The Aryl Version of the Cyclopropyl-π-Methane Rearrangement. Partitioning of a 1,4-Diradical: Mechanistic and Exploratory Organic Photochemistry[1,2]

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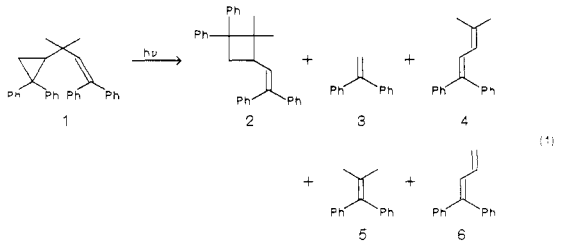
Received December 11, 1987

The photochemistry of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane (**8**) was investigated in a search for the arylcyclopropylmethane counterpart of the known vinylcyclopropylmethane reaction. Direct irradiation of arylcyclopropylmethane **8** led to 1,1-diphenylethylene (**3**) and 1-phenyl-2-methyl-1-propene (**13**) as products in addition to the usual Griffin fragmentation leading to diphenylcarbene (**15**) and 3-methyl-3-phenyl-1-butene (**7**). 1,1,3-Triphenyl-2,2-dimethylcyclobutane (**12**) was considered as a potential reaction intermediate. The cyclobutane was synthesized and found to afford alkenes **3** and **13** on irradiation. However, dynamic isotope dilution revealed that only 1% of the reaction did proceed via this intermediate, and its presence was eventually detected by FT NMR. The triplet of arylcyclopropane **8** proved unreactive. A third mechanism involving a Griffin fragmentation was considered and ruled out by independent generation of the carbene and observation of the products. Quantum yields were obtained. Also excited singlet-state lifetimes and reaction rates were determined by using single photon counting. The electronic features leading to the observed reactivities are discussed.

Introduction

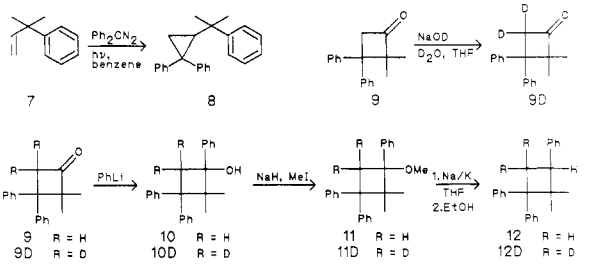
Background to the Problem. Organic photochemistry consists of two areas of endeavor. The first is the search for new excited state reactions, while the second is the elucidation of the mechanism for each new reaction discovered. The research presently under discussion began with the first objective in mind. Thus, over a decade ago we reported[4] a first example of a reaction related to the di-π-methane rearrangement; it differed in having a cyclopropyl moiety in place of a double bond. This reaction is depicted in eq 1. Here only **2**, **3**, and **4** are primary photoproducts, and alkenes **5** and **6** were found to derive from secondary photochemical fragmentation of cyclobutane **2**.



(1)

Since in the di-π-methane rearrangement[5,6] both divinyl and arylvinyl variations are known, and with the vinylcyclopropylmethane example elucidated, it was of interest to search for an arylcyclopropylmethane reaction. We selected 2-(2,2-diphenylcyclopropyl)-2-phenylpropane (**8**) for study.

Scheme I. Synthetic Details

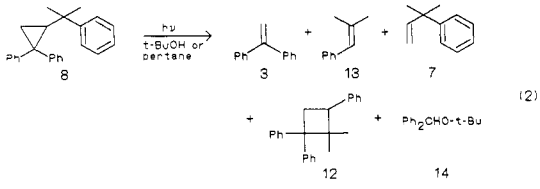


Results

Synthetic Aspects. The requisite arylcyclopropylmethane **8** was synthesized as shown in Scheme I. Also included in Scheme I is the synthesis of 1,1,3-triphenyl-2,2-dimethylcyclobutane (**12**) and its labeled counterpart (**12D**) which proved necessary during the study.

Exploratory Photochemistry of Arylcyclopropylmethane 8. With the requisite reactant **8** in hand, we proceeded to study the photochemistry of this arylcyclopropylmethane in *tert*-butyl alcohol. Under the preparative conditions used, four photoproducts were found. These were identified as 1,1-diphenylethylene (**3**), 1-phenyl-2-methyl-1-propene (**13**), 3-methyl-3-phenyl-1-butene (**7**), and diphenylmethyl *tert*-butyl ether (**14**).

Runs were also carried out in pentane. Alkenes **3**, **7**, and **13** were produced. Additionally, triphenylcyclobutane **12** was observed in a very small quantity. However, detection of this photoproduct proved difficult. These photolyses are summarized in eq 2.



(2)

In our previous study[4] starting with a cyclopropylvinylmethane, cyclobutane **2** was found to be an intermediate in formation of some of the photoproducts (**5** and **6** in eq 1). Hence the present results posed the question

(1) This is part 152 of our photochemical series and part 212 of the general series. For a preliminary report of the present study, please note ref 3.

(2) For part 151, see: Zimmerman, H. E.; Kamath, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 900-911.

(3) Zimmerman, H. E.; Carpenter, C. W.; Weber, A. M. *J. Am. Chem. Soc.* **1985**, *107*, 1073-1075.

(4) Zimmerman, H. E.; Samuel, C. J. *J. Am. Chem. Soc.* **1975**, *97*, 4025-4036.

(5) (a) One early example was that of the barrelene to semibullvalene rearrangement: Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183-184. (b) The mechanism was proposed by Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932-3933. (c) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718-1727. (d) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968** *90*, 4191-4193.

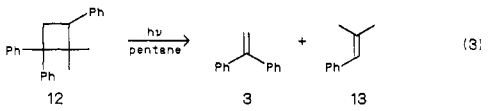
(6) (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531-551. (b) Zimmerman, H. E.; Döpp, D. *Houben-Weyl, Methods of Organic Chemistry*; G. Thieme Verlag: Stuttgart, 1975; pp 413-448. (c) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3.

0022-3263/88/1953-3298$01.50/0

of whether the triphenylcyclobutane **12** undergoes secondary photochemistry and is responsible for formation of photoproducts **3** and **13**. This point is considered below.

A final aspect of the photochemistry of cyclopropylmethylmethane **8** is its complete lack of reactivity on sensitization with acetophenone or acetone. While the triplet energy of acetophenone (ca. 74 kcal/mol[7a]) may be too low for efficient energy transfer to a phenylcyclopropyl moiety (80 kcal/mol[7b]), that of acetone (ca. 80 kcal/mol[7c]) should be sufficient for appreciable transfer.

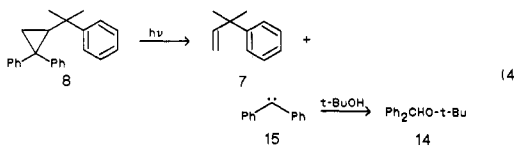
Exploratory Photochemistry of Triphenylcyclobutane 12. The question of whether triphenylcyclobutane **12** is a plausible reaction intermediate was answered affirmatively by the observation that independent direct irradiation of this compound afforded diphenylethylene **3** and phenylisobutylene **13**. Although two alternative modes of cleavage of the cyclobutane might be envisaged, the reaction was regioselective as shown in eq 3, a point



(3)

to be considered (vide infra). This evidence demonstrated that triphenylcyclobutane **12** was a potential intermediate in the arylcyclopropylmethane photochemistry, since the same two photoproducts were produced from the cyclobutane and, additionally, no products were formed in the photochemistry of the cyclobutane which were not seen in the arylcyclopropylmethane irradiations.

