heated to 90°. The products were trapped at −78° and were allowed to come to room temperature. Water was removed with a pipet, the dioxane was dissolved in ether, and the solution was dried with Drierite. Concentration and distillation gave 10.3 g (86% yield) of product, bp 148–154° at ambient pressure, 50–51° (18 Torr). The use of sulfuric acid as a catalyst led to yields in the vicinity of 50%. The two isomers were separated by vpc on column D at 170°. The earlier eluted was the *S-meso:* nmr δ 0.734 (d, J = 7 Hz, 3 H), 1.15 (d, J = 6 Hz, 7 H (obscures 1 H multiplet)), 3.16 (m, J = 6 Hz, J' = 8.5 Hz, 2 M), 4.48 (AB multiplet, 2 H).

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.51; H, 10.74.

The next eluted was the *dl* pair: nmr δ 0.8 (d, J = 6.5 Hz, 3 H), 1.13 (d, J = 6.5 Hz, 3 H), 1.17 (d, J = 6.5 Hz, 3 H), 1.67 (m, 1 H), 3.57 (m, J = J' = 6.5 Hz, 1 H), 3.92 (m, J = 6.5 Hz, J' = 7.5 Hz, 1 H), 4.71 (AB multiplet, 2 H).

Anal. Found: C, 64.40; H, 10.77.

The *S-meso* compound was contaminated by 9% of *R-meso*, as estimated by nmr. The ratio of *dl*:*meso* was 1:1.12 by vpc (uncorrected).

***dl*- and (*R*)-*meso*-3-Methylpentane-2,4-diol.** The procedure reported above for the synthesis of *dl* and *S-meso* compounds was repeated on 10 g of *trans*-3-methyl-3-penten-2-ol to give the desired compounds.

***dl*- and (*R*)-*meso*-4,5,6-Trimethyl-1,3-dioxane.** The procedure reported for the synthesis of *dl* and *S-meso* dioxanes was repeated on a mixture of *dl*- and (*R*)-*meso*-3-methylpentane-2,4-diols. Vpc separation gave the *R-meso:* nmr δ 0.884 (d, J = 6 Hz, 3 H), 1.08 (d, J = 6.5 Hz, 7 H (obscures 1 H multiplet)), 3.67 (m, J = 6.5 Hz, J' = 2 Hz, 2 H), 4.74 (AB multiplet, 2 H).

Anal. Calcd: see above. Found: C, 64.60; H, 10.70.

This was contaminated by 15% of the *S-meso* dioxane as seen by nmr. The *dl* form then eluted, as described above. The ratio of *dl*:*meso* was 2.35:1 by vpc (uncorrected).

3-Methyl-2,4-diazidopentane (Reference Mixtures). In separate sequences, the diol mixtures described above were converted into the ditosylates. The crude ditosylates were then converted into the diazides by treatment with sodium azide in HMPA (*vide supra*). Each mixture of two diol isomers gave rise to a mixture of only two diazide isomers. This specificity permitted the following assignments of resonances (all except hydrogen on carbon 3). From the *S-meso* and *dl* diols; *dl* diazide: nmr δ 0.86 (d, J = 7 Hz, 3 H), 1.28 (d, J = 7 Hz, 3 H), 1.285 (d, J = 7 Hz, 3 H), 3.38 (m, J = 7 Hz, J' = 8 Hz, 1 H), 3.9 (m, J = 7 Hz, J' = 3 Hz, 1 H). *R-meso* diazide: nmr δ 0.986 (d, J = 7 Hz, 3 H), 1.32 (d, J = 6 Hz, 6 H), 3.52 (m, J = J' = 7 Hz, 2 H). From *R-meso* and *dl* diol; *dl* diazide as above, S-*meso* diazide: nmr δ 0.876 (d, J = 7 Hz, 3 H), 1.215 (d, J = 7 Hz, 6 H), 3.55 (m, J = J' = 7 Hz, 2 H).

Reaction of (*S*)-*meso*- and *dl*-3-Methyl-2,4-dibromopentane with Potassium Azide in Aqueous Acetone. A solution of 25 g (0.39 mol) of potassium azide and 5 g (0.0485 mol) of a 1:1 mixture of dibromide isomers (produced by radical bromination of *cis*-1,2,3-trimethylcyclopropane) in 125 ml of water and 500 ml of acetone was refluxed under nitrogen for 40 hr. Acetone was removed on a Roto-vap, the residue was added to water, and the products were extracted with pentane. Concentration and distillation gave 1 g (29%) of product which was largely diazide. The isomeric identification of the starting material was made by the observation of characteristic resonances for the *R-meso* diazide (δ 0.986, d, and 3.52, m), indicating the *S* configuration for the dibromide. This was accompanied by the *dl* diazide (δ 0.86, d; and 3.38 and 3.9, m) and unidentified impurities.

Control Reaction of (*R*)-, (*S*)-, and *dl*-3-Methyl-2,4-dibromopentane with Potassium Azide. The displacement described above was repeated exactly on the mixture of dibromide isomers produced by radical bromination of *trans*-1,2,3-trimethylcyclopropane. In this case, the predominant *meso* form was the *S-meso*, identified by characteristic resonances at δ 0.876 (d) and 3.55 (m). This was clearly accompanied by the *dl* pair, but the doublet for the *R-meso* (δ 0.986) was obscured by spinning side bands (max amount <20%).

Control Equilibration of Isomers of 3-Methyl-2,4-dibromopentane. A mixture of 5 g of dibromide from bromination of *trans*-trimethylcyclopropane, 20 g of sodium bromide, and 125 ml of HMPA was stirred for 52 hr under nitrogen at 25°. The suspension was then poured into 750 ml of water, and the dibromides were extracted with pentane. The organic solution was extracted with water and with brine, dried over Drierite, and distilled to give 1.0 g of dibromide, 20% recovery. The reaction was then repeated on 2.5 g of dibromide from bromination of *cis*-trimethylcyclopropane.

In the former case the original composition was *S*:*R*:*dl* = 1:0.55:1.53, and the final composition was 1:1.68:2.28. In the latter case, the starting composition was 1:(0):1.05; the final composition was 1:1.87:2.30.

Acknowledgments. This work was supported in part by National Science Foundation Grant GP-8372, and in part by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund.

Photodimerization of Some Cyclopropenes

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Abstract: The photochemistry of three 1,2-diphenylcyclopropenes (**1**, **2**, and **3**) has been studied. Direct irradiation gives no photodimers. Sensitized irradiation gives tricyclohexane dimers (major) and cyclopropylcyclopropenes (minor). The tricyclohexanes are thermally rearranged to 1,4-cyclohexadienes at widely varying temperatures. Quantum yield measurements and isotope effects show that the dimerization of **1** occurs in stepwise fashion with a diradical intermediate. Flash photolysis measurements show the triplet state of **1** is ≈ 60 kcal/mol. Nonvertical energy transfer to cyclopropenes appears to be unimportant. When low-energy sensitizers are used, the dimerization appears to include a termolecular step and can only be explained by a process similar to the Schenck mechanism.

The photodimerization of a cyclopropene was first studied by Stechl,[1] who found that the benzophenone-sensitized irradiation of 1,3,3-trimethylcyclopropene gives two isomeric dimers of tricyclohexane structure. Obata and Moritani[2] have also reported that both 3-acetyl- and 3-benzoyl-1,2-diphenylcyclopropene undergo dimerization to tricyclohexanes upon irradiation, undoubtedly by intramolecular sensitiza-

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[1] H. H. Stechl, *Chem. Ber.*, 97, 2681 (1964).

