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Studies Dealing with the Intramolecular Hydrogen Atom Transfer Reaction of Tetrasubstituted Cyclopropenes[1a]

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Abstract: The photochemical behavior of a number of 3-alkyl substituted cyclopropenes which contain a hydrogen atom 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 state of these systems reacts 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_0/Φ_q vs. *trans*-stilbene at a constant quencher to cyclopropene ratio. The rate constants for hydrogen abstraction were found to be two orders of magnitude less than that for related phenyl alkyl ketones and increased as the strength of the C–H bond in the γ position decreased. Measurements of Arrhenius activation parameters were carried out at different temperatures. The entropy of activation was typical of a reaction proceeding via a strain-free six-center transition state. The activation energy associated with hydrogen abstraction was found to be dependent on the γ C–H bond strength. In contrast to the symmetrically substituted 1,2-diphenyl substituted cyclopropenes, the quantum efficiency of hydrogen abstraction of the 1,3 isomers was found to depend on the concentration of starting material. This dependence was rationalized in terms of an electron-transfer reaction to give a radical cation which reacts further with starting material. This interpretation is supported by the observation that the quantum yield for reaction exceeds unity at high concentrations of cyclopropene.

Alkene photochemistry is an unusually complex and versatile field of study.[2-4] The principal photochemical processes which have been observed for simple alkenes are cis $\rightleftarrows$ trans[5] isomerization and [2 + 2] cycloaddition.[6] Numerous studies have established that transfer of triplet energy to acyclic or macrocyclic olefins from suitable photosensitizers results in cis-trans isomerization of the double bond, undoubtedly as a consequence of the preferred orthogonal conformation of triplet olefins.[7] A 90° twist places the unpaired electrons in noninteracting orthogonal orbitals. The triplet state behavior of cyclohexenes, -heptenes, and -octenes has been studied in some detail by Kropp[8] and Marshall.[9] The reactions observed have been attributed to an initial cis $\rightleftarrows$ trans isomerization of the olefin followed by protonation of the resulting highly strained trans isomer. The divergent behavior exhibited by cyclopentene and other highly constrained olefins, on the other hand, is thought to be associated with the inability of these olefins to undergo cis $\rightarrow$ trans isomerization.[10] The radical-type behavior exhibited by these systems originates by intermolecular hydrogen abstraction by the π-π^* excited state itself. In fact, a number of reports have appeared in the literature which show that the excited π-π^* state of certain olefins has the ability to abstract hydrogen.[11-28] Thus, both intermolecular photoreduction and intramolecular hydrogen transfer reactions have recently been reported for alkenes. Intramolecular hydrogen abstractions by carbon have also been observed in the photochemistry of α,β-unsaturated enones.[29]

It was the purpose of the present study to investigate the triplet-induced hydrogen-abstraction reaction of a number of tetrasubstituted cyclopropenes. Formation of an orthogonal oriented triplet with these systems is inconceivable as a result of structural constraints. The photochemistry of cyclopropene derivatives has attracted considerable interest over the past several years.[30] The photochemical behavior of this highly strained ring system has been shown to be remarkably dependent on the multiplicity of the excited state involved.[31,32] Singlet states react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinyl carbenes[33] while triplet states, generated by sensitization techniques, usually give high yields of cyclopropene dimers.[34-38] Some earlier observations by DeBoer indicate that there are severe steric constraints associated with the triplet dimerization reaction.[31] Thus, 1,2-diphenylcyclopropenes, where both 3 positions are substituted with alkyl groups, do not dimerize.[31] Instead, the triplet states of tetrasubstituted cyclopropenes which possess γ hydrogen have been found to undergo an intramolecular hydrogen transfer reaction[39] by a mechanism analogous to the well-known Norrish type II photoreaction of carbonyl compounds.[40] In this paper we wish to describe some of the salient features associated with this reaction.

Results

Synthesis of Diphenylmethyl-3-alkyl Substituted Cyclopropenes. 1,2-Diphenyl-3-methyl-3-alkyl substituted cyclopropenes were prepared by treating diphenylmethylcyclopropenyl cation with Grignard reagents according to the general procedure of Breslow and co-workers.[41] In all the cases studied, nucleophilic attack by the Grignard reagent on the cyclopropenyl cation afforded the 1,2-diphenyl-3,3-disubstituted cyclopropene as the major product. This is consistent with

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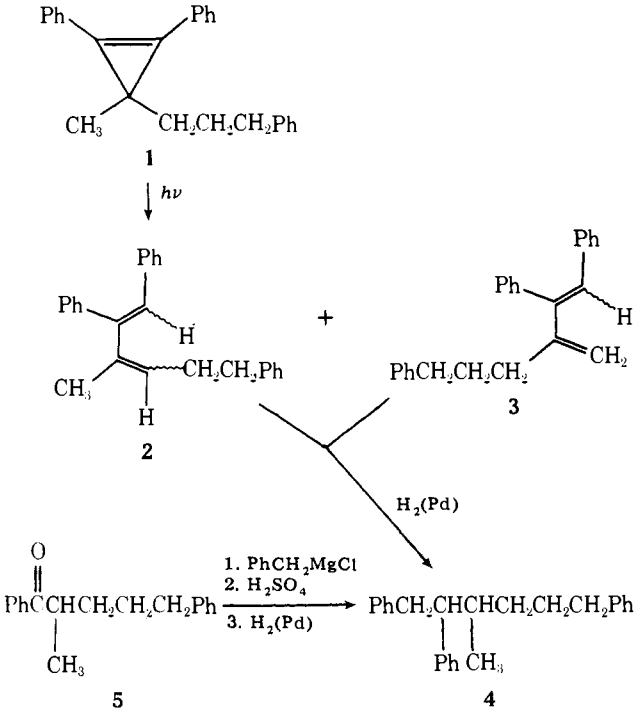
Breslow's previous observations in that nucleophilic attack occurs preferentially on the carbon atom of the cyclopropenyl cation which is best able to localize the positive charge.[41,42] The mixture of isomers could readily be separated by silica gel chromatography.

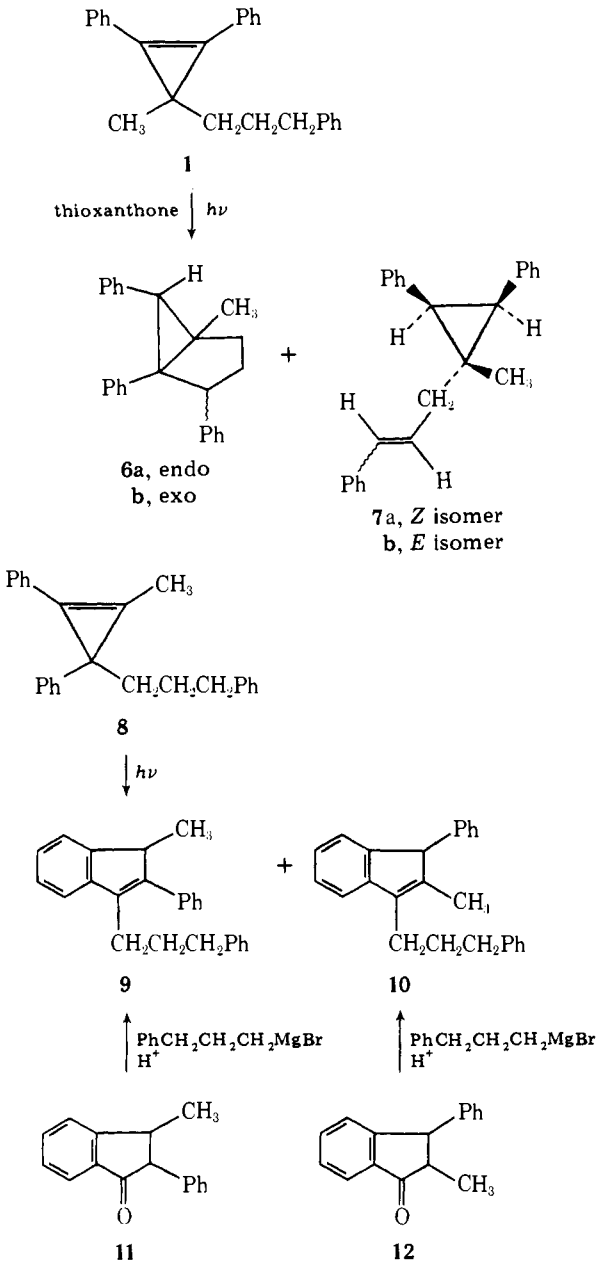
Isolation and Identification of Photoproducts. Direct irradiation of 1,2-diphenyl-3-methyl-3-(3-phenylpropyl)cyclopropene (**1**) in benzene with Pyrex-filtered light afforded a 1:1



mixture of 1,2,6-triphenyl-3-methyl-1,3-hexadiene (**2**) and 1,2-diphenyl-3-(3-phenylpropyl)-1,3-butadiene (**3**). The structures of these dienes were confirmed by catalytic reduction to 1,2,6-triphenyl-3-methylhexane (**4**), which was, in turn, independently synthesized by treating 1,5-diphenyl-2-methyl-1-pentanone (**5**) with benzylmagnesium chloride followed by dehydration and catalytic hydrogenation of the resulting olefins. The formation of **2** and **3** can be most economically accounted for by ring opening of the excited singlet state of **1** to a vinyl carbene followed by intramolecular hydrogen transfer. Insertion of vinyl carbenes onto neighboring alkyl groups to generate 1,3-butadienes has been previously described by Arnold and co-workers[43] thereby providing good analogy for the formation of dienes **2** and **3** from the irradiation of cyclopropene **1**.

In contrast to the direct photolysis, sensitized irradiation of **1** in benzene (thioxanthone) produced *endo*- (**6a**) (13%) and *exo*-5-methyl-1,2,6-triphenylbicyclo[3.1.0]hexane (**6b**) (17%) as well as *cis*-1,2-diphenyl-*cis*-3-methyl-3-(3-phenyl-2-propenyl)cyclopropane as a mixture of *Z* (**7a**) (42%) and *E* (**7b**) (28%) isomers. The product structures were in accord with the NMR, UV, IR, and mass spectral data (see Experimental Section). The *Z* and *E* isomers of cyclopropane **7** were found to be interconverted under the reaction conditions (photostationary state *Z*:*E* = 3:2) while the exo and endo isomers of bicyclohexane **6** were stable to the experimental conditions.

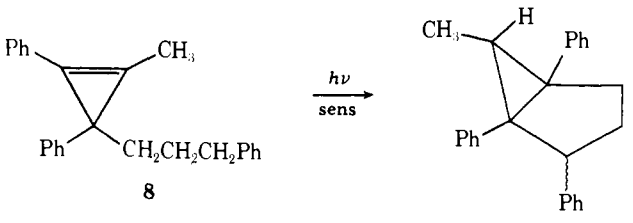
The irradiation of 1-methyl-2,3-diphenyl-3-(3-phenylpropyl)cyclopropene (**8**) provides another example of a system in which the products of the direct and triplet-sensitized photolysis are completely different. Thus, direct irradiation of **8** in benzene with Pyrex-filtered light afforded a 3:1 mixture of indenes **9** and **10** in quantitative yield. The structures of these indenes were confirmed by comparison with authentic samples prepared by treating 2-phenyl-3-methyl- (**11**) and 2-methyl-3-phenylindanone (**12**) with 3-phenylpropylmagnesium bro-



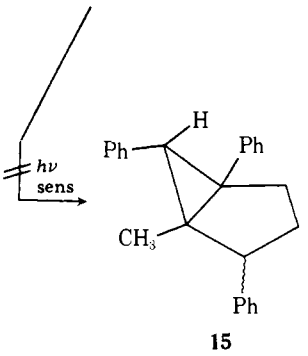
mide, followed by dehydration of the resulting alcohols. The regiospecificity observed in the rearrangement of this unsymmetrical cyclopropene is similar to that encountered with related vinyl[44] and aryl substituted cyclopropenes.[45]

The sensitized photolysis of **8** followed an entirely different course and produced a mixture of *endo*- (**13a**) (43%) and *exo*-1,2,5-triphenyl-6-methylbicyclo[3.1.0]hexane (**13b**) (13%) as well as *cis*-1,2-diphenyl-*cis*-3-methyl-2-(3-phenyl-2-propenyl)cyclopropane as a mixture of *Z* (**14a**) (25%) and *E* (**14b**) (19%) isomers. No signs of the isomeric 2,5,6-triphenyl-1-methylbicyclo[3.1.0]hexane (**15**) system could be detected in the crude photolysate.

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-alkyl substituted cyclopropenes which contain a hydrogen atom in the γ position of the side chain. In each case, products arising from a 1,5-diradical intermediate were observed. The triplet-sensitized irradiation of the symmetrically substituted cyclopropenes **16**–**18** led to mixtures of *exo*- and *endo*-bicyclo[3.1.0]hexanes **19** and *E* and *Z* olefinic cyclopropanes **20**. Similar results were obtained when the unsym-



8 → **13a**, endo; **b**, exo + **14a**, *Z* isomer; **b**, *E* isomer



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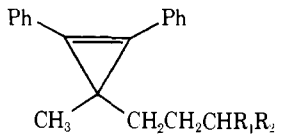
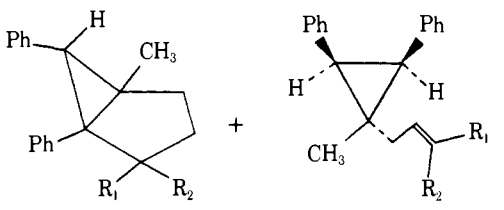
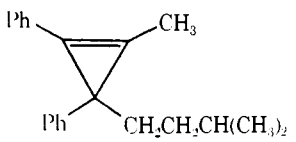


16, $R_1 = H$; $R_2 = CH_3$
17, $R_1 = R_2 = CH_3$
18, $R_1 = H$; $R_2 = -CH=CH_2$



19 + **20**



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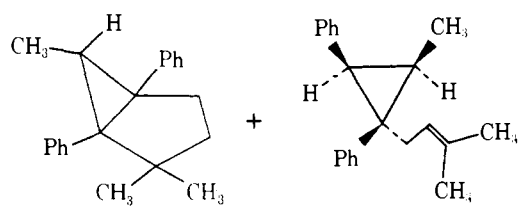
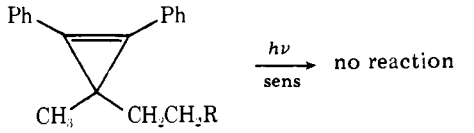


22 + **23**

metrically substituted cyclopropene **21** was irradiated in the presence of a triplet sensitizer. The structures of the photoproducts were deduced from their characteristic spectral data (see Experimental Section).

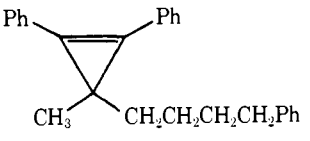
We also examined the triplet-induced photobehavior of cyclopropenes **24** and **25**. Both of these compounds were found to be stable on irradiation in the presence of a triplet photosensitizer. The reluctance of cyclopropene **24** to undergo hydrogen-atom transfer is probably due to the difficulty of



24, R = CH_3
25, R = Ph

transferring a primary hydrogen atom to the π-π^* triplet state of the cyclopropene. The lack of reactivity of cyclopropene **25**, on the other hand, is undoubtedly a result of the absence of a hydrogen atom in the γ position of the side chain.

