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Mechanistic and Exploratory Organic Photochemistry. Cyclopropene Photochemical Studies[1,2]

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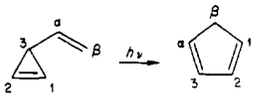
Our investigation of cyclopropene photochemistry was continued with the aim of exploring the nature and generality of the observed photochemistry as well as the reaction mechanisms utilized. Two cyclopropenes were studied. 1-Methyl-2,3-diphenyl-3-isobutenylcyclopropene and 1,2-diphenyl-3-methyl-3-isobutenylcyclopropene were found to afford cyclopentadienes and indenes in accord with previous investigations. The former on direct irradiation afforded 2,3-diphenyl-1,5,5-trimethyl-1,3-cyclopentadiene as the major photoproduct; in addition, there were formed 1,3-diphenyl-2,5,5-trimethyl-1,3-cyclopentadiene, 1-methyl-2-phenyl-3-isobutenylindene, 1-phenyl-2-methyl-3-isobutenylindene, and 1,2-diphenyl-3-methyl-3-isobutenylcyclopropene. In contrast, the sensitized photolysis of the 1-methylcyclopropene led to the 2,3-diphenylcyclopentadiene and 1,2-diphenyl-3,5,5-trimethyl-1,3-cyclopentadiene. In the case of the 3-methylcyclopropene direct irradiation yielded 1,2-diphenyl-3,5,5-trimethyl-1,3-cyclopentadiene as the major product and lesser amounts of the 1-methylcyclopropene. Sensitized photolysis gave the 1,2-diphenylcyclopentadiene as well as the 2,3-diphenylcyclopentadiene. The preferential formation of 2,3-diphenyl-1,5,5-trimethyl-1,3-cyclopentadiene in the direct irradiation of the 1-methylcyclopropene as well as the overwhelming preference for this product in the triplet runs is discussed as evidence favoring a diradical rather than a carbene mechanism. The interconversions of the different vinylcyclopropenes are understood as an incipient di-π-methane rearrangement involving a diradical mechanism. Another approach to studying the mechanism involved independent generation of that carbene which would have to be the intermediate leading to the major cyclopropene photoproduct, if one assumes a carbene mechanism. 3,4-Diphenyl-6-methyl-3,5-heptadien-2-one tosylhydrazone and 3,4-diphenyl-5-methyl-3-isobutenyl-3*H*-pyrazole were utilized as carbene precursors, with photochemical generation of S_1 carbenes. The product distribution proved different from that obtained from the cyclopropene photochemistry.

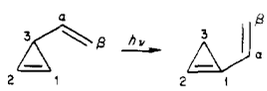
Studies in our laboratories[2b,3,4] and by Padwa and coworkers[5] have revealed the existence of some intriguing and new photochemical rearrangements. The goal of the present investigation was to enlarge the scope of these reactions, which have proven of considerable synthetic value, and also to cast further light on an especially interesting mechanistic question.

The overall structural change in one of two photorearrangements of vinylcyclopropenes can be depicted as in eq 1. For this, three reasonable, a priori mechanisms can



(1)

be written (vide infra); two have been considered previously.[2b,3,5] The other rearrangement involves a migration of the vinyl moiety in a potentially degenerate rearrangement as illustrated generally in eq 2.



(2)

For the present study we selected 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene (**1**) and 1,2-diphenyl-3-methyl-3-isobutenylcyclopropene (**2**). The 1-methylcyclopropene **1** promised to afford additional information on regioselectivity of the formation of cyclopentadienes and thus ascertain whether the pattern observed in the initial studies is indeed general. Also, this molecule seemed likely to cast light on the reaction mechanism. The 3-methyl-

(1) This is paper 119 of our photochemical series, 3 of the cyclopropene series.

(2) (a) For paper 118 of our series note H. E. Zimmerman, T. P. Gannett, and G. E. Keck, *J. Org. Chem.*, **44**, 1882 (1979). (b) For our previous paper on cyclopropene photochemistry note H. E. Zimmerman and S. M. Aasen, *J. Org. Chem.*, **43**, 1493 (1978).

(3) H. E. Zimmerman and S. M. Aasen, *J. Am. Chem. Soc.*, **99**, 2342 (1977).

(4) H. E. Zimmerman and R. A. Bunce, unpublished results.

(5) (a) A. Padwa, T. J. Blacklock, D. Getman, and N. Hatanaka, *J. Am. Chem. Soc.*, **99**, 2344 (1977); (b) A. Padwa and T. J. Blacklock, *ibid.*, **99**, 2345 (1977); (c) *idem*, *ibid.*, **100**, 1321 (1978); (d) A. Padwa, U. Chiacchio, and N. Hatanaka, *ibid.*, **100**, 3928 (1978);. (e) A. Padwa, T. J. Blacklock, D. Getman, N. Hatanaka, and R. Loza, *J. Org. Chem.*, **43**, 1481 (1978); (f) A. Padwa, R. Loza, and D. Getman, *Tetrahedron Lett.*, 2847 (1977).

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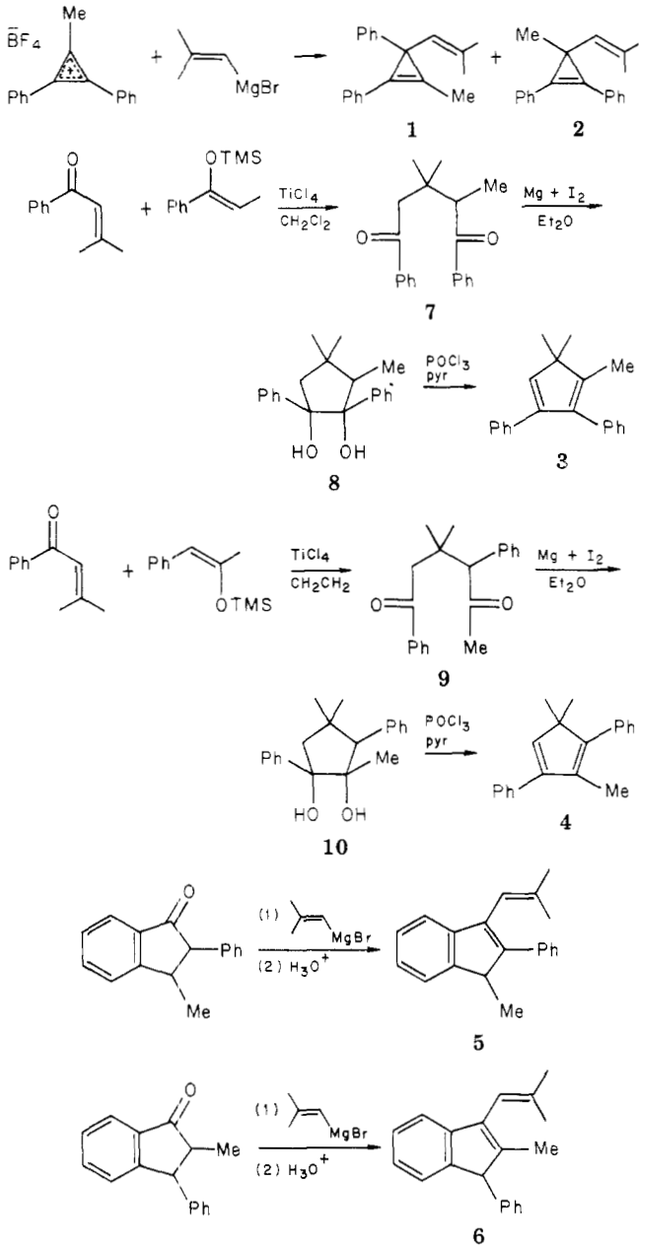
Chart I. Synthesis of Photochemical Reactants and Potential Products



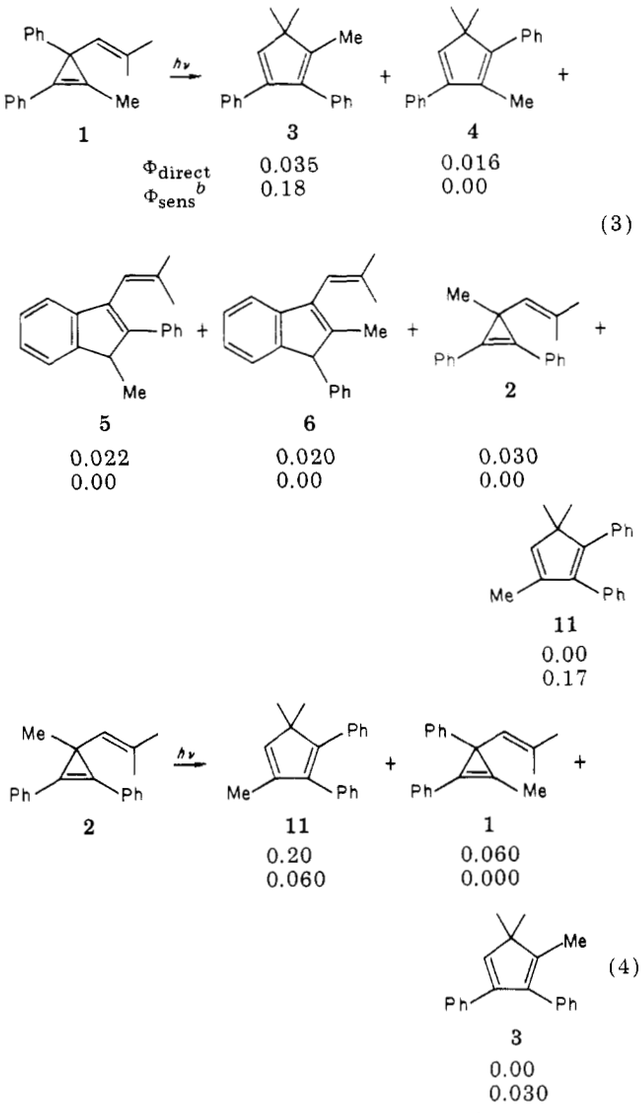
cyclopropene (2) proved to be the product of a walk rearrangement of the 1-methylcyclopropene (1) and conversely, and thus the photochemistry of this isomer (i.e., 2) was of interest, too.

Results

Synthesis of Photoreactants and Potential Photoproducts. A convenient synthesis of both desired photochemical reactants, 1 and 2, was found in the reaction of isobutenylmagnesium bromide with 1,2-diphenyl-3-methylcyclopropenium fluoborate as depicted in Chart I. Additionally, syntheses were devised for those cyclopentadienes expected as potential products from the photochemistry of the 1-methylcyclopropene 1 based on the structural change shown in eq 1. These preparations, too, are given in Chart I. Finally, the previous studies had led to indene products as well, and Chart I also contains details of synthesis of this type of product.

Exploratory Photolyses. High-conversion irradiations were run by using a 450-W immersion apparatus while

Chart II. Photochemical Transformations[a]



[a] Φ's are extrapolated to 0% conversion. [b] sens = 4-(dimethylamino)benzophenone.[10]

low-conversion photolyses were performed by using either the Black Box apparatus[6] or the organic chemist's microbench[6] previously described.

Irradiation of the 1-methylcyclopropene 1 to high conversion led to five photoproducts. Separation by traditional chromatography proved inadequate and resort was made to high-pressure LC, using preparative columns capable of separating 100-mg samples with 4500 theoretical plates. Of the photoproducts, four were among those synthesized and described above. These were the 2,3-diphenylcyclopentadiene 3, the 1,3-diphenylcyclopentadiene 4, the 2-phenylindene 5, and the 1-phenylindene 6. The remaining photoproduct was an isomer; mp 61–62 °C. The NMR spectrum revealed a vinyl quartet coupled with a methyl doublet by J = 1.3 Hz, thus suggesting the presence of the $CH{=}CCH_3$ moiety. Two equivalent methyl and two phenyl groups were also discerned. The ultraviolet spectrum was characteristic of a stilbenyl chromophore. Of two structures, 1,2-diphenyl-3,5,5-trimethyl-1,3-cyclopentadiene (11) and 1,2-diphenyl-4,5,5-trimethyl-1,3-cyclopentadiene, the former was suggested by structural analogy to related examples and

(6) H. E. Zimmerman, *Mol. Photochem.*, 3, 281 (1971).

Table I. Quantum Yield Determinations

		quantum yields								
		cyclopentadienes			indenes		cyclopropenes			
		2,3-di-Ph	1,3-di-Ph	1,2-di-Ph	2-Ph	1-Ph	1-Me	3-Me		
reactant	run[a]	3	4	11	5	6	1	2	% convrsn	sens[b]
1	1A	0.0072	0.0072	0.0040	0.0023	0.0030		0.000	51.1	
	1B	0.0068	0.0074	0.0060	0.0046	0.0050		0.000	24.2	
	1C	0.0081	0.0085	0.0070	0.0081	0.0060		0.000	10.3	
	1D	0.0075	0.0070	0.0028	0.0095	0.011		0.000	4.0	
	1E	0.023	0.010	0.000	0.018	0.020		0.027	2.6	
	1F	0.035	0.016	0.000	0.022	0.019		0.030	1.2	
1	2A	0.17	0.000	0.18	0.000	0.000		0.000	13.2	A
	2B	0.17	0.000	0.18	0.000	0.000		0.000	3.4	A
	2C	0.18	0.000	0.17	0.000	0.000		0.000	1.4	A
	2D	0.17	0.000	0.17	0.000	0.000		0.000	0.69	A
2	3A	0.000	0.000	0.025	0.000	0.000	0.0036		10.5	
	3B	0.000	0.000	0.11	0.000	0.000	0.025		3.7	
	3C	0.000	0.000	0.20	0.000	0.000	0.048		1.2	
2	4A	0.032	0.000	0.060	0.000	0.000	0.000		18.5	A
	4B	0.033	0.000	0.060	0.000	0.000	0.000		9.1	A
	4C	0.035	0.000	0.070	0.000	0.000	0.000		1.0	A

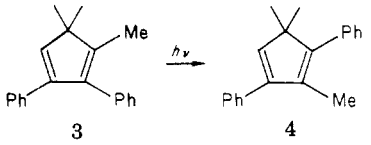
[a] Run numbers correspond to those in the Experimental Section. Runs 1A–F were analyzed by 270-MHz FT NMR, while the rest were analyzed by high-pressure LC. [b] A, 4-(dimethylamino)benzophenone (E_T = 67 kcal/mol[10]).

mechanistic conditions (vide infra). The photochemistry of the 1-methylcyclopropene **1** is depicted in Chart II.

