Photochemistry of Cyclopropene Derivatives. 17. Competition between Side-Chain Fragmentation and Ring Opening[1]

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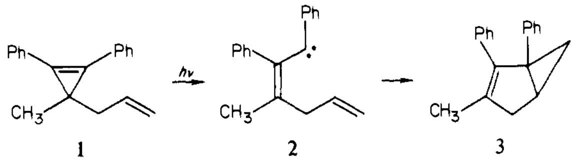
Abstract: The photochemical reactions of several 3-allyl substituted diphenylcyclopropenes have been studied. Irradiation of 2-methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-propene produced products derived from both cyclopropenyl ring opening and side-chain fragmentation. The formation of a bicyclo[3.1.0]hex-2-ene from the irradiation can be rationalized in terms of a vinylcarbene intermediate which undergoes internal cycloaddition. Successive introduction of methyl groups on the α or γ carbon of the allyl side chain was found to dramatically increase the importance of side-chain cleavage relative to ring opening. Thus, irradiation of the 3-prenyl substituted system was found to give rearranged products corresponding to a 1,2-substituent shift. The results obtained from our studies reveal the following trends: (1) excited cyclopropene singlets give products consistent with ring cleavage or side-chain fragmentation, whereas triplet states undergo intramolecular [2 + 2] cycloaddition; (2) the 1,2-substituent shift only occurs with 1,2-diphenyl substituted cyclopropenes; (3) the rearrangement is completely regiospecific leading to unsymmetrically substituted cyclopropenes; (4) side-chain fragmentation competes with ring opening as a primary process when stable radicals are produced. A mechanism involving a dissociation-reassociation process is proposed to account for the formation of the rearranged cyclopropenes.

The photochemistry of cyclopropene derivatives has attracted considerable interest over the past several years.[2,3] The photochemical behavior of this highly strained ring system has been shown to be remarkably dependent on the multiplicity of the excited state involved.[4,5] Singlet states generally react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinylcarbenes,[6] while triplet states, generated by sensitization techniques, give products in which the three membered ring has been retained.[7-11] Recent MO calculations suggest that the singlet excited state of cyclopropenes can readily open in an unactivated process to relieve the strain energy present in the ring.[12] The calculations also indicate that triplet states of cyclopropenes have a large barrier (13 kcal/mol) for ring opening. Triplet states of tetrasubstituted cyclopropenes which possess γ hydrogen have been found to undergo an intramolecular hydrogen transfer reaction[8] by a mechanism analogous to the well-known Norrish type II photoreaction of carbonyl compounds.[13] Systematic probing into the photoreactivity of a number of cyclopropene derivatives led us to the discovery that side-chain fragmentation can compete with ring cleavage as a primary process when stable radicals are produced. This finding provided the stimulus for a broad investigation into the photochemistry of a number of cyclopropene derivatives which contain different substituent groups on the 3 position of the ring. We have found that some of these compounds undergo a side-chain fragmentation reaction which is somewhat similar to the type I reaction of ketones.[14,15] In this paper we wish to describe some of the salient features associated with this reaction.

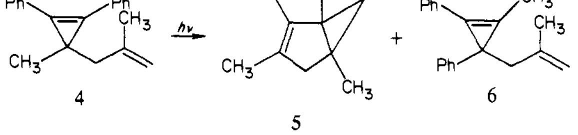
Results

We had previously found that the direct irradiation of 3-allyl-3-methyl-1,2-diphenylcyclopropene (**1**) afforded 1,2-diphenyl-3-methylbicyclo[3.1.0]hex-2-ene (**3**) as the exclusive photoproduct.[9] The most reasonable explanation to account for the formation of **3** involves ring opening of the electronically excited singlet state of **1** to a vinylcarbene intermediate (**2**). The formation of the vinylcarbene in the direct irradiation experiments can be viewed as the result of heterolytic cleavage and simultaneous rotation of the disubstituted methylene carbon.[16,17] Both electrons occupy an in-plane σ orbital with only two electrons in the conjugated π orbital. Attack of the vinylcarbene carbon on the neighboring double bond generates the bicyclo[3.1.0]hexene skeleton.



1 **2** **3**

Irradiation of the related cyclopropene **4** yields products derived from both cyclopropenyl ring opening and α-cleavage.[18] Rupture of the cyclopropene σ bond leads to bicyclohexene **5** (80%) while α-cleavage affords the isomeric cyclopropene **6** in 20% yield. The



4 **5** **6**

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[1] Photochemical Transformations of Small Ring Compounds. 114. For part 113 see A. Padwa and C. S. Chou, *J. Am. Chem. Soc.*, **102**, 3619 (1980).