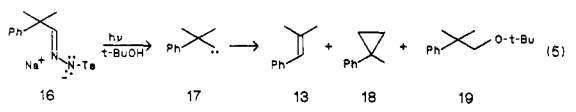
Possibility of a Griffin Fragmentation Mechanism. A second mechanism for the photochemistry was suggested by the observation of the phenylbutene **7** and the *tert*-butyl ether **14**. These clearly arise from Griffin fragmentation[8] of the three-membered ring of arylcyclopropane **8** as shown in eq 4.



(4)

An analogous Griffin fragmentation, with differing regioselectivity, seemed possible in affording the two remaining alkenes, diphenylethylene **3** and phenylisobutylene **13**. Such a fragmentation would afford **3** directly and also carbene **17**. The latter would be expected[9] to rearrange to afford the phenylisobutylene **13**.

Thus we needed to define the actual behavior of carbene **17**. This was generated by the photolysis of the sodium conjugate base of tosylhydrazone **16** as outlined in eq 5.



(5)

Indeed, phenylisobutylene **13** was formed. However, in addition, the cyclopropane **18** and *tert*-butyl ether **19** were observed, and these were products not encountered in the arylcyclopropylmethane irradiation. These results are in good agreement with those of Schechter[10] except for the observation of *tert*-butyl ether **19** due to *tert*-butyl alcohol presently being employed. The finding that carbene **17** gives different results than encountered in the photochemistry of arylcyclopropylmethane **8** makes it clear that the carbene is not an intermediate in the photochemistry of **8** presently studied. This point is considered below.

Table I. Quantum Yield Results

run	sensitizer	% convn	quantum yields 13	3	7
1	none	1.3	0.017	0.018	0.025
2	none	2.5	0.016	0.018	0.024
3	none	4.0	0.016	0.017	0.024
4	none	6.1	0.015	0.015	0.022
5	acetophenone		<0.0001	<0.0001	<0.0001
6	acetone		<0.0001	<0.0001	<0.0001

Table II. Single Photon Counting Data for Arylcyclopropylmethane 8

observable	T, K	value obtained
$^1k_{d(tot)}$	77	2.6×10^7 s^{-1}
$^1k_{d(tot)}$	293	1.1×10^9 s^{-1}
M[a]		42
τ	77	38 ns
τ	293	900 ns
^1k_r	77	1.1×10^6 s^{-1}
^1k_r	293	4.7×10^7 s^{-1}

[a] Magic multiplier.

Quantum Yield Determinations. These were determined by using the Black Box apparatus and electronic actinometer described by us previously.[11] Products were assayed by GLC as described in Experimental Section. Runs were made at varying conversions with the intent of extrapolation to 0% conversion; however, little dependence on conversion was noted. Finally, no detectible reaction was observed on sensitization with either acetophenone or acetone. The quantum yields are summarized in Table I.

Singlet Rate Studies. The singlet lifetimes of the arylcyclopropylmethane **8** were determined at 77 and 293 K by the single photon counting methods previously described.[12] The ratio of 77 K to room-temperature rates, the "magic multiplier" (cf. Experimental Section), was determined as 42. The relationship $k_r = (\phi_r)(k_{d(tot)})$ was used to determine the rate of reaction. The results of the single photon counting experiments are summarized in Table II.

Dynamic Isotope Dilution Determination of the Role of a Cyclobutane Intermediate. It has been noted that triphenylcyclobutane **12** is a potential intermediate in the conversion of arylcyclopropylmethane **8** to afford photoproducts (i.e., diphenylethylene and phenylisobutylene). To determine whether the reaction was of the type A → C or A → B → C or some combination of these pathways, we turned to the method of dynamic isotope dilution we reported earlier.[3] The method required running the photolysis to varying extents of conversion with addition of the labeled potential intermediate (i.e., dideuteriotriphenylcyclobutane, **12D**) followed by analysis of the composition of the mixtures. The method makes use of eq 6a. Here the initial amount of starting material is represented by A_0, the amount of starting material by

(7) (a) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbery, R. *J. Am. Chem. Soc.* **1957**, *89*, 5466–5468. (b) Evans, D. F. *J. Chem. Soc.* **1959**, 2753–2757. (c) Borkman, R. F.; Kerns, D. R. *J. Chem. Phys.* **1966**, *44*, 945–949.

(8) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537–547.

(9) (a) Landgrebe, J. A.; Kirk, A. G. *J. Org. Chem.* **1967**, *32*, 3499–3506. (b) Zimmerman, H. E.; Munch, J. H. *J. Am. Chem. Soc.* **1968**, *90*, 187–196.

(10) Kraska, A. R.; Chang, K.-T.; Moseley, C. G.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 1627–1630.

(11) (a) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292. (b) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochem.* **1977**, *8*, 379–385.

(12) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1973**, *95*, 5094–5095.

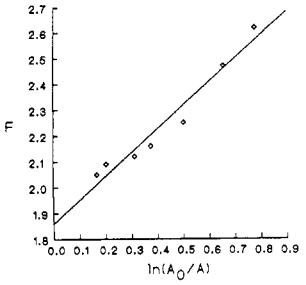
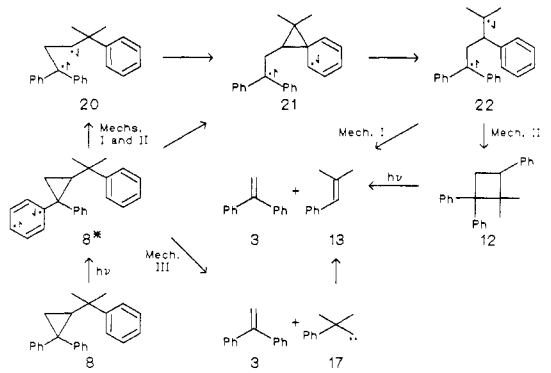


Figure 1. Dynamic isotope dilution plot of F versus ln (A_0/A).

Scheme II. Three Alternative Mechanisms Leading to Photoproducts



A, the initial amount of labeled cyclobutane **12D** by B^*_0, the amount of labeled cyclobutane remaining by B^*, and the amount of residual unlabeled cyclobutane by B. The compounds were separated by column chromatography and the deuteration of B was determined by NMR using 1024 scans.

$$F = \ln\left[\frac{B^*_0(B^*A_0 - B^*_0A)}{B^*(B^*_0B - B^*B_0)}\right] = L \ln (A_0/A) + I \quad (6a)$$

$$L = \phi_{bc}\epsilon_b/(\phi_{ab} + \phi_{ac})\epsilon_a \quad (6b)$$

$$I = \ln (1 - L)/M \text{ or } M = \ln (1 - L)/I \quad (6c)$$

$$M = \phi_{ab}/(\phi_{ab} + \phi_{ac}) \text{ or } \phi_{ab}/\phi_{ac} = M/(1 - M) \quad (6d)$$

From a plot of the seven points obtained, a slope of L = 0.93 and an intercept, I, was obtained; see Figure 1. Equation 6c, in conjunction with the value of L obtained, afforded a value of M = 0.011. This, applied to eq 6d, gives us the ratio between the two mechanistic pathways A → C and A → B → C as 91:1 (± 0.2).

Interpretive Discussion

Alternative Mechanistic Possibilities. Three reasonable mechanistic alternatives present themselves. These are termed mechanisms I, II, and III and are outlined in Scheme II. Two of the three possibilities, I and II, begin as a homo-di-π-methane rearrangement. Thus, arylcyclopropylmethane 8 is excited to its singlet, one three-membered ring bond opens to afford singlet diradical **20**, and bridging between the less stabilized diradical center and the isolated phenyl group leads to diradical species **21**. It is known that phenylcyclopropanes have lower energies than isolated phenyl groups and that there is interaction between the phenyl and cyclopropyl moieties in the excited state.[13] Thus it is possible that diradical **20** is not formed as a discrete species and that the excited phenylcyclopropyl moiety of 8* bridges directly. Also we see that diradical **21** is analogous to the half-migrated species in the free-radical 1,2-shift of a β-phenylethyl radical.[14] Completion of the migration process leads to the 1,4-diradical **22**.