It was observed in the exploratory, high-conversion runs that the ratio of the 2,3-diphenylcyclopentadiene **3** to the 1,3-diphenylcyclopentadiene **4** favored the 1,3-isomer **4**. This was structurally inconsistent with earlier regioselectivity[2b,3,5] observed, in which the preferred product was that formed by a formal 1,3-sigmatropic ring expansion utilizing the three-ring σ bond bearing the alkyl, rather than the aryl, group; thus precedent would have favored photoproduct **3**.

Indeed, at lower conversion it was found that the 2,3-diphenylcyclopentadiene **3** became the major product in over a 2:1 ratio. This is seen best in quantum yield runs extrapolated to 0% conversion described below.

The dependence of cyclopentadiene isomer distribution on extent of conversion suggested that the photochemistry of these five-ring compounds ought to be investigated. The 1,3-diphenylcyclopentadiene **4** and the 1,2-diphenylcyclopentadiene **11** proved to be photostable. However, the 2,3-diphenylcyclopentadiene **3** did rearrange in a facile reaction to afford the 1,3-isomer **4**. This is shown in eq 5.



3 4 (5)

Also, it was found that at lower conversion the 1,2-diphenylcyclopentadiene **11** was no longer formed. Additionally, this cyclopentadiene (i.e., **11**) was shown (vide supra) to be photostable. At lower conversion, in place of the 1,2-diphenylcyclopentadiene, the previously synthesized 3-methylcyclopropene **2** was formed. Hence, the cyclopentadiene **11** was a secondary photoproduct arising from the further photolysis of the cyclopropene **2**. This, also, is included in Chart II.

In view of the involvement of the 3-methylcyclopropene **2** in the photochemistry studied, it was of interest to investigate the behavior of this compound on irradiation. This photochemistry proved relatively straightforward and led to two known products, the 1-methylcyclopropene **1** and the 1,2-diphenylcyclopentadiene **11**. This photochemistry is illustrated in Chart II. The reactivity of cyclopropene **2** confirms the involvement of this compound in the secondary photochemistry in the photolysis of cyclopropene **1**.

Also, the formation of the 1,2-diphenylcyclopentadiene **11** starting with the 3-methylcyclopropene **2** is a characteristic ring expansion of the type studied and lends support to the structure assigned to **11**. Thus, the direct photochemistry of the 3-methylcyclopropene **2** is much less complex than that of the 1-methyl isomer **1** as a consequence of the symmetry of **2** and also the absence of a 3-phenyl group as needed for indene formation.

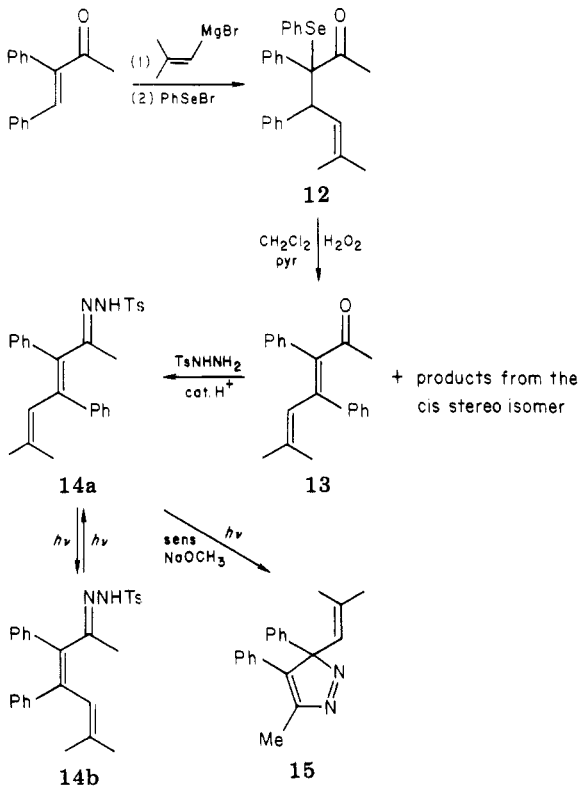
Attention was next turned to sensitization of the two cyclopropenes. Strikingly, the regioselectivity partitioning the product distribution in photolysis of the 1-methylcyclopropene **1** was so overwhelming that only the 2,3-diphenylcyclopentadiene **3** was found, with no 1,3-diphenyl isomer **4** being detected. Additionally the 1,2-diphenylcyclopentadiene **11** was isolated. Analogy to the direct irradiation suggested that this might not be a primary product but rather one arising from further reaction of the 3-methylcyclopropene **2**. Extrapolation to zero conversion, however, showed **11** to be a primary product. This, and the sensitized photochemistry of the 1-methylcyclopropene **1**, is outlined in Chart II. Next, we turned to sensitized photolysis of the 3-methylcyclopropene **2**. Interestingly, the same two products were isolated as had been observed from the sensitized irradiation of the isomeric cyclopropene **1**, namely, the 1,2-diphenylcyclopentadiene **11** and the 2,3-diphenylcyclopentadiene **3**. This photochemistry, too, is included in Chart II.

Hence, there is a dramatic difference between direct and sensitized product distributions.

Quantum Yield Determinations. Quantum yields were determined primarily by using the Black Box apparatus[6] and also the organic chemist's microbench described earlier.[6] Light measurement was performed by using our electronic actinometer,[7] with ferrioxalate[8] cal-

(7) H. E. Zimmerman, T. P. Cutler, V. R. Fitzgerald, and T. J. Weight, *Mol. Photochem.*, 8, 379 (1977).
(8) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

Chart III. Synthesis of Carbene Precursors



ibration for each run. These results are included in Chart II and also with more detail in Table I. In most cases, very low conversion runs were required to avoid secondary photochemistry; in each case runs were made to several extents of reaction at low conversion. Determinations were made by high-pressure LC and also by 270-MHz NMR spectrometry.

Synthesis of Carbene Precursors. One approach to study of the reaction mechanisms involved in the photochemistry proved to be generation of a potential reaction intermediate of the type considered in earlier studies,[2b,3,5] this being carbene **16**.

One precursor was the tosylhydrazone **14**. In view of the photochemical stereoisomerization of the conjugate base of this compound, only one isomer (i.e., *trans*-**14a**) was studied. The approach utilized is outlined in Chart III.

Another precursor used was the pyrazole **15**. Interestingly, this was formed in the sensitized irradiation of the conjugate base of tosylhydrazone **14a**. As noted below, direct irradiation led to different products and was not synthetically useful for preparation of the pyrazole.

Independent Generation of Carbene 16. Both *p*-toluenesulfonylhydrazones[11] and 3*H*-pyrazoles[12] are known as useful carbene precursors. The former is used as the conjugate base. In both cases direct irradiation was employed.

The results of photolytic generation of the desired carbene are tabulated in Chart IV. Significantly, the same product distribution arose from the two precursors. This may be due to intervention of a common diazo compound (i.e., **18**; vide infra). We note but delay for subsequent discussion that, in addition to 37% of diazepine **17**, the products of photolysis of the carbene precursors are the hydrocarbons involved in the photochemistry under investigation. This discussion must deal with a comparison of the distribution of the vinylcyclopropene photoproducts with that obtained from independent generation of carbene **16**.

Interpretative Discussion

Potential Reaction Mechanisms. In our previous publications on the vinylcyclopropene rearrangement to cyclopentadienes we have suggested two alternative reaction mechanisms.[2b,3] Padwa[5] has arrived at the same two possible pathways. These mechanisms are labeled A and B in Chart V.

Additionally, a third mechanism is included in Chart V, and this is labeled C.

Two of the three possible mechanisms, namely, A and C, are diradical processes. The third, B, utilizes a carbene intermediate (i.e., **22**). However, all three involve precisely the same overall skeletal transformation. For example, mechanism A proceeds by an initial bond b formation followed by a subsequent bond a scission. Mechanism B has these processes reversed with bond a fission to give carbene **22** being followed by formation of bond b. Mechanism C has the sequence of bond a fission and bond b formation preceded and followed by bond c formation and bond c fission.

As a consequence of the close structural relationship of the three mechanisms, useful information cannot derive from the mere location of product substituents or other (e.g., isotopic) skeletal labeling. Rather, independent mechanistic information is required such as regioselectivity, multiplicity effects, the behavior of independently generated carbene, and information provided by simultaneously occurring side reactions.

Regioselectivity. Reference to Chart II reveals a preference for one of two parallel five-ring products, namely, the 2,3-diphenylcyclopentadiene **3** in a 2.2:1 ratio to the 1,3-diphenylcyclopentadiene **4**. This is the third example of such regioselectivity.[2b,3,5]

In terms of mechanism A of Chart V, the regioselectivity is readily understood on the basis of excited-state vinyl–vinyl bridging preferentially to give the more stable of two diradical species (i.e., diradical **28** rather than diradical **29**). This is seen in eq 8.

In the case of the sensitized rearrangement, the corresponding triplet showed dramatically increased regioselectivity so that the 2,3-diphenylcyclopentadiene **3** with no 1,3-diphenylcyclopentadiene **4** is observed, and the same argument applies.

Thus mechanism A is consistent with the observed regioselectivity.

Mechanism B is not very helpful in understanding the regioselectivity. Thus, one would expect the excited three-ring to open to the more stable of two carbenes (i.e., **35**) in preference to carbene **34**, independent of whether it is the excited-state S_1 carbene, the triplet carbene T_1, or the ground-state carbene S_0 which is involved. This is shown in eq 9.

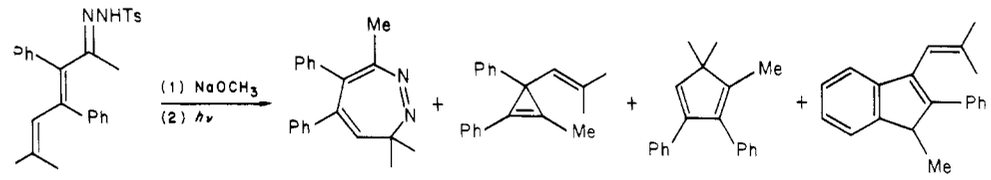
(9) G. S. Hammond as quoted in J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 360.

(10) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

(11) (a) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 2015 (1961); (b) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963); (c) G. L. Closs and W. A. Böll, *Angew. Chem., Int. Ed. Engl.*, **2**, 399 (1963); (d) H. Dürr, *Angew. Chem.*, **79**, 1104 (1967); (e) H. Dürr, *Chem. Ber.*, **103**, 369 (1970).

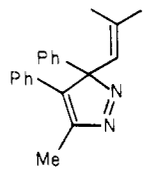
(12) (a) A. C. Day and M. C. Whiting, *J. Chem. Soc., Chem. Commun.*, 292 (1965); (b) A. C. Day and A. N. McDonald, *ibid.*, 247 (1973); (c) A. C. Day and R. N. Inwood, *J. Chem. Soc. C*, 1065 (1969); (d) M. Franck-Neumann and C. Buchecker, *Tetrahedron Lett.*, 2875 (1973); (e) L. Schrader, *Chem. Ber.*, **104**, 941 (1971); (f) M. E. Hendrick, W. J. Baron, and M. Jones, Jr., *J. Am. Chem. Soc.*, **93**, 1554 (1971); (g) G. L. Closs and W. A. Böll, *ibid.*, **85**, 3904 (1963); (h) G. L. Closs, W. A. Böll, H. Heyn, and V. Dev., *ibid.*, **90**, 173 (1968); (i) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *ibid.*, **89**, 3376 (1967); (j) M. Franck-Neumann and C. D. Buchecker, *Tetrahedron*, **34**, 2797 (1978).

Chart IV. Independent Carbene Generation



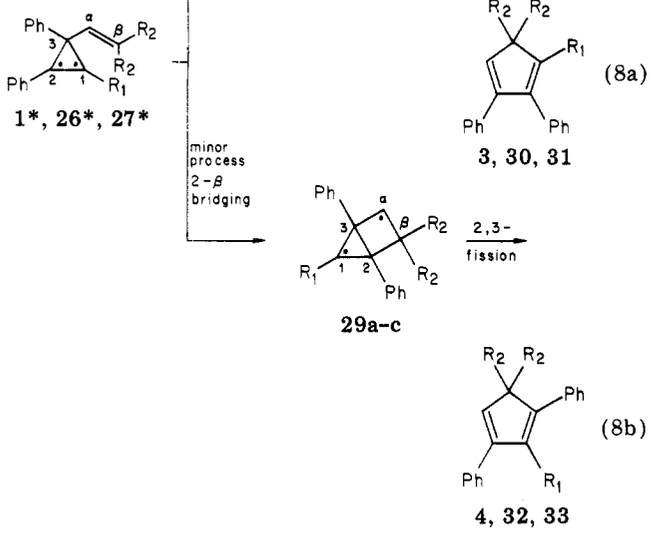
14a → 17 + 1 + 3 + 5 (6)

ratios 0.6 : 1.0 : 0.005 : 0.023

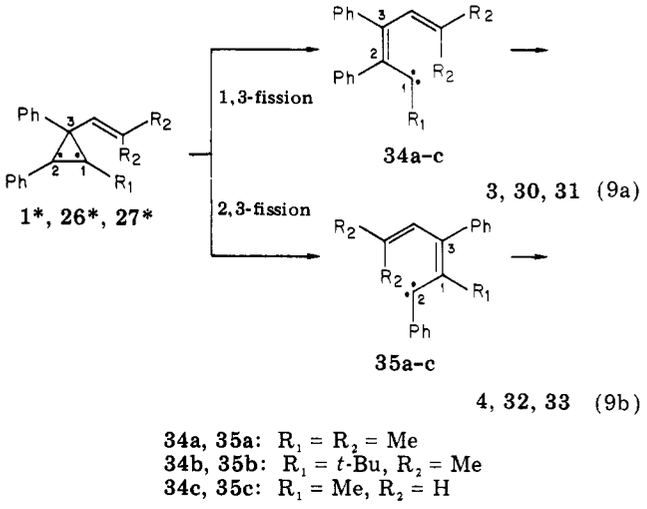


15 —hν→ 17 + 1 + 3 + 5 (7)

ratios 0.6 : 1.0 : 0.005 : 0.023



1*, 28a, 29a, 3, 4: $R_1 = R_2 = Me$ (this work)
26*, 28b, 29b, 30, 32: $R_1 = t$-Bu, $R_2 = Me$ (ref 2b, 3)
27*, 28c, 29c, 31, 33: $R_1 = Me$, $R_2 = H$ (ref 5a,e)



34a, 35a: $R_1 = R_2 = Me$
34b, 35b: $R_1 = t$-Bu, $R_2 = Me$
34c, 35c: $R_1 = Me$, $R_2 = H$

The carbene mechanism is, however, complicated by return of the opened species to reactant. Accordingly, in Chart VI if phenyl stabilization at carbon-1 in the ring-opening process (with rate·k_{ab}) were the only factor involved, one would predict either formation of the more stable of the two carbenes or no selectivity based on the possibility of a zero activation energy. We note that Pincock and Boyd[13] have predicted a zero activation energy for opening of S_1 and 13 kcal/mol for opening of T_1 of unsubstituted cyclopropene; this was based on MINDO/3 calculations.