The n-π^* triplet state of aryl ketones has been reported to undergo δ-hydrogen abstraction competitive with γ-hydrogen abstraction, especially when the δ carbon bears substituents which weaken its C-H bonds.[46-51] In order to determine whether a similar process can occur from the triplet π-π^* state of a tetrasubstituted cyclopropene, we have examined the sensitized behavior of 1,2-diphenyl-3-methyl-3-(4-phenylbutyl)cyclopropene (**26**). In this case the δ C-H bond is in-



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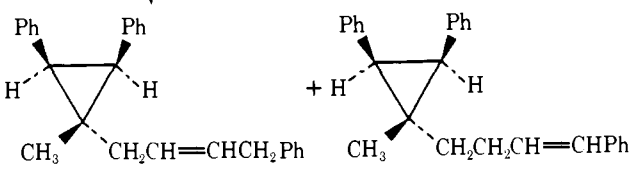
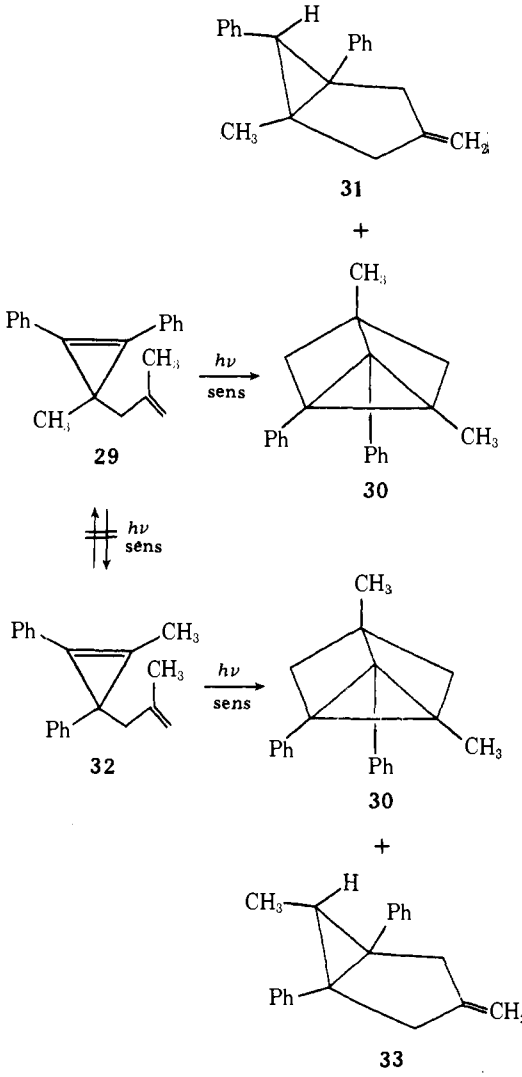
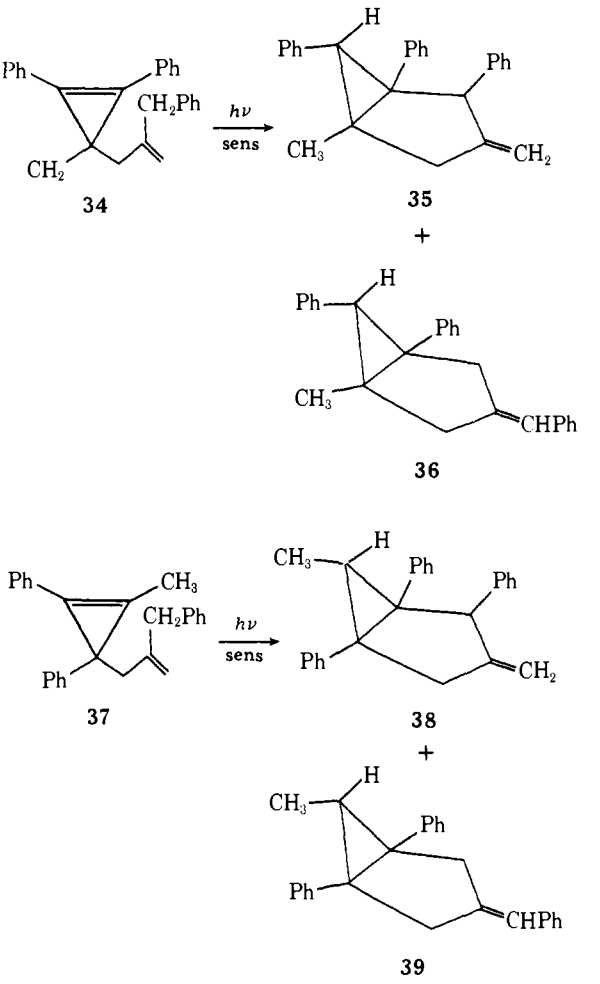


27 **28**

trinsically more reactive than the corresponding γ C-H bond. Irradiation of **25** in the presence of thioxanthone resulted in the formation of a complex mixture of photoproducts. The major products obtained were identified as cyclopropanes **27** (43%) and **28** (35%) on the basis of their characteristic spectral data. Unfortunately, it was not possible to separate the mixture of bicycloalkanes (22%) into its component parts. The predominant formation of cyclopropane **27** indicates that γ-hydrogen transfer is the preferred process. Intramolecular γ-hydrogen abstraction from **26** will produce a 1,5 biradical which can disproportionate to give both **27** and **28**. Since δ-hydrogen transfer will also give rise to cyclopropane **28**, it is not possible at this time to determine the γ/δ reactivity ratio with this system. Nevertheless, our results indicate that γ-hydrogen transfer is favored over δ abstraction. This is similar to the well-known order of 1,5 > 1,6 ≫ 1,4 in rate of intramolecular hydrogen atom transfers in acyclic systems.[52-55]

Attention was next turned to the triplet-induced photobehavior of the 3-substituted 2-methylallyl substituted cyclopropene system. The sensitized irradiation of cyclopropene **29** gave rise to a mixture of 4,6-dimethyl-1,2-diphenyltricyclo[2.2.0.$0^{2,6}$]hexane (**30**) (82%) and *exo*-1-phenyl-3-methylene-5-methyl-6-phenylbicyclo[3.1.0]hexane (**31**) (18%). The identity of tricyclohexane **30** was determined by its straightforward spectral characteristics [NMR ($CDCl_3$, 100 Hz) τ 8.76 (s, 3 H), 8.65 (s, 3 H), 7.86 (d, 1 H, J = 7.5 Hz), 7.68 (d, 1 H, J = 7.5 Hz), 7.59 (d, 1 H, J = 7.5 Hz), 7.49 (d, 1 H, J = 7.5 Hz), and 2.6-3.0 (m, 10 H)]. The structure of bicyclohexane **31** was also assigned on the basis of its spectral properties (see Experimental Section). Subjection of the isomeric cyclopropene **32** to similar photolysis conditions gave tricyclohexane **30** (48%) and bicyclo[3.1.0]hexane **33** (32%)





as the major photoproducts. In this case significantly larger quantities of the bicyclohexane ring were obtained. Appropriate control experiments established that no isomerization of the starting material was operative under the reaction conditions.

We have also studied the sensitized photolysis of the closely related 3-(2-benzylallyl) substituted cyclopropenes (i.e., **34** and **37**) and find that these compounds exhibit somewhat different photobehavior. Irradiation of a sample of cyclopropene **34** in benzene with thioxanthone gave rise to a 1:1 mixture of *exo,exo*-1,2,6-triphenyl-3-methylene-5-methylbicyclo-[3.1.0]hexane (**35**) and *exo*-1,6-diphenyl-3-benzylidene-5-methylbicyclo[3.1.0]hexane (**36**). The sensitized photolysis of **37** also resulted in the formation of a mixture of bicyclohexanes (i.e., **38** and **39**). With these systems, however, no significant quantities of a tricyclo[2.2.0.0^{2,6}]hexane could be detected in the NMR spectrum of the crude photolysate.

Determination of Reaction Efficiency and Reaction Rates. In order to derive 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 using benzophenone-benzhydrol as the chemical actinometer.[56] Degassed and sealed Pyrex tubes containing solutions of the cyclopropenes and sensitizers were irradiated through a uranium filter along with actinometer tubes in a rotating photochemical assembly. Reactions were carried out to low conversions to prevent secondary photoreactions, and yields of products were determined by analytical gas chromatography using internal standards. In these runs, concentrations were adjusted so that sensitizer singlets would decay to triplets before collision with the acceptor, but triplet energy transfer would be efficient. 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.[31,58,59] The direct observation of the triplet state of these 1,2-diphenyl substituted cyclopropenes was not possible since no emission could be found for any of the compounds at 77 K. 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.[60]

The quantum yield of hydrogen transfer for the symmetrical cyclopropenes was measured with several different high-energy sensitizers by analyzing the appearance of products by GLC analysis. The fact that the quantum yield of reaction (see Table I) was found to be independent of the nature of the sensitizer suggests that the rate of energy transfer is diffusion controlled. In general, the photosensitized reactions were reasonably efficient, with quantum yields varying from 0.03 to 0.68 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,[31,43] it is necessary to use a sensitizer to populate the triplet state. We found that *trans*-stilbene (E_T = 50 kcal/mol)[57] can act as a quencher for the triplet-sensitized hydrogen-transfer reaction of cyclopropenes **1**, **16**, and **17**. In these experiments, *trans*-stilbene intercepts both the sensitizer triplet and the cyclopropene triplet. It was assumed that both triplets (thioxanthone (E_T = 65.5

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

cyclopropene	sensitizer	Φ[c,d]	$k_{CQ}\tau^3$C, M^{-1} [e]	τ, 10^7 s^{-1}	k_r, 10^6 s^{-1}	k_d, 10^6 s^{-1}
1	acetophenone	0.42				
1	benzophenone	0.41				
1	thioxanthone	0.42	1300	2.52	1.69	2.30
16	acetophenone	0.029				
16	benzophenone	0.031				
16	thioxanthone	0.028	4900	9.52	0.03	1.02
17	acetophenone	0.38				
17	benzophenone	0.39				
17	thioxanthone	0.40	2675	5.20	0.77	1.15
8	acetophenone	0.67				
21	acetophenone	0.53				

[a] Concentration of cyclopropene ca. 2×10^{-3} M. [b] 40 °C. [c] Sum of all products. [d] ±10%. [e] ±20%.

kcal/mol)[57] and cyclopropene ($E_T \sim 55$ 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.

Recently, Cristol and co-workers have described a method for the treatment of quenching data of photosensitized reactions which allows for the determination of the lifetime of the triplet state.[61] We have used his method in order to approximate the rate of hydrogen transfer of the triplet state of the symmetrically substituted cyclopropenes **1**, **16**, and **17**. 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]hexane P, was derived from Scheme I. 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 and whose slopes divided by the intercepts give $k_{CQ}\tau^3$C values.

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

The results of a photosensitized experiment with 1,2-diphenyl-3-methyl-3-(3-phenylpropyl)cyclopropene (**1**), using a ratio of [C]/[Q] of 50, sensitized with thioxanthone and quenched with *trans*-stilbene, are displayed in Figure 1. These data, whose scatter unfortunately shows the difficulties inherent in plots with small slopes, lead to a k_{SQ}/k_{SC} ratio of 1.5 ± 0.5 and a $k_{CQ}\tau_C{}^{*3}$ value of 1300. Quantum yields and ($k_r + k_d$) values (i.e., $1/\tau$) are given in Table I for the three cyclopropenes studied. The value of k_{CQ} in benzene is taken to be 5×10^9 L mol^{-1} s^{-1}.[46] The data clearly show that the three symmetrically substituted cyclopropenes (i.e., **1**, **16**, and **17**) all accept excitation from triplet thioxanthone with a reaction

Scheme I

$$S_0 \xrightarrow{h\nu} S^{*1} \xrightarrow{k_{isc}} S^{*3}$$

$$S^{*3} + C_0 \xrightarrow{k_{SC}} C^{*3} + S_0$$

$$S^{*3} + Q_0 \xrightarrow{k_{SQ}} Q^{*3} + S_0$$

$$S^{*3} \xrightarrow{k_{SD}} S_0$$

$$C^{*3} \xrightarrow{k_r} B \longrightarrow P_0$$

$$C^{*3} \xrightarrow{k_d} C_0$$

$$C^{*3} + Q_0 \xrightarrow{k_{CQ}} C_0 + Q^{*3}$$

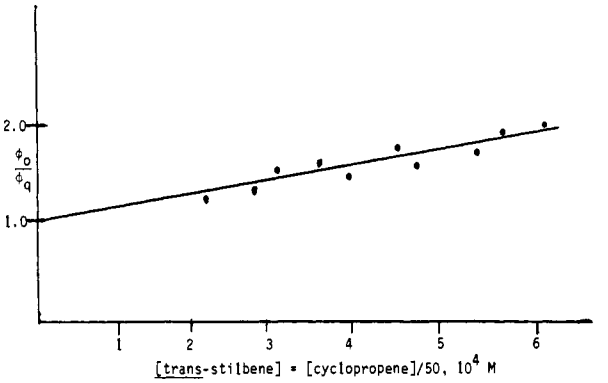


Figure 1. Quenching of thioxanthone sensitization of 1,2-diphenyl-3-methyl-3-(3-phenylpropyl)cyclopropene (**1**) with *trans*-stilbene.

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 transformation to product or to some 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 quenching experiments with the unsymmetrically substituted cyclopropenes **8** and **21**. With these two systems, however, a negative slope was obtained from the Stern-Volmer plots. A negative slope is obviously inconsistent with the mechanism outlined in Scheme I, as the result leads to a negative lifetime, clearly beyond physical reality. Treatment of the data according to Cristol's method assumes that quenching of the excited cyclopropene triplet leads away from product formation. If interaction of the excited state with either the quencher or starting material enhances the formation of product, then negative slopes will be obtained. We have measured the quantum yield of reaction of these two systems as a function of increasing concentration of starting cyclopropene and find that the quantum efficiency of reaction is actually enhanced (see Figure 2). This observation would account for the negative slopes observed in the Stern-Volmer plots. Examination of the product ratio of the two unsymmetrical cyclopropenes by NMR shows no change in distribution as a function of concentration. This unusual concentration effect was only observed with the unsymmetrically substituted cyclopropenes **8** and **21**. The quantum yield of reaction of the symmetrical cyclopropenes (i.e., **1**, **16**, and **17**) was found to be independent of the concentration of starting material. As a result of this added complication, it is not possible to obtain the triplet lifetimes of the unsymmetrically

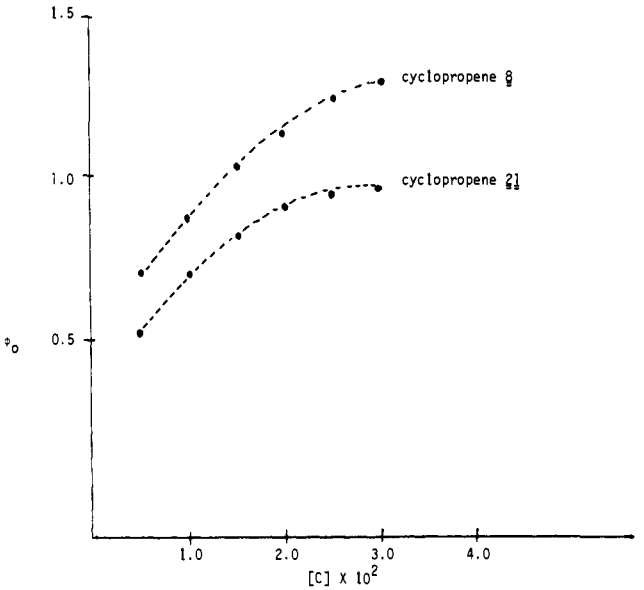


Figure 2. Quantum yield of reaction of cyclopropenes **8** and **21** vs. concentration of starting material.