Table III Comparison of Two Examples of Homo-Di-π-Methane Reactivity

reactant	quantum yield, ϕ	excited state rate ^1k_r, s^{-1}	total decay rate $^1k_{d(tot)}$, s^{-1}
1	0.018	7.0×10^8	3.9×10^{10}
8	0.018	2.0×10^7	1.1×10^9

[a] The reaction rates refer only to the portion undergoing the homo-di-π-methane rearrangement. [b] The rates are at room temperature.

It is at this juncture that the two mechanisms diverge. In one option (mechanism I) the 1,4-diradical **22** undergoes a direct 1,4-(2,3)-fragmentation[15] to afford the observed reaction products, diphenylethylene **3** and phenylisobutylene **13**. In the other option (mechanism II) the 1,4-diradical closes to form triphenylcyclobutane **12** which, in secondary photochemistry, undergoes four-membered ring fission to afford **3** and **13**. We delay further discussion of these two pathways momentarily.

Scheme II also provides the third alternative mechanism, III. Here the reaction begins with a Griffin fragmentation[8] cited as a possibility earlier. One of the two modes of Griffin fragmentation has been described in eq 4 and clearly is utilized. However, mechanism III (note Scheme II) requires a regioisomeric fission in which diphenylethylene and carbene **17** are formed. The rearrangement of **17** to phenylisobutylene has precedent.[9]

Question of Intervention of Carbene 17. There are several observations which argue against mechanism III considered above. When generated independently and photochemically (vide supra, refer to eq 5), carbene **17** undergoes insertion to form phenylmethylcyclopropane **18** and *tert*-butyl ether **19** as its reaction products. However, these were not detected in the homo-di-π-methane photochemistry. Secondly, in an elegant study, Hixson[16] has noted that in the Griffin fragmentation reaction very high regioselectivities result and that formation of the most stabilized carbene is controlling. In the present study, formation of diphenylcarbene would have to be only slightly preferred over formation of diphenylethylene **3** and phenylisobutylene **13**, both of which would result from the regioisomeric three-membered fragmentation.

Two Homo-Di-π-Methane Mechanisms. Mechanisms I and II differ in whether or not triphenylcyclobutane **12** is an intermediate. As noted above, the problem invited the use of dynamic isotope dilution which led to the observed partition of mechanism I and mechanism II in a ratio of 91:1 (vide supra), a result qualitatively consistent with the observation of minor amounts of triphenylcyclobutane **12** using NMR analysis.

Parenthetically, it needs to be clarified that the dynamic isotope dilution results may not be construed as adding to the evidence excluding mechanism III, since these merely give the ratio of a direct (i.e. A → C) versus an

(13) (a) Energy derived from: Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971; p 175. (b) Becker, R. S.; Edwards, L.; Bost, R.; Elam, M.; Griffin, G. *J. Am. Chem. Soc.* **1972**, *94*, 6584–6592.

(14) (a) Winstein, S.; Seubold, F. H. *J. Am. Chem. Soc.* **1947**, *69*, 2916–2917. (b) Rüchardt, C.; Trautwein, H. *Chem. Ber.* **1962**, *95*, 1197–1205.

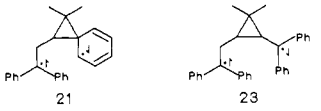
(15) (a) Alternatively[15b] this may be termed a Grob[15c] fragmentation in analogy of those polar ground-state transformations. (b) Zimmerman, H. E.; Factor, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 3538–3548. (c) Grob, C. A.; Schiess, P. W. *Angew. Chem.* **1967**, *79*, 1–14.

(16) Hixson, S. S. *J. Am. Chem. Soc.* **1973**, *95*, 6144–6145.

indirect (i.e. A → B → C) mechanism. Mechanism III, excluded on other grounds (vide supra), does qualify as a direct mechanism.

Comparison with the Diphenylvinyl Analogue. Our one previous example[4] of the homo-di-π-methane rearrangement (eq 1) proceeded with a quantum yield (ϕ = 0.018) experimentally the same as that observed presently (ϕ = 0.018). However, the S_1 reaction rate, as well as the rate of radiationless decay, was considerably higher; refer to Table III.

In the bridging of the diphenylvinyl homo-di-π-methane system of our previous study (eq 1), the reactant energy is that of the diphenylethylene S_1 excited moiety, which is approximately 100 kcal/mol[13a] above ground state. The presently studied arylcyclopropylmethane singlet 8* is 104 kcal/mol[13b] above ground state. Thus we find relatively little difference in starting S_1 energies. Starting excited state energies may well be a factor in controlling reactivity.[17] However, in comparing the diradical bridged species **23** derived from the diphenylvinyl homo-di-π-methane



reactant **1** with diradical **21** (note Scheme II) of the present study, we note loss of aromaticity of an unexcited phenyl group in **21**, a factor not involved in the diphenylvinyl case. Thus, of diradicals **21** and **23**, the latter may be seen to be considerably lower in energy. This factor may account for the ca. 20-fold difference in reaction rates.

The much slower excited state decay (note Table III) of the present system compared with diphenylvinyl accounts for the quantum efficiency being similar to the two cases, since ϕ is given by the ratio of the rate of reaction to the total rate of decay. The present lower decay rate may derive from the vertical excitation not being localized in a diphenylvinyl chromophore. An excited diphenylvinyl moiety provides a free-rotor mechanism for decay which would be faster than decay by reversible three-membered ring opening which is possible in the present example.

Lack of Triplet Reactivity of the Homo-Di-π-Methane System. The lack of reactivity on sensitization must arise from some mode of facile triplet decay. In view of the absence of free rotors which might dissipate triplet energy, it seems likely that reversible three-membered ring opening is responsible for the unreactive triplet behavior. In this interpretation, once the three-membered ring is opened any singlet diradical must bridge to afford homo-di-π-methane reaction while the triplet must revert to reactant.

Factors Controlling Fragmentation versus Ring Closure of Singlet 1,4-Diradicals. One observation of considerable interest is the preference for 1,4-(2,3)-fragmentation over closure to cyclobutane product exhibited by the singlet of 1,4-diradicals of the present system. This is reminiscent of the behavior of ground state and S_1 cyclopropyldicarbinyl diradicals occurring in the di-π-methane rearrangement where the evidence is that the S_0 diradical undergoes a 1,4-(2,3)-fragmentation (i.e. a Grob fragmentation[15]) while the S_1 diradical proceeds onward along the excited hypersurface toward the di-π-methane product.

Relative to the present chemistry, the correlation diagram given in Figure 2 is helpful. This shows that the fragmentation reaction of a homopolar 1,4-diradical is

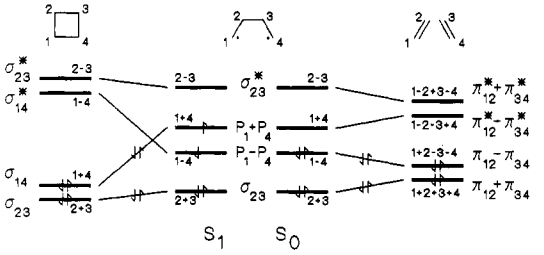


Figure 2. Correlation diagram for reactions of tetramethyl diradicals.

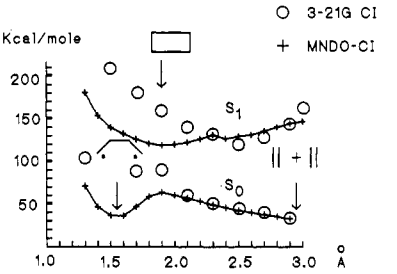


Figure 3. MNDO-CI and ab initio energies of S_0 and S_1 tetramethylene as function of stretching of bond 2–3.