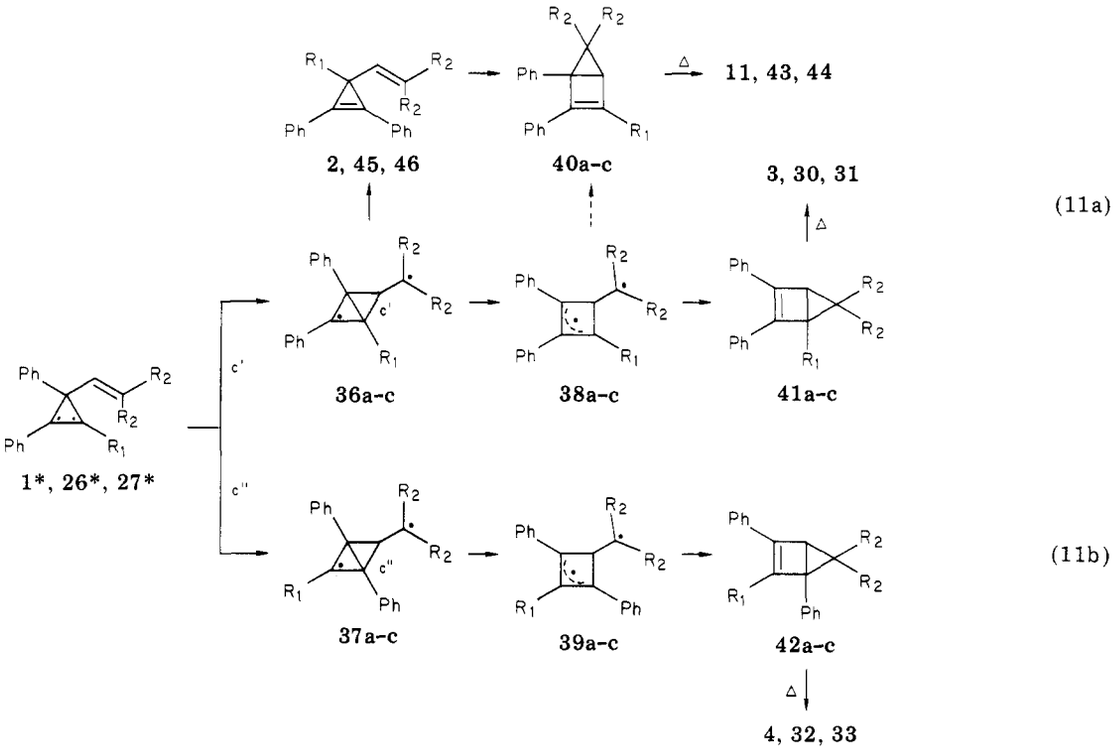
Yet, regioselectivity of three-ring opening has been found to vary with substituents on the cyclopropene double bond (positions 1 and 2 in Chart VI).[2b,3,5] Arnold and Morchat[14] recently have postulated a photochemical opening of 1,2-disubstituted cyclopropenes in which the bond bearing a methoxyphenyl group opens in preference to bonds bearing phenyl, which in turn facilitates opening more than cyanophenyl; the opened carbene rearranges by 1,4-hydrogen abstraction.

We know from our independent carbene generation that most of the carbene formed (>97%) reverts to cyclopropene (rate k_{bd} in Chart VI). With the assumption of steady-state kinetics, we arrive at the rate of formation of a given regioisomer of five-ring product (C) as given in eq 10. Here [A] is just the steady-state concentration of excited state and is common to both regiomodes of opening.

$$\text{rate of formation of five-ring product C} = dC/dt = \frac{k_{bc}}{k_{bc} + k_{bd}} k_{ab}[A] \quad (10)$$

We know that the rate of five-ring formation from carbene is slower than the rate of three-ring formation (i.e., $k_{bc} < k_{bd}$) from the independent carbene generation. The ratio $k_{bc}/(k_{bc} + k_{bd})$ represents the probability of carbene going on to form five-ring product relative to three-ring product while k_{ab} gives the rate of formation to the carbene. The question, then, is whether phenyl substitution on the opening bond could diminish the ratio $k_{bc}/(k_{bc} + k_{bd})$ more than k_{ab} is increased. We see no particular reason why k_{bc} and k_{bd} should be affected appreciably differently by phenyl substitution since both processes involve parallel carbon bonding processes. Thus

(13) J. A. Pincock and R. J. Boyd, *Can. J. Chem.*, **55**, 2482 (1977).
(14) R. M. Morchat and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, 743 (1978).



a series, **2**, **11**: $R_1 = R_2 = Me$
b series, **43**, **45**: $R_1 = t\text{-Bu}$, $R_2 = Me$
c series, **44**, **46**: $R_1 = Me$, $R_2 = H$

the ratio $k_{bc}/(k_{bc} + k_{bd})$ should tend to be less sensitive to substitution effects than a single rate such as k_{ab}. But considering that Pincock and Boyd[13] predict a zero activation energy for the singlet cyclopropene opening, it is possible that the effect of substitution on k_{ab} might be very small. However, with a 13 kcal/mol predicted activation energy for the triplet, this would no longer be a difficulty and we do observe complete regioselectivity. Interestingly, for the singlet the observation of regioselectivity of Arnold and Morchat[14] is quite parallel from the kinetic viewpoint although the reaction is quite different.

In summary, mechanism B remains possible but not particularly helpful in rationalizing the observations discussed thus far.

We now turn to mechanism C (note Chart V). Although this is a diradical mechanism, it is more related to carbene mechanism B than diradical mechanism A. This derives from mechanism C utilizing the same sequence of bond a fission followed by bond b formation as mechanism B except that these steps are preceded by bond c formation and followed by bond c scission. Bond a fission in species such as **36** and **37** is a known[15a] type of reaction. Mechanism C does properly rationalize the observed regioselectivity as is seen from eq 11. In diradical **36** there is extra delocalization by phenyl favoring this species over diradical **37**. Some evidence in favor of mechanism C comes from the observation of the vinyl-migrated 3-methylcyclopropene **2** as a product of the direct irradiation of 1-methylcyclopropene **1**. Thus species **36**, the product of the first step of mechanism C, must be formed. Also, mechanism C accounts for the formation of sensitized photoproduct 1,2-diphenylcyclopentadiene **11** (note eq 3 of Chart I) as a primary photoproduct. The proposed housenes should proceed onward with facility thermally[15b-d] if not photochemically.

Mechanism C, however, is incompatible with the singlet photochemistry. Thus, cyclobutenyl diradical **38a** is common to both photochemical reactions, that starting with the 1-methylcyclopropene **1** and that starting with the 3-methylcyclopropene **2**. For simplicity, let us focus attention on only two photoproducts, namely, the 2,3-diphenylcyclopentadiene **3** and the 1,2-diphenylcyclopentadiene **11**. Chart II (eq 3 and 4) and Chart VII reveal that direct irradiation of the 1-methylcyclopropene **1** gives only the 2,3-diphenylcyclopentadiene **3**. In contrast, the singlet of the 3-methylcyclopropene **2** leads only to the 1,2-diphenylcyclopentadiene **11**. This rules out mechanism C for the singlet.

Turning to the triplet, we find that the triplets of the 1-methylcyclopropene **1** and the 3-methylcyclopropene **2** both lead to the two cyclopentadienes **3** and **11**. Now, however, we observe formation of the 1,2-diphenylcyclopentadiene **11** from the 1-methylcyclopropene **1**; this is a reaction which is not accommodated by mechanisms A and B but is accounted for by mechanism C. Similarly, the formation of the 2,3-diphenylcyclopentadiene **3** from the 3-methylcyclopropene **2** is accounted for only by mechanism C.

Still, the ratio of cyclopentadienes **3** and **11** from the sensitized irradiations of the two cyclopropenes **1** and **2** does differ (i.e., 1:1 vs. 1:2). With mechanism C being mandatory for formation of **11** from **1** and **3** from **2**, the discrepancy in product ratios must derive from intervention of some alternative mechanism (i.e., A or B) affording additional **3** from **1** or **11** from **2**. Chart VII depicts the differing product distributions upon which the above reasoning rests.

Thus, mechanism C seems required to account for part of the triplet reaction, yet it cannot account for all of the reaction course nor can it account for the singlet rear-

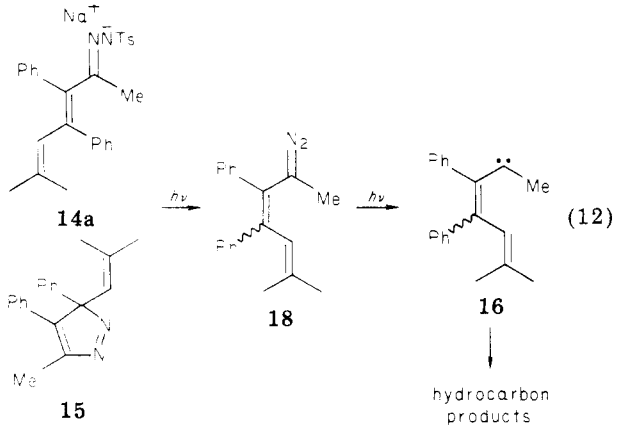
(15) (a) J. E. Baldwin and A. H. Andrist, *J. Chem. Soc., Chem. Commun.*, 1561 (1970); (b) J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *J. Am. Chem. Soc.*, **92**, 5249 (1970); (c) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969); (d) G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, **99**, 4853 (1977).

rangement.

The close relationship between the three mechanisms A, B, and C has been noted (vide supra). This leads us to the possibility of a composite mechanism embodying the features of all three extremes with timing depending upon structure and multiplicity. Such a mechanism would involve the bicycling[17] of carbene carbon C-1 from C-3 to the terminus of the vinyl moiety.

Significance of the Product Distribution in Independent Carbene Generation. The objective of studying the photochemistry of tosylhydrazone **14** and 3*H*-pyrazole **15** was to determine the actual behavior of carbene **16** and then to compare this with the cyclopropene photochemistry. This would then be a comparison of "fingerprints".[16]

As noted above the product distribution derived from both carbene precursors is the same. This is in agreement with the literature[11e,12e,g,h,18] indicating that both of these are precursors to the corresponding diazo compound (in this case **18**). The formations of diazepine **17** from the tosylhydrazone **14a**, the diazoalkene **18** or the 3*H*-pyrazole **15** have precedent[19] and are probably independent reactions, since the diazepine was photostable. The diazo compound **18** on loss of nitrogen affords the desired carbene **16**. Note eq 12.

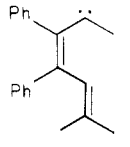


Thus we need to compare the product distributions in eq 3 (photochemical products) and 6 or 7 (i.e., carbene products). Reference to Table II is helpful. In this table, focusing attention on two ratios is utilized as a mode of comparison. Thus, the ratio of indene to cyclopentadiene product characterizes the nature of the intermediate involved as does the ratio of total five-ring product (i.e., cyclopentadiene **3** plus indene **5**) to three-ring (i.e., cyclopropene **1**) product. The ratio of indene to cyclopentadiene product is 4.5 from the independent carbene generation but 0.63 from the direct irradiation, thus suggesting that the same species (i.e., carbene **16**) is not involved in both experiments. There is the possibility that this difference arises from a different ratio of the two possible stereoisomeric carbenes (**16a** and **16b**) being generated photochemically from the cyclopropene **1** as contrasted with the photolyses of the tosylhydrazone salt (**14a** conjugate base) and the 3*H*-pyrazole **15**. The diazo compound **18** formed seems likely to be generated with a preference for the bulky phenyl groups trans, thus accounting for the 0.23:0.005 ratio of indene **5** (having transoid phenyls) to cyclopentadiene **3** (having cisoid phenyls). However, in the cyclopropene photolysis, to account for an inverted ratio of indene **5** to cyclopentadiene **3** based on stereochemical factors, we need to postulate a preference for formation of cisoid carbene in the three-ring (**1**) opening. This seems unreasonable if van der Waals repulsions are the controlling factor. Still, if as the three-ring were opened, the carbene generated selected the more reactive group (i.e., vinyl rather than phenyl) for attack, the stereochemistry could be accommodated. However, concerted (i.e., overlapping in time) carbene generation and reaction become tantamount to intervention of mechanism A above (note Chart V).

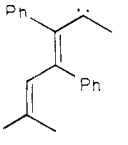
Table II. Experimental and Hypothetical Product Ratios

rel amt			ratios[a]	
cyclopropene 1	cyclopentadiene 3	indene 5	indene 5/cyclopentadiene 3	5-ring/3-ring
Independent Generation of Carbene 16				
1.0	0.005	0.023	4.5	0.028
If Carbene 16 Is Involved in Irradiation of 1[b]				
assumed $\Phi_{opening}$				
1.0	0.95	0.033	0.021	0.63	0.057
0.75	0.93	0.044	0.027	0.63	0.076
0.5	0.90	0.063	0.039	0.63	0.11
0.25	0.81	0.11	0.071	0.63	0.23
general	<0.95	>0.033	>0.021	0.63	>0.057

[a] 3-ring refers to the 1-methylcyclopropene **1**; 5-ring refers to the sum of the 2,3-diphenylcyclopentadiene **3** plus indene **5**. [b] $\Phi_{opening}$ represents the quantum yield of 3-ring opening to yield carbene **16**.



cisoid carbene **16a**



transoid carbene **16b**

Returning to our "fingerprint" treatment, we find that the ratio of five-ring product (cyclopentadiene plus indene) to three-ring product is different in the independent generation than in the photochemistry of cyclopropene **1** (note Table II). Here we need to assume different possible efficiencies of three-ring openings in S_1, and these are tabulated (note Table II). The best fit is obtained by assuming three-ring opening with unit efficiency. Again a stereochemical basis is possible since a preference for transoid geometry in the independent carbene generation would lead to greater three-ring formation due to nonavailability of the cyclopentadiene cyclization process while the cisoid carbene generated photochemically would revert less to three-ring **1** due to capture of the carbene by the available vinyl group. However, this implies that the carbenoid carbon begins bonding as it is formed, and a

(16) (a) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1967); (b) H. E. Zimmerman and K. G. Hancock, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract 0-130; (c) H. E. Zimmerman and R. L. Morse, *J. Am. Chem. Soc.*, **90**, 954 (1968).