Table II. Variation of the Relative Quantum Yield, $k_q\tau$, and $1/\tau$ Values of Photoreaction with Temperature

cyclopropene	T, °C	$k_q\tau$, M^{-1}	$10^6(1/\tau)$, s^{-1}	Φ
1	40	1300	3.85	0.42
1	55	1025	4.88	0.51
1	70	850	5.88	0.58
16	40	4900	1.02	0.028
16	55	4200	1.19	0.049
16	70	4000	1.25	0.091
17	40	2675	1.87	0.40
17	55	2000	2.50	0.49
17	70	1550	3.23	0.57

substituted cyclopropenes. A possible explanation to account for this effect will be described in the Discussion section.

Arrhenius Activation Parameters. We have also studied the temperature dependence of the sensitized photoreaction of cyclopropenes **1**, **16**, and **17** in competition with the triplet quenching by *trans*-stilbene. Stern–Volmer quenching experiments were performed on 10^{-3} M solutions of the cyclopropene in benzene between 40 and 70 °C. The values obtained from a series of Stern–Volmer plots were plotted in an Arrhenius form and fitted by the least-squares treatment. In order to obtain the absolute activation energies for the hydrogen abstraction, it is necessary to know the temperature dependence of k_q. Viscosities were measured for solutions containing substrate, sensitizer, and quencher and the rates of diffusion were calculated using the Debye equation.[62]

$$k_{diff} = 8RT/3000\eta$$

The results are given in Table II. Computer-generated Arrhenius plots of the data resulted in the activation parameters listed in Table III.

During the course of our studies we found that the distribution of the photoproducts was also dependent on the temperature of the reaction. The variation of product yield as a function of temperature is shown in Table IV (see Experimental Section). With all of the systems studied, an increase in temperature resulted in a pronounced increase in the overall yield of bicyclohexane and a corresponding decrease in the yield of the olefinic cyclopropanes. The predominant olefinic cyclopropane isolated always corresponded to the Z isomer and the ratio of Z:E olefins increased slightly with increasing

Table III. Arrhenius Activation Parameters[a] for Hydrogen Abstraction

cyclopropene	E_a, kcal/mol	$\Delta S^{\ddagger}$, gibbs[b]	r[c]
1	5.38 ± 0.46	−14.9 ± 1.4	0.94
16	10.22 ± 0.32	−7.51 ± 2.0	0.96
17	6.48 ± 0.50	−12.9 ± 1.5	0.95

[a] Error limits are deviations from least squares. [b] Entropies of activation calculated for 25 °C. [c] Correlation coefficients of least-squares plot.

Table IV. Variation of Yield of Photoproduct as a Function of Temperature

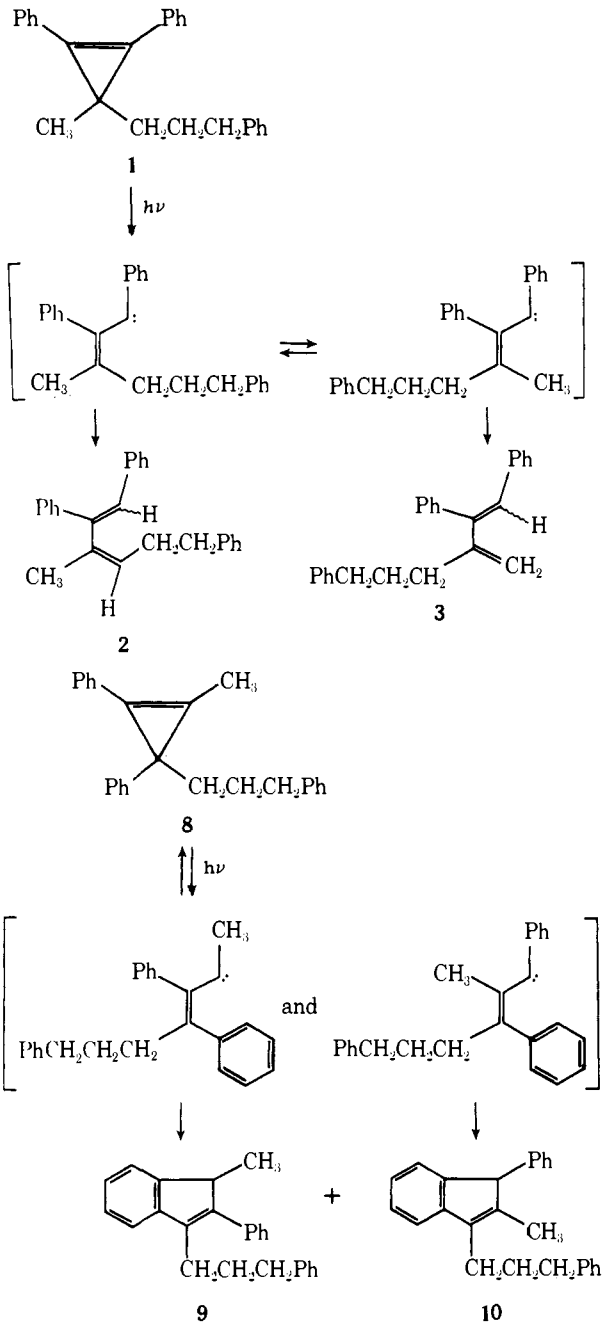
		% yield of photoproduct			
		bicyclohexane		3-allyl substituted cyclopropane	
cyclopropene	temp, °C	exo	endo	Z	E
1	−15	12	11	48	29
1	25	18	13	42	27
1	80	22	19	36	23
1	130	26	19	35	20
8	−15	10	38	30	22
8	25	13	43	25	19
8	80	18	43	23	16
8	130	20	41	23	15
17	−15	15		85	
17	25	20		80	
17	80	23		77	
17	130	26		74	
21	−15	21		79	
21	25	26		74	
21	80	29		71	
21	130	32		68	

temperature. The major bicyclohexane produced from the sensitized irradiation of **1** corresponded to the exo isomer whereas the endo bicyclohexane was the major isomer isolated from the sensitized irradiation of the unsymmetrically substituted cyclopropene **8**.

Discussion

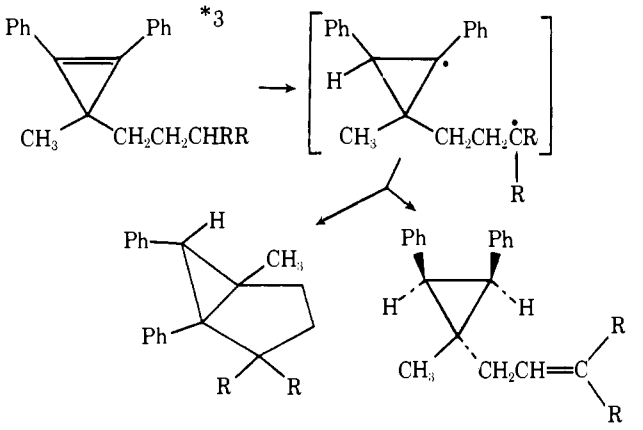
The photochemistry of cyclopropene derivatives has been shown to be remarkedly dependent on the multiplicity of the excited state involved.[30] Singlet states react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinyl carbenes.[30] Thus, the formation of dienes **2** and **3** from the direct irradiation of cyclopropene **1** can readily be accounted for in terms of a vinyl carbene intermediate. In this case, the products obtained correspond to 1,4-hydrogen transfer from the methyl and methylene groups adjacent to the double bond. The low quantum efficiency observed (Φ = 0.02) is probably a result of a rapid return of the carbene intermediate to the corresponding cyclopropene.

Yet another reaction undoubtedly resulting from a vinyl carbene intermediate is the formation of indenes **9** and **10** from the irradiation of cyclopropene **8**. This reaction proceeds via an isoindene intermediate which subsequently undergoes a thermally allowed 1,5-sigmatropic hydrogen shift to give the aromatic indene system. Earlier work by Padwa[45] and Zimmerman[44] has shown that an unusual substituent effect operates in the photorearrangement of a series of unsymmetrically substituted cyclopropenes. The major product obtained from the irradiation of a 1,3-diphenyl-2-methyl substituted cyclopropene was always found to correspond to preferential cleavage of the cyclopropene bond which is methyl rather than phenyl substituted. This unusual regioselectivity was attributed to a funneling of the excited state of the cyclopropene to the



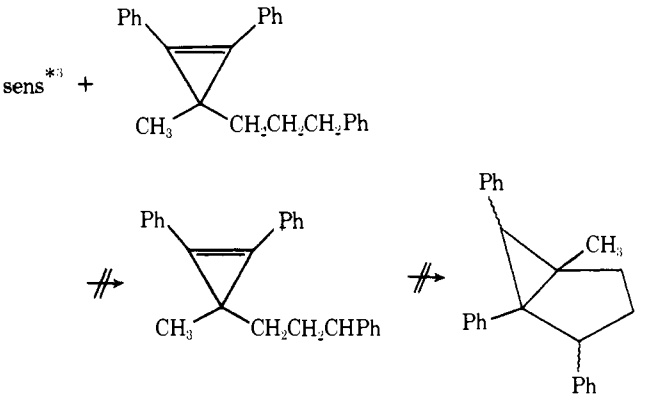
energy surface of the higher lying carbene state.[45] Thus the formation of indene **9** as the major photoproduct obtained from the irradiation of **8** is perfectly compatible with the earlier observations.

Recent MINDO/3 semiempirical MO calculations by Pincock and Boyd[38] indicate that the triplet state of cyclopropene possesses a large barrier (~13 kcal/mol) to ring opening and is therefore long lived enough to undergo bimolecular reactions such as dimerization. Triplet states of tetrasubstituted cyclopropenes, however, do not dimerize as a consequence of the severe steric factors which exist in the transition state. Instead, these systems abstract a hydrogen from the γ-carbon atom of the side chain via a six-membered transition state to produce a 1,5 biradical which either couples to give a bicyclo[3.1.0]hexane or disproportionates to afford a mixture of olefinic cyclopropanes. As was mentioned earlier, there are a number of reports in the literature which indicate that hydrogen-transfer reactions occur in the photochemistry of alkenes.[11-28] In fact, a closely related hydrogen atom transfer reaction of a cyclopropenyl ketone was previously proposed by van Tamelen and Whitesides[63] and provides ex-



cellent chemical analogy for the first step of the above sequence.

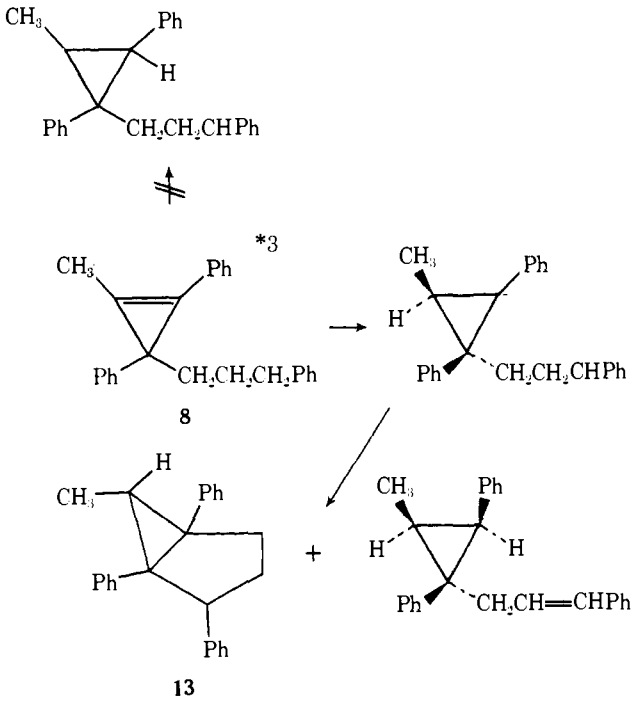
While tetrasubstituted cyclopropenes which bear a γ hydrogen on the side-chain substituent undergo smooth photochemical reorganization on triplet sensitization, the homologous 3-phenylethyl substituted cyclopropene **25** is inert under similar reaction conditions. This widely differing behavior can be attributed to the necessity of having a hydrogen in the γ position of the side chain for reaction to occur. A mechanism involving benzylic hydrogen abstraction by the excited sensitizer followed by radical addition to the neighboring double bond would not rationalize the data obtained. This process would be expected to give rise to a mixture of the 6-endo and 6-exo bicyclohexanes. In fact, the 6-endo isomer should be the



major product since further abstraction of a hydrogen atom would be expected to occur from the least hindered side. The exclusive formation of the 6-exo isomer is only compatible with coupling of the 1,5-biradical intermediate since the geometry of the cyclopropyl biradical precludes formation of the 6-endo isomer. The bimolecular abstraction reaction also fails to account for the formation of the olefinic cyclopropanes (70%). Control experiments with 1,2-diphenyl-3,3-dimethylcyclopropene showed that this system was perfectly stable to the sensitized conditions. Photoreduction of the cyclopropene double bond did not occur even under prolonged irradiation.

Further studies with the structurally related cyclopropene **8** have shown that the triplet state of this system affords bicyclohexane **13** and cyclopropane **14** as the exclusive photoproducts. Thus, the reaction is completely regiospecific and involves hydrogen atom transfer to the carbon bearing the methyl group. This 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. Similar behavior was observed with the closely related cyclopropene **21**.

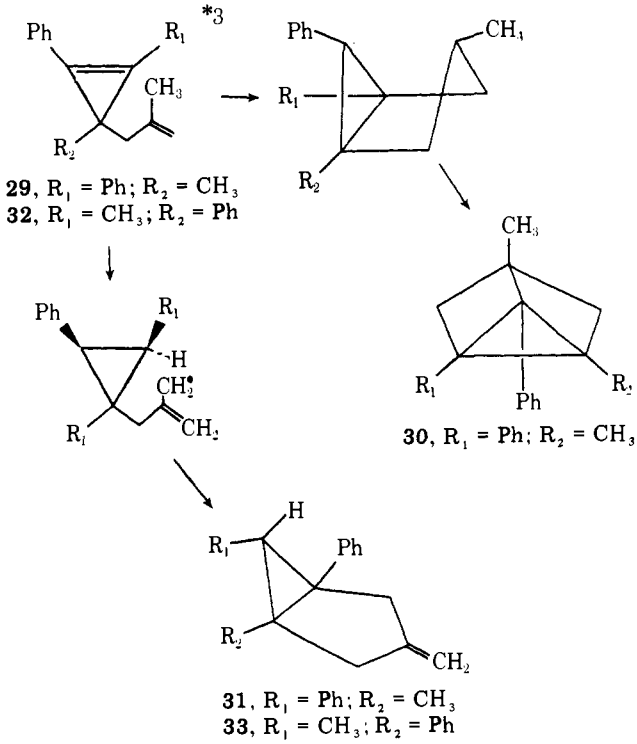
Another aspect of interest is that the triplet-sensitized reaction of cyclopropene **29** gives rise to a [2 + 2] cycloadduct



8

13

30 (82%) and a 3-methylene substituted bicyclo[3.1.0]hexane **31** (18%). Similar results were encountered with cyclopropene **32**, although in this case only one of the two possible bicyclo-

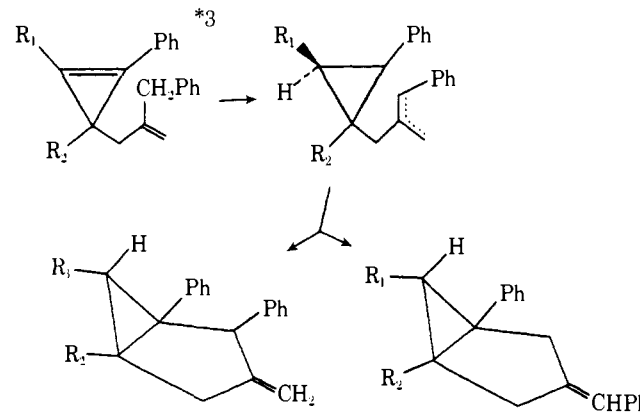


29, R_1 = Ph; R_2 = CH_3
32, R_1 = CH_3; R_2 = Ph

30, R_1 = Ph; R_2 = CH_3

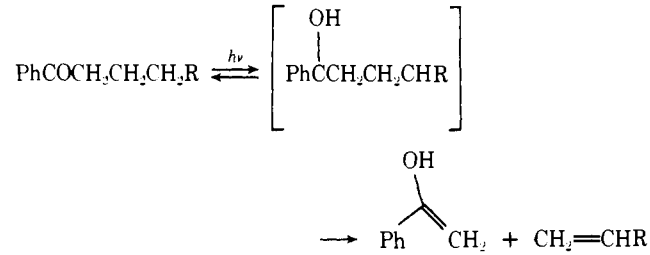
31, R_1 = Ph; R_2 = CH_3
33, R_1 = CH_3; R_2 = Ph

hexanes was produced (ratio **30**:**31** = 5:3). The formation of the bicyclohexane ring proceeds via an intramolecular hydrogen atom transfer reaction while the formation of the tricyclo[2.2.0.$0^{2,6}$]hexane involves a novel intramolecular [2 + 2] cycloaddition reaction. Both products were equally quenched with added triplet quenchers, thereby indicating that they are both derived from a common triplet state. The fact that larger quantities of the 3-methylene substituted bicyclo[3.1.0]hexane (i.e., **31**) is obtained from the sensitized irradiation of **32** is probably the result of an enhanced rate of hydrogen abstraction by the methyl-bearing carbon atom of the cyclopropene ring. When the allylic methyl group is replaced by a benzyl group (i.e., structures **34** and/or **37**), the



hydrogen-abstraction reaction becomes the exclusive path followed. In this case a mixture of two bicyclohexanes, corresponding to biradical coupling at both allylic positions, was obtained. The failure of the triplet state to give the tricyclo[2.2.0.$0^{2,6}$]hexane ring is undoubtedly related to the ease with which the doubly activated (benzylic-allylic) hydrogen is transferred.