[2] N. Obata and I. Moritani, *Tetrahedron Lett.*, 1503 (1966).

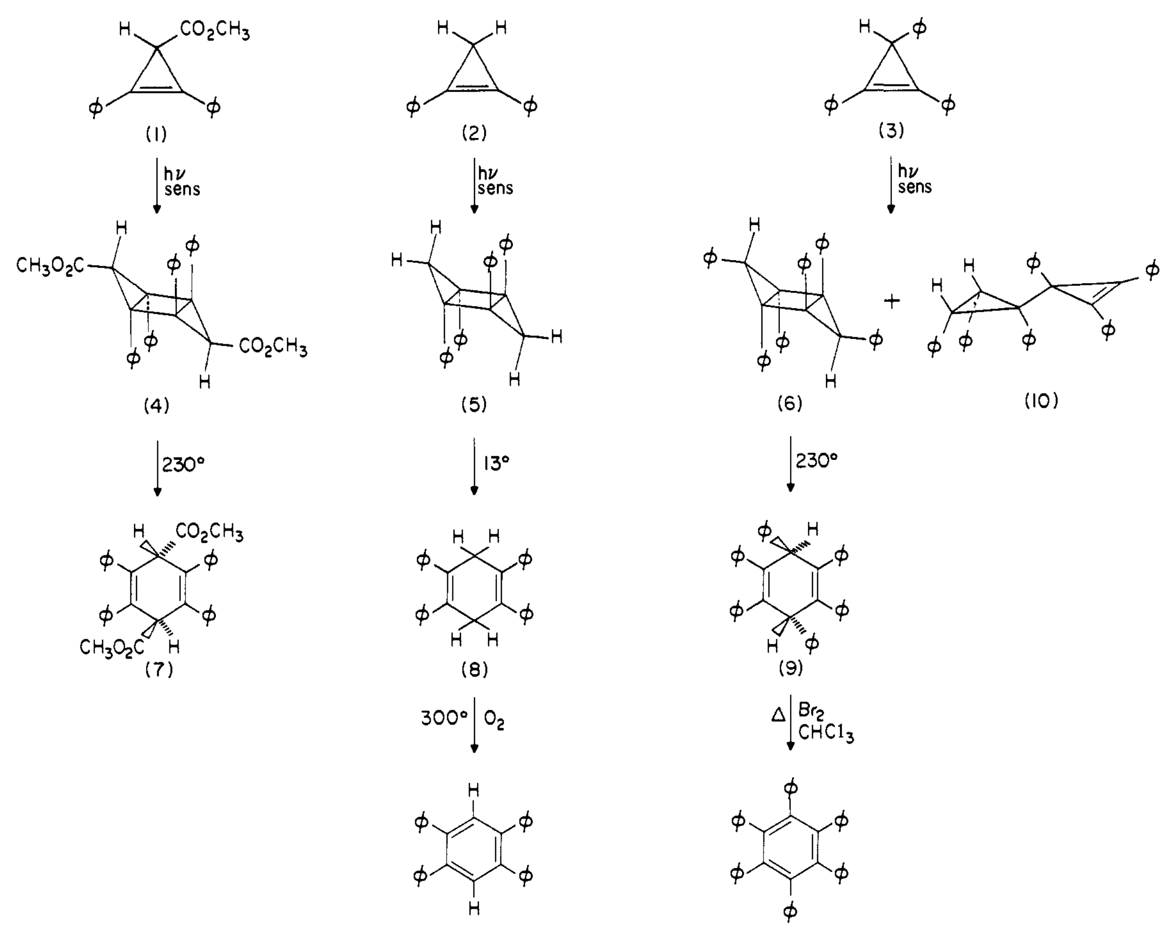

Figure 1.

tion. The literature concerning the photodimerization of 1,2,3-triphenylcyclopropene, reported by DeBoer and Breslow[3] and by Durr,[4] is in disagreement with regard to the products of the reaction and the triplet energy of the substrate. The photodimerization of cyclopropenes seemed interesting enough to warrant a careful examination of the problem, particularly since review articles have appeared giving inconsistent data.[5] We have therefore undertaken a careful study of the products and mechanism of the photodimerization of three cyclopropenes: methyl 1,2-diphenylcyclopropene-3-carboxylate (**1**), 1,2-diphenylcyclopropene (**2**), and 1,2,3-triphenylcyclopropene (**3**). Taken together, the observations we have made on the dimerization of these three cyclopropenes make a consistent and satisfying mechanistic picture.

Results and Discussion

Products. The products were determined by irradiating degassed sealed samples of each cyclopropene in benzene, sensitized with 5×10^{-4} *M* thioxanthone. Filtered (Corning 0-52 and 7-39 color filters) 366-nm radiation was used and the reaction was carried to about 50% conversion. The benzene was then evaporated under a stream of nitrogen, the residue was totally dissolved in $CDCl_3$, and the nmr spectrum of the total product mixture of each cyclopropene was taken. These spectra were then compared with the spectra of the products isolated from the usual kind of preparative irradiations (see Experimental Section). In this way we determined that we had not lost or ignored any of the principal products, nor had the products undergone any change in the preparative irradiation or work-up.

Figure 1 diagrams the photochemistry observed. Compound **1** gave a major tricyclohexane product as well as about 10% of other products which were not isolated, but which were observed as several small peaks in the nmr spectrum of the total product mixture. Only a single dimer could be seen in the nmr spectrum of the total product mixture from **2**. In the case of **3**, the nmr spectrum of the total product mixture showed only two products in a 60:40 ratio. The minor product proved identical in all respects with the thermal dimer of **3**, including the remarkable high-temperature thermal rearrangement of the dimer to triphenylazulene and stilbene.[6] This dimer has been assigned the cyclopropylcyclopropene structure **10** by Breslow and Dowd.[6] Although **10** constituted 40% of the products of the photodimerization of **3**, it was not reported among the photoproducts isolated by Durr.[4] This discrepancy may reflect a solvent effect, or possibly the consumption of **10** by secondary photoreactions.

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(3) C. D. DeBoer and R. Breslow, *Tetrahedron Lett.*, 1033 (1967).

(4) H. Durr, *ibid.*, 1649 (1967); *Justus Liebigs Ann. Chem.*, **723**, 102 (1969).

(5) N. J. Turro, J. C. Dalton, and D. S. Weiss in "Organic Photochemistry," Vol. II, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, p 34; N. J. Turro, D. M. Pond, D. R. Morton, and J. C. Dalton, *Annu. Rev. Photochem.*, **3**, 58 (1971); **1**, 63 (1967).

(6) R. Breslow and P. Dowd, *J. Amer. Chem. Soc.*, **85**, 2729 (1963).