(17) Bicycling refers to motion of a doubly substituted carbon atom, carbenoid in nature and having two sp^5 orbitals. For further definition and examples note; H. E. Zimmerman and T. P. Cutler, *J. Org. Chem.*, **43**, 3283 (1978); *J. Chem. Soc., Chem. Commun.*, 232 (1978).

(18) (a) H. Hartzler in "Carbenes", R. A. Moss and M. Jones, Jr., Eds., Wiley, New York, N.Y., 1975, p 59; (b) D. R. Arnold, R. W. Humphreys, W. J. Leigh, and G. E. Palmer, *J. Am. Chem. Soc.*, **98**, 6225 (1976); (c) G. E. Palmer, J. R. Bolton, and D. R. Arnold, *J. Am. Chem. Soc.*, **96**, 3708 (1974); (d) J. A. Pincock, R. Morchat, and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 7536 (1973).

(19) (a) A. A. Reid, J. T. Sharp, H. R. Sood, and P. B. Thorogood, *J. Chem. Soc., Perkin Trans. 1*, 2543 (1973); (b) J. T. Sharp, R. H. Findlay, and P. B. Thorogood, *ibid.*, 102 (1975); (c) C. D. Anderson, J. T. Sharp, H. R. Sood, and R. S. Strathdee, *J. Chem. Soc., Chem. Commun.*, 613 (1975).

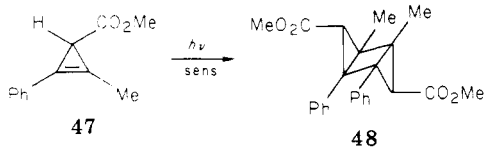
mechanism approaching A is suggested.

Hence, independent generation of carbene **16** has provided reasonable but not absolute evidence against this discrete species being involved in the photochemistry of cyclopropene 1.

Significance of the Triplet Photochemistry of Cyclopropene 1. One striking result is the very high efficiency of the triplet rearrangement of the 1-methylcyclopropene 1. Equally dramatic is the total regioselectivity observed for the triplet compared with the direct irradiation product distribution.

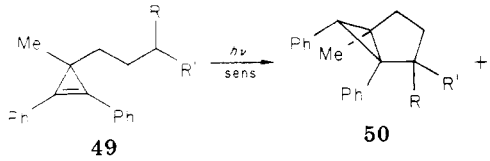
A first conclusion is that in the direct irradiation within 0.2% experimental error, the 1,3-diphenylcyclopentadiene 4 must arise from the singlet, since this product is not encountered from the triplet.

The high triplet efficiency for the vinylcyclopropene rearrangement is significant in light of the literature of cyclopropenes which indicates an almost total lack of ring-opening reactions from their triplets, with dimerization being the common reaction by default. Thus, Pincock observed the formation of a furan product from (carbomethoxy)cyclopropene **47** on direct irradiation but only dimer on sensitization[20] (note eq 13). Again, Padwa

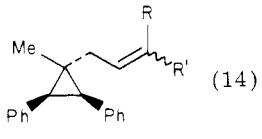


47 48 (13)

encountered a ring-opening reaction to give dienes, presumably via a carbene intermediate, from the singlet of cyclopropene **49** whereas the triplet yielded products with the three-ring still intact; note eq 14.[5d] Similarly, cy-



49 50



(14)

51

clopropene **47** racemizes 2.5 times as fast as it reacts to give furan, again via the carbene, on direct irradiation but, as noted above, only forms dimer from the triplet.[20]

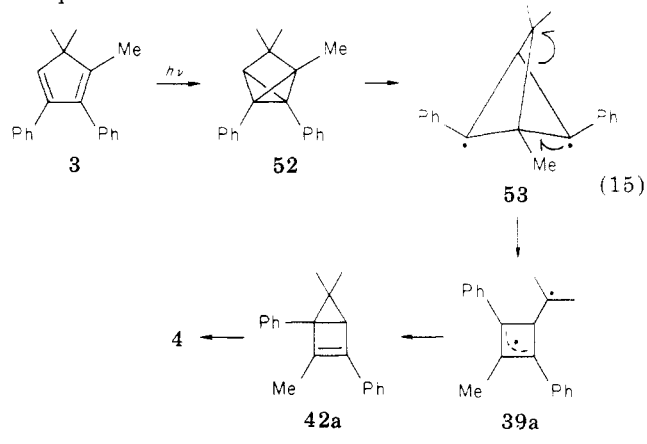
While this literature is limited, it nevertheless begins to form a pattern suggesting that triplet cyclopropenes open inefficiently, consistent with the high activation energy[13] calculated for this process. Thus, we are tempted to ascribe the high triplet efficiency of the 1-methylcyclopropene 1 to a mechanism other than ring opening, namely, mechanisms A or C.

The high regioselectivity observed for the triplet is understood on the basis of mechanisms A or C, since in each case that diradical is formed which is most stabilized by a delocalizing phenyl group on the three-ring and formation of a diradical with electrons separated maximally is especially favored by the triplet.[21,22]

The lack of free-rotor triplet-energy dissipation[23] probably arises from steric inhibition of rotation encountered when the potential free rotor is isobutenyl.[2b] Molecular models of the space-filling variety suggest less steric hindrance to free rotation in the case of the 3-methylcyclopropene 2 where the triplet efficiency is lower.

The Walk Rearrangement. We still need to deal with the related reaction in which the vinyl moiety undergoes a 1,2 shift (i.e., the formation of the 3-methylcyclopropene 2 from the 1-methylcyclopropene 1 and the reverse reaction (note Chart II and eq 3 and 4)). This walk reaction is experimentally separable in the case of the singlet photochemistry while in the case of the triplets cyclopentadiene rearrangement products are observed which may arise from such 1,2-vinyl walk products but are shown by the quantum yield results to arise directly. Equation 11 includes the sequence **1*** → **36a** → **2** which illustrates the most simple and reasonable mechanism for the walk rearrangment in the singlet of the 1-methylcyclopropene 1.

Photorearrangement of the 2,3-Diphenylcyclopentadiene 3. The rearrangement of the 2,3-diphenylcyclopentadiene 4 (note eq 5) is a reaction which has several close analogies. Morrison[24a,b] and Padwa[5e,f] have observed several instances of rearrangements of indenes in which the sp^3 and adjacent sp^2 atoms are exchanged. Analogously, several cyclopentadienes have been shown by labeling studies to rearrange via housene intermediates.[15,24c] For the presently studied rearrangement, a plausible mechanism for the transformation **3** → **4** is shown in eq 15.



3 52 53 (15) 42a 39a

Indeed, both the photoconversion of a cyclopentadiene to a tricyclopentane[24c] such as **52** and the reverse[25] (i.e., **52** → **4**) are known types of reactions.

Two alternative mechanisms are a priori possibilities but seem ruled out by lack of side reactions in the cyclopentadiene rearrangement. The two mechanisms are the microscopic reverse of mechanisms A and B leading from cyclopropene to cyclopentadiene. For example, 1,3 bridging of the 2,3-diphenylcyclopentadiene **3** leads to housane diradical **28a** (note eq 8a) already considered in the forward reaction affording cyclopentadiene. Then

(20) J. A. Pincock and A. A. Moutsokapas, *Can. J. Chem.*, **55**, 979 (1977).
(21) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 8749 (1972).
(22) J. Michl, *Mol. Photochem.*, **4**, 257 (1972).
(23) (a) H. E. Zimmerman and C. O. Bender, *J. Am. Chem. Soc.*, **92**, 4366 (1970); (b) H. E. Zimmerman, R. J. Boettcher, and W. Braig, *ibid.*, **95**, 2159 (1973); (c) H. E. Zimmerman, D. W. Kurtz, and L. M. Tolbert, *ibid.*, **95**, 8210 (1973); (d) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973); (e) H. E. Zimmerman, K. S. Kamm, and D. P. Werthemann, *J. Am. Chem. Soc.*, **97**, 3718 (1975); (f) H. E. Zimmerman, F. X. Albrecht, and M. J. Haire, *ibid.*, **97**, 3726 (1975); (g) H. E. Zimmerman and L. M. Tolbert, *ibid.*, **97**, 5497 (1975); (h) H. E. Zimmerman and R. T. Klun, *Tetrahedron*, **34**, 1775 (1977).
(24) (a) F. J. Palensky and H. A. Morrison, *J. Am. Chem. Soc.*, **99**, 3507 (1977); (b) D. Giacherio and H. Morrison, *ibid.*, **100**, 7109 (1978); (c) G. D. Andrews and J. E. Baldwin, *ibid.*, **99**, 4851 (1977).
(25) G. L. Closs, *Tetrahedron Lett.*, 287 (1965).

Chart V. Three Alternative Reaction Mechanisms

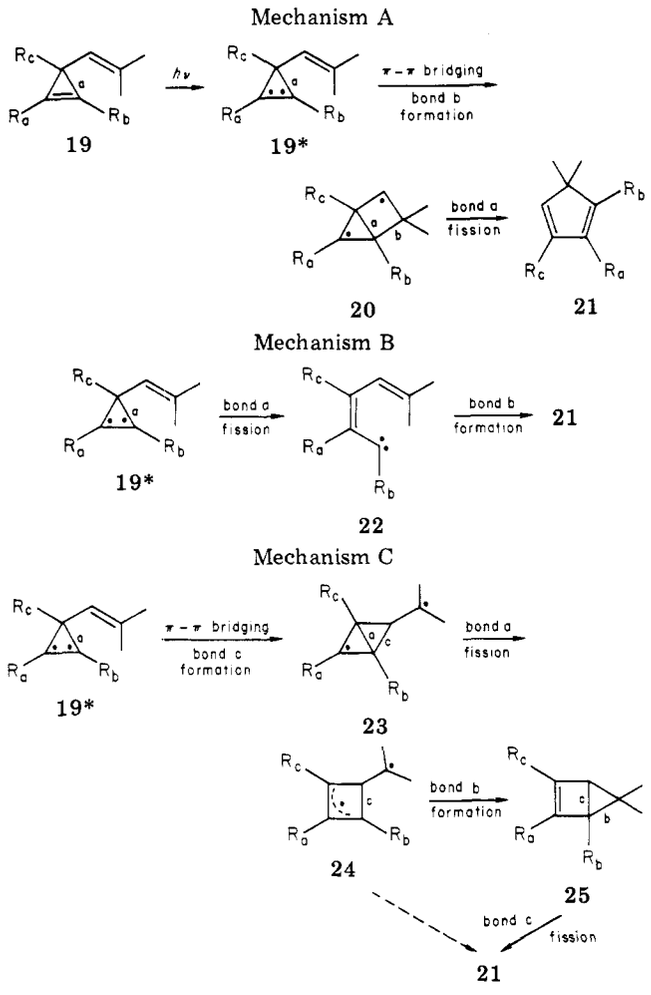
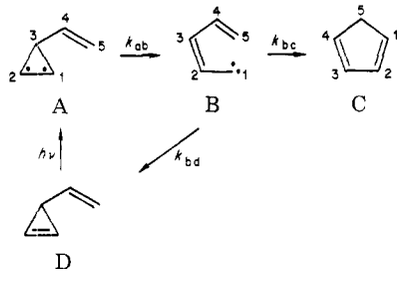


Chart VI. Kinetic Scheme for Carbene Formation and Dissipation

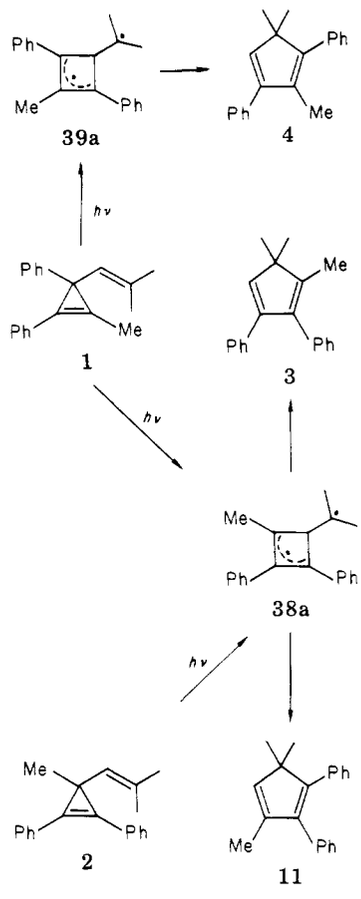


reversal to cyclopropene **1** is a possibility. While photolysis of this cyclopropene would lead to formation of the 1,3-diphenylcyclopentadiene **4**, it would also give rise to indenes **5** and **6**; however, these were not formed in the cyclopentadiene isomerization. Similarly, no 3-methylcyclopropene **2** was formed. This signifies that cyclopropene **1** is not an intermediate in the cyclopentadiene interconversion.

A parallel situation is encountered in a mechanism in which bond 1–5 of cyclopentadiene **3** is severed directly giving carbene **34a**; note eq 9a. Such a carbene could revert to cyclopropene and thence to isomerized cyclopentadiene by secondary photolysis. However, again the lack of all the cyclopropene photoproducts indicates that this mechanism is not utilized.

Consideration of the Three Mechanisms. We have shown that in the case of the singlet reaction, mechanism C cannot operate, while in the case of the triplet, it must operate but not solely. To the extent that the literature

Chart VII. Common Intermediates in Mechanism C



quantum yields starting from 1	2	
0.016	0.000	singlet
0.000	0.000	triplet
0.035	0.000	singlet
0.18	0.030	triplet
0.00	0.20	singlet
0.17	0.060	triplet

pattern of lack of three-ring opening of triplet cyclopropenes is significant, the carbene mechanism B seems unlikely for the triplet.

In the case of the singlet, the behavior of the independently generated carbenes argues that these are not reaction intermediates unless incipiently formed carbenes are entertained. In the latter case, we are dealing with mechanism A.

The regioselectivity, in which the more stable of two diradicals would be involved in mechanisms A and C but the less stable of two carbenes would be required in mechanism B, argues in favor of mechanisms A and C. Support of mechanism A has been noted earlier.[2b,3,5]

The occurrence of the walk rearrangement reveals that diradical species of the type **36** (note eq 11) are indeed formed in the singlet photochemistry. This pathway also leads to mechanism C.

Triplet photochemistry of cyclopropenes **1** and **2** is readily explained in terms of mechanism C. The walk rearrangement interconverting cyclopropenes **1** and **2** is seen not to occur in the triplet state. Instead, a diversion of intermediate **36a** (note eq 11a) to afford **38a**, and ultimately both cyclopentadienes **3** and **11**, occurs.

In considering all three mechanisms, we note that they differ in chronology; the same bonds are formed and broken overall. It is quite possible that the actual reaction mechanism is a composite varying in weighting of the bonding and bond-breaking contributions as structure is varied by changing multiplicity or reactant nature. The major conclusion which can be made is that we may be dealing with mechanistic gradations rather than totally discrete alternatives. Our future efforts are aimed at assessing these gradations.