The intramolecular photoelimination of ketones with a hydrogen atom on the γ carbon to give a shorter chain ketone and an olefin is a well-documented reaction which has been known for some time.[40,64] The results described above indicate that the triplet-induced reaction of tetrasubstituted cyclopropenes containing a γ hydrogen in the side chain proceeds via a mechanism analogous to that accepted for the Norrish type II reaction of ketones. The enhancement of the quantum yield



for the Norrish type II reaction of aryl ketones in polar as opposed to nonpolar solvents has been reported by Wagner and co-workers.[40,65] The solvent effect was explained in terms of a mechanism involving a biradical intermediate. It was postulated that radiationless decay occurs from the 1,4 biradical by reversal of the hydrogen-abstraction step to give the ground state of the starting ketone. In polar solvents the hydroxyl group of the biradical is hydrogen bonded to the solvent and reversal of the hydrogen abstraction is hindered. The increase in quantum efficiency to unity in a hydroxylic solvent suggests that radiationless decay occurs solely from the biradical and not from the triplet state itself. As a consequence of this reversal, one cannot readily separate $1/\tau$ values into rates of abstraction (k_r) and decay (k_d) in nonpolar solvents. The situation is quite different with the triplet state of the tetrasubstituted cyclopropenes. With these systems it is highly unlikely that the initially produced 1,5 biradical will regenerate the highly strained (53 kcal/mol)[66] cyclopropene ring when it has two lower energy pathways available to it (i.e., coupling and disproportionation).[67] It should be noted that the quantum yield for H-atom transfer approaches unity with the unsymmetrical cyclopropenes, thereby providing good support for the contention that the 1,5-biradical intermediate does not regenerate the cyclopropene ring. By making the reasonable assumption that the fraction of biradical reversion is close to zero, one can easily dissect k_r and k_d values from τ (Table I) with these systems.

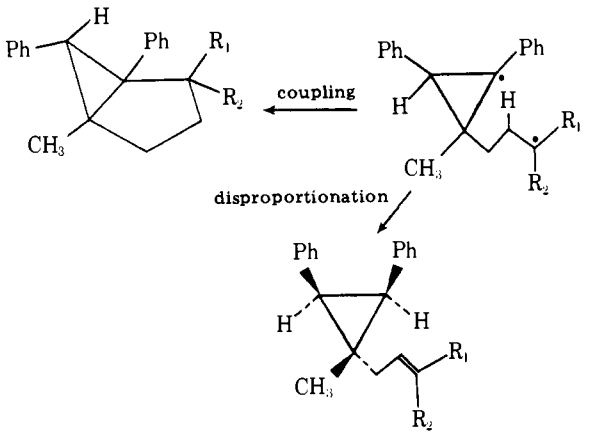
$$k_r = \Phi/\tau \text{ and } k_d = 1/\tau - k_r$$

The rate constants for hydrogen abstraction (k_r) and nonradiative decay (k_d) are given in Table I and represent one of the rare determinations of the rate constant for hydrogen abstraction of the triplet state of an olefin.[13] Several results in Table I are of interest and merit comment. First, the triplet lifetimes of the cyclopropenes are ~100 times greater than those for the related phenyl alkyl ketones.[68,69] The longer lifetime of the cyclopropenes may very well reflect the weaker C-H bond being formed in the abstraction reaction. Secondly, the rate of hydrogen abstraction for cyclopropene **1** is ca. 250 times smaller than that for α-phenylbutyrophenone (**40**).[40,69] The larger rate constant observed for the aryl ketone is undoubtedly a reflection of the greater strength of the OH bond being formed in the reaction. Similar differences in reactivity were also observed with cyclopropenes **16** and **17** when compared with valerophenone (**41**) and phenyl isopentyl ketone (**42**) (i.e., **41**:**16** ~ 4×10^3 and **42**:**17** ~ 600). Thirdly, the rate constant for abstraction increases as the strength of the γ C-H bond decreases (**1**:**17**:**16** = 56:26:1.0). 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 to be expected 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. Finally, the quantum efficiency of the abstraction is directly related to the triplet-state reactivity since the initially produced biradical intermediate does not undergo reverse hydrogen transfer as was observed in the phenyl alkyl ketone system.

Recent work by Rosenberg and Servé on the photoreduction of 1,1-diphenylethylene (DPE) by 2-propanol has pointed out the similarities in the chemistry of the benzophenone and diphenylethylene reactive excited states.[13] It is worthy of note that the bimolecular rate constant for triplet DPE hydrogen abstraction ($k_r = 1.4 \times 10^9$ M^{-1} s^{-1}) is considerably greater than the corresponding value reported for benzophenone triplet (10^6 M^{-1} s^{-1}).[70] The excited DPE triplet state would be expected to twist rapidly to an orthogonal structure.[71] Interaction between the electrons on C-1 and C-2 is thus minimized by their orthogonal relationship as well as the extensive delocalization of the C-2 electron, with both factors combining to create a C-1 radical analogous to the lone nonbonding electron in an n-π* state. The much lower rate constant of hydrogen abstraction encountered with the diphenyl substituted cyclopropenes is probably related to radical delocalization by the attached phenyl groups and perhaps also to a lower reactivity of this planar π-π* state.[72]

The Arrhenius activation energies for cyclopropenes **1** and **17** are almost within experimental error of each other (Table III). The activation energy associated with cyclopropene **16** is ca. 4 kcal larger than that for cyclopropenes **1** and **17** while there is little difference in the entropies of activation of the three systems. The entropy of activation for all three compounds is quite typical of a reaction proceeding via a strain-free six-center transition state[73,74] (i.e., valerophenone photoelimination, $\Delta S^{\ddagger} = -12.5$ eu).[75] Scaiano and co-workers have demonstrated that the activation energy of the Norrish type II reaction (E_a ~ 3-6 kcal/mol) is dependent upon the γ C-H bond strength.[76] For example, the activation energy of butyrophenone photoelimination is ca. 2.0 kcal/mol larger than that for valerophenone.[76,77] This correlation also holds with the tetrasubstituted cyclopropenes. With this system the activation energies are even larger than with the corresponding ketones. Cyclopropenes **1** and **17** possess identical π-π* triplet energies and the C-H bonds being broken have similar bond strengths. Thus it is not surprising to find that the activation energies are approximately the same. Cyclopropene **16**, on the other hand, possesses a significantly larger activation energy thereby accounting for its slow rate of hydrogen abstraction. Since the entropy of activation for the hydrogen abstractions is the same, the large variation in rate constants must be due entirely to the differences in activation energy. The failure to detect reaction with the triplet state of cyclopropene **24** at room temperature can be readily understood since the activation energy associated with this reaction will be very large. The large values of the activation energy of the cyclopropenes are undoubtedly related to the weak C-H bond that is being formed in the hydrogen-abstraction reaction.

As was noted previously, the 1,5-biradical intermediate produced on γ-hydrogen abstraction can undergo cyclization or disproportionation. The most dramatic effect of temperature on the reaction products is the increase in the percentage of coupling with an increase in temperature. For example, the percentage of cyclization of the biradical obtained from cyclopropene **1** increases from 23% at −15 °C to 45% at 130 °C. Similar increases were observed with the other systems (see Table IV). This temperature effect is most readily explained in terms of the biradical conformation necessary for the disproportionation reaction. The transition state for disproportionation requires that the C-H bond in the β position of the side chain be in close proximity to the radical center on the



cyclopropane ring. As the temperature is raised it becomes more difficult to achieve this conformation and consequently an increase in the amount of cyclization occurs.

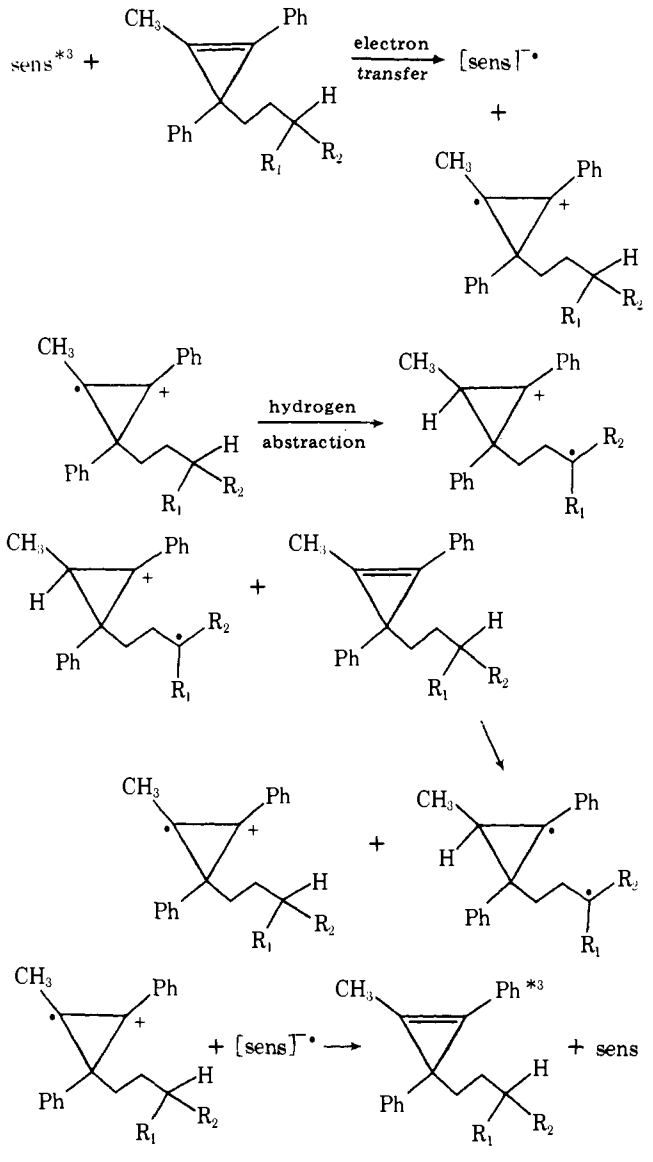
The quantum yield for reaction of the triplet state of the symmetrically substituted 1,2-diphenylcyclopropenes in benzene is independent of concentration, indicating that the reaction is intramolecular. The mechanism of the reaction involves (1) triplet energy transfer from sensitizer, (2) intramolecular hydrogen abstraction, and (3) cyclization or disproportionation to products. The situation is quite different with the unsymmetrically 1,3-diphenyl substituted cyclopropenes. With these systems 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.[61] At low concentration the quantum yield for reaction of cyclopropene **21** is 0.53. At higher concentrations it levels off to a value of ca. 0.96. With cyclopropene **8**, a concentration dependence is also observed, but in this case the quantum efficiency actually exceeds unity (see Figure 2). A simple intramolecular hydrogen atom transfer will not explain this concentration dependence. The reaction with cyclopropene **8** apparently involves some bimolecular step which proceeds via a short radical chain.

A reasonable rationale which could account for the unusual concentration effect observed with the unsymmetrical cyclopropenes is based on the assumption that triplet energy transfer from the sensitizer (thioxanthone, E_T = 65 kcal/mol) to the unsymmetrical cyclopropene is an endothermic process. The triplet energy of the 1,3-diphenyl substituted cyclopropene

should be much larger than the corresponding 1,2-diphenyl substituted isomer. In recent years it has become clear that, in many cases where electronic energy transfer is endothermic, the primary process leading to quenching of aromatic carbonyl triplets is formation of a triplet exciplex, the stability of which should depend on the electron-donating and -accepting properties of the quencher and excited state, respectively. Based on the pioneering work by Weller and co-workers[78] it has been suggested[79] that the relationship between the rate constant for charge-transfer quenching of an aromatic ketone excited state and the relevant physical properties of the reactants may be approximated by the relationship

$$-\log k_q \propto \Delta G_c \sim IP_Q - [\Delta E_{0,0} + E(A^-/A)] + C$$

In this expression IP_q is the quencher ionization potential, $\Delta E_{0,0}$ is the electronic energy of the excited state, and $E(A^-/A)$ is the half-wave reduction potential of the ground-state carbonyl compound. It has been suggested that such a relationship should hold for reactions which are endothermic by several kcal/mol. Caldwell,[80] Kochevar and Wagner,[81] and Gupta and Hammond[82] have argued persuasively that simple olefins quench aromatic ketone triplets via a triplet exciplex. More recently, Arnold[83] and Farid[59] have shown that photoinduced electron transfer reactions can readily occur with diphenyl substituted cyclopropenes. Thus, the radical cation produced on electron transfer from the cyclopropene to the sensitizer triplet might then undergo intramolecular hydrogen abstraction to give rise to a new radical cation. Reaction of this species with another molecule of cyclopropene would generate the same 1,5-biradical intermediate expected from a simple hydrogen-transfer reaction. Recombination of the radical ion pairs would also be expected to lead to triplet formation.[84] According to the above scheme, the quantum efficiency of the reaction could exceed unity. It should be noted that a number of olefins are known to dimerize via a photochemically produced radical cation.[85-88] Some of these dimerizations proceed via a chain mechanism, in which the chain propagation step involves an electron transfer from a monomeric olefin to a dimeric radical cation.[85,87] This type of reaction provides good analogy for the process outlined above. Actually, the mechanism involved with the unsymmetrically substituted cyclopropenes may proceed by both an intramolecular and bimolecular component. At high concentrations of starting material, the bimolecular radical cation process would be expected to become progressively more important. Although we have no firm evidence for this pathway, it does have the advantage of rationalizing the increase in quantum yield as a function of concentration and also accounts for the absence of this effect with the symmetrical cyclopropenes. With these systems, triplet energy transfer should be exothermic by at least 5 kcal/mol. We are continuing to examine the triplet-sensitized behavior of unsymmetrically substituted cyclopropenes and will report additional findings at a later date.