Table I. Physical Constants of the Reaction Products

Compd	Mp, °C	Nmr	Mass spectrum	Ir
4	Rearranges to **7**	δ 3.33 (6 H) δ 3.75 (2 H) δ 7.29 (20 H)	Rearranges to **7**	1679 (vs) 1600 (w) 1495 (m) 1446 (m) 1433 (m) 1395 (m)
5	Rearranges to **8**	(d) δ 2.62 (2 H) (d) δ 2.90 (2 H) $J = 4.5$ cps δ 7.0–7.8 (20 H)	Rearranges to **8**	
6	Rearranges to **9**	δ 4.10 (2 H) δ 7.20 (30 H)	Rearranges to **9**	1600 (s) 1496 (s) 1457 (w) 1442
7	250–252	δ 3.06 (6 H) δ 5.10 (2 H) δ 7.17 (20 H)	500, 469, 468 *441*, *409*, 397 382, 305, 304 303, 302, 289 105, 91, 78 77, 59	1672 (vs) 1600 (w) 1490 (m) 1440 (m) 1428 (m)
8	257–258.5	δ 3.63 (4 H) $\delta \approx 7.4$ (20 H)	384, 307, 293 215, 167, 115 91, 78	1600 (m) 1575 (w) 1490 (s) 1441 (s) 1418 (m)
9	330–335 (open capillary)	δ 5.00 (2 H) δ 7.28 (30 H)	536, 458, 457 445, 369, 367 291, 167	1597 (w) 1490 (m) 1452 (m) 1440 (m)
10	179–180	δ 3.22 (2 H) δ 7.20 (30 H)		

As shown in Figure 1, the major dimer of all three cyclopropenes undergoes a thermal rearrangement (at widely differing temperatures) to an isomeric cyclohexadiene (see below). In the case of the dimer of **3**, this thermally rearranged isomer (**9**) was reported as a primary photoproduct.[4] Presumably this was due to secondary photolysis, since the photolysis of pure **3** to **9** has been observed.[4] In our work, careful examination of nmr spectra of the total product mixture revealed none of the thermally rearranged dimer **9** in the photoproducts.

Table I gives the physical data of all the products and Figure 1 shows their chemical transformations. The assignment of the structure of the dimer of diphenylcyclopropene is the most straightforward and will be discussed first.

Since the thermal rearrangement of **5** occurs with a half-life of about 5 min at 13°, the nmr spectrum of **5** was taken on a sample prepared by irradiating a thioxanthone-sensitized solution of **2** in dichloromethane in a sealed, degassed nmr tube at −80°. The nmr spectrum was then scanned at successively increasing temperatures until the thermal rearrangement occurred at 13° (Figure 2). The resolution of the spectra is poor because undissolved dimer was suspended in the solution at all times. The assignment of the structure 1,2,4,5-tetraphenyl-1,4-cyclohexadiene (**8**) to the thermally rearranged material rests on the nmr spectrum (4-proton singlet at δ 3.63), the mass spectrum (384 parent ion, reasonable cracking pattern), the elemental analysis, and ir spectrum (consistent with **8**) as well as the chemical behavior of **8** (partial oxidation 1,2,3,4,5-tetraphenylbenzene upon heating in a sealed tube under air to 300°). A similar oxidation of **9** upon heating has been reported.[4] The only reasonable structure for **5** which will then fit the nmr spectrum and the easy thermal rearrangement to **8** is the tricyclohexane structure shown in Figure 1. The assignment of the structure of **8** as the cyclohexadiene is particularly important in this work since **8** serves as a model for the absorption spectrum of **7** and **9**. Although we cannot unambiguously assign **5**

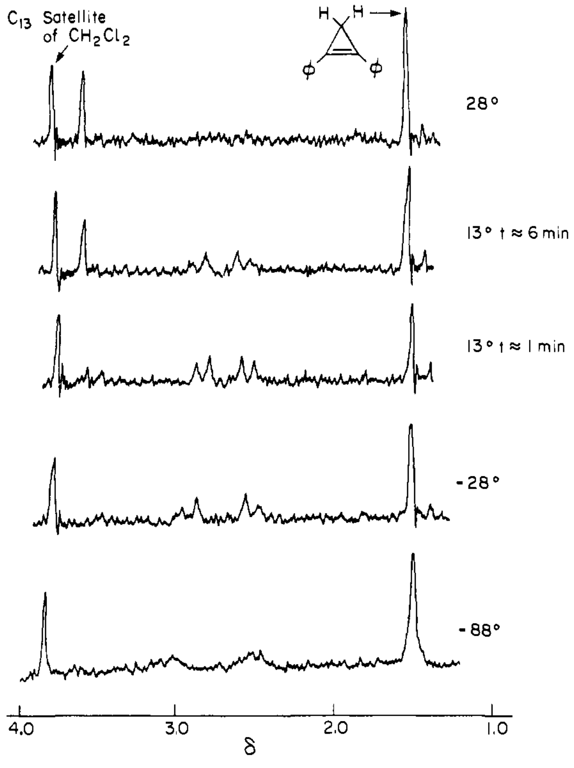


Figure 2. Nmr spectra of the −80° photoproduct of **2** in methylene chloride.

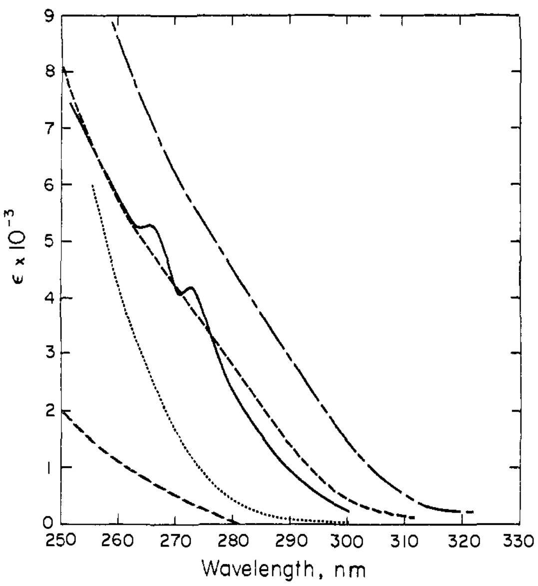


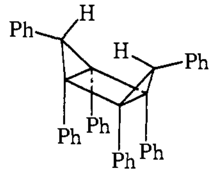
Figure 3. Absorption spectra of the photoproducts in $CHCl_3$: (— — — —) 4, (. . . . . . .) 6, (————) 9, (- - - - -) 7; (— — —) 8.

the cis-anti-cis configuration shown in Figure 1, in the Mechanism section it will be shown that the cyclopropene dimerization is extremely sensitive to steric factors which favor the cis–anti–cis configuration.

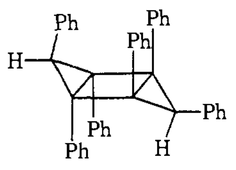
The dimers **4** and **6** also undergo thermal rearrangements, but at much higher temperatures. When **4** is heated rapidly to 230° in a melting-point capillary, it melts and then resolidifies, whereas in the case of **6** a phase change can be seen to move through the crystalline mass. These rearrangements do not appear to occur rapidly below about 200°, although accurate thermal measurements have not been made. The much higher temperatures required for the rearrangements of **4** and **6** are apparently a consequence of steric crowding. Since the thermal rearrangement of a tricyclohexane to a cyclohexadiene is forbidden by Woodward-Hoffmann rules,[7] it can be assumed that the transition state will resemble a diradical and that resonance with the phenyl rings will be important. Inspection of Dreiding stereomodels reveals that the cyclohexadienes **7** and **9** are considerably more crowded than **8**, which tends to push the phenyls on the double bonds out of the resonance plane. Presumably it is this crowding which so raises the activation energy for rearrangement of **4** and **6**. The rearrangement of **4** has also been observed at room temperature in dimethyl sulfoxide solution. This is similar to the cleavage of α-lumicolchicine in dimethyl sulfoxide,[8] but the mechanism of the rearrangement is not obvious.