Experimental Section[26]

1-Methyl-2,3-diphenyl-3-isobutenylcyclopropene and 1,2-Diphenyl-3-methyl-3-isobutenylcyclopropene. To a stirred slurry of 3.04 g (10.4 mmol) of 1,2-diphenyl-3-methylcyclopropenium fluoborate[2b] in 30 mL of tetrahydrofuran at 0 °C under nitrogen was added dropwise 22 mL of 1.0 M isobutenylmagnesium bromide[27] in tetrahydrofuran. After 4 h of stirring at room temperature under nitrogen, the reaction was poured into saturated aqueous ammonium chloride and hexane extracted twice. The combined organic layers were washed with saturated sodium chloride, dried, and concentrated leaving an orange oil which was combined with three other runs on 2.5-, 2.89-, and 3.03-g quantities of 1,2-diphenyl-3-methylcyclopropenium fluoborate run in parallel fashion. The combined crude products were triturated with hexane at −18 °C and filtered, and the solution was concentrated leaving 10.6 g of an orange oil. Chromatography on a 2.0 × 250 cm silica gel column slurry packed and eluted with hexane in 40-mL fractions gave the following: fractions 1–63, nil; fractions 64–122, 4.92 g (18.9 mmol, 48%) of colorless 1,2-diphenyl-3-methyl-3-isobutenylcyclopropene; fractions 123–228, 760 mg (2.92 mmol, 7.4%) of colorless 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene; fractions 229–240, nil.

Crystallization of 1,2-diphenyl-3-methyl-3-isobutenylcyclopropene from methanol gave 4.50 g (17.3 mmol, 44%) of colorless flat plates, mp 53–54 °C. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.35 (m, 4 H, aromatic), 2.57 (m, 4 H, aromatic), 2.70 (m, 2 H, aromatic), 4.48 (septet, 1 H, J = 1.1 Hz, vinyl), 8.34 (s, 3 H, CH_3), 8.34 (d, 3 H, J = 1.1 Hz, CH_3), 8.40 (d, 3 H, J = 1.3 Hz, CH_3); CMR ($CDCl_3$) 18.7 (CH_3), 24.5 (CH_3), 27.0 (CH_3), 53.0 (C-3 of cyclopropene), 121.9, 128.0, 128.7, 129.2, 130.0, 131.0 ppm; IR ($CHCl_3$) 3.28, 3.34, 3.38, 3.47, 3.52, 5.53, 6.27, 6.70, 6.92, 7.30, 9.35, 9.90, 10.4, 11.0 μm; UV (EtOH) λ_{max} 334 (ϵ 24600), 317 (ϵ 31300), 307 sh (ϵ 26900), 237 sh (ϵ 19400), 228 (ϵ 27300) nm; high-resolution mass spectrometry for $C_{20}H_{20}$ m/e(calcd) 260.157, m/e(found) 260.156.

Anal. Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.75. Found: C, 92.38; H, 7.67.

Crystallization of 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene from methanol gave 554 mg (2.13 mmol, 5.4%) of colorless prisms, mp 58–59 °C. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.7–3.0 (m, 10 H, aromatic), 4.32 (septet, 1 H, J = 1.1 Hz, vinyl), 7.68 (s, 3 H, CH_3), 8.22 (d, 3 H, J = 1.3 Hz, CH_3), 8.36 (d, 3 H, J = 1.1 Hz, CH_3); CMR ($CDCl_3$) 9.6 (CH_3), 19.8 (CH_3), 25.4 (CH_3), 31.1 (C-3 of cyclopropene), 114.0, 116.0, 124.5, 126.8, 127.7, 127.8, 128.5, 128.7, 135.1, 146.7, 147.2 ppm; IR ($CHCl_3$) 3.25, 3.27, 3.33, 3.43, 3.70, 5.48, 6.25, 6.68, 6.88, 7.13, 7.27, 8.60, 8.80, 10.0, 11.7 μm; UV (EtOH) λ_{max} 266 (ϵ 17000) nm; high-resolution mass spectrometry for $C_{20}H_{20}$ m/e(calcd) 260.157, m/e(found) 260.157.

Anal. Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.75. Found: C, 92.30; H, 7.76.

1,4-Diphenyl-3,3-dimethylhexane-1,5-dione. Following the general procedure of Mukaiyama,[28] a solution of 2.26 g (11.0 mmol) of 1-phenyl-2-(trimethylsilyloxy)propene in 3.0 mL of methylene chloride was added to a stirred solution of 1.7 g (10.7 mmol) of 1-phenyl-3-methylbut-2-en-1-one and 1.1 mL of titanium tetrachloride in 11 mL of methylene chloride at −78 °C under nitrogen. Stirring at −78 °C was continued for 1 h. The solution was poured into dilute aqueous sodium carbonate and the aqueous phase was methylene chloride extracted. The combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give 3.43 g (11.0 mmol, 100%) of the dione as colorless crystals, mp 39–44 °C. Crystallization from hexane afforded 3.11 g (10.5 mmol, 96%) of colorless prisms, mp 49–50 °C. The spectral data were as follows: 100-MHz NMR ($CDCl_3$) τ 1.95–2.13 (m, 2 H, aromatic), 2.4–3.0 (m, 8 H, aromatic), 5.66 (s, 1 H, CH), 6.91 (AB q, 2 H, J_{AB} = 16 Hz, CH_2), 8.00 (s, 3 H, CH_3), 8.82 (s, 3 H, CH_3), 8.93 (s, 3 H, CH_3); CMR ($CDCl_3$) 25.6 (q, CH_3), 26.4 (q, CH_3), 31.6 (q, CH_3CO), 36.9 (s, C-3), 46.4 (t, C-2), 64.8 (d, C-4), 127.2, 127.4, 128.0, 128.2, 128.4, 128.7, 130.6, 132.7, 135.3, 200.4 (s, benzoyl carbonyl), 208.6 (s, acyl carbonyl); IR (thin film) 3.25, 3.30, 3.38, 3.48, 5.87, 5.98, 6.28, 6.34, 6.70, 6.80, 6.90, 7.39, 8.04, 8.17, 8.49, 8.68, 9.31, 9.90, 11.0 μm; high-resolution mass spectrometry for $C_{20}H_{22}O_2$ m/e(calcd) 294.162, m/e(found) 294.160.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.59; H, 7.54. Found: C, 81.67; H, 7.56.

1,3-Diphenyl-2,4,4-trimethyl-1,2-cyclopentanediol. To a stirred ether (100 mL) suspension, under nitrogen, of 1.46 g (60.0 mg-atom) of magnesium powder was added 7.15 g (28.2 mmol) of iodine in small portions. When the iodine color had disappeared, an ether solution containing 2.91 g (9.89 mmol) of 1,4-diphenyl-3,3-dimethylhexane-1,5-dione was added. The reaction mixture was stirred for 2 h. The mixture was hydrolyzed by addition of saturated aqueous ammonium chloride. The aqueous solution was ether extracted, and the combined ether extracts were washed with saturated aqueous sodium chloride. The ether solution was dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to afford 2.28 g of oily crystals. Recrystallization from hexane–ether gave 1.07 g (3.61 mmol, 37%) of colorless needles, mp 146.5–149.5 °C. The spectral data were as follows: 100-MHz NMR ($CDCl_3$) τ 2.35–2.94 (m, 10 H, aromatic), 6.42 (s, 1 H, CH), 7.27 (br s, 1 H, OH), 7.32 (br s, 1 H, OH), 7.63 (AB q, 2 H, J_{AB} = 15 Hz, CH_2), 8.79 (s, 3 H, CH_3), 8.85 (s, 3 H, CH_3), 9.36 (s, 3 H, CH_3); CMR ($CDCl_3$) 25.5, 28.0, 30.4, 40.1, 55.6, 63.8, 83.9, 84.7, 126.5, 126.8, 127.6, 127.7, 131.4, 137.6, 145.3 ppm; IR ($CDCl_3$) 2.77 (sharp, OH), 2.85 (br, OH), 3.27, 3.30, 3.38, 3.49, 6.26, 6.80, 6.92, 7.28, 7.32, 8.30, 8.81, 9.07, 9.47, 9.73, 10.2, 10.7, 12.1 μm; high-resolution mass spectrometry for $C_{20}H_{24}O_2$ m/e(calcd) 296.178, m/e(found) 296.178.

Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.03; H, 8.17. Found: C, 81.04; H, 8.20.

1,3-Diphenyl-2,5,5-trimethyl-1,3-cyclopentadiene. To a solution of 439 mg (1.48 mmol) of 1,3-diphenyl-2,4,4-trimethyl-1,2-cyclopentanediol in 5.0 mL of dry pyridine was added 1.0 mL of phosphorous oxychloride. The solution was refluxed for 9.5 h under nitrogen. After the reaction mixture was cooled, it was poured into aqueous ammonium chloride. The aqueous solution was ether extracted twice, and the combined ether extracts were washed with aqueous sodium bicarbonate, water, and brine. The dried solution was concentrated in vacuo to give 239 mg (0.92 mmol, 62%) of an oily brown crystalline mixture which was chromatographed on a 20 × 20 × 0.2 cm preparative silica gel plate eluted twice with 0.5% ether in hexane. The first band (largest R_f) contained 205 mg (0.79 mmol, 53%) of the desired cyclopentadiene as a colorless oil. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.4–3.0 (m, 10 H, aromatic), 3.736 (s, 1 H, vinyl), 8.182 (s, 3 H, CH_3), 8.787 (s, 6 H, $C(CH_3)_2$); CMR ($CDCl_3$) 13.2 (q, CH_3), 22.2 (q, $C(CH_3)_2$), 52.5 (s, C-5), 126.5, 126.7, 127.8, 128.0, 128.6, 129.3, 133.6 (s), 137.1 (s), 137.6 (d), 142.5 (d), 144.1 (s), 152.1 (s) ppm; IR (thin film) 3.25, 3.27, 3.30, 3.38, 3.42, 3.50, 6.27, 6.70, 6.85, 6.94, 7.23, 7.40, 9.35, 9.73, 10.4, 11.0 μm; UV (EtOH) λ_{max} 230 (ϵ 13000) nm; high-resolution mass spectrometry for $C_{20}H_{20}$ m/e(calcd) 260.157, m/e(found) 260.158.

Anal. Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.75. Found: C, 92.09; H, 7.78.

1,5-Diphenyl-2,3,3-trimethyl-1,5-pentanedione. Following the general method of Mukaiyama,[28] a solution of 10.2 g (49.0 mmol) of 1-phenyl-1-(trimethylsilyloxy)propene in 5.0 mL of methylene chloride was added to a stirred solution of 7.93 g (49.5 mmol) of 1-phenyl-3-methylbut-2-en-1-one and 5.5 mL (50 mmol) of titanium tetrachloride in 30 mL of methylene chloride at −78 °C under nitrogen. Stirring at −78 °C was continued for 40 min. The solution was poured into dilute aqueous sodium carbonate,

(26) (a) All melting points were determined by using a calibrated hot-stage apparatus. Mass spectra were obtained with an AEI MS-902 mass spectrometer at 70 eV. Proton nuclear magnetic resonance spectra were obtained with a JEOL MH-100, Varian T-60, or Bruker WH-270 spectrometer. Carbon nuclear magnetic resonance spectra were obtained with a JEOL FX-60 spectrometer. High-pressure liquid chromatography was performed on a Waters Model ALC-100 liquid chromatograph by employing an LDC 254-nm UV detector which was calibrated for the relative responses of detected compounds and standards. Column chromatography was performed on silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) packing mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored by a hand-held UV lamp. Preparative thin-layer chromatography was performed by using MN-Kieselgel G/UV-254 silica gel. (b) *tert*-Butyl alcohol (Commercial Grade, Eastman Kodak Chemicals) was refluxed over and distilled from calcium hydride immediately prior to use.

(27) H. Normandt, *Adv. Org. Chem.*, **2**, 1 (1960).

(28) T. Mukaiyama, K. Soai, and K. Narasaka, *Chem. Lett.*, 1223 (1974).

and the aqueous phase was methylene chloride extracted. The combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give 16.1 g of a pale yellow oil. Chromatography on a 4 × 85 cm silica gel column slurry packed and eluted with 2% ether in hexane gave the following: fraction 1, 1.0 L, 9.7 g of a mixture of propiophenone and 1-phenyl-3-methylbut-2-en-1-one; fraction 2, 2.3 L, 6.39 g (21.7 mmol, 44%) of colorless 1,5-diphenyl-2,3,3-trimethyl-1,5-pentanedione as an oil. The spectral data were as follows: 100-MHz NMR ($CDCl_3$) τ 2.1 (m, 4 H, aromatic), 2.7 (m, 6 H, aromatic), 5.96 (q, 1 H, J = 7 Hz, CH), 4.96 (AB q, 2 H, J_{AB} = 16 Hz, CH_2), 8.82 (s, 3 H, CH_3), 8.85 (s, 3 H, CH_3), 8.85 (d, 3 H, J = 7 Hz, CH_3); CMR ($CDCl_3$) 13.2, 25.9, 36.4, 46.2, 127.9, 128.2, 128.4, 128.5, 132.6, 138.4, 200.1, 205.1 ppm; IR ($CHCl_3$) 3.26, 3.36, 3.46, 5.96, 6.28, 6.33, 6.82, 6.88, 7.35, 7.70, 8.13, 8.45, 9.89, 9.99, 10.4 μm; UV (EtOH) λ_{max} 322 (ϵ 116), 245 (ϵ 20 400) nm; high-resolution mass spectrometry for $C_{20}H_{22}O_2$ m/e(calcd) 294.162, m/e(found) 294.162.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.59; H, 7.54. Found: C, 81.36; H, 7.32.