Experimental Section[89]

Preparation of 1,2-Diphenyl-3-methyl-3-(3-phenylpropyl)cyclopropene (1) and 1-Methyl-2,3-diphenyl-3-(3-phenylpropyl)cyclopropene (8). To a suspension containing 6.0 g of methyldiphenylcyclopropenyl perchlorate[45] in 50 mL of anhydrous tetrahydrofuran at −78 °C was added 50 mL of a 1.0 M 3-phenylpropylmagnesium bromide solution in ether. After the addition was complete, the mixture was allowed to warm to 25 °C and was stirred at this temperature for 12 h. 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 yellow residue was chromatographed on a silica gel column using hexane as the eluent. The first component isolated from the column contained 2.86 g (45%) of 1,2-diphenyl-3-methyl-3-(3-phenylpropyl)cyclopropene (**1**) as a clear oil: IR (neat) 3.30, 3.42, 5.51, 6.23, 6.70, 6.91, 7.30, 9.31, 9.70, 10.94, 13.21, and 14.53 μ; UV (95% ethanol) 337, 320, and 312 nm (ε 21 000, 28 200, and 23 700); NMR ($CDCl_3$, 100 MHz) τ 8.56 (s, 3 H), 8.05-8.60 (m, 4 H), 7.48 (t, 2 H, J = 8.0 Hz), and 2.30-2.97 (m, 15 H); *m/e* 324 (M^+), 262, 244, 220 (base), 205, 186, 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.54; H, 7.43.

The second component isolated from the column contained 3.28 g (51%) of a clear oil whose structure was assigned as 1-methyl-2,3-diphenyl-3-(3-phenylpropyl)cyclopropene (**8**) on the basis of its characteristic data: IR (neat) 3.31, 3.43, 5.40, 6.26, 6.72, 6.95, 7.90, 9.30, 9.68, 10.93, 13.11, and 14.33 μ; UV (95% ethanol) 262 nm (ε 16 300); NMR ($CDCl_3$, 100 MHz) τ 8.14-8.59 (m, 2 H), 7.72 (s, 3 H), 7.70-7.86 (m, 2 H), 7.36 (t, 2 H, J = 8.0 Hz), and 2.44-2.91 (m, 15 H); *m/e* 324 (M^+), 220 (base), 205, 105, 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.59; H, 7.41.

Direct Irradiation of 1,2-Diphenyl-3-methyl-(3-phenylpropyl)cyclopropene (1). A solution containing 117 mg of **1** in 125 mL of benzene was irradiated with a 450-W Hanovia mercury lamp equipped with a Pyrex filter sleeve for 3 h. Removal of the solvent under reduced pressure left a pale yellow oil whose NMR spectrum indicated it to be a mixture of 1,2,6-triphenyl-3-methyl-1,3-hexadiene (**2**) and 1,2-diphenyl-3-(3-phenylpropyl)-1,3-butadiene (**3**). All attempts to separate the mixture into its component parts failed: NMR ($CDCl_3$, 100 MHz) τ 7.28-8.80 (m, 6 H), 4.76-5.20 (m, 2 H), 2.40-3.70 (m, 16 H). The crude reaction mixture was taken up in 50 mL of glacial acetic acid and was subjected to hydrogenation using a Parr apparatus with 200 mg of 5% palladium on calcium sulfate as a catalyst under 45 psi of hydrogen gas at 60 °C for 20 h. The catalyst was filtered and the solution was concentrated under reduced pressure. The resulting

residue was subjected to preparative thick layer chromatography using a 5% benzene–hexane mixture to give 89 mg of a diastereomeric mixture of 1,2,6-triphenyl-3-methylhexane (**4**) as a clear oil: IR (neat) 3.32, 3.43, 6.22, 6.69, 6.89, 9.31, 9.66, 13.36, and 14.34 μ; NMR ($CDCl_3$, 100 MHz) τ 9.23 (d, 3 H, J = 7.0 Hz), 9.02 (d, 3 H, J = 7.0 Hz), 8.10–9.0 (m, 5 H), 6.91–7.64 (m, 5 H), and 2.62–3.40 (m, 15 H); *m/e* 328 (M^+), 237, 159, 145 (base), 117, 105, 91, and 77.

Anal. Calcd for $C_{25}H_{28}$: C, 91.41; H, 8.59. Found: C, 91.25; H, 8.73.

The structure of this material was verified by comparison with an independently synthesized sample. A 6.5-g sample of propiophenone in 50 mL of dimethyl sulfoxide was added to a mixture containing 1.3 g of sodium hydride in 50 mL of dimethyl sulfoxide. The reaction mixture was stirred for 1 h at 25 °C and then 10.0 g of 1-bromo-3-phenylpropane in 50 mL of dimethyl sulfoxide was added. After stirring for 12 h at 25 °C, the reaction mixture was poured onto 300 mL of ice–water and extracted with hexane. The hexane solution was washed with water and dried over magnesium sulfate. Removal of the solvent left 12.1 g of a clear oil. This material was dissolved in 150 mL of methanol which contained 15 mL of a 10% hydrochloric acid solution. The resulting mixture was stirred at 25 °C for 1 h in order to destroy any enol ether formed in the alkylation step. The reaction mixture was poured onto water and the organic layer was taken up in ether, washed with water and a 5% sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent left a clear oil which was subjected to fractional distillation. The second fraction collected contained 5.97 g of 2-methyl-1,5-diphenyl-1-pentanone (**5**): bp 130–132 °C (0.1 mm); IR (neat) 5.95, 6.91, 8.15, 10.26, and 13.40 μ; NMR ($CDCl_3$, 100 MHz) τ 8.88 (d, 3 H, J = 6.0 Hz), 8.0–8.72 (m, 4 H), 7.74 (t, 2 H, J = 6.0 Hz), 6.64 (sextet, 1 H, J = 6.0 Hz), and 2.2–3.2 (m, 10 H).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.62; H, 7.96.

To a solution containing 1.26 g of the above ketone in 50 mL of anhydrous ether was added 50 mL of a 0.5 M benzylmagnesium chloride solution in ether at 0 °C. The reaction mixture was allowed to stir at 25 °C for 12 h and was then quenched by the addition of a saturated ammonium chloride solution. The ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent left 1.70 g of a clear oil whose NMR spectrum indicated it to be a diastereomeric mixture of 1,2,6-triphenyl-3-methyl-2-hexanol: NMR ($CDCl_3$, 100 MHz) doublets at τ 9.16 and 8.96 (3 H, J = 7.0 Hz), 7.84–8.80 (m, 5 H), 7.20–7.64 (2 H), 6.84 (broad s, 2 H), 5.40 (s, 1 H), and 2.60–3.40 (m, 15 H). This material was used without further purification.

A solution containing 0.80 g of the above alcohol in 30 mL of glacial acetic acid and 5 mL of 10% sulfuric acid was heated at reflux for 15 h. The reaction mixture was poured onto ice–water, extracted with ether, washed with water and 5% sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded 0.57 g of a 1:1 mixture of 1,2,6-triphenyl-3-methyl-1-hexene and 1,2,6-triphenyl-3-methyl-2-hexene: NMR 1-hexene ($CDCl_3$, 100 MHz) τ 8.96 (d, 3 H, J = 6.5 Hz), 7.3–8.8 (m, 7 H), 3.68 (s, 1 H), and 2.6–3.4 (m, 15 H); NMR 2-hexene ($CDCl_3$, 100 MHz) τ singlets at 8.44 and 8.14 (3 H), 7.3–8.8 (m, 6 H), 6.38 (s, 2 H), and 2.6–3.4 (m, 15 H).

Anal. Calcd for $C_{25}H_{26}$: C, 91.97; H, 8.03. Found: C, 91.93; H, 7.98.

The mixture of isomeric 1,2,6-triphenyl-3-methylhexenes was subjected to hydrogenation in 50 mL of acetic acid using 200 mg of 5% palladium on calcium sulfate under 45 psi of hydrogen gas at 60 °C for 20 h. Removal of the solvent under reduced pressure followed by Florisil chromatography using hexane as the eluent gave the same diastereomeric mixture of 1,2,6-triphenyl-3-methylhexanes (**4**) as was obtained from the reduction of the crude photolysate derived from the irradiation of **1**.

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(3-phenylpropyl)cyclopropene (1). A solution containing 990 mg of **1** and 100 mg of thioxanthone in 450 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium glass filter sleeve for 3 h. Removal of the solvent under reduced pressure left a pale yellow oil which was subjected to silica gel chromatography using a 5% benzene–hexane mixture as the eluent. The first band isolated from the column contained 432 mg of a mixture of two compounds. The two components could be separated by preparative gas chromatography using a 3 ft 10% Carbowax 20M column on Chromosorb W 60/80 mesh at 270 °C. The faster moving component (retention time 4.1 min) contained 108 mg of a clear oil whose structure was assigned as *exo*-5-methyl-1,2,6-triphenylbicyclo[3.1.0]hexane (**6b**) on the basis of its characteristic spectra: IR (neat 3.31, 3.44, 6.26, 6.72, 6.93, 9.69, 13.21, and 14.31 μ; UV (95% ethanol) 220 nm (shoulder, ϵ 18 500); NMR ($CDCl_3$, 100 MHz) τ 8.75 (s, 3 H), 7.70–8.20 (m, 4 H), 7.34 (s, 1 H), 6.63 (dd, 1 H, J = 10.0 and 6.0 Hz), and 2.80–3.40 (m, 15 H); *m/e* 324 (M^+), 309, 220 (base), 206, 193, 131, 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.54; H, 7.43.

The second component isolated by preparative gas chromatography (retention time 8.3 min) contained 320 mg of *cis*-1,2-diphenyl-*cis*-3-methyl-3-(*cis*-3-phenyl-2-propenyl)cyclopropane (**7a**). The structure of this material was assigned on the basis of its characteristic spectral properties: IR (neat) 3.30, 6.23, 6.69, 6.92, 9.26, 9.67, 12.93, and 14.29 μ; UV (95% ethanol) 231 nm (ϵ 21 200); NMR ($CDCl_3$, 100 MHz) τ 8.96 (s, 3 H), 7.70 (s, 2 H), 7.44 (dd, 2 H, J = 7.0 and 1.0 Hz), 4.22 (dt, 1 H, J = 12.0 and 7.0 Hz), 3.55 (dt, 1 H, J = 12.0 and 1.0 Hz), and 2.74–3.27 (m, 15 H); *m/e* 324 (M^+), 220, 207 (base), 129, 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.81; H, 7.39.

The second band isolated from the silica gel chromatography column also contained two components (360 mg) which could be separated by gas chromatography. The first peak isolated (retention time 4.1 min) contained 128 mg of *endo*-5-methyl-1,2,6-triphenylbicyclo[3.1.0]hexane (**6a**) as a colorless oil: IR (neat) 3.27, 3.39, 6.19, 6.66 6.87, 9.25, 9.62, 12.57, 13.01, and 14.30 μ; UV (95% ethanol) 220 nm (shoulder, ϵ 17 400); NMR ($CDCl_3$, 100 MHz) τ 8.66 (s, 3 H), 7.54–8.28 (m, 4 H), 7.69 (s, 1 H), 6.54 (d, 1 H, J = 6.0 Hz), and 2.80–3.65 (m, 15 H); *m/e* 324 (M^+), 309, 220 (base), 205, 193, 131, 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.60; H, 7.40.

The second peak isolated from the gas chromatograph (retention time 10.3 min) contained 200 mg of a colorless oil whose structure was assigned as *cis*-1,2-diphenyl-*cis*-3-methyl-3-(*trans*-3-phenyl-2-propenyl)cyclopropane (**7b**) on the basis of its characteristic spectra: IR (neat) 3.32, 6.23, 6.69, 6.95, 9.30, 10.31, 13.37, and 14.26 μ; UV (95% ethanol) 246 nm (ϵ 19 500); NMR ($CDCl_3$, 100 MHz) τ 8.94 (s, 3 H), 7.69 (s, 2 H), 7.62 (d, 2 H, J = 6.5 Hz), 3.51–3.92 (m, 2 H), and 2.72–3.30 (m, 15 H); *m/e* 324 (M^+), 220, 207, 205, 131 (base), 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.76; H, 7.40.

The stereochemistry of the phenyl group at position C_6 in bicyclohexanes **6a** and **6b** was made on the basis of its chemical shift (i.e., C_6H (**6a**) δ 7.69; C_6H (**6b**) δ 7.34). If the phenyl group were located in the endo position, the C_6 proton would be shielded by the cis phenyl ring and would be expected to appear at a higher chemical field. The exo, exo stereochemistry of **6b** was assigned on the basis that it showed a strong intramolecular nuclear Overhauser effect. In the NMR spectrum of **6b**, application of an intense radio frequency at the transition energy of proton H_2 (δ 6.63) produced a NOE at proton H_6 (31% intensity increase), whereas similar irradiation of the H_2 proton in the endo isomer **6a** (δ 6.54) had no effect. Accordingly, protons H_2 and H_6 in **6b** must be proximal, an observation which requires the spatial relationship embodied uniquely in the exo,exo isomer. The exo and endo assignments at position C_2 were made on the basis of the coupling constants. The fact that proton H_2 in **6a** is a doublet (6.0 Hz) fixes the phenyl group in the endo position. Molecular models show that the dihedral angle for the H_2 proton in the exo position with the endo-H_3 proton is ca. 90°. On the other hand, proton H_2 in the exo isomer **6b** is coupled with both protons at C_3 and appears as a doublet of doublets. In addition, proton H_6 in **6a** (δ 7.69) appears at a higher field relative to proton H_6 with **6b** (δ 7.34). This is consistent with the expected shielding effect with the neighboring phenyl ring at C_2 in the endo isomer **6a**. Similar arguments lead to the assignments of bicyclohexanes **13**, **19**, **22**, **31**, **33**, **35**, **36**, **38**, and **39**. The stereochemistry at C_3 of cyclopropanes **7a** and **7b** was based on the chemical shift of the methyl group which is shielded by both phenyl rings. In addition, irradiation of the allylic protons with an external field produced a NOE at the cyclopropyl protons. No comparable effect was noted when the methyl group at C_3 was saturated with an external field. Similar arguments lead to the assignment of stereochemistry of cyclopropanes **14**, **20**, **23**, **27**, and **28**.

The structures of cyclopropanes **7a** and **7b** were further established by a photosensitized isomerization. Irradiation of either isomer in the presence of thioxanthone resulted in the same photostationary state which contained 60% of the cis isomer **7a** and 40% of the trans isomer **7b**. Further support for the above assignments was obtained by an iodine-catalyzed isomerization of the cis isomer **7a** to the corresponding trans isomer **7b**. A solution containing 14.5 mg of the cis isomer and a catalytic quantity of iodine in 5 mL of benzene was heated at reflux under a nitrogen atmosphere. After 215 h of heating, the mixture contained 10% of unreacted cis starting material and 90% of the corresponding trans isomer **7b**.