[2] A. Padwa, *Acc. Chem. Res.*, **12**, 310 (1979).

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[9] A. Padwa and T. J. Blacklock, *J. Am. Chem. Soc.*, **99**, 2345 (1977); **101**, 3390 (1979).

[10] D. R. Arnold and R. M. Morchat, *Can. J. Chem.*, **55**, 393 (1977).

[11] K. A. Brown-Wensley, S. L. Mattes, and S. Farid, *J. Am. Chem. Soc.*, **100**, 4162 (1978).

[12] J. A. Pincock and R. J. Boyd, *Can. J. Chem.*, **55**, 2482 (1977).

[13] P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).

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[16] R. M. Morchat and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, 743 (1978).

[17] J. H. Davis, W. A. Goddard, and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 4015 (1976); **99**, 2427 (1977).

[18] For a preliminary report see A. Padwa, T. J. Blacklock, and R. Loza, *Tetrahedron Lett.*, 219 (1979).

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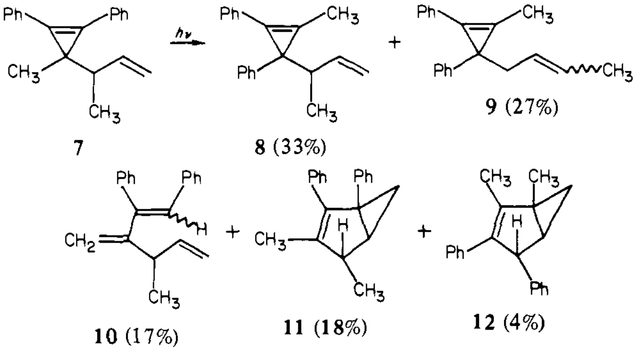
NMR spectrum of bicyclohexene **5** consists of a doublet at δ 0.83 (1 H, J = 4.0 Hz), a three-proton singlet at δ 0.94 and 1.80, a doublet at δ 1.49 (J = 4.0 Hz), an AB quartet at δ 2.68 (2 H, J = 17.0 Hz), and the aromatic multiplet (10 H) at δ 6.95–7.28. The structure of cyclopropene **6** was confirmed by comparison with an authentic sample.

The photochemistry of 3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**7**) was found to proceed differently from that of **4** in that the major products (**8** and **9**) are now derived from α-cleavage (60% overall). The two minor components (35% overall) in the reaction mixture (**10** and **11**) can be considered to be formed from a transient vinylcarbene intermediate which either inserts into the methyl group or undergoes addition to the neighboring π system. In addition to structure **11** another bicyclohexene (**12**) was isolated from the irradiation (4%). The structure of this material was assigned as 1,2-dimethyl-3,4-diphenylbicyclo[3.1.0]hex-2-ene on the basis of its characteristic NMR spectrum, which showed a triplet at δ 0.22 (1 H, J = 4.0 Hz), a doublet of doublets at δ 0.84 (1 H, J = 8.0 and 4.0 Hz), a broad singlet at δ 1.38 (4 H), a doublet at δ 1.89 (3 H, J = 2.0 Hz), a broad singlet at δ 3.93 (1 H), and a multiplet at δ 7.30 (10 H). The lack of coupling between protons H_4 and H_5 necessitates that the phenyl group in the 4 position be located in the exo orientation.



7

8 (33%)

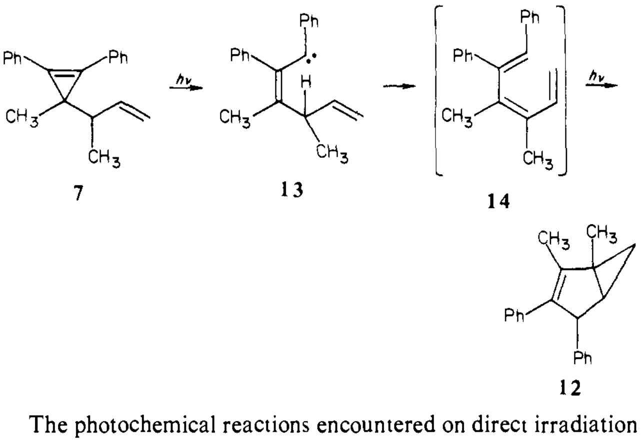
9 (27%)