1,2-Diphenyl-3,4,4-trimethyl-1,2-cyclopentanediol. An ether (5 mL) solution of 6.38 g (21.7 mmol) of 1,5-diphenyl-2,3,3-trimethyl-1,5-pentanedione was added to a solution of the magnesium–iodine reagent (sixfold excess), prepared as described above, and the solution was stirred for 1.45 h. The usual workup afforded 5.77 g (19.5 mmol, 90%) of orange crystals. Recrystallization twice from hexane gave 4.86 g (16.4 mmol, 76%) of colorless prisms, mp 93–94 °C. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.97–3.29 (m, 10 H, aromatic), 6.67 (br s, 2 H, OH), 7.67 (q, 1 H, J = 7 Hz, CH), 7.72 (AB q, 2 H, J_{AB} = 15 Hz, CH_2), 8.72 (s, 3 H, CH_3), 8.74 (s, 3 H, CH_3), 9.25 (d, 3 H, J = 7 Hz, CH_3); CMR ($CDCl_3$) 7.66 (q, CH_3), 27.7 (q, CH_3), 29.7 (q, CH_3), 38.0 (s, C-4), 47.8 (d, C-3), 55.6 (t, C-5), 85.8 (s, C-1 or C-2), 88.3 (s, C-2 or C-1), 126.1, 126.4, 126.7, 126.9, 127.1, 142.1 (s), 144.3 (s) ppm; IR ($CDCl_3$) 2.78 (sharp), 2.82 (br), 3.23, 3.27, 3.32, 3.37, 3.48, 6.71, 6.88, 7.34, 8.29, 8.40, 8.49, 8.71, 8.85, 9.42, 9.66, 10.3 μm; high-resolution mass spectrometry for $C_{20}H_{24}O_2$ m/e(calcd) 296.178, m/e(found) 296.180.

Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.03; H, 8.17. Found: C, 81.26; H, 8.30.

2,3-Diphenyl-1,5,5-trimethyl-1,3-cyclopentadiene. To a solution of 1.5 g (5.1 mmol) of 1,2-diphenyl-3,4,4-trimethyl-1,2-cyclopentanediol in 30 mL of dry pyridine was added 3.0 mL (33 mmol) of phosphorous oxychloride. The solution was refluxed for 4.5 h under nitrogen. The usual workup afforded 1.28 g (4.92 mmol, 96%) of brown crystals which by NMR was a 1:1 mixture of the desired cyclopentadiene and an unidentified compound. Separation of the compounds was effected by preparative high-pressure liquid chromatography, using one 2 ft × $^3/_8$ in. column packed with 7–12-μm porous silica gel beads[29] and eluting with dry hexane. When appropriate cuts were taken, a typical 100-mg injection gave 45 mg of pure 2,3-diphenyl-1,5,5-trimethyl-1,3-cyclopentadiene as colorless crystals from the slower eluting band and 35 mg of the unidentified compound from the faster eluting band. Crystallization of the cyclopentadiene from methanol gave colorless prisms, mp 73–73.5 °C. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.60–3.19 (m, 10 H, aromatic), 3.673 (s, 1 H, vinyl), 8.165 (s, 3 H, CH_3), 8.792 (s, 6 H, $C(CH_3)_2$); CMR ($CDCl_3$) 22.5 ($C(\mathbf{C}H_3)_2$), 29.8 (CH_3), 51.8 (C-4), 126.1, 126.4, 126.9, 127.6, 127.8, 127.9, 136.6, 141.7 ppm; IR ($CHCl_3$) 3.27, 3.33, 3.46, 3.52, 3.59, 6.22, 6.33, 6.68, 6.80, 6.88, 7.36, 7.69, 9.30, 9.92, 10.6, 10.9, 11.3, 11.5, 12.3 μm; UV (EtOH) λ_{max} 280 (ϵ 4000), 237 (ϵ 24 600), 227 sh (ϵ 22 500) nm; high-resolution mass spectrometry for $C_{20}H_{20}$ m/e(calcd) 260.157, m/e(found) 260.156.

Anal. Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.75. Found: C, 92.43; H, 7.77.

The 270-MHz FT NMR spectrum ($CDCl_3$) of the unknown compound is as follows: τ 2.5–2.7 (m, 10 H, aromatic), 5.219 (s, 1 H), 5.346 (s, 1 H), 7.169 (s, 2 H), 8.718 (s, 6 H).

1,2-Diphenyl-3,5,5-trimethyl-1,3-cyclopentadiene. A methanol (200 mL) solution of 1.07 g (4.12 mmol) of 1,2-diphenyl-3-methyl-3-isobutenylcyclopropene was irradiated according to the general procedure for exploratory photolyses (see below) for a period of 1.0 h and then concentrated leaving 1.05 g of a colorless oil which crystallized spontaneously. The solid was recrystallized from methanol to give 0.85 g (3.27 mmol, 79%) of colorless prisms, mp 60–62 °C. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.90 (m, 10 H, aromatic), 3.98 (q, 1 H, J = 1.3 Hz, vinyl), 8.114 (d, 3 H, J = 1.3 Hz, CH_3), 8.776 (s, 6 H, $C(CH_3)_2$); CMR ($CDCl_3$) 14.8 (q, CH_3), 22.5 (q, $C(CH_3)_2$), 52.7 (s, C-5), 126.1, 127.6, 129.4, 129.5, 136.5, 137.3, 137.6, 141.4, 152.3 ppm; IR (CCl_4) 3.25, 3.28, 3.32, 3.39, 3.44, 3.51, 6.28, 6.74, 6.85, 6.94, 7.28, 7.41, 7.73, 9.46, 9.90, 10.7, 11.2 μm; UV (EtOH) λ_{max} 287 (ϵ 5000), 230 (ϵ 17 000) nm; high-resolution mass spectrometry for $C_{20}H_{20}$ m/e(calcd) 260.157, m/e(found) 260.156.

Anal. Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.75. Found: C, 92.20; H, 7.78.

1-Methyl-2-phenyl-3-isobutenylindene. To a stirred solution containing 50 mmol of isobutenylmagnesium bromide[27] in 50 mL of tetrahydrofuran was added 474 mg (2.13 mmol) of solid 2-phenyl-3-methylindanone. The solution was refluxed 2 h under nitrogen, and a saturated ammonium chloride solution was added. The organic phase was separated, washed with brine, and dried over magnesium sulfate. Concentration afforded 0.933 g of a pale yellow oil of crude indanol and several other products. This material was used in the next step without further purification. To this crude indanol was added 20 mL of a mixture containing 17 mL of glacial acetic acid, 2 mL of sulfuric acid, and 1 mL of water. The solution was stirred for 5 min and then diluted with water. The solution was neutralized with sodium bicarbonate and extracted with ether. The ether extracts were washed with water and dried over magnesium sulfate. Removal of the solvent in vacuo left 710 mg of a yellow oil which was a mixture of the desired indene, 2,5-dimethyl-2,4-hexadiene, starting indanone, and several other products. The crude material was percolated through a 1 × 50 cm silica gel column with hexane to separate the hydrocarbon fraction as 231 mg of a colorless oil. The dimethylhexadiene was removed under vacuum, and the indene was purified by preparative high-pressure liquid chromatography, using one 2 ft × $^3/_8$ in. column packed with 7–12 μm porous silica gel beads[29] and eluting with dry hexane. When appropriate cuts were taken, a typical 50-mg injection gave 25 mg of the indene as a colorless oil from the slower eluting band. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.50–2.81 (m, 10 H, aromatic), 3.908 (septet, 1 H, J = 1.1 Hz, vinyl), 6.084 (d of q, 1 H, J = 1.1, 7.8 Hz, CH), 8.114 (d, 3 H, J = 1.3 Hz, CH_3), 8.562 (d, 3 H, J = 1.2 Hz, CH_3), 8.746 (d, 3 H, J = 7.5 Hz, CH_3); CMR ($CDCl_3$) 17.1 (CH_3), 20.4 (CH_3), 25.6 (CH_3), 45.1 (CH), 118.2, 120.4, 122.5, 124.7, 126.4, 128.1, 128.5, 128.6, 135.5, 136.7, 137.8, 145.0, 146.9, 148.2 ppm; IR ($CHCl_3$) 3.25, 3.32, 3.35, 3.40, 3.43, 3.47, 5.98, 6.22, 6.63, 6.78, 7.25, 8.39, 8.48, 8.66, 8.88, 9.00, 10.9, 12.1 μm; UV (EtOH) λ_{max} 299 (ϵ 15 000), 238 (ϵ 20 000) nm; high-resolution mass spectrometry for $C_{20}H_{20}$ m/e(calcd) 260.157, m/e(found) 260.157.

Anal. Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.75. Found: C, 92.37; H, 7.70.

1-Phenyl-2-methyl-3-isobutenylindene. To a stirred solution containing 15 mmol of isobutenylmagnesium bromide[27] in 15 mL of tetrahydrofuran was added 2.59 g (11.7 mmol) of 2-methyl-3-phenylindanone. The solution was stirred 1 h under nitrogen, and a saturated aqueous ammonium chloride solution was added. The organic phase was separated, washed with brine, and dried over magnesium sulfate. Concentration afforded 3.2 g (11.7 mmol, 100%) of the crude indanol as a yellow oil. This material was used in the next step without further purification. To this crude indanol was added a mixture containing 18 mL of glacial acetic acid, 2 mL of sulfuric acid, and 2 mL of water. The solution was stirred for 15 min and then diluted with water. The solution was neutralized with sodium bicarbonate and extracted with ether. The ether extracts were washed with water and dried over magnesium sulfate. Removal of the solvent in vacuo left 2.97 g (11.4 mmol, 98% based on indanone) of the indene as a yellow oil. The crude material was percolated with hexane through a 1.7 × 30 cm silica gel column affording 1.56 g (6.0 mmol, 51%) of the pure indene as a colorless oil. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.6–3.1 (m, 10 H, aromatic), 3.986 (m, 1 H, vinyl), 5.696 (br s, 1 H, CH), 8.064 (d, 3 H, J = 1.3 Hz, CH_3), 8.246 (narrow m, 3 H, CH_3), 8.357 (d, 3 H, J = 1.1 Hz, CH_3); CMR ($CDCl_3$) 13.7 (q, CH_3), 20.3 (q, CH_3), 25.6 (q, CH_3), 59.3 (d, CH), 117.5 (d, vinyl), 119.1, 123.4, 124.2, 126.5, 128.1, 128.2,

(29) H. E. Zimmerman, T. R. Welter, D. Tartler, and R. A. Bunce, unpublished results.

128.5, 129.0, 136.0 (s), 137.7 (s), 140.3 (s), 143.6 (s), 145.8 (s), 147.5 (s) ppm; IR (thin film) 3.28, 3.33, 3.40, 3.44, 3.47, 3.54, 6.27, 6.72, 6.92, 7.33, 8.47, 9.43, 9.65, 9.80 μm; UV (EtOH) λ_{max} 226 (ε 8800) nm; high-resolution mass spectrometry for $C_{20}H_{20}$ *m/e*(calcd) 260.157, *m/e*(found) 260.156.

Anal. Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.75. Found: C, 92.27; H, 7.75.

3-Phenylseleno-3,4-diphenyl-6-methyl-5-hepten-2-one. To a solution of 82 mmol of isobutenylmagnesium bromide[27] in 130 mL of tetrahydrofuran under nitrogen at 0 °C was added 1.09 g (5.72 mmol) of cuprous iodide. After 10 min a solution of 8.87 g (40 mmol) of 1,2-diphenyl-1-buten-3-one in 25 mL of tetrahydrofuran was added dropwise over 20 min. Stirring was continued 15 min at 0 °C. The magnesium enolate was quenched by addition of a solution of 80 mmol of phenylselenium bromide[30] in 25 mL of tetrahydrofuran, and the mixture was stirred 15 min. The mixture was hydrolyzed by dropwise addition of 100 mmol of ammonium chloride dissolved in a minimum amount of water. The precipitate was filtered and washed twice with ether. The filtrate and washings were concentrated in vacuo to give a dark orange oil which was chromatographed on a 2.5 × 95 cm silica gel column slurry packed and eluted in hexane, and the following 300-mL fractions were collected: fractions 1–3, 6.1 g of diphenyl diselenide; fractions 4–10, 12 g (28 mmol, 70%) of the desired phenylseleno ketone; fractions 11–13, 3.2 g of an unidentified orange oil. Fractions 4–10 were recrystallized from ethanol to give 11.2 g (25.8 mmol, 64%) of colorless prisms, mp 137–139 °C. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.2–3.4 (m, 15 H, aromatic), 4.186 (d of septets, 1 H, *J* = 1.1, 9.2 Hz, vinyl), 5.702 (d, 1 H, *J* = 9.4 Hz, CH), 7.832 (s, 3 H, CH_3CO), 8.261 (d, 3 H, *J* = 1.1 Hz, CH_3), 8.831 (d, 3 H, *J* = 1.2 Hz, CH_3); CMR ($CDCl_3$) 18.2, 25.8, 28.1, 45.3, 74.2, 125.6, 126.6, 127.2, 127.8, 128.6, 129.5, 130.8, 131.2, 132.1, 135.3, 137.2, 141.7, 198.8 ppm; IR ($CHCl_3$) 3.26, 3.33, 3.41, 3.43, 5.86, 6.23, 6.32, 6.65, 6.73, 7.25, 7.33, 8.38, 8.43, 9.20, 9.27, 9.77, 9.96, 10.8, 11.4 μm; high-resolution mass spectrometry for $C_{26}H_{26}SeO$ *m/e*(calcd) 434.115, *m/e*(found) 434.114.

Anal. Calcd for $C_{26}H_{26}SeO$: C, 71.87; H, 6.04. Found: C, 71.75; H, 5.98.

***trans*-3,4-Diphenyl-6-methyl-3,5-heptadien-2-one.** To a solution of 3.39 g (7.8 mmol) of 3-phenylseleno-3,4-diphenyl-6-methyl-5-hepten-2-one in 35 mL of methylene chloride containing 0.5 mL (6.2 mmol) of pyridine was added 19.5 mmol of hydrogen peroxide (2.2 mL of 30% hydrogen peroxide in 2.2 mL of water).[30] After vigorous stirring for 3 h, the reaction was poured into methylene chloride and saturated sodium bicarbonate extracted. The aqueous layer was methylene chloride extracted, and the combined organic layers were washed with 5% hydrochloric acid, water, and brine, dried, and concentrated leaving 2.0 g of a brown solid. Crystallization from ethanol gave 1.36 g (4.92 mmol, 63%) of the dienone as colorless needles, mp 120–121 °C. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.76 (narrow m, 10 H, aromatic), 4.12 (septet, 1 H, *J* = 1.3 Hz, vinyl), 8.06 (s, 3 H, CH_3CO), 8.32 (d, 3 H, *J* = 1.3 Hz, CH_3), 8.81 (d, 3 H, *J* = 1.1 Hz, CH_3); CMR ($CDCl_3$) 20.2, 26.7, 31.6, 125.2, 127.4, 128.1, 128.4, 129.2, 129.8, 138.5, 139.9, 141.3, 141.8, 142.5, 206.0 ppm; IR ($CHCl_3$) 3.24, 3.27, 3.32, 3.36, 3.41, 3.43, 5.96, 6.26, 6.42, 6.70, 6.91, 7.26, 7.39, 8.38, 8.48, 9.32, 9.73, 11.67 μm; UV (EtOH) λ_{max} 298 (ε 9600), 230 (ε 14 300) nm; high-resolution mass spectrometry for $C_{20}H_{20}O$ *m/e*(calcd) 276.151, *m/e*(found) 276.152.