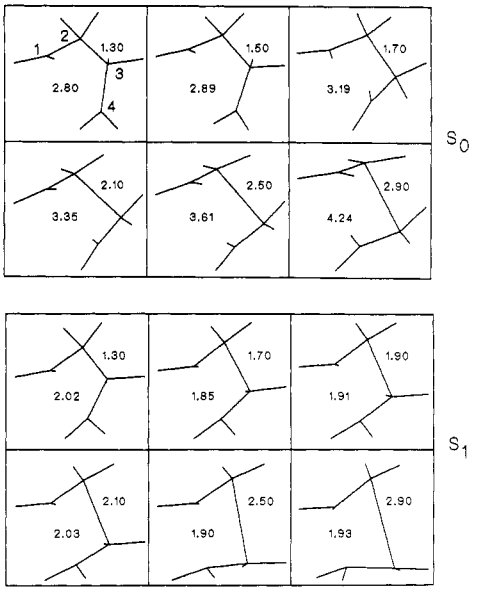


Figure 4. Geometry changes on stretching of bond 2–3 of S_0 and S_1 tetramethylene diradical. Distances 1–4 and 2–3 are in Å.

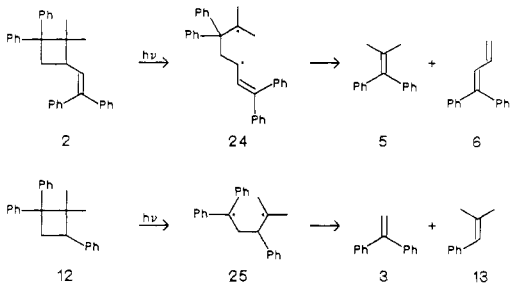
ground-state allowed and excited-state forbidden while ring closure to cyclobutane product is excited-state allowed and ground-state forbidden.

Also relevant are the results of a MNDO-CI and ab initio calculations on central bond stretching of the tetramethylene 1,4-diradical.[18] These calculations were carried out in the cisoid conformation optimizing geometry both

(17) Zimmerman, H. E.; Gruenbaum, W. T.; Klun, R. T.; Steinmetz, M. G.; Welter, T. R. *J. Chem. Soc., Chem. Commun.* **1978**, 228–230.

(18) (a) Our computations were carried out only on the cisoid conformer in order to assess the tendency of this conformer to fragment versus to close. Thus, we have carried out an exploration of only a part of the hypersurface. (b) In Figure 3, it needs to be recognized that the S_0 and S_1 curves are not contained in precisely the same hypersurface cross section but have in common only the distance between atoms 2 and 3; thus the bond distance 1–4 differs for these two states at any given distance 2–3. (c) Computations have been carried out on tetramethylene diradical with different geometries and generally for S_0 rather than S_1,[18d-g] most commonly trans. (d) Segal, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 7892–7898. (e) Doubleday, C.; Camp, R. N.; King, J. W.; McIver, J.; Mullally, D.; Page, M. *J. Am. Chem. Soc.* **1984**, *106*, 447–448. Doubleday, C.; McIver, J. W., Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 3768–3770. These authors found a very flat S_0 surface.

Scheme III. Regioselectivity and Mechanism of Cyclobutane Fragmentations



for the S_0 and S_1 states using MNDO. For S_0 the open diradical leads to the Grob fragmented pair of ethylenes. Increasing CI diminishes an apparent barrier while the ab initio 3-21G with CI, but using MNDO geometry, leads to essentially no barrier. Note Figure 3. In contrast, for S_1 an energy minimum occurs. This species corresponds to rectangular geometry in the case of MNDO computations.

Stretching bond 2–3 in S_1 further leads to a rise in energy and an attempt of atoms 1 and 4 to approach one another. The contrast between the S_0 and S_1 behavior is seen in Figures 4a and 4b which depict the change in optimized geometry as bond 2–3 is stretched.

Hence, cyclobutane formation is expected from cisoid S_1 and Grob fragmentation is anticipated from S_0. In the present study involving direct irradiation we see primarily Grob fragmentation. The small amount of cyclobutane formation most likely derives from the initial S_1 excited state formed on direct irradiation. The predominance of fragmentation then derives either from a facile radiationless decay to S_0, or alternatively, an initial formation of the transoid tetramethylene diradical which sterically cannot close as rapidly as radiationless decay occurs.

Mechanism and Regioselectivity of the Cyclobutane Cleavage. In both our previous study and the present one, the photochemical cleavage of the cyclobutanes occurred in a regioselective manner as depicted in Scheme III. The common factor controlling the regioselectivity seems to be formation of the lowest energy diradical. In the case of cyclobutane **2**, the lowest energy and initial excitation is in the diphenylvinyl chromophore, and one can expect an adjacent bond to be opened which leads to the most stable diradical.

In the present case, that of cyclobutane **12**, excitation seems likely to be distributed among the three phenyl groups. Nevertheless, regioselectivity is observed. The product, again, is the one deriving from the most stable diradical (i.e. **25**).

A further point derives from consideration of the correlation diagram of Figure 2. The S_1 formation of cyclobutane from diradical **25** was noted to be allowed. Similarly, the reverse reaction converting the cyclobutane to the diradical is allowed. Furthermore, HOMO and LUMO cross in the correlation diagram, thus providing a mode of S_1 to S_0 decay and a route to the S_0 1,4-diradical **25** which is then expected to fragment by an allowed pathway. This is suggested[18b] in the approach of S_0 and S_1 surfaces in the SCF-CI results as depicted in Figure 3.

Conclusion. The present study provides a second example of the homo-di-π-methane rearrangement. Beyond this, however, it is noted that there is consistency in the behavior of electronically excited states. Thus, the homo-di-π-methane rearrangement extends to the arylcyclopropylmethane system just as the di-π-methane rearrangement extends to the arylvinyl version. Yet each new system exhibits reactivity characteristic of the given excited state structure. Hence our aim continues to be the exploration of excited state chemistry until this field of endeavor has reached the level of sophistication characteristic of ground-state mechanisms where a priori predictions of reactivity are more likely to be successful.

Experimental Section[19]

2-(2,2-Diphenylcyclopropyl)-2-phenylpropane (8). A solution of 5.54 g (30.4 mmol) of diphenyldiazomethane in 20 mL of photolysis-grade benzene was slowly added to a solution of 2.15 g (14.7 mmol) of 3-methyl-3-phenyl-1-butene[20] in 120 mL of photolysis-grade benzene as irradiation was done through a Pyrex glass filter. The mixture was photolyzed for 4 h as the addition took place. After addition was complete, the mixture was photolyzed 0.5 h more, concentrated in vacuo, and chromatographed on a 120 × 3 cm silica gel column eluting with hexane: fraction 1, 700 mL, 0.63 g of 3-methyl-3-phenyl-1-butene; fraction 3, 500 mL, 1.22 g of crude 2-(2,2-diphenylcyclopropyl)-2-phenylpropane as a white solid, mp 91–103 °C. Recrystallization from HPLC hexane afforded 1.07 g (24%) of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane as colorless prisms, mp 113–114 °C.

The spectral data were as follows: ($CHCl_3$) 3070, 3010, 2975, 2880, 1605, 1585, 1495 (s), 1450, 1395, 1370, 1165, 1105, 1085, 1040, 705, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0–7.3 (m, 15 H, Ar), 2.052 (dd, 1 H, J = 9.5 Hz, 7.2 Hz, cyclopropyl), 1.685 (dd, 1 H, J = 5.0 Hz, 7.2 Hz, cyclopropyl), 1.170 (dd, 1 H, J = 5.0, 9.5 Hz, cyclopropyl), 1.089 (s, 3 H, CH_3), 1.046 (s, 3 H, CH_3); UV λ_{max} (EtOH) 273 sh (ϵ 350), 266 (700), 259 (850), 253 nm (720); MS, m/e 312.1875 (calcd for $C_{24}H_{24}$, m/e 312.1877).

Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.23; H, 7.73.

2,2-Dimethyl-1,3,3-triphenylcyclobutanol (10). Phenylmagnesium bromide was prepared from 2.0 g (82.2 mmol) of magnesium turnings and 8.0 mL (76 mmol) of bromobenzene in 70 mL of anhydrous ether. A solution of 2.218 g (8.86 mmol) of 2,2-dimethyl-3,3-diphenylcyclobutanone[4] in 50 mL of ether was added dropwise, and the mixture was stirred for 1 h. Neutral workup[19] gave 2.59 g (89%) of crude 2,2-dimethyl-1,3,3-triphenylcyclobutanol as a yellowish solid, mp 106–109 °C. Recrystallization from hexane afforded 2.44 g (84%) of 2,2-di-

(19) Melting points were determined on a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, TN 37921. All reactions were performed under an atmosphere of dry nitrogen unless stated otherwise. Anhydrous magnesium sulfate or sodium sulfate was used as drying agent. Neutral workup involved quenching the reaction with water, thorough ether extraction, washing the organic phase with water and brine, drying, filtering, and concentration in vacuo. Exploratory photolyses were done by using an immersion Hanovia 450-W medium pressure mercury arc lamp equipped with the appropriate 2-mm filter. All photolyses were thoroughly purged with deoxygenated nitrogen prior to the photolysis. Photolyses in *tert*-butyl alcohol and benzene were also purged during the course of photolysis, while photolyses in pentane were carried out with an atmosphere of nitrogen maintained over the solution of the photochemical reactant.

Column chromatography was performed on silica gel (Matheson, Coleman, and Bell, grade 62, 60–200 mesh) mixed with Sylvania 2282 phosphor slurry packed into Vycor columns, which permitted monitoring with a hand-held UV lamp. Preparative thin layer chromatography was carried out with MN Kieselgel G/UV 254 silica gel or Merck aluminum oxide 60 GF 254 neutral (type E) alumina. Analytical gas–liquid chromatography (GLC) was performed on a Varian series 2100 chromatograph with a 0.32 × 150 cm glass column packed with 10% QF-1 on 100–120-mesh Varaport 30, with nitrogen as the carrier gas at a flow rate of 40 mL/min.

Tetrahydrofuran (THF) and dimethoxyethane (DME) were purified by storage over potassium hydroxide, followed by successive distillation under a nitrogen atmosphere from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. *tert*-Butyl alcohol used for photolyses was distilled from calcium hydride prior to use. Pentane used for photolyses was washed with nitric acid and sulfuric acid (1:1), water, saturated aqueous sodium bicarbonate, and brine, dried over anhydrous calcium chloride, passed through neutral alumina, and distilled from calcium hydride. Benzene used for photolyses was washed with saturated potassium permanganate in 10% aqueous sulfuric acid, water, saturated aqueous sodium bicarbonate, and brine, dried over anhydrous calcium chloride, and distilled from calcium hydride. Sodium hydride was obtained as a 56% dispersion in mineral oil, which was washed with ether and dried before use.

(20) Swafford, R. L. Ph.D. Thesis, University of Wisconsin, 1981.

methyl-1,3,3-triphenylcyclobutanol as colorless prisms, mp 114–115 °C.

The spectral data were as follows: IR ($CHCl_3$) 3560, 3350 (br), 3080, 3050, 2990, 2965, 2930, 1600, 1580, 1495 (s), 1465, 1450, 1390, 1370, 1190, 1155, 1140, 1095, 1070, 1030, 1015, 990, 975, 915, 895, 865, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7–6.9 (m, 15 H, Ar), 3.42 (AB q, J = 12 Hz, 2 H, CH_2), 1.90 (br s, 1 H, OH), 1.38 (s, 3 H, CH_3), 0.79 (s, 3 H, CH_3); MS, m/e 328.1826 (calcd for $C_{24}H_{24}O$, m/e 328.1826).

Anal. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.36. Found: C, 87.69; H, 7.38.

2,2-Dimethyl-1-methoxy-1,3,3-triphenylcyclobutane (11). To a solution of 2.15 g (6.55 mmol) of 2,2-dimethyl-1,3,3-triphenylcyclobutanol and 1.0 mL (2.28 g, 16.1 mmol) of methyl iodide in 50 mL of dimethoxyethane was added 0.375 g (15.7 mmol) of sodium hydride. The mixture was stirred at reflux for 16 h and then subjected to neutral workup[19] which yielded 2.11 g (94%) of crude 2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane as a yellow solid, mp 108–112 °C. Recrystallization from pentane afforded 2.01 g (90%) of pure 2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane as colorless prisms, mp 117.0–117.5 °C.

The spectral data were as follows: IR ($CHCl_3$) 3085, 3060, 3010, 2970, 2940, 2825, 1685, 1655, 1600, 1560, 1540, 1510, 1490, 1465, 1445, 1390, 1365, 1290, 1155, 1135, 1085, 1075, 980, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–6.9 (m, 15 H, Ar), 3.30 (AB q, J = 12 Hz, 2 H, CH_2), 2.82 (s, 3 H, OCH_3), 1.35 (s, 3 H, CH_3), 0.71 (s, 3 H, CH_3); MS, m/e 342.1984 (calcd for $C_{25}H_{26}O$, m/e 342.1983).

Anal. Calcd for $C_{25}H_{26}O$: C, 87.68; H, 7.65. Found: C, 87.78; H, 7.61.

2,2-Dimethyl-1,1,3-triphenylcyclobutane (12). To a solution of 0.516 g (1.51 mmol) of 2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane in 10 mL of ether was added 0.050 mL (1.47 mmol) of 1:1 (mole ratio, w/w 37:63) sodium–potassium alloy via hypodermic syringe. After an induction period of 10 min, the solution turned deep red. The solution was stirred for 75 min and then quenched with 5.0 mL of ethanol. Neutral workup[19] gave 0.53 g of a colorless foam. NMR analysis of the crude product indicated approximately 40% conversion to the desired 2,2-dimethyl-1,1,3-triphenylcyclobutane. The rest of the material was unreacted 2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane. The mixture was chromatographed on a 37 × 2 cm silica gel column eluting with hexane taking 250-mL fractions: fractions 2–4, 209 mg (44%) of 2,2-dimethyl-1,1,3-triphenylcyclobutane as a colorless solid, mp 105–107 °C; fraction 5, 23.8 mg of a mixture of 2,2-dimethyl-1,1,3-triphenylcyclobutane and 2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane; fractions 6–8, 226.2 mg of 2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane. Recrystallization from pentane afforded 201 mg (43%) of 2,2-dimethyl-1,1,3-triphenylcyclobutane, mp 108–109 °C.

The spectral data were as follows: IR ($CHCl_3$) 3085, 3060, 3030, 3010, 2970, 2940, 2925, 2865, 1605, 1495, 1465, 1455, 1445, 1385, 1365, 1220, 1215, 1140, 1035, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6–7.0 (m, 15 H, Ar), 3.46 (dd, J = 6 Hz, 10 Hz, 1 H, cyclobutyl), 3.28 (dd, J = 6 Hz, 10 Hz, 1 H, cyclobutyl), 2.95 (t, J = 10 Hz, 1 H, cyclobutyl), 1.06 (s, 3 H, CH_3), 0.81 (s, 3 H, CH_3); UV (EtOH) λ_{max} 269 (ε 420), 265 (sh) (520), 262 (sh) (650), 259 (700), 254 (600), 249 nm (470); MS, m/e 312.1877 (calcd for $C_{24}H_{24}$, m/e 312.1877).

Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.74.