10 (17%)

11 (18%)

12 (4%)

The most reasonable mechanism to account for the formation of **12** involves insertion of the carbene carbon into the butenyl side chain to give hexatriene **14** as a transient species. It is not unreasonable to expect this highly absorbing compound to be converted into bicyclohexene **12** via an intramolecular photo-Diels–Alder reaction.[19]



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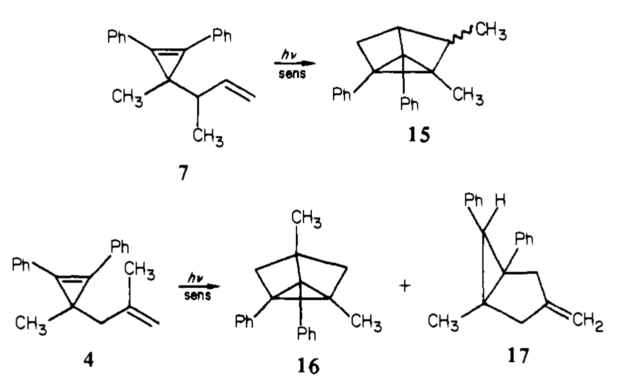
14

12

The photochemical reactions encountered on direct irradiation of **7** proceed through the singlet manifold since sensitization with thioxanthone gave a 1:1 epimeric mixture of tricyclo[2.2.0.0^{2,6}]hexane **15** as the exclusive photoproduct. The triplet-sensitized reaction of cyclopropene **4** gave rise to cycloadduct **16** (82%) and a 3-methylene substituted bicyclo[3.1.0]hexane **17** (18%). The formation of the bicyclohexane ring **17** proceeds via an intramolecular hydrogen atom transfer reaction[8] while the formation of the tricyclo[2.2.0.0^{2,6}]hexane involves an intramolecular [2 + 2]-cycloaddition reaction. Both products were equally quenched with added triplet quenchers, thereby indicating that they are both derived from a common triplet state. These results clearly indicate that the photochemical behavior of the cyclopropene ring is markedly dependent on the multiplicity of the excited state involved.



7

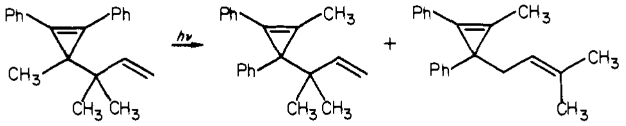
15

4

16

17

Further studies have shown that the successive introduction of methyl groups on the α carbon of the side chain dramatically increases the importance of side-chain cleavage relative to ring opening. Thus, irradiation of cyclopropene **18** afforded a 1:1 mixture of the isomeric cyclopropenes **19** and **20** as the exclusive photoproducts. Close examination of the crude photolysate showed the complete absence of products derived from ring opening.

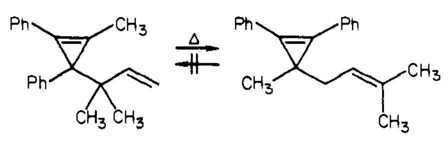


18

19

20

In order to determine whether ring opening would also be suppressed by additional methylation at the γ position, we decided to irradiate a sample of 3-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**21**). 1,2-Diphenyl-3-methyl-3-allyl substituted cyclopropenes are generally prepared by treating diphenylmethylcyclopropenyl cation with allylic Grignard reagents according to the general procedure of Breslow and co-workers.[20] In all the cases studied, nucleophilic attack by the Grignard reagent on the cyclopropenyl cation selectively occurs at the more substituted γ position to furnish high yields of the 3-methyl-3-cyclopropenyl substituted 1-butenes as the major products (i.e., structure **18** from prenyl Grignard and the cyclopropenyl cation). The formation of the substituted 1-butenyl system is entirely analogous to previous results obtained by Young and co-workers.[20] The regioselectivity of addition can be reconciled with a cyclic mechanism of coupling or addition.[21] Since it was not possible to prepare sufficient quantities of **21** from the Grignard approach, we resorted to an alternate approach in which cyclopropene **19** was subjected to thermolysis. Previous work from our laboratory has shown that heating 1,3-diphenyl-3-allyl substituted cyclopropenes results in a novel Cope rearrangement giving rise to the thermodynamically more stable 1,2-diphenyl-3-allyl substituted system as the major product.[22] In agreement with our earlier findings, thermolysis of **19** at 175 °C for 1 h gave **21** in 93% isolated yield. In this case the reaction was irreversible, since extended heating of **21** did not produce any detectable quantities of **19**.