Anal. Calcd for $C_{20}H_{20}O$: C, 86.91; H, 7.30. Found: C, 86.80; H, 7.27.

***trans*-3,4-Diphenyl-6-methyl-3,5-heptadien-2-one Tosylhydrazone.** A mixture of 1.78 g (6.45 mmol) of *trans*-3,4-diphenyl-6-methyl-3,5-heptadien-2-one, 1.20 g (6.45 mmol) of tosylhydrazine, and 0.01 mL of concentrated hydrochloric acid in 5.0 mL of ethanol was refluxed under nitrogen for 5.5 h. The dark brown mixture was diluted with 10 mL of ethanol and kept at −18 °C for 18 h. The mixture was filtered and the residue washed twice with cold ethanol. Crystallization from methanol gave 670 mg (1.51 mmol, 23%) of the tosylhydrazone as fine colorless needles, mp 178–180 °C. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.44 (m, 2 H, aromatic), 2.7–2.9 (m, 12 H, aromatic), 4.192 (septet, 1 H, *J* = 1.1 Hz, vinyl), 7.572 (s, 3 H, CH_3), 8.359 (d, 3 H, *J* = 1.3 Hz, CH_3), 8.478 (s, 3 H, $CH_3C{=}N$), 8.869 (d, 3 H, *J* = 1.1 Hz, CH_3); IR (KBr) 3.05–3.23, 3.26, 3.42, 5.23, 6.27, 6.79, 6.80, 6.92, 7.07, 7.25, 7.45, 7.52, 7.66, 7.75, 8.28, 8.43, 8.55, 8.60, 8.95, 9.20, 8.82, 10.8, 12.3 μm; UV (EtOH) λ_{max} 304 (ε 10 800), 232 (ε 21 700) nm; high-resolution mass spectrometry for $C_{27}H_{28}N_2O_2S$ *m/e*(calcd) 444.187, *m/e*(found) 444.187.

Anal. Calcd for $C_{27}H_{28}N_2O_2S$: C, 72.94; H, 6.35. Found: C, 72.78; H, 6.35.

3,4-Diphenyl-3-isobutenyl-5-methyl-3*H*-pyrazole. A solution of 1.58 g (3.55 mmol) of *trans*-3,4-diphenyl-6-methyl-3,5-heptadien-2-one tosylhydrazone and 490 mg (9.07 mmol) of sodium methoxide in 750 mL of dry tetrahydrofuran was stirred 17 h, shielded from direct light and under nitrogen. The yellow slurry was transferred via cannula to a 750-mL photolysis cell and 1.63 g (6.07 mmol) of Michler's ketone was added. The reaction mixture was stirred and dry nitrogen was bubbled through as it was irradiated for 7.5 h on the Wisconsin Black Box apparatus, using filter combination E (vide infra). Concentration of the photolysate gave a yellow solid mass which was triturated five times with pentane. The pentane filtrates were concentrated in vacuo, leaving 600 mg (2.29 mmol, 64%) of the 3*H*-pyrazole as pale yellow crystals, mp 86–89.5 °C. Purification of the acid-sensitive 3*H*-pyrazole was effected by preparative high-pressure liquid chromatography, using one 1 ft × $^3/_8$ in. column packed with 15–25-μm porous silica gel beads[29] and eluting with 20% anhydrous ether in anhydrous hexane. When appropriate cuts were taken, a typical 100-mg injection gave 85 mg of pure 3,4-diphenyl-3-isobutenyl-5-methyl-3*H*-pyrazole as colorless prisms, mp 92.5–93.5 °C. The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.74 (m, 6 H, aromatic), 2.95 (m, 4 H, aromatic), 4.66 (septet, 1 H, *J* = 1.1 Hz, vinyl), 7.41 (s, 3 H, CH_3), 8.18 (d, 3 H, *J* = 1.3 Hz, CH_3), 8.24 (d, 3 H, *J* = 1.1 Hz, CH_3); IR ($CHCl_3$) 3.27, 3.36, 3.44, 3.52, 6.25, 6.68, 6.92, 7.27, 7.57, 8.50, 8.58, 9.37, 10.5, 11.0 μm; CMR ($CDCl_3$) 13.1, 21.0, 27.1, 47.3, 116.8, 118.4, 126.1, 126.9, 128.0, 128.4, 128.7, 129.8, 130.6 ppm; UV (EtOH) λ_{max} 307 (ε 5900), 271 (ε 5700) nm; high-resolution mass spectrometry for $C_{20}H_{20}N_2$ *m/e*(calcd) 288.163, *m/e*(found) 288.163.

Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99. Found: C, 83.44; H, 6.94.

General Procedure for Exploratory Photolyses. All irradiations were through a 2-mm Corex or Pyrex filter, using a Hanovia 450-W medium-pressure mercury lamp and benzene[31] or *tert*-butyl alcohol[26b] as the solvent. All runs were purged with purified nitrogen[32] for 0.75 h before and during the photolysis.

Exploratory Photolysis of 1-Methyl-2,3-diphenyl-3-isobutenylcyclopropene. A solution of 360 mg (1.38 mmol) of 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene in 500 mL of *tert*-butyl alcohol[26b] was irradiated for 110 min through a Corex filter and then concentrated leaving 365 mg of a yellow oil. Chromatography on a 2.2 × 300 cm silica gel column slurry packed and eluted with hexane in 40-mL fractions gave the following: fractions 1–52, nil; fractions 53–60, 26.2 mg of 1,3-diphenyl-2,5,5-trimethylcyclopentadiene; fractions 61–72, 89.0 mg of a 1:1.4:1 mixture of 2,3-diphenyl-1,5,5-trimethylcyclopentadiene, 1,3-diphenyl-2,5,5-trimethylcyclopentadiene, and 1-methyl-2-phenyl-3-isobutenylindene; fractions 73–80, 34.3 mg of a 1:1:3 mixture of 2,3-diphenyl-1,5,5-trimethylcyclopentadiene, 1,2-diphenyl-3,5,5-trimethylcyclopentadiene, and 1-phenyl-2-methyl-3-isobutenylindene; fractions 81–84, 19.2 mg of a 1:1:2 mixture of 1,2-diphenyl-3,5,5-trimethylcyclopentadiene, 1-phenyl-2-methyl-3-isobutenylindene, and 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene; fractions 85–102, 80.9 mg of pure 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene (mass balance 68%). The ternary mixtures from the above fractions were separated into their constituents by preparative high-pressure liquid chromatography, using two 2 ft × $^3/_8$ in. columns packed with 7–12-μm porous silica gel beads[29] and eluting with hexane

(30) H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975).

(31) H. E. Zimmerman and R. Daniel Little, *J. Am. Chem. Soc.*, **96**, 4623 (1974).

(32) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

which was distilled from calcium hydride and then passed through alumina. Mass balances from high-pressure LC separation of each set of fractions from above were poor for the pure compounds because of the severe overlap of the components in the ternary mixtures even upon reinjection, taking appropriate cuts, and recycling. In each injection, however, inclusion of the overlapping cuts resulted in an overall mass balance of greater than 95%. The spectral data (plus mixture melting points in the cases of 1,3-diphenyl-2,5,5-trimethylcyclopentadiene, 2,3-diphenyl-1,5,5-trimethylcyclopentadiene, and 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene) were identical with those of independently synthesized material (vide supra).

Exploratory Photolysis of 1,2-Diphenyl-3-methyl-3-isobutenylcyclopropene. A solution of 2.076 g (7.98 mmol) of 1,2-diphenyl-3-methyl-3-isobutenylcyclopropene in 200 mL of benzene was irradiated for 110 min through a Pyrex filter and then concentrated leaving 2.03 g of colorless crystals. Chromatography on a 2.0 × 200 cm silica gel column slurry packed and eluted with hexane in 25-mL fractions gave the following: fractions 1–40, nil; fractions 41–46, 109 mg (0.42 mmol, 5.2%) of 1,2-diphenyl-3-methyl-3-isobutenylcyclopropene; fractions 47–52, nil; fractions 53–65, 1.88 g (7.2 mmol, 90%) of 1,2-diphenyl-3,5,5-trimethylcyclopentadiene; fractions 66–67, nil; fractions 68–88, 86 mg (0.33 mmol, 4%) of 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene (mass balance 100%). The spectral data for the three compounds were identical with those of independently synthesized materials (vide supra).

Photolysis Apparatus for Quantum Yield Determinations. All quantum yield determinations were run on either the "Wisconsin Black Box"[6] or microoptical bench.[6] Light output was measured for each run by a digital electronic actinometer[7] calibrated by ferrioxalate actinometry.[8] Microoptical bench photolyses employed an Osram HBO 200-W high-pressure mercury lamp and a Bausch and Lomb Model 33-86-79 monochromator with a 5.2-mm entrance slit and 3.0-mm exit slit giving a bandpass of 22 nm at half-peak height. For Black Box photolyses the bandpass was controlled by one of a series of filter solution combinations held in a 750 mL total volume three compartment quartz faced filter solution cell. The filter solutions employed were as follows. Filter A: cell 1, 0.14 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 1.0 M cobalt sulfate heptahydrate in 10% sulfuric acid; cell 3, 0.8 M stannous chloride dihydrate in 10% hydrochloric acid (transmission: 0% below 332 nm, 24% at 355 nm, 0% above 390 nm). Filter B: cell 1, 2 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 2 M cobalt sulfate heptahydrate in 5% sulfuric acid; cell 3, 0.0002 M bismuth trichloride in 10% hydrochloric acid (transmission: 0% below 255 nm, 18% at 282 nm, 0% above 305 nm). Filter C: cell 1, 0.5 M nickel sulfate heptahydrate in 10% sulfuric acid; cell 2, 0.8 M cobalt sulfate heptahydrate in 10% sulfuric acid; cell 3, 0.021 M stannous chloride dihydrate in 10% hydrochloric acid (transmission: 0% below 308 nm, 32.5% at 330 nm, 0% above 368 nm). Filter D: cell 1, 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 0.8 M cobalt sulfate heptahydrate in 10% sulfuric acid; cell 3, 0.1 M copper sulfate pentahydrate in 10% sulfuric acid (transmission: 0% below 285 nm, 36% at 316 nm, 0% above 355 nm). Filter E: cell 1, water; cell 2, 0.8 M cobalt sulfate heptahydrate in 10% sulfuric acid; cell 3, 0.1 M sodium metavanadate in 1.0 M sodium hydroxide (transmission: 0% below 356 nm, 36.5% at 379 nm, 0% from 432 to 565 nm, gradually rising to 24% at 700 nm).

All quantum yield photolyses were purged with purified nitrogen[32] for 0.75 h before and during each run. The glassware utilized in the quantum yield determinations was soaked in 50% ammonium hydroxide for 3 h and then rinsed with ethanol, ether, and benzene prior to each run, in order to minimize complications due to acid-catalyzed reactions of the vinylcyclopropenes.[33a]

Summary of Quantum Yield Results for 1-Methyl-2,3-diphenyl-3-isobutenylcyclopropene. All direct runs were analyzed by 270-MHz FT NMR. The internal standard was *trans*-3,4-diphenyl-6-methyl-3,5-heptadien-2-one. The sensitized runs were analyzed by high-pressure liquid chromatography, using two 2 ft × $^3/_8$ in. columns packed with 7–10-μm porous silica gel beads[29] and eluting with anhydrous hexane. The sensitizer used was 4-(dimethylamino)benzophenone (enough to absorb >99% of the light). The internal standard used was 1,2-diphenyl-3-methyl-3-isobutenylcyclopropene. All runs are summarized in Table III.

Summary of Quantum Yield Results for 1,2-Diphenyl-3-methyl-3-isobutenylcyclopropene. All direct and sensitized runs were analyzed by high-pressure liquid chromatography, using two 2 ft × $^3/_8$ in. columns packed with 7–10-μm porous silica gel beads[29] and eluting with anhydrous hexane. The sensitizer used was 4-(dimethylamino)benzophenone (enough to absorb >99% of the light). The internal standard used was *trans*-3,4-diphenyl-6-methyl-3,5-heptadien-2-one. All runs were summarized in Table IV.

Independent Generation of Singlet Carbene Intermediates. General Procedure. In each run, the crude photolysate was injected onto the high-pressure liquid chromatograph, using one 1 ft × $^3/_8$ in. column packed with 15–25-μm porous silica gel beads[29] and eluting with 20% anhydrous ether in anhydrous hexane. The first peak, representing the entire hydrocarbon fraction, was collected, concentrated in vacuo, and analyzed by using 270-MHz FT NMR. For each compound listed, all its characteristic NMR peaks were observed in each run, and in the proper integration. Error on the chemical shifts was estimated at ±0.002 ppm over a large number of spectra run in the course of this study.

Method 1. From the Tosylhydrazone Sodium Salt. A mixture of 279 mg (0.63 mmol) of *trans*-3,4-diphenyl-6-methyl-3,5-heptadien-2-one tosylhydrazone and 92.1 mg (1.70 mmol) of sodium methoxide in 750 mL of anhydrous tetrahydrofuran was stirred 15 h at room temperature under nitrogen and shielded from direct light. The resulting yellow solution was irradiated for 3.00 h through filter C on the Wisconsin Black Box apparatus with vigorous stirring and absorbed 5.64 mEinsteins of light. The resulting near-colorless suspension of fine needles was concentrated in vacuo and the residue partitioned between water and pentane. The aqueous layer was pentane extracted four times and the combined organic extracts were concentrated in vacuo to afford 48.0 mg of a colorless oil. Analysis of the crude material by 270-MHz FT NMR showed two major products: 5,6-diphenyl-3,3,7-trimethyl-3*H*-1,2-diazepine and 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene in a ratio of 1:1.6. Also observed were 1-methyl-2-phenyl-3-isobutenylindene and 2,3-diphenyl-1,5,5-trimethylcyclopentadiene in the ratio of 4.5:1.0. The ratio of 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene to 2,3-diphenyl-1,5,5-trimethylcyclopentadiene was estimated to be 1:0.005. Injection of the crude mixture on the high-pressure LC[29] effected separation of the hydrocarbons from the slower moving diazepine. Analysis of the hydrocarbon mixture by 270-MHz FT NMR showed no change in the ratios of the component compounds.