The rearrangement products **7** and **9** show a downfield shift of the methine proton compared to their precursors of about 1 ppm and longer wavelength absorption in the uv (Figure 3). The spectra of **7** and **9** show parallel absorption at about 10 nm shorter wavelength than **8**, where there is no question of the cyclohexadiene structural assignment. The slightly shorter wavelength absorption of **7** and **9** is presumably due to the increased steric hindrance compared to **8**. On the basis of the spectral data given in Figure 3 and Table I, as well as the oxidation of **9** to hexaphenylbenzene (Figure 1), we have assigned **7** and **9** the 1,4-cyclohexadiene structures and their precursors, **4** and **6**, the tricyclohexane structures shown in Figure 1.[8a] As in the case of **5**, the reasons for the assignment of the cis–anti–cis configuration to **4** and **6** will become clear in the Mechanism section.

It has been argued that **9** is not a cyclohexadiene, but rather an isomeric tricyclohexane, **9a** or **9b**,[4] on



9a



9b

the basis that the absorption spectrum of **9** does not resemble that of *cis*-stilbene. However, the sterically less hindered *cis*-stilbene is not a good model for the spectrum of **9**. Fortunately, the nmr spectra shown in Figure 2 make the assignment of **5** and **8** unambiguous, and **8** can serve as a model for the absorption spectrum of **9**. In addition to the comparison of the absorption spectra of **8** and **9** shown in Figure 3, there are several other arguments against the assignment of structure **9a** or **9b**. First, **9a** and **9b** would be thermodynamically unfavored, since they are sterically more crowded than **6**, and the thermal rearrangement would be expected to proceed in the opposite direction to that observed. Second, the cyclopropane protons of **9a** and **9b** would be expected to appear at higher field in the nmr spectrum than those of the precursor, **6**, because of decreased shielding from the adjacent phenyl rings. In fact, they are observed at lower fields, consistent with the cyclohexadiene structure **9**.

We think the structural assignments of the major photodimers of **1**, **2**, and **3** are now secure. It is probable that the minor product or products from **1** are cyclopropylcyclopropenes similar to **10**, for reasons that will become clear in the Mechanism section, but no attempt has been made to isolate or characterize these products.

Mechanism of Dimerization

Multiplicity of the Reactive State. Irradiation of a 0.1 *M* solution of **3** in degassed benzene with 335-nm radiation for extended periods of time produces no measurable changes. A conservative estimate of the quantum yield for reaction under these conditions is less than 10^{-3}. On the other hand, irradiation of 0.1 *M* solutions of **1** and **3** in the presence of 10^{-3} *M* thioxanthone (E_t = 65 kcal/mol, ϕ_{isc} = 1.0)[9] with 366-nm radiation (100% absorbed by thioxanthone) gives dimers with quantum yields over one-half. These two facts, along with the data that follow, make it clear that reaction is occurring from the triplet state of the cyclopropene. This is in dramatic contrast to the case of 1,2-diphenylcyclobutene, where dimeriza-

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[7] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 395 (1965).

[8] D. J. Pasto, "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 178.

[8a] Note Added in Proof: Comparison of the ^{13}C nmr spectra and laser Raman spectra of compounds 4, 7, and 8 entirely confirms these structural assignments, according to T. H. Regan and T. J. Davis of these laboratories.

[9] All triplet energies and intersystem crossing ratios were taken from N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

tion occurs only from the singlet state (*via* an excimer) and sensitized irradiation gives no products.[10]

Triplet Energies of 1,2-Diphenylcyclopropenes. The triplet energy of **3** has been estimated as less than 55 kcal/mol, on the basis that biacetyl (E_t = 55 kcal/mol) will sensitize the reaction while anthracene (E_t = 43 kcal/mol) will not.[4] However, this estimate ignores the fact that endothermic energy transfer can occur at rates sufficiently fast to cause dimerization.

If energy transfer from a low-energy sensitizer is faster than decay of the sensitizer triplet, a significant quantum yield for photochemical reaction can be observed. For example, in the case of *cis*-stilbene (E_t = 57 kcal/mol), the rate of energy transfer from benzanthracene triplets (E_t = 47 kcal/mol) is 6×10^7 l./(mol sec).[11] Since the decay of the benzanthracene triplet is only 300 sec^{-1},[11] at a concentration of 10^{-3} *M cis*-stilbene the quantum yield of stilbene isomerization will still be high, *even with a sensitizer of triplet energy 10 kcal below the acceptor.* Clearly triplet energies cannot be established from qualitative evaluations of sensitizer efficiencies alone.

The direct observation of the triplet state of **1** or **3** was not possible since no emission could be found from either compound at 77°K. This contrasts sharply with the case of 1,2-diphenylcyclobutene, where the fluorescence emission at room temperature in degassed hexane is 99%.[10] Presumably this is due to relief of ring strain in the cyclopropene excited state, since it has been estimated that the strain energy of a cyclopropene is about 20 kcal/mol higher than that of a cyclopropane (a model for the cyclopropene excited state), whereas the strain energies of cyclobutenes and cyclobutanes are nearly equal.[12]

We have made an indirect estimate of the triplet energy of **1** from a flash photolysis experiment in which the rate of energy transfer from the triplet state of chrysene to **1** was measured. The rate of decay of the chrysene triplet was measured with and without 1.60×10^{-5} *M* **1**. The first-order component of the decay was extracted through a nonlinear regression computer analysis of the decay curves, and from these numbers the rate of energy transfer from the chrysene triplet (E_t = 57 kcal/mol)[9] to **1** was calculated to be 1.1×10^9 l./(mol sec).

In comparison, the rate of energy transfer from chrysene triplets to *cis*-stilbene (E_t = 57 kcal/mol) is 2.5×10^9 l./(mol sec).[11] This allows us to place the triplet energy of **1** slightly higher than *cis*-stilbene, about 60 kcal/mol. Since the chromophore is the same in cyclopropenes **2** and **3**, we assume their triplet energies are also about 60 kcal/mol. It has been suggested that the effect of strain relief in the triplet state of **1**, where the double bond is broken, would produce a lower triplet energy in **1** than in *cis*-stilbene.[9] The fact that this was not observed probably means that the triplet state of **1** initially formed by energy transfer has the same geometry and therefore the same strain energy as the ground state; *i.e.*, the Frank–Condon principle holds for triplet energy transfer from sensitizers to **1**. A rapid relaxation of the initially formed triplet to a less strained configuration would then be consistent with the lack of emission from **1** and **3**. This point is being further investigated by a flash photolysis study of the rate of energy transfer from several sensitizers to **1**, which will appear later.

If this effect withstands more detailed examination, it will be a striking example of a limitation on the kind of geometric distortion permitted during nonvertical energy transfer. The high strain energy of a cyclopropene relative to a cyclopropane makes the lack of observation of nonvertical energy transfer to cyclopropenes highly important in the development of a theory adequate to explain the general case of nonvertical energy transfer.