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21

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[19] G. J. Fonken, *Org. Photochem.*, **1**, 222 (1967).

[20] J. F. Lane, J. D. Roberts, and W. G. Young, *J. Am. Chem. Soc.*, **66**, 543 (1944); J. D. Roberts and W. G. Young, *ibid.*, **67**, 148, 319 (1945); **68**, 649 (1946).

[21] W. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 1472 (1946).

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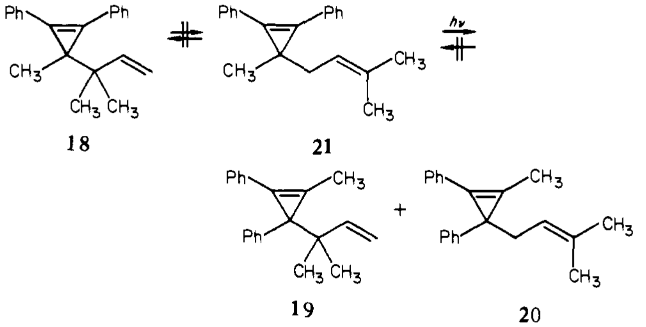
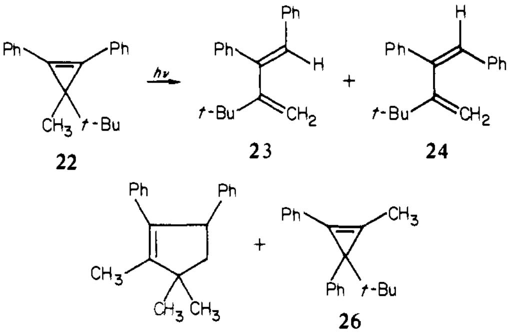
When the irradiation of **21** was carried out in benzene for 30 min, a 1:3 mixture of cyclopropenes **19** and **20** was obtained. The structures of these compounds were confirmed by comparison with authentic samples. Control experiments showed that **18** and **21** were not interconverted under the photolytic conditions. Further irradiation of **19** and **20** did not afford **18** or **21** but instead gave indenes derived from a vinylcarbene intermediate.[23]



18 **21** **19** **20**

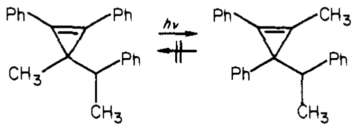
The yields and efficiencies of photochemical α-cleavage reactions of carbonyl compounds have frequently been observed to depend on the stability of the pair of radicals or biradical that is formed.[24-26] In an attempt to assess the importance of this effect with tetrasubstituted cyclopropenes, we have studied the photochemical behavior of 1,2-diphenyl-3-methyl-3-*tert*-butyl- (**22**) and 3-(β-phenethyl)cyclopropene (**27**). Cyclopropene **22** was prepared by treating 3-*tert*-butyl-1,2-diphenylcyclopropenylium perchlorate with methylmagnesium bromide followed by separation of the mixture of isomeric cyclopropenes. Irradiation of **22** with Pyrex-filtered light resulted in the formation of four products which could be separated and purified by silica gel chromatography. Structures **23** (32%) and **24** (32%) were assigned on the basis of their characteristic spectral properties and were further verified by comparison with independently synthesized samples.



22 **23** **24** **25** **26**

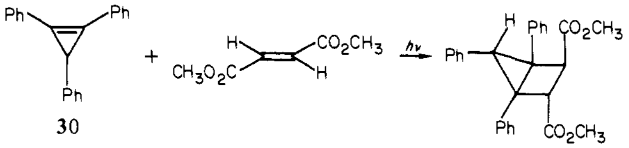
The two dienes were readily interconverted under the photolytic conditions employed. The minor component present in the reaction mixture (4%) was identified as cyclopropene **26** by comparison with an authentic sample. Cyclopentene **25** (17%) was identified on the basis of its spectral data: NMR ($CDCl_3$, 100 MHz) δ 1.12 (s, 3 H), 1.18 (s, 3 H), 1.67 (dd, 1 H, J = 12.6 and 8.4 Hz), 1.79 (d, 3 H, J = 2.2 Hz), 2.34 (1 H, dd, J = 12.6 and 8.4 Hz), 4.20 (dd, 1 H, J = 8.4 and 2.2 Hz), and 6.99–7.24 (m, 10 H).

