV (95% ethanol) 339 nm (ϵ 22 400), 311 (shoulder, 23 800), 321 (28 900), 238 (13 900); m/e 324 (M^+), 238, 219, 205, 186, 105 (base).

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.48; H, 7.50.

Irradiation of a benzene solution of **28** in the presence of thioxanthone for 5 h resulted in the complete recovery of starting material. Further photolysis for 16 h also gave back recovered starting material.

Preparation and Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-anisyl)cyclopropene (29). A 3.6 M solution of *o*-methoxyphenyl magnesium bromide was added to 1.4 g of diphenylcyclopropenyl perchlorate to give 1.02 g (70%) of 1,2-diphenyl-3-(*o*-anisyl)cyclopropene: NMR ($CDCl_3$, 100 MHz) τ 6.48 (s, 1 H), 6.07 (s, 3 H), 2.13–3.34 (m, 14 H). To 1.0 g of the cyclopropene in 30 mL of acetonitrile was added 2.0 g of trityl perchlorate at 0 °C. After being stirred for 2 h at 25 °C, the mixture was diluted with 350 mL of ether and the solid was filtered and washed with ether to give 980 mg (74%) of 1,2-diphenyl-3-(*o*-anisyl)cyclopropenyl perchlorate (mp 221 °C).

To a suspension containing 980 mg of 1,2-diphenyl-3-(*o*-anisyl)-cyclopropenyl perchlorate in 30 mL of tetrahydrofuran at −78 °C was added 10 mL of a 3.0 M solution of methylmagnesium bromide in ether. The mixture was allowed to stir at −78 °C for 2 h and was warmed to room temperature. The excess Grignard reagent was destroyed with a saturated ammonium chloride solution, and the organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the resulting oil was subjected to silica gel chromatography with use of a 1% ether–hexane mixture as the eluant. The first fraction isolated from the column contained 125 mg (16%) of a crystalline solid (mp 81–82 °C) whose structure was assigned as 1,2-diphenyl-3-methyl-3-methyl-3-(*o*-anisyl)cyclopropene (**29**): IR (KBr) 3.51, 5.58, 6.28, 6.77, 7.01, 7.32, 7.68, 7.88, 8.09, 8.45, 8.98, 9.52, 9.76, 10.90, 12.94, 13.26, 14.31 μm; UV (95% ethanol) 356 nm, 310 (ϵ 18 600, 24 500); NMR ($CDCl_3$, 100 MHz) τ 8.17 (s, 3 H), 6.12 (s, 3 H), 2.03–3.41 (m, 14 H).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.38; H, 6.40.

Irradiation of a benzene solution of **29** in the presence of thioxanthone for 16 h resulted in the complete recovery of starting material.

Preparation of 1,2-Diphenyl-3-methyl-3-(*o*-methyl-d_3-phenyl)cyclopropene (30) and 1,3-Diphenyl-2-methyl-3-(*o*-methyl-d_3-phenyl)cyclopropene (31). A sample of *o*-bromo-α,α,α-trideuteriotoluene was prepared from *o*-bromobenzoic acid following the method of Okubo and co-workers.[93] The trideuterio-labeled *o*-bromotoluene was converted into the corresponding Grignard reagent which, in turn, was allowed to react with 3-methyl-1,2-diphenylcyclopropenyl perchlorate according to the procedure previously described. Chromatography of the crude reaction mixture on silica gel gave a 25% yield of 1,2-diphenyl-3-methyl-3-(*o*-methyl-d_3-phenyl)cyclopropene (**30**) (m/e 299 (M^+, base), 284) and 3% yield of 1,3-diphenyl-2-methyl-3-(*o*-methyl-d_3-phenyl)cyclopropene (**31**) (m/e 299 (M^+, base), 284).

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-methyl-d_3-phenyl)cyclopropene (30). A solution containing 162 mg of **30** and

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20 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium filter sleeve for 10 h. The crude photolysate was concentrated under reduced pressure, and the residue was chromatographed on a silica gel column with use of hexane as the eluant. The major component isolated from the column was a crystalline solid (mp 106-107 °C) whose structure was assigned as 1-methyl-5,6-diphenyl-4,4,6-trideuterio-2,3-benzobicyclo[3.1.0]hexene: NMR ($CDCl_3$, 100 MHz) τ 8.48 (s, 3 H), 2.48-3.46 (m, 14 H); *m/e* 299 (M^+), 284, 222, 207, 206, 205 and 168.

Triplet-Sensitized Irradiation of 1,3-Diphenyl-2-methyl-3-(*o*-methyl-d_3-phenyl)cyclopropene (31). A solution containing 120 mg of **31** and 15 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium filter sleeve for 90 min. The solution was concentrated under reduced pressure, and the resulting residue was chromatographed on a thick-layer plate. The first fraction contained 65 mg of unreacted starting material. The second fraction consisted of 40 mg (33%) of a white solid (mp 78-79 °C) whose structure was assigned as 1,5-diphenyl-6-methyl-4,4,6-trideuterio-2,3-benzobicyclo[3.1.0]hexene: NMR ($CDCl_3$, 100 MHz) τ 8.83 (s, 3 H), 2.50-3.41 (m, 14 H); *m/e* 299 (M^+), 284 (base), 222, 220, 207, 206, 205, 204.