4,4-Dideuterio-2,2-dimethyl-3,3-diphenylcyclobutanone (9D). A solution of sodium deuteroxide in deuterium oxide, prepared by adding 4.4 mL (4.9 g, 240 mmol) of deuterium oxide (99.8% D) to 28.9 mg (1.26 mmol) of sodium metal under nitrogen, was added to 2.486 g (9.93 mmol) of 2,2-dimethyl-3,3-diphenylcyclobutanone in 25 mL of tetrahydrofuran. The mixture was stirred for 1 h, neutralized with 10 mL of 0.1 N hydrochloric acid, and quickly subjected to neutral workup,[19] to yield 2.30 g (92%) of crude 2,2-dimethyl-3,3-diphenylcyclobutanone which was found by NMR analysis to be 78% deuteriated. This procedure was repeated with the partially deuteriated 2,2-dimethyl-3,3-diphenylcyclobutanone in 25 mL of THF, using sodium deuteroxide in D_2O from 32.8 mg (1.43 mmol) of sodium and 5.0 mL (5.5 g, 280 mmol) of deuterium oxide (99.8% D). The same workup gave 1.86 g (81%) of crude 2,2-dimethyl-3,3-diphenylcyclobutanone, determined by NMR to be 91% deuteriated. A third exchange over a period of 5 h (25.7 mg (1.11 mmol) of sodium, 5.0 mL (5.5 g, 280 mmol) of deuterium oxide) yielded 1.70 g (91%) of crude 4,4-dideuterio-2,2-dimethyl-3,3-diphenylcyclobutanone, mp 79–80 °C, which was found to be >99% deuteriated by NMR analysis. Recrystallization from methanol gave 1.64 g (66% yield overall) of 4,4-dideuterio-2,2-dimethyl-3,3-diphenylcyclobutanone, mp 81.0–81.5 °C.

The spectral data were as follows: IR ($CHCl_3$) 3090, 3060, 3030, 3010, 2980, 2970, 2940, 2905, 2865, 2235, 1775 (s), 1600, 1495, 1460, 1445, 1390, 1365, 1150, 1105, 1080, 1010, 925, 890, 805, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (m, 10 H, Ar), 1.12 (s, 6 H, CH_3); MS, m/e 226.1326 (calcd for $C_{18}H_{14}D_2O$, m/e 226.1327).

4,4-Dideuterio-2,2-dimethyl-1,3,3-triphenylcyclobutanol (10D). To a solution of 1.29 g (5.10 mmol) of 4,4-dideuterio-2,2-dimethyl-3,3-diphenylcyclobutanone in 20 mL of ether was added 10.0 mL of phenyllithium (0.88 M in ether, 11.3 mmol). The mixture was stirred for 2 h. Neutral workup[19] afforded 1.36 g (81%) of crude 4,4-dideuterio-2,2-dimethyl-1,3,3-triphenylcyclobutanol, mp 107–110 °C. Recrystallization from ether–hexane afforded 1.29 g (77%) of pure 4,4-dideuterio-2,2-dimethyl-1,3,3-cyclobutanol, mp 114–115 °C.

The spectral data were as follows: IR ($CHCl_3$) 3560, 3350 (br), 3080, 3050, 2990, 2965, 2930, 2245, 1600, 1580, 1495 (s), 1465, 1450, 1390, 1370, 1190, 1155, 1140, 1095, 1070, 1030, 1015, 990, 975, 915, 895, 865, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7–6.9 (m, 15 H, Ar), 1.90 (s, 1 H, OH), 1.38 (s, 3 H, CH_3), 0.79 (s, 3 H, CH_3); MS, m/e 330.1954 (calcd for $C_{24}H_{22}D_2O$, m/e 330.1952).

4,4-Dideuterio-2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane (11D). To a solution of 1.292 g (3.91 mmol) of 4,4-dideuterio-2,2-dimethyl-1,3,3-triphenylcyclobutanol and 1.0 mL (2.28 g, 16.1 mmol) of methyl iodide in 50 mL of DME was added 0.375 g (15.7 mmol) of sodium hydride. The mixture was stirred at reflux for 16 h. Neutral workup[19] gave 1.16 g (82%) of crude 4,4-dideuterio-2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane, mp 111–113 °C. Recrystallization from pentane afforded 1.08 g (80%) of pure 4,4-dideuterio-2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane, mp 117.0–117.5 °C.

The spectral data were as follows: IR ($CHCl_3$) 3085, 3060, 3010, 2970, 2940, 2825, 2250, 1685, 1655, 1600, 1560, 1540, 1510, 1490, 1465, 1445, 1390, 1365, 1290, 1155, 1135, 1085, 1075, 980, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–6.9 (m, 15 H, Ar), 2.82 (s, 3 H, OCH_3), 1.35 (s, 3 H, CH_3), 0.71 (s, 3 H, CH_3); M/S, m/e 344.2111 (calcd for $C_{25}H_{24}D_2O$, m/e 344.2109).

4,4-Dideuterio-2,2-dimethyl-1,1,3-triphenylcyclobutane (12D). To a solution of 0.518 g (1.51 mmol) of 4,4-dideuterio-2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane in 7.0 mL of ether was added 0.050 mL (1.47 mmol) of 1:1 (mole ratio, w/w 37:63) sodium–potassium alloy via hypodermic syringe. After an induction period of 15 min, the solution turned deep red. The solution was stirred for 80 min and then quenched with 5 mL of *tert*-butyl alcohol. Neutral workup[19] afforded 0.52 g of a colorless foam. NMR analysis of the crude product indicated approximately 70% conversion. The mixture was chromatographed on a 35 × 2 cm silica gel column eluting with hexane taking 250-mL fractions: fractions 2–4, 363 mg (73%) of 4,4-dideuterio-2,2-dimethyl-1,1,3-triphenylcyclobutane as a colorless solid, mp 104–107 °C; fraction 5, 31.7 mg of a mixture of 4,4-dideuterio-2,2-dimethyl-1,1,3-triphenylcyclobutane and 4,4-dideuterio-2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane; fraction 6–9, 112 mg of 4,4-dideuterio-2,2-dimethyl-1-methoxy-1,3,3-triphenylcyclobutane. Recrystallization from pentane afforded 345 mg (69%) of 4,4-dideuterio-2,2-dimethyl-1,1,3-triphenylcyclobutane, mp 108–109 °C. Analysis by NMR showed the compound to be >99% deuteriated.

The spectral data were as follows: IR ($CHCl_3$) 3085, 3060, 3030, 3010, 2970, 2940, 2925, 2865, 2260, 1605, 1495, 1465, 1455, 1445, 1385, 1365, 1220, 1215, 1140, 1035, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6–7.0 (m, 15 H, Ar), 3.46 (s, 1 H, cyclobutyl CH), 1.06 (s, 3 H, CH_3), 0.81 (s, 3 H, CH_3); UV (EtOH) λ_{max} 269 (ε 410), 265 (sh) (510), 262 (sh) (640), 259 (680), 254 (590), 249 nm (460); MS, m/e 314.2002 (calcd for $C_{24}H_{22}D_2$, m/e, 314.2003).