Quantum Yields of Dimerization. Cyclopropene **2** was thermally less stable than **1** and **3** and was not obtained in a pure enough state to warrant quantum-yield measurements,[13] but from preparative irradiation experiments we are able to estimate that the quantum yield of dimerization sensitized by thioxanthone is greater than 0.5.

The quantum yields of dimerization of **3** were measured with several sensitizers by analyzing the appearance of dimers by nmr spectroscopy, since thermal side reactions prevented vpc analysis. Unfortunately, the values obtained by this method were limited to about ±15% accuracy. This accuracy did not permit a careful study of the mechanism of dimerization through variation of the concentration of **3** and of the sensitizer. The values that were obtained are given in Table II.

The disappearance of **1** upon irradiation can be followed by vpc analysis, since thermolysis of the dimer **4** gives the cyclohexadiene **7** rather than the monomer, as is commonly observed with cyclobutane photodimers.[14] Our most accurate quantum yields were measured in this way. The full description of the method of analysis and the various checks performed to ensure the validity of our results are given in the Experimental Section. The quantum yields measured are given in Table II. They fall into three groups.

(Q-1) Quantum Yields with High-Energy Sensitizers. The fact that the quantum yield of dimerization is independent of the concentration of **1** with high-energy sensitizers (Table II), yet not equal to unity, is consistent with the mechanism given in Scheme I, where the species (**1**, **1**) may be either an exciplex or a diradical intermediate with one of the two cyclobutane bonds formed. This sort of mechanism has been reported in the literature several times recently.[15]

From the expression for ϕ^{-1} in Scheme I and the data of Table II, it can be calculated that k_w/k_p = 0.25 and that the limit for $k_d/k_r \approx 10^{-4}$, by assuming a 10% change in the quantum yield of dimerization could be detected. The value for k_w/k_p is surprisingly low considering the high strain energy and steric hindrance of the product. The photodimer of indene is considerably less strained, yet the value for k_w/k_p is 5.0 in this case.[15] A possible rationalization of this

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[10] C. D. DeBoer and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **90**, 803 (1968).

[11] W. G. Herkstroeter, Ph.D. Thesis, California Institute of Technology, 1965.

[12] R. Breslow, J. Lockhart, and A. Small, *J. Amer. Chem. Soc.*, **84**, 2793 (1962).

[13] The nmr spectrum of **2** showed no impurities, but crystals of **2** were pale yellow, indicating that the material was contaminated.

[14] G. O. Schenck, W. Hartman, S.-P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962).

[15] C. D. DeBoer, *J. Amer. Chem. Soc.*, **91**, 1855 (1969), and references cited therein.

Table II. Quantum Yields of Cyclopropene Dimerizations in Benzene

Cyclopropene	Concn, *M*	Sensitizer	Concn, *M*	ϕ^a
3	0.04	Benzophenone	0.1	0.5 ± 0.07
	0.04	Michler's ketone	10^{-3}	0.7
	0.04	2-Acetonaphthone	0.1	0.4
	0.04	Chrysene	0.05	0.2
	0.04	Fluorenone	0.1	0.5
	0.04	Benzil	0.05	0.5
	0.04	1,2-Benzanthracene	0.05	0.3
	0.04	Acridine	10^{-2}	0.2
	0.04	Anthracene	10^{-2}	$<10^{-2}$
1	0.1	Benzophenone	0.06	0.80 ± 0.015
	0.1	Thioxanthone	10^{-4}	0.70 ± 0.014
	0.05	Thioxanthone	10^{-4}	0.75 ± 0.015
	0.02	Thioxanthone	10^{-4}	0.76 ± 0.015
	0.01	Thioxanthone	10^{-4}	0.75 ± 0.015
	0.001	Thioxanthone	10^{-4}	0.74 ± 0.015
	0.1	1,2-Benzanthracene	0.0087	0.21 ± 0.02
	0.1	1,2-Benzanthracene	0.0069	0.21 ± 0.02
	0.1	1,2-Benzanthracene	0.0044	0.24 ± 0.02
	0.1	1,2-Benzanthracene	0.0029	0.22 ± 0.02
	10^{-3}	Fluorenone	0.0226	0.164 ± 0.005
	10^{-3}	Fluorenone	0.0337	0.086 ± 0.002
	10^{-3}	Fluorenone	0.0446	0.044 ± 0.002
	10^{-3}	Fluorenone	0.0574	0.0315 ± 0.002
	10^{-3}	Fluorenone	0.100	$<10^{-3}$
	2×10^{-3}	Fluorenone	0.0222	0.347 ± 0.005
	2×10^{-3}	Fluorenone	0.0334	0.225 ± 0.005
	2×10^{-3}	Fluorenone	0.0445	0.167 ± 0.005
	2×10^{-3}	Fluorenone	0.0556	0.111 ± 0.005
	2×10^{-3}	Fluorenone	0.0668	0.095 ± 0.005
	4×10^{-3}	Fluorenone	0.0222	0.664 ± 0.005
	4×10^{-3}	Fluorenone	0.0445	0.237 ± 0.005
	4×10^{-3}	Fluorenone	0.0668	0.142 ± 0.005
	6×10^{-3}	Fluorenone	0.0222	0.57 ± 0.005

[a] Corrected for ϕ_{isc} of the sensitizer.

Scheme I

$$\text{sensitizer} \xrightarrow{h\nu} \text{sensitizer}^3$$

$$\text{sensitizer}^3 + \mathbf{1} \xrightarrow{k_{\text{et}}} \mathbf{1}^3 + \text{sensitizer}$$

$$\mathbf{1}^3 \xrightarrow{k_{\text{d}}} \mathbf{1}$$

$$\mathbf{1}^3 + \mathbf{1} \xrightarrow{k_{\text{r}}} (\mathbf{1},\mathbf{1})$$

$$(\mathbf{1},\mathbf{1}) \xrightarrow{k_{\text{w}}} \mathbf{1} + \mathbf{1}$$

$$(\mathbf{1},\mathbf{1}) \xrightarrow{k_{\text{p}}} \text{dimers}$$

$$\phi = \left(\frac{k_{\text{p}}}{k_{\text{p}} + k_{\text{w}}}\right)\left(\frac{k_{\text{r}}[\mathbf{1}]}{k_{\text{r}}[\mathbf{1}] + k_{\text{d}}}\right)$$

$$\phi^{-1} = \left(1 + \frac{k_{\text{w}}}{k_{\text{p}}}\right)\left(1 + \frac{k_{\text{d}}}{k_{\text{r}}[\mathbf{1}]}\right)$$

observation can be made by assuming intermediate (**1**, **1**) is a thermally equilibrated diradical. The relief of ring strain in the intermediate would then provide a barrier to fragmentation of the intermediate in the case of **1**, but not in the case of the less strained indene. This relief of ring strain is unique to cyclopropene in the class of monocyclic olefins. In all larger rings the difference in strain energy between the saturated and unsaturated case is small (taking the saturated ring as a rough model for the triplet state where the π electrons are nonbonding). It appears likely that the principal limitation on the quantum yield of dimerization of cyclic olefins is the amount of cleavage of the intermediate diradical.[15] Because of ring strain, the cyclopropenes offer a unique way around this limitation. It is interesting to note that the same ring strain argument should hold for photoadditions between cyclopropenes and other unsaturated molecules, raising the possibility of controlling the course of photochemical cross addition reactions. However, whether (**1**, **1**) in Scheme I is an exciplex or a diradical, the ratio $k_{\text{w}}/k_{\text{p}}$ would be expected to be a sensitive function of several steric and electronic factors, and therefore difficult to predict quantitatively.