In contrast to the plethora of compounds obtained from the irradiation of **22**, cyclopropene **27** gave rise to a single photoproduct whose structure was established as 2-methyl-3-(β-phenethyl)-1,3-diphenylcyclopropene (**28**) by comparison with an authentic sample. This result clearly demonstrates that the facility with which the 1,2 substituent shift occurs is markedly dependent on the nature of the substituent group located on the 3 position of the ring.



27 **28**

One additional system which was also studied involved the photochemistry of 3-methoxycarbonyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-propene (**29**). Arnold and Morchat[27] had previously reported that the direct irradiation of the charge-transfer complex between 1,2,3-triphenylcyclopropene (**30**) and dimethyl fumarate gives the bicyclo[2.1.0]pentane **31**. The mechanism proposed for this reaction involved initial excitation of the charge-transfer complex followed by an intersystem-crossing process which led to formation of the cyclopropene triplet. Product formation was attributed to the reactivity of the cyclopropene triplet. The formation of the triplet dimers of cyclopropene **30** as coproducts in this reaction[4] provides additional support for the argument that the irradiation of the charge-transfer complex produces the triplet state of the cyclopropene. There are a number of other examples in the literature where irradiation of a charge-transfer complex leads ultimately to the triplet state of one of the components.[11,28,29] This process has recently been reviewed.[30] It should be noted that the direct irradiation of 1,2-diphenylcyclopropenes does not produce appreciable quantities of triplets. Apparently, intersystem crossing is not able to compete with other processes which deactivate the excited singlet state. It would seem, however, that excitation of the charge-transfer complex formed from a diphenyl-substituted cyclopropene and an electron-deficient olefin will populate the triplet state on direct irradiation.



30 **31**

Our search for an intramolecular version of Arnold's reaction led us to examine the photochemistry of cyclopropene **29**. This compound was prepared by treating 1-methyl-2,3-diphenyl-2-cyclopropen-1-acetaldehyde with carbomethoxytriphenylphosphorane. Our original hope was that this system would form a strong charge-transfer complex which would absorb at long wavelengths and thus allow efficient generation of the triplet state. Earlier results from our laboratory have shown that the triplet states of 3-allyl substituted cyclopropenes undergo smooth intramolecular [2 + 2] cycloaddition to produce tricyclo$[2.2.0.0^{2,6}]$hexanes in high yield.[9] In spite of the significant number of charge-transfer complexes studied by Arnold and Morchat,[27] it remains difficult to predict whether the triplet state of the cyclopropene portion of the complex will be formed upon direct irradiation. We could not obtain any evidence for charge-transfer complex formation between the cyclopropene ring and the electron-deficient double bond present in structure **29**. A benzene solution of **29** had an absorption curve which was superimposable upon that of a benzene solution of 3-allyl substituted cyclopropene **1**. The irradiation of **29** was carried out through a uranium glass filter sleeve in order to maximize excitation by the charge-transfer transition of the complex. The cyclopropene portion of the molecule does have absorption which tails out beyond 370 nm, so direct excitation can occur as well. After 7 h of irradiation,

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(23) A. Padwa, T. J. Blacklock, D. Getman, and N. Hatanaka, *J. Am. Chem. Soc.*, **99**, 2344 (1977); A. Padwa, T. J. Blacklock, D. Getman, N. Hatanaka, and R. Loza, *J. Org. Chem.*, **43**, 1481 (1978).

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(27) R. M. Morchat and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, 743 (1978); D. R. Arnold and R. M. Morchat, *Can. J. Chem.*, **55**, 393 (1977); P. C. Wong and D. R. Arnold, *ibid*, **57**, 1037 (1979).