2-Methyl-2-phenylpropanal (*p*-Tolylsulfonyl)hydrazone (16). A solution of 2.65 g (18.1 mmol) of 2-methyl-2-phenylpropanal, 3.38 g (18.1 mmol) of *p*-tolylsulfonylhydrazide, and 0.2 mL of acetic acid in 50 mL of methanol was refluxed for 10 h. On cooling to 0 °C, a yellowish solid precipitated, which was

Table IV. Summary of Quantum Yield Results for 2-(2,2-Diphenylcyclopropyl)-2-phenylpropane

			product 13		product 3		product 7		
run	reactant 8, mmol	light abs, mE	mmol	ϕ	mmol	ϕ	mmol	ϕ	% convn
1	0.724	0.222	0.0038	0.0171	0.0040	0.0180	0.0055	0.0248	1.3
2	0.565	0.313	0.0051	0.0163	0.0055	0.0176	0.0076	0.0243	2.5
3	0.503	0.496	0.0079	0.0159	0.0085	0.0171	0.0117	0.0236	4.0
4	0.455	0.728	0.0108	0.0148	0.0112	0.0154	0.0163	0.0224	6.1

Table V. Summary of Quantum Yield Results for 2,2-Dimethyl-1,1,3-triphenylcyclobutane

			product 13		product 3		
run	reactant 12, mmol	light abs, mE	mmol	ϕ	mmol	ϕ	% convn
1	0.421	0.165	0.0083	0.0503	0.0084	0.0509	2.0
2	0.406	0.280	0.0139	0.0496	0.0141	0.0504	3.5
3	0.336	0.378	0.0186	0.0492	0.0189	0.0500	5.6
4	0.361	0.345	0.0172	0.0499	0.0173	0.0501	4.8

filtered and dried to give 4.42 g (78%) of crude 2-methyl-2-phenylpropanal (*p*-tolylsulfonyl)hydrazone, mp 108–111 °C. Recrystallization from methanol yielded 4.04 g (71%) of 2-methyl-2-phenylpropanal (*p*-tolylsulfonyl)hydrazone as colorless prisms, mp 120.0–120.5 °C.

The spectral data were as follows: IR ($CHCl_3$) 3210 (s), 3155, 2970, 2920, 2870, 1660, 1635, 1600 (s), 1490, 1465, 1445, 1420, 1360, 1320, 1180, 1165 (s), 1090, 1030, 1015, 1005, 945, 905, 850, 810, 765, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–6.9 (m, 10 H, Ar and HC=N), 2.47 (s, 3 H, $PhCH_3$), 1.59 (s, 1 H, NH), 1.34 (s, 6 H, $C(CH_3)_2$); MS, *m/e* 316.1243 (calcd for $C_{17}H_{20}N_2O_2S$, *m/e* 316.1245).

Anal. Calcd for $C_{17}H_{20}N_2O_2S$: C, 64.94; H, 6.41. Found: C, 64.85; H, 6.37.

Exploratory Direct Photolysis of 2-(2,2-Diphenylcyclopropyl)-2-phenylpropane in *tert*-Butyl Alcohol. A solution of 157 mg (0.502 mmol) of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane in 120 mL of *tert*-butyl alcohol was photolyzed for 2 h through a Vycor filter. Concentration in vacuo gave 144 mg (92%) of a yellowish oil which was shown by NMR spectroscopy to be a mixture of the starting 2-(2,2-diphenylcyclopropyl)-2-phenylpropane, 1,1-diphenylethylene, 2-methyl-1-phenylpropene, diphenylmethyl *tert*-butyl ether, and 3-methyl-3-phenyl-1-butene. This was chromatographed on a 20 × 20 cm preparative thin-layer silica gel plate, eluting once with pentane, to give five bands: 1, 5.3 mg (8%) of 2-methyl-1-phenylpropene; 2, 8.7 mg (12%) of 3-methyl-3-phenyl-1-butene; 3, 10.9 mg (12%) of 1,1-diphenylethylene; 4, 97.3 mg (62%) of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane; 5, 19.4 mg (16%) of diphenylmethyl *tert*-butyl ether. Each product was spectroscopically identical with authentic material.

Exploratory Direct Photolysis of 2-(2,2-Diphenylcyclopropyl)-2-phenylpropane in Pentane. A solution of 97.1 mg (0.311 mmol) of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane in 150 mL of pentane was irradiated for 30 min by using Vycor filter. Concentration in vacuo gave 85.4 mg (88%) of a yellow oil which was shown by NMR spectroscopy to be a mixture of the starting 2-(2,2-diphenylcyclopropyl)-2-phenylpropane, 1,1-diphenylethylene, 2-methyl-1-phenylpropene, and 3-methyl-3-phenyl-1-butene. A trace (less than 1%) of 2,2-dimethyl-1,1,3-triphenylcyclobutane could also be seen. Chromatography on a 20 × 20 cm preparative thin-layer silica gel plate eluting once with pentane gave four bands: 1, 4.5 mg (11%) of 2-methyl-1-phenylpropene; 2, 6.9 mg (15%) of 3-methyl-3-phenyl-1-butene; 3, 6.2 mg (11%) of 1,1-diphenylethylene; 4, 58.6 mg (62%) of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane. Each product was spectroscopically identical with authentic material.

Exploratory Acetone-Sensitized Photolysis of 2-(2,2-Diphenylcyclopropyl)-2-phenylpropane. A solution of 170 mg (0.544 mmol) of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane in 150 mL of acetone was photolyzed for 4 h by using a Vycor filter. The solvent was removed in vacuo to give 172 mg (101%) of a white solid. Analysis by NMR showed that the material was the starting 2-(2,2-diphenylcyclopropyl)-2-phenylpropane.

Exploratory Acetophenone-Sensitized Photolysis of 2-(2,2-Diphenylcyclopropyl)-2-phenylpropane. A solution of 122 mg (0.390 mmol) of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane and 16.0 mL (129 mmol) of acetophenone in 150 mL of pentane was photolyzed for 4 h through a Pyrex filter. Concentration in vacuo and removal of the acetophenone (50 °C, 0.1 Torr) gave 125 mg (103%) of a white solid which was shown to be the starting 2-(2,2-diphenylcyclopropyl)-2-phenylpropane by NMR analysis.

Exploratory Direct Photolysis of 2,2-Dimethyl-1,1,3-triphenylcyclobutane. A solution of 87.1 mg (0.278 mmol) of 2,2-dimethyl-1,1,3-triphenylcyclobutane in 150 mL of pentane was irradiated for 10 min by using a Vycor filter. The solvent was removed in vacuo to 83.4 mg (96%) of yellowish oily solid. NMR analysis of the product revealed 1,1-diphenylethylene, 2-methyl-1-phenylpropene, and starting material. This was chromatographed on a 20 × 20 cm preparative thin-layer silica gel plate which gave three bands: 1, 5.5 mg (15%) of 2-methyl-1-phenylpropene; 2, 7.6 mg (15%) of 1,1-diphenylethylene; 3, 69.0 mg (79%) of 2,2-dimethyl-1,1,3-triphenylcyclobutane. Each product was spectroscopically identical with authentic material.

Photochemical Carbene Generation from 2-Methyl-2-phenylpropanal (4-Tolylsulfonyl)hydrazone in Pentane–THF. A solution of 0.466 g (1.47 mmol) of 2-methyl-2-phenylpropanal (4-tolylsulfonyl)hydrazone in 20 mL of THF and 120 mL of pentane was prepared. To this solution was added 65 mg (2.6 mmol) of sodium hydride, and the mixture was purged with nitrogen for 30 min. The mixture was photolyzed for 20 min through a Pyrex filter as it was stirred. Neutral workup[19] gave 0.194 g of a yellow-orange oil which was chromatographed on a 20 × 20 cm preparative thin-layer silica gel plate, eluting once with pentane. Of two bands, the faster moving one contained 79.6 mg (41%) of 1-methyl-1-phenylcyclopropane and the slower moving band afforded 36.8 mg (19%) of 2-methyl-1-phenylpropene.

Photochemical Carbene Generation from 2-Methyl-2-phenylpropanal (4-Tolylsulfonyl)hydrazone in *tert*-Butyl Alcohol. A solution of 0.236 g (0.746 mmol) of 2-methyl-2-phenylpropanal (4-tolylsulfonyl)hydrazone and 0.584 g (5.20 mmol) of potassium *tert*-butoxide in 150 mL of *tert*-butyl alcohol was photolyzed for 2 h through a Pyrex filter. Neutral workup[19] gave 0.103 g of a yellow oil which was chromatographed on a 10 × 20 cm preparative thin-layer alumina plate, eluting once with pentane to give three bands: 1, 44.5 mg (45%) of 1-methyl-1-phenylcyclopropane; 2, 20.6 mg (21%) of 2-methyl-1-phenylpropene; 3, 5.8 mg (4%) of 2-methyl-2-phenylpropyl *tert*-butyl ether.