(Q-2) Quantum Yield in the Presence of Low-Energy Quenchers. Measurements of the quantum yield of dimerization of **1** in the presence of quenchers can be used to calculate the rate constant k_{r}. If the quencher used in such measurements undergoes an isomerization upon quenching the triplet state of **1**, then one can obtain values for k_{r} by observing either the isomerization of the quencher or the dimerization of **1**. In this case we have chosen to use *trans*-stilbene as the quencher and observe the stilbene isomerization rather than the dimerization of **1** for the following reasons.

Since the intersystem crossing quantum yield for **1** is zero, it is necessary to use a sensitizer to excite **1** to the triplet state, but the quencher as well as **1** will capture sensitizer triplets. It is a good assumption that the rate of energy transfer from a high-energy sensitizer such as thioxanthone (E_{t} = 65 kcal/mol) will be diffusion-controlled to both **1** (E_{t} = 60 kcal/mol) and to *trans*-stilbene (E_{t} = 50 kcal/mol). In order to minimize the amount of energy transfer from the sensitizer to the quencher, it is important to keep the ratio of [**1**]:[stilbene] as high as possible. However, if we follow the dimerization of **1** by disappearance of starting material, by the time enough dimerization has occurred to give an accurate measurement, the stilbene quencher will be at the photostationary state which is predominantly *cis*-stilbene. Since *cis*-stilbene has about the same triplet energy as **1**, we cannot be sure of the rate of energy transfer from $\mathbf{1}^3$ to *cis*-stilbene, a necessary number for the calculation of the k_r. Therefore, we have measured the isomerization of *trans*-stilbene in the presence of **1** and thioxanthone, because short irradiation times and low conversions of *trans*- to *cis*-stilbene can be used. The reactions in Scheme II must be added to those given in Scheme I. Then we can write eq 1, where k_d has

$$\phi_{cis\text{-stilbene}} = \left(\frac{k_c}{k_c + k_t}\right)\left(\frac{k_{et}[trans\text{-stilbene}]}{k_{et}[trans\text{-stilbene}] + k_r[\mathbf{1}]}\right) \times \left(\frac{[\mathbf{1}]}{[\mathbf{1}] + [trans\text{-stilbene}]}\right) + \left(\frac{k_c}{k_c + k_t}\right) \times \left(\frac{[trans\text{-stilbene}]}{[trans\text{-stilbene}] + [\mathbf{1}]}\right) \quad (1)$$

been neglected and the ratio of [**1**]:[stilbene] is large.

Scheme II

$$\text{sensitizer}^3 + trans\text{-stilbene} \xrightarrow{k_{et}} \text{stilbene}^3 + \text{sensitizer}$$

$$\mathbf{1}^3 + trans\text{-stilbene} \xrightarrow{k_{et}} \text{stilbene}^3 + \mathbf{1}$$

$$\text{stilbene}^3 \xrightarrow{k_t} trans\text{-stilbene}$$

$$\text{stilbene}^3 \xrightarrow{k_c} cis\text{-stilbene}$$

The measured values for the quantum yield of stilbene isomerization sensitized by thioxanthone with added **1** are given in Table III, along with the calculated value of k_r, using the equation given in Scheme II. All three concentrations of stilbene used give about the same value for k_r, $1.1 \pm 0.1 \times 10^8$ l./(mol sec).

Table III. Stilbene Isomerization in the Presence of **1**

[Stilbene],[a] *M*	[**1**], *M*	ϕ_0/ϕ	k_r[b]
4.44×10^{-3}	0.10	1.60	1.20×10^8
6.66×10^{-3}	0.10	1.37	0.99×10^8
8.88×10^{-3}	0.10	1.30	1.02×10^8

[a] 10^{-4} *M* thioxanthone as sensitizer. [b] Calculated from equations in Scheme II.

In the derivation of the expression for $\phi_{cis\text{-stilbene}}$ in Scheme II, it has been assumed that the rates of energy transfer to both stilbene and to **1** are diffusion-controlled and therefore equal. This has been shown to be a good assumption for high-energy sensitizers.[11] From the limiting value of $k_d/k_r < 10^{-4}$ established in section Q-1 and the data of Table III, it can be estimated that $k_d < 10^4$ sec^{-1}. In comparison, the rate of unimolecular decay of the stilbene triplet has been estimated to be greater than 10^7 sec^{-1}.[16] This difference is laid to the inability of the stilbene chromophore to twist in a three-membered ring, since twisting brings the triplet and ground states closer together and thereby increases the probability of intersystem crossing.

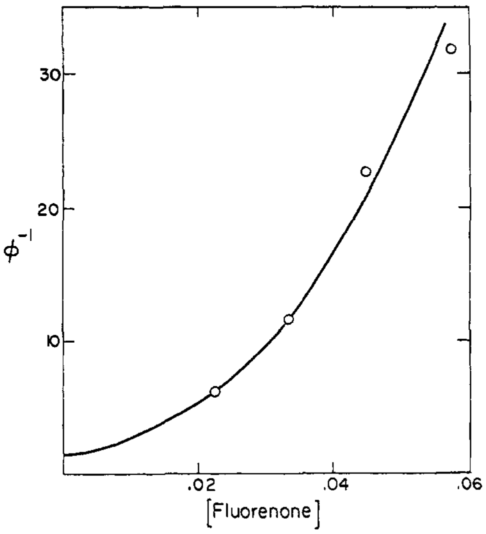

Figure 4. Stern–Volmer plot for 10^{-3} *M* **1** dimerization sensitized by fluorenone.

(Q-3) Low-Energy Sensitizers. With low-energy sensitizers one would expect the mechanism to be complicated by reversible energy transfer from the cyclopropene triplet to ground state sensitizer. In this case kinetic analysis shows ϕ^{-1} should be proportional to the concentration of ground state sensitizer. We have measured the quantum yields of dimerization of **1** sensitized by 9-fluorenone and 1,2-benzanthracene, both low-energy sensitizers for **1**. The quantum yield of dimerization is independent of the benzanthracene concentration. With fluorenone a concentration dependence is observed, but a plot of ϕ^{-1} *vs.* [fluorenone] deviates greatly from linearity, as Figure 4 shows. The simple addition of reversible energy transfer to the mechanism of Scheme I will not explain these data. In fact, these results are difficult to explain by any of the commonly held concepts of organic photochemistry. In order to clarify the mechanism as much as possible, we have measured the fluorescence spectrum of a 0.004 *M* benzene solution of 1,2-benzanthracene at room temperature with and without 0.1 *M* **1**. The spectra were identical in all respects, including intensity. This experiment shows the dimerization must be occurring from the benzanthracene triplet state. The mechanism of the reaction will apparently require a termolecular step such as

$$\text{benzanthracene}^{*3} + \mathbf{1} \longrightarrow \text{complex}$$

$$\text{complex} + \mathbf{1} \longrightarrow \text{dimer} + \text{benzanthracene}$$

The nature of the complex in this mechanism is the key to the problem. The complex cannot be quenched by ground state benzanthracene; therefore it does not much resemble the triplet state of **1**. If the complex were a simple biradical such as **11**, the mechanism becomes simply the Schenck mechanism[17] and, in fact, the best example of the Schenck mechanism yet reported. However, if this were the correct explanation of the results, one would probably expect that the product ratio

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(16) E. F. Ullman, *J. Amer. Chem. Soc.*, **86**, 5357 (1964); W. A. Henderson, Jr., *ibid.*, **89**, 4930 (1967).