Direct Irradiation of 1-Methyl-2,3-diphenyl-3-(3-phenylpropyl)-cyclopropene (8). A solution containing 200 mg of **8** in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 2 h. Removal of the solvent under reduced pressure left a yellow oil which was shown to contain two components in a 3:1 ratio by NMR analysis. The mixture was chromatographed over silica gel using a 10% benzene–hexane mixture as the eluent. The major component (75%) isolated was a clear oil whose structure was assigned as 1-methyl-2-phenyl-3-(3-phenylpropyl)indene (**9**) on the basis of its spectroscopic properties: IR (neat) 3.27, 3.39, 5.08, 6.20, 6.67, 6.83, 7.30, 7.85, 8.60, 9.25, 9.62, 10.88, 12.95, 13.37, and 14.29 μ; NMR ($CDCl_3$, 100 MHz) τ 8.85 (d, 3 H, J = 7.0 Hz), 8.02 (quintet, 2 H, J = 7.0 Hz), 7.37 (t, 4 H, J = 8.0 Hz), 6.24 (q, 1 H, J = 7.0 Hz), and 2.29–3.34 (m, 14 H); UV (95% ethanol) 292 nm (ϵ 13 500) and 227 (shoulder, 14 200); *m/e* 324 (M^+), 323 (base), 220, 219, 206, 205, 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.61; H, 7.05.

The structure of this material was unequivocally confirmed by an independent synthesis. A 500-mg sample of 2-phenyl-3-methylindanone (**11**)[90] in 50 mL of ether was treated with 8 mL of a 0.5 M solution of 3-phenylpropylmagnesium bromide in ether at 0 °C followed by heating at reflux for 1 h and then stirring at room temperature for an additional 1 h. The reaction mixture was hydrolyzed with a saturated ammonium chloride solution and the ether layer was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude residue was added to 4.5 mL of glacial acetic acid, 0.5 mL of concentrated sulfuric acid, and 0.2 mL of water. The mixture was stirred for 30 min at room temperature and then poured onto ice water and extracted with ether. The ethereal layer was washed with a saturated sodium bicarbonate solution and water and then dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude residue was purified by silica gel chromatography using a 10% benzene–hexane mixture as the eluent. The major component isolated was identical in every detail with the major compound obtained from the photolysis of cyclopropene **8**.

The minor component isolated from the crude photolysate was a clear oil whose structure was assigned as 1-phenyl-2-methyl-3-(3-phenylpropyl)indene (**10**) on the basis of its characteristic data: IR (neat) 3.29, 3.40, 5.06, 6.21, 6.67, 6.83, 8.42, 8.61, 9.27, 9.66, 10.92, 13.32, and 14.31 μ; NMR ($CDCl_3$, 100 MHz) τ 8.24 (s, 3 H), 8.05 (quintet, 2 H, J = 7.0 Hz), 7.22–7.56 (m, 4 H), 5.80 (s, 1 H), and 2.61–3.54 (m, 14 H); UV (95% ethanol) 264 nm (ϵ 10 400); *m/e* 324 (M^+), 323, 220 (base), 219, 205, 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.39; H, 7.03.

The structure of this material was established by comparison with an independently synthesized sample. A 1.0-g sample of 2-methyl-3-phenylindanone (**12**)[91] dissolved in 50 mL of anhydrous ether was treated with 9 mL of a 0.8 M solution of 3-phenylpropylmagnesium bromide in ether. The mixture was stirred for 2 h at 25 °C and was then hydrolyzed with a saturated ammonium chloride solution. The ethereal layer was separated, washed with water, and dried over magnesium sulfate. Removal of the solvent left a crude oil which was taken up in 20 mL of glacial acetic acid, 2 mL of concentrated sulfuric acid, and 1 mL of water. The mixture was stirred at room temperature for 30 min, poured onto ice-water, and extracted with ether. The ether layer was washed with a saturated sodium bicarbonate solution and water and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was chromatographed on a silica gel column using a 10% benzene–hexane mixture as the eluent. The major fraction contained a clear oil whose structure was identical in every detail with the minor component isolated from the irradiation of cyclopropene **8**.

Triplet-Sensitized Irradiation of 1-Methyl-2,3-diphenyl-3-(3-phenylpropyl)cyclopropene (8). A solution containing 1.574 g of **8** and 150 mg of thioxanthone in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium glass filter sleeve for 4 h. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed through a Florisil column to remove the thioxanthone. The resulting oil was then chromatographed on a 1.5 × 160 cm silica gel column using a 1% ether–hexane mixture as the eluent. The first component isolated from the column contained 438 mg (25%) of *cis*-1,2-diphenyl-*cis*-3-methyl-2-(*cis*-3-phenyl-2-propenyl)cyclopropane (**14a**) as a colorless oil: IR (neat) 3.31, 6.21, 6.66, 6.90, 9.24, 9.63, 10.85, 13.04, and 14.29 μ; NMR ($CDCl_3$, 100 MHz) τ 8.89 (d, 3 H, J = 7.0 Hz), 8.33–8.68 (m, 1 H), 7.81 (d, 1 H, J = 10.0 Hz), 7.40 (d, 2 H, J = 7.0 Hz), 4.26 (dt, 1 H, J = 11.5 and 7.0 Hz), 3.58 (d, 1 H, J = 11.5 Hz), and 2.67–3.40 (m, 15 H); UV (95% ethanol) 231 nm (ϵ 20 100); *m/e* 324 (M^+), 233, 220, 207, 193, 129, 106, and 105 (base).

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.35; H, 7.32.

The second component isolated from the column contained 676 mg (43%) of *endo*-1,2,5-triphenyl-6-methylbicyclo[3.1.0]hexane (**13a**) as a clear oil: IR (neat) 3.29, 3.38, 6.20, 6.65, 6.84, 9.24, 9.62, 13.12, and 14.26 μ; NMR ($CDCl_3$, 100 MHz) τ 9.09 (d, 3 H, J = 6.0 Hz), 7.18–8.47 (m, 5 H), 6.36 (d, 1 H, J = 7.5 Hz), and 2.50–3.12 (m, 15 H); UV (95% ethanol) 220 nm (ϵ 15 200); *m/e* 324 (M^+), 309, 220 (base), 205, 193, 178, 129, 115, 105, 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.63; H, 7.38.

The third component isolated from the column contained 305 mg (19%) of *cis*-1,2-diphenyl-*cis*-3-methyl-2-(*trans*-3-phenyl-2-propenyl)cyclopropane (**14b**) as a clear oil: IR (neat) 3.33, 6.25, 6.70, 6.92, 9.29, 9.66, 10.32, 13.01, 13.39, and 14.25 μ; NMR ($CDCl_3$, 100 MHz) τ 8.86 (d, 3 H, J = 7.0 Hz), 8.20–8.54 (m, 1 H), 7.71 (d, 1 H, J = 9.5 Hz), 7.39–7.54 (m, 2 H), 3.72–3.89 (m, 2 H), and 2.59–3.36 (m, 15 H); UV (95% ethanol) 254 nm (ϵ 18 400); *m/e* 324 (M^+), 220, 205, 193, 129, 115, 106, 105 (base), 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.47; H, 7.47.

The fourth component isolated from the column contained 20.6 mg (13%) of *exo*-1,2,5-triphenyl-6-methylbicyclo[3.1.0]hexane (**13b**) as a clear oil: IR (neat) 3.35, 3.45, 6.26, 6.73, 6.95, 9.32, 9.68, 13.01, 13.24, and 14.26 μ; NMR ($CDCl_3$, 100 MHz) τ 8.93 (d, 3 H, J = 6.5 Hz), 7.86–8.39 (m, 3 H), 7.41–7.63 (m, 2 H), 6.36 (dd, 1 H, J = 1.5 and 8.0 Hz), and 2.66–3.03 (m, 15 H); UV (95% ethanol) 220 nm (ϵ 17 800); *m/e* 324 (M^+), 309, 246, 220 (base), 193, 178, 115, 91, and 77.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.50; H, 7.53.

Preparation of 3-Butyl-1,2-diphenyl-3-methylcyclopropene (16). To a suspension containing 4.0 g of methyldiphenylcyclopropenyl perchlorate[45] in 50 mL of anhydrous tetrahydrofuran at −78 °C was added 50 mL of a 1.0 M butylmagnesium bromide solution in ether. After the addition was complete, the reaction mixture was stirred at room temperature for 12 h. 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 residue was chromatographed on a silica gel column using hexane as the eluent. The first component isolated from the column contained 1.61 g (47%) of 3-butyl-1,2-diphenyl-3-methylcyclopropene (**16**) as a clear oil: IR (neat) 3.47, 5.53, 6.27, 6.71, 6.93, 7.30, 9.33, 9.72, 10.97, 13.30, and 14.61 μ; NMR ($CDCl_3$, 100 MHz) τ 9.18 (t, 3 H, J = 6.5 Hz), 8.62–8.86 (m, 4 H), 8.54 (s, 3 H), 8.16 (t, 2 H, J = 7.6 Hz), and 2.31–2.86 (m, 10 H); UV (95% ethanol) 338 nm (ϵ 21 700), 321 (28 900), and 229 (17 200); *m/e* 262 (M^+), 233, 219, 205 (base), 115, 91, and 77.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.54; H, 8.49.

The second component isolated from the column contained 1.52 g (44%) of 3-butyl-1,3-diphenyl-2-methylcyclopropene as a clear oil: IR (neat) 3.44, 5.40, 6.25, 6.72, 6.93, 9.32, 10.96, 13.19, and 14.47 μ; NMR ($CDCl_3$, 100 MHz) τ 9.11 (t, 3 H, J = 6.0 Hz), 8.57–8.82 (m, 4 H), 7.85 (t, 2 H, J = 7.6 Hz), 7.71 (s, 3 H), and 2.49–2.95 (m, 10 H); UV (95% ethanol) 263 nm (ϵ 17 500); *m/e* 262 (M^+), 219, 205 (base), 120, 105, 91, and 77.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.69; H, 8.66.

Triplet-Sensitized Irradiation of 3-Butyl-1,2-diphenyl-3-methylcyclopropene (16). A solution containing 455 mg of 3-butyl-1,2-diphenyl-3-methylcyclopropene (**16**) and 40 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. Removal of the solvent left a pale yellow oil which was subjected to preparative thick layer chromatography using hexane as the eluent. The first band isolated from the thick layer plate contained 82 mg of an inseparable mixture (6:5) of *exo*- and *endo*-1,6-diphenyl-2,5-dimethylbicyclo[3.1.0]-hexane: IR (neat) 3.46, 6.26, 6.72, 6.93, 7.30, 9.32, 13.11, and 14.31 μ; NMR ($CDCl_3$, 100 MHz) τ 9.29 (d, 3 H, J = 6.5 Hz), 9.02 (d, 3 H, J = 6.5 Hz), 8.80 (s, 3 H), 8.69 (s, 3 H), 7.45–8.18 (m, 6 H), 2.52–3.46 (m, 10 H); UV (95% ethanol) 225 nm shoulder (ϵ 13 600); *m/e* 262 (M^+), 247, 220, 205, 154, 131 (base), 115, 105, 91, and 77.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.84; H, 8.54.

The second band isolated from the thick layer plate contained 117 mg of a mixture of (*Z*)- and (*E*)-*cis*-1,2-diphenyl-*cis*-3-methyl-3-(2-butenyl)cyclopropane which could be separated by preparative gas chromatography using a 10% 5 ft Carbowax 20M on Chromosorb W (60/80) column at 215 °C. The first peak collected contained 72 mg of *cis*-1,2-diphenyl-*cis*-3-methyl-3-((*E*)-2-butenyl)cyclopropane: IR (neat) 3.27, 3.41, 6.19, 6.65, 6.88, 10.27, 12.85, 13.18, and 14.29 μ; NMR ($CDCl_3$, 100 MHz) τ 8.98 (s, 3 H), 8.31 (d, 3 H, J = 4.5 Hz), 7.80 (d, 2 H, J = 4.0 Hz), 7.73 (s, 2 H), 4.36–4.49 (m, 2 H), and 2.73–3.16 (m, 10 H); UV (95% ethanol) 225 nm shoulder (ϵ 13 800); *m/e* 262 (M^+), 207 (base), 178, 129, 91, and 77.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.35; H, 8.63.

The second peak collected off the GC column contained 21 mg of *cis*-1,2-diphenyl-*cis*-3-methyl-3-((*Z*)-2-butenyl)cyclopropane as a clear oil: IR (neat) 3.34, 3.44, 6.25, 6.69, 6.94, 9.35, 12.79, and 14.31 μ; NMR ($CDCl_3$, 100 MHz) τ 8.97 (s, 3 H), 8.32 (d, 3 H, J = 4.5 Hz), 7.68 (d, 2 H, J = 4.5 Hz), 7.66 (s, 2 H), 4.30–4.46 (m, 2 H), and 2.70–3.14 (m, 10 H); UV (95% ethanol) 225 nm shoulder (ϵ 13 800); *m/e* 262 (M^+), 207 (base), 178, 129, 91, and 77.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.39; H, 8.56.

Preparation of 1,2-Diphenyl-3-methyl-3-(3-methylbutyl)cyclopropene (17) and 1,3-Diphenyl-2-methyl-3-(3-methylbutyl)cyclopropene (21). To a suspension containing 4.0 g of methyldiphenylcyclopropenyl perchlorate[45] in 50 mL of anhydrous tetrahydrofuran at −78 °C was added 50 mL of a 1.0 M solution of 3-methylbutylmagnesium bromide in ether. After the addition was complete, the mixture was allowed to warm to 25 °C and was stirred at this temperature for 12 h. 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. Removal of the solvent left a yellow residue which was chromatographed over silica gel using hexane as the eluent. The first material isolated from the column contained 1.69 g (47%) of 1,2-diphenyl-3-methyl-3-(3-methylbutyl)cyclopropene (**17**) as a clear oil: IR (neat) 3.59, 5.55, 6.26, 6.73, 6.94, 7.33, 9.34, 9.73, 10.98, 13.29, and 14.61 μ; NMR ($CDCl_3$, 100 MHz) τ 9.18 (d, 6 H, J = 6.5 Hz), 8.67–8.96 (m, 2 H), 8.42–8.63 (m, 1 H), 8.55 (s, 3 H), 8.02–8.27 (m, 2 H), and 2.31–2.87 (m, 10 H); UV (95% ethanol) 338, 321, and 229 nm (ϵ 21 500, 28 600, and 16 800); *m/e* 276 (M^+), 233, 219, 205 (base), 186, 129, 115, 105, 91, and 77.

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.43; H, 8.72.

The second component isolated from the column contained 1.46 g (40%) of 1,3-diphenyl-2-methyl-3-(3-methylbutyl)cyclopropene (**21**) as a clear oil: IR (neat) 3.45, 5.41, 6.25, 6.72, 6.94, 7.33, 9.32, 10.96, 13.18, and 14.49 μ; NMR ($CDCl_3$, 100 MHz) τ 9.18 (d, 6 H, J = 6.5 Hz), 8.63–8.94 (m, 2 H), 8.28–8.59 (m, 1 H), 7.67–7.94 (m, 2 H), 7.70 (s, 3 H), and 2.48–2.98 (m, 10 H); UV (95% ethanol) 264 nm (ϵ 16 600); *m/e* 276 (M^+), 233, 219, 205 (base), 105, 91, and 77.

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.28; H, 8.78.

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(3-methylbutyl)cyclopropene (17). A solution containing 231 mg of cyclopropene **17** and 20 mg of thioxanthone in 125 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium glass filter for 2 h. Removal of the solvent under reduced pressure left a pale yellow oil which was subjected to preparative thick layer chromatography using hexane as the eluent. The first component isolated from the plate contained 35 mg of 1,6-diphenyl-2,2,5-trimethylbicyclo[3.1.0]hexane as a clear oil: IR (neat) 3.42, 6.23, 6.66, 6.86, 7.34, 8.60, 13.03, 13.28, and 14.26 μ; NMR ($CDCl_3$, 100 MHz) τ 9.25 (s, 3 H), 8.96 (s, 3 H), 8.76 (s, 3 H), 8.29–8.63 (m, 2 H), 7.84–8.07 (m, 2 H), 7.79 (s, 1 H), 3.40–3.57 (m, 2 H), and 2.70–3.09 (m, 8 H); UV (95% ethanol) 225 nm shoulder (ϵ 13 700); *m/e* 276 (M^+), 262, 219, 205 (base), 105, 91, and 77.