Photolysis Apparatus for Quantum Yield Determinations. All quantum yield determinations were performed by using the "Wisconsin Black Box".[11a] Light output for each run was measured by using a digital actinometer[11b] calibrated by ferrioxalate actinometry.[21] The filter solution combination (filter A) was cell 1, 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 0.8 M cobalt sulfate heptahydrate in 5% sulfuric acid; cell 3, 2.5 × 10^{-3} M bismuth trichloride monohydrate in 20% hydrochloric acid; transmission, 0% below 250 nm, 17% at 282 nm, 0% above 306 nm. Photolyses were carried out in 750-mL photo-grade pentane in a stirred cell and purged for 1 h before each run. Analysis by GLC[19] used triphenylmethane as an internal standard.

(21) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A*, **1956**, *23*, 518–521.

Table VI. Dynamic Isotope Dilution Data[a,b]

run	A_0, mmol[c]	A, mmol[c]	B^*_0, mmol	B, mmol	B^*, mmol	A_0/A	F
1	0.151	0.123	0.0832	0.0024	0.0773	0.205	2.09
2	0.120	0.0825	0.0518	0.0030	0.0455	0.376	2.16
3	0.107	0.0773	0.0728	0.0029	0.0686	0.314	2.12
4	0.0882	0.0746	0.0528	0.0014	0.0508	0.168	2.05
5	0.136	0.0818	0.0477	0.0045	0.0422	0.502	2.25
6	0.177	0.0810	0.0416	0.0056	0.0357	0.778	2.62
7	0.120	0.0628	0.359	0.0042	0.313	0.656	2.47

Results: L = 0.93; intercept = 1.86; M = 0.0109; ϕ_{ab}/ϕ_{ac} = 0.011

[a] B_0 was zero in all runs. [b] Estimated error ±10%. [c] Corrected values.

Temperature programming was used as follows: 5 min at 100 °C, increased at 4 °C/min to 180 °C, then held at 180 °C for the duration of the run. Retention times were 3-methyl-3-phenyl-1-butene, 2.9 min; 2-methyl-1-phenylpropene, 3.3 min; 1,1-diphenylethylene, 13.8 min; triphenylmethane, 24.8 min; 2-(2,2-diphenylcyclopropyl)-2-phenylpropane, 40.7 min; 2,2-dimethyl-1,1,3-triphenylcyclobutane, 58.9 min.

Quantum yield results for 2-(2,2-diphenylcyclopropyl)-2-phenylpropane and 2,2-dimethyl-1,1,3-triphenylcyclobutane are summarized in Tables IV and V, respectively.

General Procedure for Photolytic Deuterium-Labeled Dynamic Isotope Dilution Experiments. Photolyses were carried out in 750 mL of pentane in a stirred cell on the "Black Box"[11a] apparatus using filter A and purging for 1 h before irradiation. The photolysate was concentrated in vacuo and chromatographed on a 50 × 1.0 cm silica gel column eluted with hexane in 50-mL fractions to isolate 2,2-dimethyl-1,1,3-triphenylcyclobutane, which was analyzed by 200-MHz NMR spectroscopy using 1024 scans for the relative amounts of deuteriated to protiated material that had been recovered. Starting and final amounts of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane and 2,2-dimethyl-1,1,3-triphenylcyclobutane were determined by GLC[19] with triphenylmethane as a standard. Retention times (temperature 190 °C) were triphenylmethane, 4.5 min; 2-(2,2-diphenylcyclopropyl)-2-phenylpropane, 13.6 min; 2,2-dimethyl-1,1,3-triphenylcyclobutane, 22.7 min.

Dynamic Isotope Dilution Experiment. Determination of the Amount of Direct Production of 2,2-Dimethyl-1,1,3-triphenylcyclobutane.[3] In these experiments, A_0 represents the corrected amount of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane at time zero, A is the corrected amount of 2-(2,2-diphenylcyclopropyl)-2-phenylpropane at the conclusion of photolysis, B_0 is the amount of 2,2-dimethyl-1,1,3-triphenylcyclobutane at time zero (zero presently), B is the amount of 2,2-dimethyl-1,1,3-triphenylcyclobutane after completion of the photolysis, B^*_0 is the quantity of 4,4-dideuterio-2,2-dimethyl-1,1,3-triphenylcyclobutane at time zero, and B^* is the quantity of 4,4-dideuterio-2,2-dimethyl-1,1,3-triphenylcyclobutane at the conclusion of photolysis. The correction factor of 0.420 (ϕ_{ac}/ϕ_{dis}) was applied to A and A_0 to account for the existence of the separate Griffin fragmentation pathway. The results are summarized in Table VI.

Single Photon Counting. Determination of the Rate of Excited Singlet-State Rearrangement of 2-(2,2-Diphenylcyclopropyl)-2-phenylpropane. The apparatus and procedure have been described previously.[12] 2-(2,2-Diphenylcyclopropyl)-2-phenylpropane used in single photon counting measurements was recrystallized five times from HPLC-grade hexane and twice from fluorescence-grade methylcyclohexane. Solvents were methylcyclohexane (Kodak Spectral Grade) and isopentane purified as described previously.[12] Individual samples were prepared in a 4:1 methylcyclohexane–isopentane solution to give an optical density in the range 0.8–1.5, thoroughly degassed by at least 4 freeze–thaw cycles on a vacuum line immediately before counting and counted at 77 K until a minimum of 2000 counts in the maximum channel (512 channels) was obtained. Data were collected at less than 5% of the 30–40-kHz lamp flash rate to ensure exclusion of double-photon counting. In separate runs excitation was varied from 265 to 275 nm and emission was monitored over the range 300–315 nm with an RCA 8850 photomultiplier. The decay rate was independent of excitation and emission wavelengths employed. A single exponential decay function was found in all runs. Six runs were carried out. The data are summarized in Table II.

Magic Multiplier. For each run, the fluorescence spectrum was recorded in 4:1 methylcyclohexane–isopentane solution at 77 and 293 K under otherwise identical conditions using an Aminco-Kiers spectrofluorometer with a Hanovia 901C-1 150-W xenon lamp. Concentrations were adjusted to give an optical density in the range of 1.0–2.0 to minimize scatter. An excitation wavelength of 250 nm was used. The magic multiplier was obtained from a single sample by integrating the emission intensities obtained at the two temperatures. The value obtained was M = 42 (5 runs).

Quantum Mechanics Calculations. Quantum mechanics calculations for the tetramethylene diradical were performed with the MOPAC program package[22a] utilizing the MNDO approximation[22b] with two electron configuration interaction involving the HOMO and LUMO. Geometries were fully optimized (with the exception of bond 2–3, which was varied) with MOPAC using MINDO/3.[22c]

Acknowledgment. Support of this research by the National Science Foundation and NIH Grant GM07487 is gratefully acknowledged. The synthetic portions were supported by the National Institutes of Health while the mechanistic aspects were supported by NSF.

Registry No. **3**, 530-48-3; **7**, 18321-36-3; **8**, 94597-03-2; **9**, 56405-91-5; **9d**, 114274-24-7; **10**, 114274-27-0; **10d**, 114274-25-8; **11**, 114274-28-1; **11d**, 114274-26-9; **12**, 114274-29-2; **12d**, 114274-30-5; **13**, 768-49-0; **14**, 28567-35-3; **16**, 82518-00-1; **18**, 2214-14-4; **19**, 114274-31-6; Ph_2CN_2, 883-40-9; 2-methyl-2-phenylpropanal, 3805-10-5.

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