Preparation of 1,2-Diphenyl-3-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (32) and 1,3-Diphenyl-2-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (33). A solution containing 1.9 g of *o*-bromo-α,α,α-trideuteriotoluene was converted to the corresponding Grignard reagent. A 4.0-g sample of diethyl carbonate in 25 mL of ether was added to the above Grignard reagent, the mixture was heated at reflux for 10 h. At the end of this time the mixture was quenched with a saturated ammonium chloride solution. The organic layer was taken up in ether, washed with a 10% hydrochloric acid solution and a 5% sodium bicarbonate solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure to give 920 mg (51%) of ethyl *o*-methyl-d_3-benzoate: NMR ($CDCl_3$, 100 MHz) τ 8.82 (t, 3 H, J = 7.0 Hz), 5.93 (q, 2 H, J = 7.0 Hz), 2.16-3.24 (m, 4 H).

To the above material in 50 mL of ether was added 200 mg of lithium aluminum hydride. The mixture was heated at reflux for 3 h followed by quenching with water. The ether layer was dried over magnesium sulfate and concentrated under reduced pressure to give 605 mg (90%) of *o*-methyl-d_3-benzyl alcohol: NMR ($CDCl_3$, 100 MHz) τ 7.83 (br s, 1 H), 5.47 (s, 2 H), 2.72-3.12 (m, 4 H). A sample of the above alcohol was taken up in ether and heated with 10 mL of concentrated hydrochloric acid for 4 h. The mixture was extracted with ether, washed with water, and dried over magnesium sulfate to give 580 mg (85%) of *o*-methyl-d_3-benzyl chloride: NMR ($CDCl_3$, 100 MHz) τ 5.44 (s, 2 H), 2.55-2.87 (m, 4 H).

A sample of *o*-methyl-d_3-benzyl chloride was converted into the corresponding Grignard reagent which, in turn, was allowed to react with 3-methyl-1,2-diphenylcyclopropenyl perchlorate according to the procedure previously described. Chromatography of the crude reaction mixture on silica gel gave a 10% yield of 1,2-diphenyl-3-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (**32**) (*m/e* 313 (M^+)) and a 31% yield of 1,3-diphenyl-2-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (**33**) (*m/e* 313 (M^+)).

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (32) and 1,3-Diphenyl-2-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (33). The irradiation of cyclopropenes **32** and **33** were carried out as previously described. The crude reaction mixtures were subjected to thick-layer chromatography in order to isolate pure samples of the photoproducts. The thioxanthone sensitized irradiation of **32** gave 1,7-diphenyl-6-methyl-2,2,7-trideuterio-3,4-benzobicyclo-[4.1.0]heptene as the exclusive photoproduct: NMR ($CDCl_3$, 100 MHz) τ 8.72 (s, 3 H), 6.85 (s, 2 H), 2.31-3.26 (m, 14 H); *m/e* 313 (M^+), 298, 207 (base), 206, 77. The sensitized irradiation of cyclopropene **33** gave 1,6-diphenyl-7-methyl-2,2,7-trideuterio-3,4-benzobicyclo[4.1.0]heptene as the sole photoproduct: NMR ($CDCl_3$, 100 MHz) τ 8.89 (s, 3 H), 6.94 (d, 1 H, J = 16.0 Hz), 6.57 (d, 1 H, J = 16.0 Hz), 2.51-3.23 (m, 14 H); *m/e* 313 (M^+).

Quantum Yield Determinations. Quantum yields were determined by using a "merry-go-round" apparatus[94] equipped with a 450-W Hanovia lamp housed in a quartz well at the center of the carriage. Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in five freeze-thaw cycles and then sealed. Benzophenone-benzhydrol actinometry was used for quantum yield determinations. An actinometer yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 M.[32] For the sensitized runs a filter solution of potassium dichromate in aqueous potassium carbonate was circulated through the well and the entire unit allowed to run for 1 h prior to use.[95] A Uranium glass filter sleeve and Corning 7-54 filters were also used in conjunction with the filter solution. The concentrations were adjusted so that the sensitizer absorbed more than 98% of the light. Analyses were performed on a 6 ft 10% Carbowax 20 M column on chromosorb P at 265 °C. The conversions were run to 25% or less. The mass balance in these runs was generally better than 98%. *trans*-Stilbene was used as the triplet quencher in the Stern-Volmer plots.

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Supplementary Material Available: Table II, the positional and thermal parameters obtained from the least-squares refinement (3 pages). Ordering information is given on any current masthead page.

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Chemiluminescence of Secondary Peroxyesters[1]

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Abstract: The thermolysis of 1-phenylethyl peroxyacetate and a series of substituted 1-phenylethyl peroxybenzoates was investigated. Thermolysis in benzene gives acetophenone and the corresponding carboxylic acid. The study of the reaction kinetics and kinetic isotope effect indicates that the unimolecular thermolysis proceeds by homolysis of the oxygen-oxygen bond. Electronically excited states are formed in the thermolyses of these peroxyesters. These are detected by their characteristic direct chemiluminescence or by indirect chemiluminescence. In the presence of easily oxidized catalysts these peroxyesters give excited states by the chemically initiated electron-exchange luminescence (CIEEL) path. The mechanism of these luminescent reactions was investigated.

The chemical generation of electronically excited states from the thermolysis of appropriate organic peroxides is an area of active and increasing interest.[2] Most of the peroxides thus far found to generate excited states are cyclic compounds. This fact is the

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