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.34; H, 9.00.

The second component isolated from the thick layer plate contained 130 mg of *cis*-1,2-diphenyl-*cis*-3-methyl-3-(3-methyl-2-butenyl)-cyclopropane as a clear oil: IR (neat) 3.46, 6.25, 6.71, 6.93, 7.25, 9.29, 9.70, 12.82, 13.76, and 14.33 μ; NMR ($CDCl_3$, 100 MHz) τ 8.98 (s, 3 H), 8.33 (s, 3 H), 8.24 (s, 3 H), 7.76 (d, 2 H, J = 8.0 Hz), 7.71 (s, 2 H), 4.66 (t, 1 H, J = 8.0 Hz), and 2.72–3.16 (m, 10 H); UV (95% ethanol) 223 nm shoulder (ϵ 14 500); *m/e* 276 (M^+), 262, 219, 205 (base), 105, 91, and 77.

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.27; H, 8.68.

Triplet-Sensitized Irradiation of 1,3-Diphenyl-2-methyl-3-(3-methylbutyl)cyclopropene (21). A solution containing 260 mg of **21** and 10 mg of thioxanthone in 100 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium glass filter sleeve for 2 h. The solvent was removed under reduced pressure and the resulting residue was passed through a short Florisil column with hexane to remove the thioxanthone. The resulting oil was subjected to thick layer chromatography using hexane as the eluent. The first component isolated from the plate contained 61 mg (23%) of 1,5-diphenyl-2,2,6-trimethylbicyclo[3.1.0]hexane (**22**) as a crystalline solid: mp 82–83 °C; IR (KBr) 3.42, 6.23, 6.69, 6.80 6.93, 7.25, 7.35, 13.04, 13.27, 14.13, and 14.24 μ; NMR ($CDCl_3$, 100 MHz) τ 9.15 (s, 3 H), 9.11 (d, 3 H, J = 7.0 Hz), 9.02 (s, 3 H), 8.36–8.79 (m, 3 H), 7.58–8.02 (m, 2 H), and 2.69–3.21 (m, 10 H); UV (95% ethanol) 225 nm (ϵ 17 000); *m/e* 276 (M^+), 260, 220 (base), 205, 157, 145, 129, 115, 105, 91, and 77.

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 90.94; H, 8.69.

The second component isolated from the thick layer plate contained 123 mg (47%) of a clear oil whose structure was assigned as *cis*-3-methyl-2-(3-methyl-2-butenyl)cyclopropane (**23**) on the basis of the following data: IR (neat) 3.44, 6.23, 6.69, 6.93, 7.27, 9.64, 11.24, 13.05, and 14.21 μ; NMR ($CDCl_3$, 100 MHz) τ 8.93 (d, 3 H, J = 6.0 Hz), 8.78 (s, 3 H), 8.30–8.59 (m, 1 H), 8.41 (s, 3 H), 7.84 (d, 1 H, J = 9.0 Hz), 7.75 (d, 2 H, J = 8.0 Hz), 4.87 (t, 1 H, J = 8.0 Hz), and 2.79–3.53 (m, 10 H); UV (95% ethanol) 220 nm (ϵ 15 200); *m/e* 276 (M^+), 233, 220, 207, 205, 145, 143, 129 (base), 115, 105, 91, and 77.

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.14; H, 8.67.

Preparation of 1,2-Diphenyl-3-methyl-3-(4-pentenyl)cyclopropene (18). To a suspension containing 4.0 g of methyldiphenylcyclopropenyl perchlorate[45] in 100 mL of anhydrous tetrahydrofuran at −78 °C was added 10 mL of a 0.67 M 4-pentenylmagnesium bromide solution in ether. After the addition was complete, the mixture was allowed to warm to 25 °C and was stirred at this temperature for 4 h. The solution was then quenched with a saturated ammonium chloride solution and the organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded a yellow oil which was subjected to silica gel chromatography using hexane as the eluent. The first component isolated from the column was a clear oil (2.09 g, 58%) whose structure was assigned as 1,2-diphenyl-3-methyl-3-(4-pentenyl)cyclopropene (**18**): IR (neat) 3.31, 3.48, 5.57, 6.13, 6.30, 6.76, 6.98, 9.37, 10.99, 13.27, and 14.60 μ; UV (95% ethanol) 337, 319, and 223 nm (ϵ 21 100, 28 200, and 17 000); NMR ($CDCl_3$, 100 MHz) τ 8.38–8.89 (m, 2 H), 8.49 (s, 3 H), 7.89–8.18 (m, 4 H), 4.99 (broad d, 1 H, J = 11.0 Hz), 4.97 (broad d, 1 H, J = 16.0 Hz), 3.85–4.32 (m, 1 H), and 2.02–2.64 (m, 10 H); *m/e* 274 (M^+), 220, 205 (base), 178, 91, and 77.

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.89; H, 8.10.

The second component isolated from the column contained 1.18 g (33%) of a clear oil whose structure was assigned as 1-methyl-2,3-diphenyl-3-(4-pentenyl)cyclopropene on the basis of its characteristic data: IR (neat) 3.30, 3.45, 5.41, 6.10, 6.26, 6.72, 6.94, 9.32, 10.96, 13.16, 14.33, and 14.47 μ; UV (95% ethanol) 263 nm (ϵ

15 500); NMR ($CDCl_3$, 100 MHz) τ 8.42-8.79 (m, 2 H), 7.63-8.08 (m, 4 H), 7.70 (s, 3 H), 5.03 (broad d, 1 H, J = 10.0 Hz), 4.99 (broad d, 1 H, J = 18.0 Hz), 3.90-4.35 (m, 1 H), and 2.34-2.83 (m, 10 H); *m/e* 274 (M^+), 259, 220, 205 (base), 141, 91, and 77.

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.87; H, 8.08.

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(4-pentenyl)cyclopropene (18). A solution containing 914 mg of **18** and 100 mg of thioxanthone in 450 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium glass filter sleeve for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed on a Florisil column in order to remove the thioxanthone. The major component isolated was subjected to thick layer chromatography using hexane as the eluent. The fastest moving band contained 620 mg (68%) of a colorless oil whose spectral properties indicated it to be a 3:2 mixture of *exo*- and *endo*-2-vinyl-5-methyl-1,6-diphenylbicyclo[3.1.0]hexane. All attempts to separate the isomeric mixture were unsuccessful: IR (neat) 3.46, 6.12, 6.25, 6.72, 10.96, 13.07, 13.62, and 14.25 μ; UV (95% ethanol) end absorption; NMR ($CDCl_3$, 100 MHz) singlets at τ 8.82 and 8.73 (3 H), 7.84-8.64 (m, 4 H), 7.78 and 7.74 (s, 1 H), 6.94-7.31 (m, 1 H), 5.39 (broad d, 1 H, J = 15.0 Hz), 5.13 (broad d, 1 H, J = 10.0 Hz), 3.97-4.64 (m, 1 H), and 2.66-3.54 (m, 10 H); *m/e* 274 (M^+, base), 259, 220, 205, 131, 91, and 77.

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.81; H, 8.12.

The second component isolated from the column contained 163 mg (18%) of a clear oil. This material was further purified by preparative gas chromatography using a 6 ft 10% OV-17 on Chromosorb W column at 250 °C. The major component in the mixture was a clear oil whose structure was assigned as *cis*-1,2-diphenyl-*cis*-3-methyl-3-(2,4-pentadienyl)cyclopropane on the basis of the following data: IR (neat) 3.38, 3.46, 6.24, 6.71, 6.93, 8.32, 9.32, 9.93, 10.48, 11.04, 12.83, 13.26, 13.74, and 14.32 μ; NMR ($CDCl_3$, 100 MHz) τ 8.94 (s, 3 H), 7.68 (d, 2 H, J = 6.0 Hz), 7.67 (s, 2 H), 4.98 (d, 1 H, J = 10.0 Hz), 4.85 (d, 1 H, J = 16.0 Hz), 3.32-4.28 (m, 3 H), and 2.57-3.24 (m, 10 H); UV (95% ethanol) 227 nm (ϵ 18 400); *m/e* 274 (M^+), 259, 245, 219, 207 (base), 183, 178, 165, 129, 105, 91, and 77.

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.75; H, 8.14.

Preparation of 1,2-Diphenyl-3-methyl-3-propylcyclopropene (24). To a suspension containing 4.0 g of methyldiphenylcyclopropenyl perchlorate[45] in 50 mL of anhydrous tetrahydrofuran at −78 °C was added 50 mL of a 1.0 M propylmagnesium bromide solution in ether. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 12 h. The reaction was quenched by the addition of a saturated ammonium chloride solution. The organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was subjected to silica gel chromatography using hexane as the eluent. The first component isolated from the column contained 1.30 g (40%) of 1,2-diphenyl-3-methyl-3-propylcyclopropene (**24**) as a clear oil: IR (neat) 3.39, 5.50, 6.24, 6.69, 6.92, 9.33, 10.95, 13.20, and 14.53 μ; NMR ($CDCl_3$, 100 MHz) τ 9.16 (t, 3 H, J = 8.0 Hz), 8.63-8.92 (m, 2 H), 8.58 (s, 3 H), 8.07-8.28 (m, 2 H), and 2.28-2.80 (m, 10 H); UV (95% ethanol) 338 nm (ϵ 21 700), 321 (28 900), and 229 (16 300); *m/e* 248 (M^+), 233, 219, 205 (base), 105, 91, and 77.

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.58; H, 8.16.

The second component isolated from the column contained 1.18 g (36%) of 1,3-diphenyl-2-methyl-3-propylcyclopropene as a clear oil: IR (neat) 3.40, 5.38, 6.23, 6.90, 9.29, 13.13, 14.32, and 14.44 μ; NMR ($CDCl_3$, 100 MHz) τ 9.11 (t, 3 H, J = 7.0 Hz), 8.53-8.91 (m, 2 H), 7.78-7.99 (m, 2 H), 7.74 (s, 3 H), and 2.44-2.99 (m, 10 H); UV (95% ethanol) 264 nm (ϵ 16 300); *m/e* 248 (M^+ and base), 219, 205, 105, 91, and 77.

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.79; H, 8.24.

Irradiation of a benzene solution of **24** in the presence of thioxanthone for 15 h resulted in the complete recovery of starting material.

Preparation and Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(2-phenylethyl)cyclopropene (25). To a suspension containing 4.0 g of 1,2-diphenyl-3-methylcyclopropenyl perchlorate in 200 mL of tetrahydrofuran at −78 °C was added 50 mL of a 0.55 M solution of 2-phenylethylmagnesium bromide in ether. The mixture was stirred at −78 °C for 4 h and then allowed to warm to room temperature. The solution was quenched with a saturated ammonium chloride solution and extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a clear oil which was chromatographed on a silica gel column using 10% benzene-hexane as the eluent. The first component isolated contained 2.1 g (52%) of 1,2-diphenyl-3-methyl-3-(2-phenylethyl)cyclopropene (**25**) as a clear oil: IR (neat) 3.29, 3.32, 3.45, 5.51, 6.23, 6.70, 7.28, 9.26, 9.65, 10.97, 13.12, and 14.26 μ; UV (95% ethanol) 338 nm (ϵ 19 100), 321 (25 000), 312 (20 800), 238 (13 200), and 227 (17 400); NMR ($CDCl_3$, 100 MHz) τ 8.49 (s, 3 H), 7.82 (t, 2 H, J = 9.0 Hz), 7.38 (t, 2 H, J = 9.0 Hz), and 2.24-2.97 (m, 15 H); *m/e* 310 (M^+), 295, 218, 209, 204, 105, 91 (base), and 77.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.75; H, 7.17.

Irradiation of a benzene solution of **25** in the presence of thioxanthone for 25 h resulted in the complete recovery of starting material. Further photolysis also gives back recovered starting material.

Preparation and Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(4-phenylbutyl)cyclopropene (26). To a suspension containing 5.0 g of 1,2-diphenyl-3-methylcyclopropene perchlorate in 200 mL of tetrahydrofuran at −78 °C was added 50 mL of a 0.45 M solution of 4-phenylbutylmagnesium bromide in ether. The mixture was stirred at −78 °C for 3 h and was allowed to warm to room temperature. The solution was quenched with a saturated ammonium chloride solution and extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a clear oil which was chromatographed on a silica gel column using a 5% benzene-hexane mixture as the eluent. The first component isolated from the column contained 2.14 g (39%) of 1,2-diphenyl-3-methyl-3-(4-phenylbutyl)cyclopropene (**26**): IR (neat) 3.30, 3.34, 3.51, 5.54, 6.28, 6.72, 6.95, 7.30, 9.31, 9.69, 10.92, 13.25, and 14.29 μ; UV (95% ethanol) 338 nm (ϵ 21 600), 321 (28 700), 312 (23 700), 238 (12 600), and 229 (16 500); NMR ($CDCl_3$, 100 MHz) τ 8.53 (s, 3 H), 8.32-8.81 (m, 4 H), 8.10 (t, 2 H, J = 8.0 Hz), 7.48 (t, 2 H, J = 8.0 Hz), and 2.23-3.03 (m, 15 H); *m/e* 338 (M^+), 310, 295, 219, 205, 178, 131, 91 (base), and 77.

Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.23; H, 7.77.

A solution containing 313 mg of **26** and 35 mg of thioxanthone in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium filter sleeve for 5 h. The solvent was removed under reduced pressure and the residue was passed through a Florisil column with hexane to remove thioxanthone. All attempts to separate the resulting oil into its component parts failed. Analysis of the crude reaction mixture by NMR spectroscopy showed the presence of the cis (15%) and trans (20%) olefinic isomers of *cis*-1,2-diphenyl-*cis*-3-methyl-3-(4-phenyl-3-butenyl)cyclopropane (**28**) as well as *cis*-1,2-diphenyl-*cis*-3-methyl-3-(4-phenyl-2-butenyl)cyclopropane (**27**) (43%). The olefinic protons of the cis and trans isomers of **28** were essentially identical in shape and position with structures **7a** and **7b** obtained from the photolysis of 1,2-diphenyl-3-methyl-3-(3-phenylpropyl)cyclopropene (**1**).

Preparation of 1,2-Diphenyl-3-methyl-3-(2-methylallyl)cyclopropene (29) and 1,3-Diphenyl-2-methyl-3-(2-methylallyl)cyclopropene (32). A solution containing 2.5 g of methylallylmagnesium chloride in 50 mL of anhydrous tetrahydrofuran was prepared according to the procedure of Rieke.[92] The solution was added at −78 °C to a slurry of 3.0 g of methyldiphenylcyclopropenyl perchlorate in 50 mL of anhydrous tetrahydrofuran. The reaction mixture was stirred for 30 min at −78 °C and was then allowed to warm to room temperature. A saturated ammonium chloride solution was added to the mixture and the reaction mixture was stirred until both phases became clear. The organic phase was taken up in ether, washed twice with equal volumes of water and a saturated salt solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 2.7 g of a yellow oil which was chromatographed on a 1.5 × 100 cm column of silica gel using hexane as the eluent. The first component isolated contained 1.15 g (40%) of a colorless oil which was identified as 1,2-diphenyl-3-methyl-3-(2-methylallyl)cyclopropene (**29**) on the basis of its spectral properties: IR (neat) 3.26 3.41, 5.50, 6.05, 6.24, 6.67, 6.88, 7.27, 9.28, 11.18, 13.18, and 14.5 μ; NMR ($CDCl_3$, 100 MHz) τ 8.55 (s, 3 H), 8.36 (s, 3 H), 7.44 (s, 2 H), 5.30 (s, 2 H), and 2.20-2.80 (m, 10 H); UV (95% ethanol) 337, 321 and 229 nm (ϵ 19 250, 26 750, and 19 100); *m/e* 260 (M^+), 245, and 205 (base).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.78.