(17) (a) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964); (b) K. Gollnick and G. O. Schenck in "Organic Photochemistry," IUPAC, Butterworths, London, 1965, p 507.

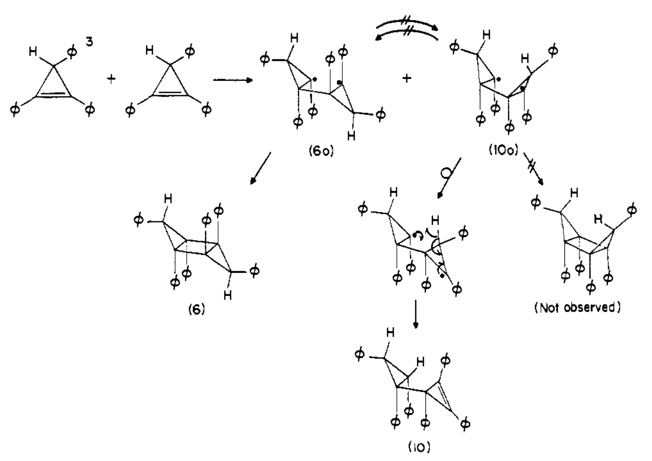
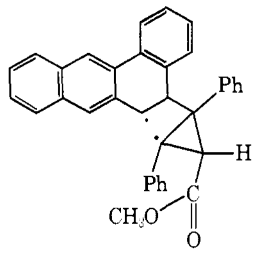


Figure 5.



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of **6** to **10** would change when benzanthracene was used to sensitize the dimerization of **3**, because of the bulky sensitizer covalently attached to the cyclopropene during the bond forming step which determines the ratio of **6** to **10**. Examination of the product ratio by nmr shows no change with sensitizer. This weakens the case for the Schenck mechanism but does not eliminate it from consideration.

At the present time we cannot offer an adequate explanation for these interesting results. It does seem likely that further experiments on the photochemistry of cyclopropenes will be similarly fruitful.

Isotope Effects. Since **3** gives two photodimers in nearly equal amounts, only one of which involves a hydrogen transfer, an isotope experiment was done with **3**. A mixture of about one-third deuterated and two-thirds nondeuterated **3** was photodimerized with Michler's ketone as sensitizer. The two dimers **6** and **10** were then isolated as described in the Experimental Section and the mass spectrum of each dimer was measured. As Table IV shows, both dimers had identical isotope ratios within experimental error.

Table IV. Isotope Ratios of Labeled Dimers of **3**

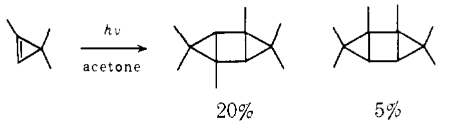
Dimer	Peak height[a] *m/e* 536	 *m/e* 537	 *m/e* 538
6	65.5	100	58.6
10	67.5	100	59.4

[a] Measured on a Du Pont 21-110-B mass spectrometer at 70 eV. Repetitive scans gave values within 3% of those shown.

This result requires that there be no isotope effect on the hydrogen transfer leading to dimer **10** and implies that the hydrogen-transfer step is not rate determining. This is explained as follows. If bond formation in the dimerization occurs in a stepwise fashion, two different diradical intermediates can be formed which are not interconvertible by rotations around σ bonds (Figure 5). In the cis–anti–cis form these diradicals lead to the observed products of the reaction, whereas in the "boat" form, diradical **10a** would give the syn isomer of **6**, which is not observed. Since the diradicals are not interconvertible, and since there would be a negligible isotope effect on the formation of the diradical intermediates, no isotope effect on the products is observed.

Because the isotope experiment clearly shows stepwise bond formation with a diradical intermediate, it is reasonable to suppose that the mechanistic intermediate (**1, 1**) in Scheme I is this same diradical intermediate observed in the isotope experiment. About 20% of the diradical intermediates would then have an alternative pathway to dimer formation, that of cleavage to monomer, as required by Scheme I. If the fragmentation pathway were important for diradical **10a**, an isotope effect would be observed with dimer **10**, because deuterated **10a** would fragment more than protonated **10a**. Since one was not, we are left with two possible conclusions: (1) intermediate (**1, 1**) in Scheme II is an exciplex which leads to diradicals **6a** and **10a**; (2) only diradical **6a** breaks to monomer. Diradical **10a** always proceeds to dimer (at least to the extent we are able to measure). The choice between these possibilities must remain pending further experimental or theoretical developments.

This analysis of the isotope-effect experiment with reaction occurring only from the cis–anti–cis configuration of the intermediate diradical also helps to make clear our preference for assignment of the cis–anti–cis structure to the tricyclohexanes **4**, **5**, and **6**. The implication of these results is that there are severe steric constraints on the cyclopropene photodimerizations. This is further indicated by the fact that 1,2-diphenylcyclopropenes where both 3 positions are substituted with groups larger than a hydrogen atom do not dimerize. For example, we have been unable to obtain dimers from 3-methyl-1,2,3-triphenylcyclopropene, methyl 1,2-diphenyl-3-chlorocyclopropene-3-carboxylate, methyl 1,2-diphenyl-3-hydroxycyclopropene-3-carboxylate, and methyl 1,2-diphenyl-3-methoxycyclopropene-3-carboxylate. Even in the case of simpler cyclopropenes such as 1,3,3-trimethylcyclopropene, the major product is the one determined by steric advantage rather than by consideration of the most stable biradical intermediate.[1]



Experimental Section

Materials. Mallinckrodt Nanograde benzene was used as received. All other solvents and reagents were Eastman reagent grade materials.

Methyl 1,2-diphenylcyclopropene-3-carboxylate (1) was synthesized by the method of Breslow, Winter, and Battiste.[18]

1,2-Diphenylcyclopropene was synthesized from 1,2-diphenylcyclopropenone by the method of Perkins and Wadsworth.[19]

3-Methyl-1,2,3-triphenylcyclopropene was synthesized by the method of Breslow and Dowd.[6]

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(18) R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, 24, 415 (1959).

(19) W. C. Perkins and D. H. Wadsworth, *ibid.*, in press.

Methyl 1,2-diphenyl-3-chlorocyclopropene-3-carboxylate, methyl 1,2-diphenyl-3-hydroxycyclopropene-3-carboxylate, and methyl 1,2-diphenyl-3-methoxycyclopropene-3-carboxylate were synthesized by the method of DeBoer.[20]

1,2,3-Triphenylcyclopropene was synthesized by the method of Breslow and Chang.[6,21]

Preparative irradiations were carried out in a Pyrex-glass vessel swept with a nitrogen stream which had first been saturated with the solvent used. The lamp (450-W, medium-pressure mercury arc) was contained by a tube of uranium yellow glass (essentially a 366 nm + visible filter) held in a water-cooled quartz jacket which was immersed in the reaction vessel. From 1 to 5 g of the cyclopropene (**1**, **2**, or **3**) was dissolved in 500 ml of benzene with 5 mg of thioxanthone as sensitizer. The disappearance of starting material was followed by tlc during the irradiation. After irradiation, the solvent was evaporated and the residue recrystallized from benzene. In the case of **3**, the residue was first extracted with ether to remove **10**, which was then chromatographed on a 4-in. alumina column with hexane–benzene and recrystallized from benzene–hexane. The nmr spectra of the dimers were taken in $CDCl_3$ on a Varian A-60 spectrometer. (When dimethyl-d_6 sulfoxide was used, the ring-opened products **7** and **9** were observed.) The ir spectra were determined on a Perkin-Elmer 700 spectrometer in KBr disks. The uv spectra were taken in $CHCl_3$ on a Cary 14 spectrometer. The mass spectra were taken on a Hitachi RMS-4 spectrometer. Melting points were determined in open capillary tubes on a Melt-Temp heating block and are uncorrected. The spectral data of the dimers are given in Table I and Figure 3.