Method 2. From the 3*H*-Pyrazole. A solution of 28 mg (0.097 mmol) of 3,4-diphenyl-3-isobutenyl-5-methyl-3*H*-pyrazole in 240 mL of benzene was irradiated for 1.25 h through filter C on the Wisconsin Black Box apparatus. The light absorbed was 0.505 mEinstein. The pale yellow photolysate was concentrated to give 28 mg of a yellow oil. Analysis of the crude oil by 270-MHz FT NMR showed 85% conversion of the 3*H*-pyrazole to a mixture of several products, including 5,6-diphenyl-3,3,7-trimethyl-3*H*-1,2-diazepine, 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene, and three other heterocyclic compounds. There were also minute amounts of 1-methyl-2-phenyl-3-isobutenylindene and 2,3-diphenyl-1,5,5-trimethylcyclopentadiene in the ratio of 4.5:1.0. Injection of the crude mixture on the high-pressure LC[29] effected separation of the hydrocarbons from the slower moving heterocycles. Analysis of the hydrocarbon mixture by 270-MHz FT NMR showed a 200:4.5:1.0 mixture of 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene, 1-methyl-2-phenyl-3-isobutenylindene, and 2,3-diphenyl-1,5,5-trimethylcyclopentadiene. The internal standard used was *trans*-3,4-diphenyl-6-methyl-3,5-heptadien-2-one.

Independent Generation of Triplet Carbene Intermediates. A solution of 25.3 mg (0.088 mmol) of 3,4-diphenyl-3-isobutenyl-5-methyl-3*H*-pyrazole and 58.0 mg (0.26 mmol) of

(33) (a) For full details of the acid-catalyzed, thermal, and silver-cation-catalyzed rearrangements of vinylcyclopropenes 1 and 2, see ref 33b. (b) M. C. Hovey, Ph.D. Thesis, University of Wisconsin, Madison, 1978.

Table III. Photolysis of 1-Methyl-2,3-diphenyl-3-isobutenylcyclopropene

run	reactant, mmol	conditions[a]	added sens, mmol	light abs, mEinstein	% convrsn	photoproduct, mmol	Φ
1A	0.100	A	b	2.36	51.1	0.017[e]	0.0072[e]
						0.017[f]	0.0072[f]
						0.0055[g]	0.0023[g]
						0.0094[h]	0.0040[h]
						0.0071[i]	0 0030[i]
						d	0.0[d,j]
1B	0.139	A	b	1.14	24.2	0.0077[e]	0.0068[e]
						0.0084[f]	0.0074[f]
						0.0052[g]	0.0046[g]
						0.0068[h]	0.0060[h]
						0.0057[i]	0.0050[i]
						d	0.0[d,j]
1C	0.105	A	b	0.284	10.3	0.0023[e]	0.0081[e]
						0.0024[f]	0.0085[f]
						0.0023[g]	0.0081[g]
						0.0020[h]	0.0070[h]
						0.0017[i]	0.0060[i]
						d	0.0[d,j]
1D	0.190	A	b	0.201	4.0	0.0015[e]	0.0075[e]
						0.0014[f]	0.0070[f]
						0.0019[g]	0.0095[g]
						0.0057[h]	0.028[h]
						0.0023[i]	0.011[i]
						d	0.0[d,j]
1E	0.198	A	b	0.0646	2.6	0.0015[e]	0.023[e]
						0.00068[f]	0.010[f]
						0.0012[g]	0.018[g]
						d	0.0[h]
						0.0013[i]	0.020[i]
						0.0017[j]	0.027[j]
1F	0.203	A	b	0.0197	1.2	0.00068[e]	0.035[e]
						0.00032[f]	0.016[f]
						0.00042[g]	0.022[g]
						d	0.0[h]
						0.00038[i]	0.019[i]
						0.00059[j]	0.030[j]
2A	0.158	B	1.64[c]	0.0606	13.2	0.0102[e]	0.168[e]
						0.106[h]	0.175[h]
2B	0.154	B	1.62[c]	0.0151	3.4	0.00263[e]	0.174[e]
						0.00264[h]	0.175[h]
2C	0.207	B	1.79[c]	0.00810	1.4	0.00145[e]	0.179[e]
						0.00141[h]	0.174[h]
2D	0.159	B	1.63[c]	0.00321	0.69	0.000543[e]	0.169[e]
						0.000557[h]	0.174[h]

[a] A: Black Box, 240 mL of benzene, filter B. B: microbench, 30 mL of benzene, 360 nm. [b] None added. [c] 4-(Dimethylamino)benzophenone.[10] [d] None detected. [e] 2,3-Diphenyl-1,5,5-trimethylcyclopentadiene. [f] 1,3-Diphenyl-2,5,5-trimethylcyclopentadiene. [g] 1-Methyl-2-phenyl-3-isobutenylindene. [h] 1,2-Diphenyl-3,5,5-trimethylcyclopentadiene. [i] 1-Phenyl-2-methyl-3-isobutenylindene. [j] 1,2-Diphenyl-3-methyl-3-isobutenylcyclopropene.

Table IV. Photolysis of 1,2-Diphenyl-3-methyl-3-isobutenylcyclopropene

run	reactant, mmol	conditions[a]	added sens, mmol	light abs, mEinstein	% convrsn	photoproduct, mmol	Φ
3A	0.224	A	b	0.826	10.5	0.0206[f]	0.025[f]
						0.0030[g]	0.0036[g]
3B	0.227	C	b	0.064	3.7	0.0068[f]	0.11[f]
						0.0016[g]	0.025[g]
3C	0.227	C	b	0.021	1.2	0.0042[f]	0.20[f]
						0.0010[g]	0.048[g]
4A	0.19	B	2.82[c]	0.380	18.5	0.012[e]	0.032[e]
						0.023[f]	0.060[f]
4B	0.21	B	2.69[c]	0.183	9.1	0.006[e]	0.033[e]
						0.011[f]	0.060[f]
4C	0.21	B	2.23[c]	0.020	1.0	0.0007[e]	0.035[e]
						0.0014[f]	0.070[f]

[a] A: Black Box, 240 mL of benzene, filter D. B: microoptical bench, 30 mL of benzene, 360 nm. C: Black Box, 240 mL of benzene, filter C. [b] None added. [c] 4-(Dimethylamino)benzophenone.[10] [d] None detected. [e] 2,3-Diphenyl-1,5,5-trimethylcyclopentadiene. [f] 1,2-Diphenyl-3,5,5-trimethylcyclopentadiene. [g] 1-Methyl-2,3-diphenyl-3-isobutenylcyclopropene.

p-(dimethylamino)benzophenone[10] in 30 mL of benzene was irradiated for 6.74 h at 360 nm on the microoptical bench. The light absorbed was 0.26 mEinstein. Concentration of the crude photolysate in vacuo left 81 mg of a pale yellow crystalline mass. Analysis of the crude photolysate by 270-MHz FT NMR showed ca. 1% conversion of the 3*H*-pyrazole to a mixture of four products in roughly equal amounts: 5,6-diphenyl-3,3,7-trimethyl-3*H*-1,2-diazepine, 1-methyl-2,3-diphenyl-3-isobutenylcyclopropene,

1,2-diphenyl-3,5,5-trimethylcyclopentadiene, and 2,3-diphenyl-1,5,5-trimethylcyclopentadiene. The quantum yield of disappearance of the 3*H*-pyrazole was approximately 0.003. Separation of the mixture of the above four products from the sensitizer was effected by preparative high-pressure liquid chromatography.[29] Analysis of the faster moving bands by 270-MHz FT NMR revealed the presence of the same four compounds and the absence of any indene photoproducts (the threshold limit was approximately 0.01%).

Control Experiments

Photostability of 1,2-Diphenyl-3,5,5-trimethylcyclopentadiene. A solution of 159 mg (0.61 mmol) of 1,2-diphenyl-3,5,5-trimethylcyclopentadiene in 200 mL of benzene was irradiated through a Pyrex filter for 5.50 h on the Hanovia apparatus previously described. Upon concentration of the photolysate, no isomeric cyclopentadiene, indene, or vinylcyclopropene was detectable by 270-MHz FT NMR. It is estimated that 0.01% could have been detected. In addition to those of starting material, there were small peaks in the NMR spectrum indicative of a 2% conversion to 1,2-diphenyl-3,5,5-trimethylbicyclo[2.1.0]pent-2-ene.[15] The spectral data were as follows: 270-MHz FT NMR ($CDCl_3$) τ 3.580 (q, 1 H, J = 1.4 Hz, bridgehead CH), 8.167 (d, 3 H, J = 1.3 Hz, CH_3), 8.225 (s, 3 H, $C(CH_3)_2$), 8.273 (s, 3 H, $C(CH_3)_2$).

Photostability of 1-Phenyl-2-methyl-3-isobutenylindene. The irradiation was performed on the Wisconsin Black Box apparatus previously described, using filter B. A solution of 422 mg (1.62 mmol) of 1-phenyl-2-methyl-3-isobutenylindene in 240 mL of benzene absorbed 4.1 mEinsteins of light. Upon concentration of the solution no isomeric indene, cyclopentadienes, or vinylcyclopropenes were detectable by 270-MHz FT NMR. It is estimated that 0.01% conversion (Φ = 0.0004) could have been detected.

Photostability of 1,3-Diphenyl-2,5,5-trimethylcyclopentadiene. The irradiation was performed on the Wisconsin Black Box apparatus previously described, using filter B. A solution of 255 mg (0.98 mmol) of 1,3-diphenyl-2,5,5-trimethylcyclopentadiene, in 240 mL of benzene absorbed 2.55 mEinsteins of light. Upon concentration of the solution no isomeric cyclopentadienes, indenes, or vinylcyclopropenes were detectable by 270-MHz FT NMR. It is estimated that 0.01% ($\Phi < 10^{-4}$) could have been detected.

Photostability of 2,3-Diphenyl-1,5,5-trimethylcyclopentadiene. The irradiation was performed on the organic chemist's microoptical bench previously described, using a wavelength of 310 nm. A solution of 8.0 mg (0.031 mmol) of 2,3-diphenyl-1,5,5-trimethylcyclopentadiene in 30 mL of benzene absorbed 0.088 mEinstein of light. Concentration of the photolysate, followed by analysis using 270-MHz FT NMR, revealed a 35% conversion to isomeric 1,3-diphenyl-2,5,5-trimethylcyclopentadiene. The quantum yield was estimated by NMR integration to be 0.11. The internal standard used was *trans*-3,4-diphenyl-6-methyl-3,5-heptadien-2-one.

Photostability of 5,6-Diphenyl-3,3,7-trimethyl-3*H*-1,2-diazepine. The irradiation was performed on the organic chemist's microoptical bench previously described, using a wavelength of 320 nm. A solution of 35 mg (0.12 mmol) of 5,6-diphenyl-3,3,7-trimethyl-3*H*-1,2-diazepine in 30 mL of benzene absorbed 0.19 mEinstein of light. Upon concentration of the solution, no other products were detected by 270-MHz FT NMR analysis.

Pyrolysis of *trans*-3,4-Diphenyl-6-methyl-3,5-heptadien-2-one Tosylhydrazone Conjugate Base. The method of Sharp[19] was used. Thus 109 mg (0.245 mmol) of *trans*-3,4-diphenyl-6-methyl-3,5-heptadien-2-one tosylhydrazone and 16.0 mg (0.296 mmol) of sodium methoxide in 20 mL of dry tetrahydrofuran were stirred for 5 h at room temperature under nitrogen while shielded from direct light. The resulting colorless slurry was vacuum pumped free of solvent, treated with 10 mL of dry toluene, and heated 8 h at reflux under nitrogen. Concentration in vacuo left colorless crystals plus a yellow oil which was triturated with hexane, filtered, and concentrated to afford 59 mg of a yellow oil (0.205 mmol, 84%) of 5,6-diphenyl-3,3,7-trimethyl-3*H*-1,2-diazepine, identified by its NMR and IR spectra. Analysis of the crude reaction product by 270-MHz FT NMR showed the absence of any hydrocarbon products (i.e., indenes, cyclopentadienes, or vinylcyclopropenes; vide supra). Injection on a $^3/_8$ in. × 1 ft high-pressure LC column[29] eluted with 20% anhydrous ether in anhydrous hexane also showed the absence of any hydrocarbon products.

The spectral properties of the 3*H*-1,2-diazepine are as follows: 270-MHz FT NMR ($CDCl_3$) τ 2.3–2.9 (m, 10 H, aromatic), 3.769 (s, 1 H, vinyl), 7.738 (s, 3 H, CH_3), 8.541 (s, 3 H, CH_3), 8.710 (s, 3 H, CH_3); IR (thin film) 6.21 (w), 6.37 (w) μm; high-resolution mass spectrometry for $C_{20}H_{20}N_2$ m/e (calcd) 288.163, m/e(found) 288.162.

Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99. Found: C, 83.34; H, 7.11.

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Registry No. 1, 70320-31-9; **2**, 62937-84-2; **3**, 70320-32-0; **4**, 70320-33-1; **5**, 70320-34-2; **6**, 70320-35-3; **7**, 70320-36-4; **8**, 70320-37-5; **9**, 70320-38-6; **10**, 70320-39-7; **11**, 70320-40-0; **12**, 70320-41-1; **13**, 70320-42-2; **14a**, 70320-43-3; **15**, 70320-44-4; **17**, 70320-45-5; **40a**, 70320-46-6; 1,2-diphenyl-3-methylcyclopropenium fluoroborate, 65102-02-5; 1-phenyl-2-(trimethylsilyloxy)propene, 43108-63-0; 1-phenyl-1-(trimethylsilyloxy)propene, 37471-46-8; 1-phenyl-3-methylbut-2-en-1-one, 5650-07-7; 2-phenyl-3-methylindanone, 62907-55-5; 2-methyl-3-phenylindanone, 52957-74-1; 1,2-diphenyl-1-buten-3-one, 1722-69-6; phenylselenium bromide, 34837-55-3; isobutenyl bromide, 3017-69-4; propiophenone, 93-55-0; 2,5-dimethyl-2,4-hexadiene, 764-13-6; diphenyl diselenide, 1666-13-3; **14a** sodium salt, 70320-47-7.

Regiospecific Synthesis of α,β-Unsaturated Azoxy Compounds (Diazene *N*-Oxides)[1]

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The regiospecific synthesis of α,β-unsaturated azoxyalkene **7** by the condensation of α,β-dihalonitroso compound **4** and *N*,*N*-dichlorourethane (**5**) followed by dehalogenation is described. Best results were obtained with the α-bromo-β-chloroazoxy precursor when subjected to iodide as promoter. The isomeric α-chloro-β-bromo compound was resistant to dehalogenation. Other dehalogenating agents were examined. The mechanistic features of dehalogenation by iodide are discussed.

Previously we reported a novel, regiospecific synthesis of unsymmetrical azoxy compounds by the reaction of *N*,*N*-dichloroamino compounds with nitroso substrates in the presence of basic promoters.[4] Yields were low for

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