The second component isolated contained 0.83 g (29%) of a colorless oil which was identified as 1,3-diphenyl-2-methyl-3-(2-methylallyl)-cyclopropene (**32**) on the basis of its spectral properties: IR (neat) 3.39, 3.45, 5.40, 6.04, 6.24, 6.71, 6.92, 7.39, 9.30, 10.94, 11.22, 13.18, and 14.48 μ; NMR ($CDCl_3$, 100 MHz) τ 8.30 (s, 3 H), 7.64 (s, 3 H), 7.46 (d, 1 H, J = 17.0 Hz), 6.80 (d, 1 H, J = 17.0 Hz), 5.21 (s, 2 H), and 2.5–3.0 (m, 10 H); UV (95% ethanol) 263 nm (ϵ 17 790); *m/e* 260 (M^+), 245, and 205 (base).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.79.

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(2-methylallyl)cyclopropene (29). A solution containing 250 mg of cyclopropene **29** and 70 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium glass filter sleeve for 15 min. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed through a silica gel column with hexane. The first fraction isolated contained 200 mg (82%) of a colorless oil whose structure was assigned as 4,6-dimethyl-1,2-diphenyltricyclo[2.2.0.$0^{2,6}$]hexane (**30**) on the basis of its spectral properties: IR (neat) 3.25, 3.40, 3.50, 6.24, 6.64, 6.90, 7.22, 7.58, 13.05, 13.75, and 14.32 μ; NMR ($CDCl_3$, 100 MHz) τ 8.76 (s, 3 H), 8.65 (s, 3 H), 7.86 (d, 1 H, J = 7.5 Hz), 7.68 (d, 1 H, J = 7.5 Hz), 7.59 (d, 1 H, J = 7.5 Hz), 7.49 (d, 1 H, J = 7.5 Hz), and 2.6–3.0 (m, 10 H); UV (95% ethanol) 263 nm (ϵ 13 100); *m/e* 260 (M^+, base), 245, 169, and 105.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.78. Found: C, 92.02; H, 7.84.

The second fraction isolated from the column contained 45 mg (18%) of a crystalline solid, mp 60–61 °C, whose structure was assigned as *exo*-1-phenyl-3-methylene-5-methyl-6-phenylbicyclo-[3.1.0]hexane (**31**): IR (neat) 3.30, 3.45, 6.04, 6.24, 6.67, 6.96, 9.39, 9.72, 11.24, 12.98, and 14.24 μ; NMR ($CDCl_3$, 100 MHz) τ 8.76 (s, 3 H), 7.94 (s, 1 H), 7.0–7.52 (m, 4 H), 5.05 (br s, 2 H), and 2.7–3.4 (m, 10 H); *m/e* 260 (M^+, base), 245, 205, 169, 167, 105, and 91; UV (95% ethanol) 225 nm (ϵ 14 900).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.13; H, 7.78.

Triplet-Sensitized Irradiation of 1,3-Diphenyl-2-methyl-3-(2-methylallyl)cyclopropene (32). A solution containing 200 mg of cyclopropene **32** and 90 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium filter sleeve for 45 min. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed through a silica gel column with hexane. The first fraction isolated contained 95 mg (48%) of tricyclohexane **30.** The second component isolated from the column contained 63 mg (32%) of a colorless oil whose structure was assigned as *exo*-6-methyl-3-methylene-1,5-diphenylbicyclo[3.1.0]hexane (**33**) on the basis of its spectral properties: IR (neat) 3.26, 3.34, 5.95, 6.24, 6.69, 6.94, 7.21, 8.06, 9.29, 9.62, 11.24, 13.09, and 14.21 μ; NMR ($CDCl_3$, 100 MHz) τ 9.00 (d, 3 H, J = 6.5 Hz), S.64 (br q, 1 H, J = 6.5 Hz), 7.22 (br d, 2 H, J = 15.0 Hz), 6.95 (td, 2 H, J = 15.0 and 2.0 Hz), 5.08 (t, 2 H, J = 2.0 Hz), and 2.6–3.0 (m, 10 H); *m/e* 260 (M^+), 245, 205, 169, 167, 142, 129, 115, 105, 91 (base), and 77.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.78. Found: C, 92.21; H, 7.78.

Preparation of 1,2-Diphenyl-3-methyl-3-(2-benzylallyl)cyclopropene (34) and 1-Methyl-2,3-diphenyl-3-(2-benzylallyl)cyclopropene (37). To a suspension containing 2.0 g of methyldiphenylcyclopropenyl perchlorate in 200 mL of anhydrous tetrahydrofuran at 0 °C was added 100 mL of a 0.12 M solution of 2-benzylallylmagnesium chloride in tetrahydrofuran. The mixture was stirred at 0 °C for 1 h and was then allowed to warm to room temperature for an additional 2 h. 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 using hexane as the eluent. The first component isolated from the column contained 350 mg (15%) of a clear oil whose structure was characterized as 1,2-diphenyl-3-methyl-3-(2-benzylallyl)cyclopropene (**34**) on the basis of its spectral properties: IR (neat) 3.28, 3.42, 5.50, 6.05, 6.23, 6.67, 6.91, 7.29, 9.28, 9.66, 11.15, 13.14, and 14.60 μ; NMR ($CDCl_3$, 100 MHz) τ 8.49 (s, 3 H), 7.44 (s, 2 H), 6.78 (s, 2 H), 5.32 (broad s, 1 H), 5.14 (broad s, 1 H), and 2.2–3.0 (m, 15 H); UV (95% ethanol) 338 nm (ϵ 18 200), 321 (24 800), 238 (shoulder, 13 500), and 228 (17 500); *m/e* 336 (M^+), 246, 245 (base), 244, 230, 205, 105, 91, and 77.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.69; H, 7.24.

The second component isolated from the column contained 362 nm (16%) of 1-methyl-2,3-diphenyl-3-(2-benzylallyl)cyclopropene (**37**): IR (neat) 3.23, 3.30, 3.42, 5.36, 6.02, 6.20, 6.67, 6.89, 9.24, 9.63, 11.10, 12.61, 13.08, 13.45, and 14.26 μ; NMR ($CDCl_3$, 100 MHz) τ 7.68 (s, 3 H), 7.47 (d, 1 H, J = 16.0 Hz), 6.89 (d, 1 H, J = 16.0 Hz), 6.75 (s, 2 H), 5.24 (broad s, 1 H), 5.10 (broad s, 1 H), and 2.48–2.98 (m, 15 H); UV (95% ethanol) 262 nm (ϵ 17 200); *m/e* 336 (M^+), 245, 205, 131, 105, 91 (base), and 77.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.60; H, 7.28.

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(2-benzylallyl)cyclopropene (34). A solution containing 200 mg of 1,2-diphenyl-3-methyl-3-(2-benzylallyl)cyclopropene (**34**) and 25 mg of thioxanthone in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium filter sleeve for 1 h. Removal of the solvent under reduced pressure left 192 mg of a pale yellow oil which was subjected to silica gel chromatography using a 1.5 × 100 cm column containing 10% silver nitrate with a 8% ether–hexane mixture as the eluent. The first component isolated from the column contained 90 mg (45%) of a crystalline solid, mp 123–124 °C, whose structure was assigned as *exo,exo*-1,2,6-triphenyl-3-methylene-5-methylbicyclo[3.1.0]hexane (**35**) on the basis of its characteristic spectral properties: IR (KBr) 3.31, 3.46, 6.26, 6.72, 6.92, 9.31, 11.23, 12.61, 13.06, and 14.36 μ; NMR ($CDCl_3$, 100 MHz) τ 8.60 (s, 3 H), 7.75 (s, 1 H), 7.15 (d, 1 H, J = 16.0 Hz), 6.80 (broad d, 1 H, J = 16.0 Hz), 5.96 (s, 1 H), 4.96 (s, 1 H), 4.88 (s, 1 H), and 2.78–3.48 (m, 15 H); UV (95% ethanol) 223 nm (shoulder on end absorption) (ϵ 22 500); *m/e* 336 (M^+), 321, 245, 205, 105, 91 (base), and 77.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.51; H, 7.42.

The second fraction isolated from the column contained 100 mg of a clear oil which was subjected to preparative gas chromatography using a 10% OV-17 3 ft column on Chromosorb W at 260 °C. The major component isolated (90 mg, 45%) was a crystalline solid, mp 153–154 °C, whose structure was assigned as *exo*-1,6-diphenyl-3-benzylidene-5-methylbicyclo[3.1.0]hexane (**36**): IR (KBr) 3.40, 3.55, 6.32, 6.75, 6.98, 9.33, 9.80, 10.88, 13.21, and 14.28 μ; NMR ($CDCl_3$, 100 MHz) τ 8.65 (s, 3 H), 8.02 (s, 1 H), 6.8–7.2 (m, 4 H), 3.3–3.6 (m, 1 H), and 2.56–3.04 (m, 15 H); UV (95% ethanol) 248 nm (ϵ 15 100); *m/e* 336 (M^+), 321, 245, 232, 219, 205, 115, 105, and 91 (base).

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.71; H, 7.50.

Triplet-Sensitized Irradiation of 1-Methyl-2,3-diphenyl-3-(2-benzylallyl)cyclopropene (37). A solution containing 210 mg of cyclopropene **37** and 25 mg of thioxanthone in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium filter sleeve for 1 h under an argon atmosphere. Removal of the solvent under reduced pressure left a yellow oil which was subjected to chromatography on a 10% silver nitrate–silica gel column using a 6% ether–hexane mixture as the eluent. The first component isolated from the column contained 92 mg (45%) of a clear oil whose structure was assigned as *exo,exo*-1,2,5-triphenyl-3-methylene-6-methylbicyclohexane (**38**) on the basis of its spectral properties: IR (neat) 3.35, 3.49, 6.01, 6.31, 6.70, 6.91, 9.28, 9.65, 11.23, 13.06, 13.52, and 14.38 μ; NMR ($CDCl_3$, 60 MHz) τ 9.05 (d, 3 H, J = 6.0 Hz), 8.60 (q, 1 H, J = 6.0 Hz), 7.08 (d, 1 H, J = 16.0 Hz), 6.58 (broad d, 1 H, J = 16.0 Hz), 5.93 (broad s, 1 H), 4.99 (broad s, 1 H), and 2.58–3.10 (m, 15 H); UV (95% ethanol) 256 nm (ϵ 2000); *m/e* 336 (M^+), 321, 245, 232, 205, 115, 105, 91 (base), and 77.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.66; H, 7.23.

The second component isolated from the column contained 68 mg (34%) of a clear oil which was further purified by preparative gas chromatography using a 3 ft 10% OV-17 on Chromosorb W column at 265 °C. The structure of this material was identified as *exo*-1,5-diphenyl-3-benzylidene-6-methylbicyclo[3.1.0]hexane (**39**): IR (neat) 3.34, 3.46, 6.27, 6.70, 6.94, 8.96, 9.31, 9.70, 10.90, 10.81, 13.02, and 14.31 μ; NMR ($CDCl_3$, 100 MHz) τ 9.02 (d, 3 H, J = 6.0 Hz), 8.76 (q, 1 H, J = 6.0 Hz), 6.52–7.08 (m, 4 H), 3.54 (broad s, 1 H), and 2.6–3.0 (m, 15 H); *m/e* 336 (M^+), 321, 245, 141, 115, 105, 91 (base), and 77.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.66; H,

7.22.

Quantum Yield Determinations. Quantum yields were determined using a "merry-go-round" apparatus[93] 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.[56] 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.[94] 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 20M 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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Crystal Structure of 9-Hydroxyphenalenone: a Very Short Intramolecular Hydrogen Bond System

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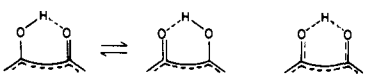
Abstract: 9-Hydroxyphenalenone ($C_{13}H_8O_2$) crystallizes in the monoclinic system with lattice constant a = 8.8941 (2) Å, b = 28.8159 (4) Å, c = 7.2117 (2) Å, β = 97.937 (1)°, and eight molecules in the unit cell. The space group is $P2_1/c$. The structure was solved by direct methods and refined by the method of least squares. The final indicator R = 0.068 for the 2270 reflections with $|F_{obsd}|^2 > 3\sigma|F_{obsd}|^2$. One of the two independent molecules is disordered leading to reduced dimensional accuracy. The other molecule has effective $mm2$ symmetry. The intramolecular O···O distance is 2.486 (4) Å; all dimensions in this molecule are consistent with a symmetric hydrogen bond or a situation in which the hydrogen is undergoing exchange between two closely spaced equilibrium positions. The disordered molecule equally occupies two major orientations, approximately related by a 120° rotation in the molecular plane. Diffuse X-ray scattering indicates appreciable short-range correlations between the orientations of the disordered molecule. Two phase transitions have been detected: one is at 252 K, the other occurs in the range 330–395 K.

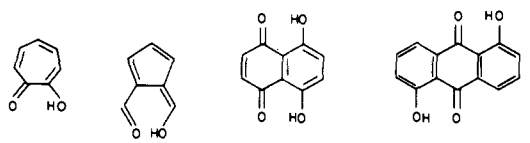
Introduction

Hydrogen bonding in solids continues to attract considerable attention, with particular emphasis being placed on systems involving potentially symmetric intramolecular hydrogen bonds. Most investigations have focused on molecules incorporating the hydroxy ketone unit (**1**). Such bistable molecules



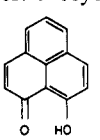
1a 1b 1c

are of general interest for possible information storage at the molecular level, in photochemical hole burning,[2] and for the possible involvement of proton tunneling in the primary event of vision.[3] Compounds involving the unit **1** fused to a conjugated ring system, for which crystallographic information is available, fall into two categories: (i) nonalternant π-electron systems with a single hydrogen bond, e.g., tropolone (**2**)[4a] and 6-hydroxy-2-formylfulvene (**3**);[4b] and (ii) dihydroxyquinones with two sets of hydrogen bonds attached to benzenoid ring systems, e.g., naphthazarin (**4**)[5a] and 1,5-dihydroxyanthraquinone (**5**).[5b] In category i, the bonding hydrogen atom is required to be part of a five- or seven-membered ring, whereas ii requires a six-membered ring.



2 3 4 5

The present work reports a compound which combines some features of both categories. 9-Hydroxyphenalenone (**6**)[6] is



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benzenoid and incorporates a single hydrogen bond as part of a six-membered ring. The compound is known to possess a very strong hydrogen bond:[6] an IR study[7] found no evidence for an absorption due to the O–H stretching vibration. Very recent ESCA[8] (gas phase) and DQR[9] (solution phase) studies indicate that 9-hydroxyphenalenone possesses m rather than $mm2$ ground-state symmetry (i.e., **1a–1b** rather than **1c**). 9-Hydroxyphenalenone in the condensed state is shown vide infra to contain one of the shortest O···O distances, <2.5 Å, documented in a neutral intramolecularly hydrogen-bonded molecule.

Experimental Section

X-ray Study. Transparent amber-colored crystals with dimensions as large as 5 mm were grown by slow cooling of saturated 9-hydroxyphenalenone in benzene solution, using a sealed container: (010) formed the principal platelet face. A sphere of radius 0.24 (1) mm was ground and mounted,[10] in random orientation, on a Pyrex capillary. Integrated intensity measurements were made on a PDP 11/40-8e computer-controlled Enraf-Nonius CAD-4 diffractometer, using

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