Thermal rearrangements of dimers **4** and **6** were accomplished by sealing 250 mg of each dimer in a degassed Pyrex tube and heating the tube in a 300° molten salt bath ($NaNO_2$ + KNO_3) for 5 min. Upon cooling, the tubes were opened and the material was recrystallized from benzene to give cyclohexadienes **7** and **9**. Dimer **8** was unchanged by this treatment, except for a slight (<10%) conversion to tetraphenylbenzene, noted in the mass spectrum (by comparison with authentic material). This conversion was increased when the tubes were sealed without degassing.

Oxidation of 9 to hexaphenylbenzene was accomplished by treating 268 mg of **9** in 25 ml of refluxing chloroform with 160 mg of bromine and 10 ml of chloroform. When the color had been discharged, the solvent was evaporated in a nitrogen stream and the residue was recrystallized twice from 3 ml of diphenyl ether, the crystals being washed with benzene after filtration. The hexaphenylbenzene was identified by mixture melting point with authentic material.

Low-temperature irradiation of 2 was done by dissolving 50 mg of **2** in 0.5 ml of methylene chloride with 1 mg of thioxanthone as sensitizer. This solution was degassed and sealed in an nmr tube. The tube was irradiated with the focused radiation from a PEK 202 high-pressure mercury arc lamp (200-W) filtered by 5 cm of water (to remove ir radiation) and a Corning 7-39 color filter to isolate the 365-nm mercury line. A lens was used to focus the radiation down to a 0.5-cm² spot on the tube which was held in a windowed dewar flask filled with methanol cooled to −78° (Dry Ice).

From time to time the tube was rotated or raised and lowered as solid dimer formed in the radiation path. When visual inspection showed that a substantial amount of dimer had formed (about 1 hr), the tube was removed from the dewar and placed in the cooled probe (−80°) of a Varian A-60 nmr spectrometer. The spectrum was then scanned at successively higher temperature as shown in Figure 2.

Quantum yields were measured by irradiating degassed (three freeze–pump–thaw cycles with an oil diffusion pump vacuum), sealed Pyrex test tubes (13 × 100 mm) containing 3.2 ml of a solution of **1** or **3** in benzene (along with a concentration of sensitizer sufficient to give an absorbance of 3 or greater at 365 nm) on a rotating tube-holder. The radiation source at the center of the tube-holder was a 450-W, medium-pressure mercury arc lamp in a Pyrex water jacket which had four sets of 2-in.-square Corning color filters (0-52 and 7-39) taped to the wall of the jacket with the remaining areas of the jacket taped up to exclude radiation which did not pass through the filters. The actinometer used to monitor the radiation was the 0.1 *M* benzophenone-sensitized isomerization of 0.1 *M* *trans*-stilbene, for which a value of ϕ was assigned as 0.5.[22–24] The isomerization was generally carried out to between 5 and 10% and was corrected for back reaction by the formula of Lamola and Hammond.[25] The extent of stilbene isomerization was measured by vpc columns packed with 10% silicon oil at 180°. A 50-μl sample was used in the analysis and the peaks were cut and weighed and corrected for the 5% smaller response of *cis*-stilbene relative to *trans*-stilbene. This lamp–actinometer combination was reproducible within the limits of our measurement (≈1%). With a distance of about 4 in. from the lamp to the tube-holder, this assembly will provide about 2 μeinsteins of 365-nm radiation per tube per minute. Tests showed that the temperature of the solutions in the tubes remained within 2° of the ambient temperature.

The cyclopropene solutions were irradiated along with the actinometer tubes for a precalculated length of time sufficient to give between a 25 and 50% decrease in the monomer concentration and then analyzed by vpc in the case of **1** for disappearance of starting material and by nmr in the case of **3** for both disappearance of starting material and appearance of products. In the case of **1**, a known solution of the dimer of **1** was injected into the gas chromatograph under the conditions used for the analysis (the same columns were used as for the actinometer, but at 230°), and no peaks were seen at the retention time of **1**. Repetitive injections of 50 μl of the solutions before irradiation gave the same peak areas for **1** within 2%. Furthermore, the peak areas were strictly proportional to the concentration of **1** in the solution. Thus simple comparison of the peak areas before and after irradiation gave the fraction of **1** lost to dimers. At least duplicate analyses were done in each case. The quantum yields were then calculated from eq 2.

$$\Phi = 2\left(\frac{(\mu\text{mol of } \mathbf{1} \text{ lost})/(\text{tube min})}{\mu\text{einsteins } h\nu \text{ absorbed}/(\text{tube min})}\right) \qquad (2)$$

These quantum yields were then corrected for differences in the sensitizers' intersystem crossing ratios between the actinometer and the cyclopropene tube, if any.

Flash photolysis experiments were done with an apparatus similar to that described by Herkstroeter and Hammond.[11] The decay of the chrysene triplet was monitored at 5541 Å. The output from the flashlamps was focused onto the cell with two elliptical mirrors and passed through 6-in.-square Corning 7-54 filters to minimize scattered light at the monitoring wavelength. The cells contained a breakseal to a side compartment containing the quencher (**1**), to minimize variations in sample preparation. Polaroid snapshots of the oscilloscope traces were photographically enlarged to 10 × 14 in. and points on the curve were measured by hand. These points were then fitted to the best curve described by the equation

$$(1/A_t)(\mathrm{d}A_t/\mathrm{d}t) = \alpha + \beta A_t$$

where A_t is the absorbance at time *t*. This was done by a nonlinear regression program on an IBM 360 computer letting α, β, and the integration constant float. The values obtained in this way for α were taken as the rates of radiationless decay of the chrysene triplet. The difference between α with and without quencher then equals k_q[quencher]. A full treatment of this method can be found in the thesis of Herkstroeter.[11]

Isotope Experiments. Deuterium-labeled **3** was prepared by reduction of 5% triphenylcyclopropenium bromide in ethanol with excess $NaBD_4$. The product was recrystallized from methanol and from hexane. The deuterated material was mixed with protonated material and the mixture recrystallized. The mass spectrum of the mixture showed about 33% deuterium labeling. After dimerization the dimers were isolated as described before and recrystallized to constant melting point. The pure dimers were then analyzed by mass spectrometry, and the ratios of the isotopes were measured by the peak heights of the spectrum.

Acknowledgments. This work was begun during postdoctoral studies of one of us (C. D. DeBoer) with Professor Ronald Breslow of Columbia University, and his encouragement and inspiration are gratefully acknowledged. We also thank Mr. John Mead for measuring a number of the quantum yields.

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