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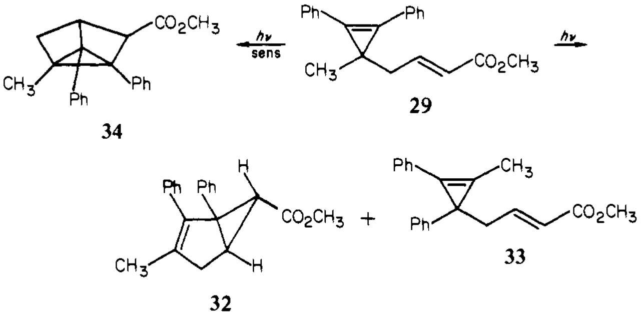
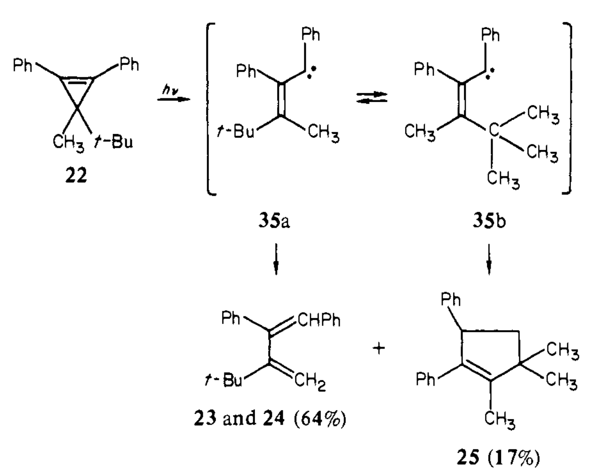
(30) S. Nagakura in "Excited States", Vol. 2, E. C. Lim, Ed., Academic Press, New York, 1975, p 321.

all the cyclopropene had been consumed and the product mixture consisted of bicyclo[3.1.0]hex-2-ene (**32**) and cyclopropene **33** in a 6:1 ratio. Analysis of the crude reaction mixture by NMR spectroscopy revealed the complete absence of tricyclohexane **34**. This material could be produced, however, from the thioxanthone-sensitized irradiation of cyclopropene **29**.

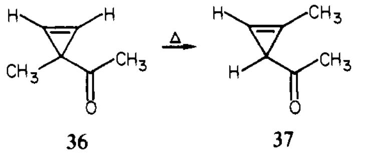


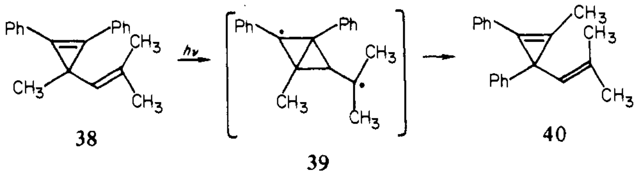
Discussion

During the past several years, considerable research has been directed toward an understanding of the chemistry of electronically excited cyclopropene derivatives.[2,3] Analysis of the data obtained from this research has revealed that cyclopropenes are capable of undergoing four general types of reaction in condensed media: (1) ring opening, (2) side-chain cleavage, (3) [2 + 2] cycloaddition, and (4) intramolecular hydrogen atom transfer. The latter two processes are unimolecular reactions of the electronically excited triplet state. The ring-opening reaction of 1,2-diphenyl-3,3-disubstituted cyclopropenes occurs from the singlet state and gives rise to a vinylcarbene intermediate. The vinylcarbene species can cyclize back to the cyclopropene[5,31] or undergo reactions characteristic of a singlet or triplet methylene. These include intramolecular hydrogen abstraction,[32] insertion into a C–H bond,[33] alkyl group migration,[34] electrocyclization,[23,35-39] and cycloaddition to π bonds.[40,41] The formation of bicyclohexenes **3**, **5**, **11**, and **32** from irradiation of the appropriate cyclopropene can readily be rationalized in terms of intramolecular addition of the carbene carbon onto the neighboring double bond. Insertion of the vinylcarbene into the neighboring C–H bond nicely accounts for the formation of butadienes **10**, **23**, and **24** from the irradiation of cyclopropenes **7** and **22**. With cyclopropene **22**, the products obtained correspond to insertion of the carbene carbon into both the methyl and *tert*-butyl groups. Ring opening of the cyclopropene could lead to either of two stereoisomeric vinylcarbenes (**35a** or **35b**). The fact that dienes **23** and **24** are the major products (64%) obtained suggests either that **35a** is preferentially formed or that insertion of the carbene onto the methyl group proceeds at a faster rate. The low quantum efficiency observed ($\Phi = 0.1$) can be attributed to the rapid return of the vinylcarbene intermediate to the cyclopropene ring.



A limited number of examples are also available where the electronically excited singlet state of the cyclopropene retains the three-membered ring. In these special cases, the photoreaction observed corresponds to a 1,2-substituent shift. It is this reaction upon which we focus our attention in the present investigation. The first example of a 1,2-substituent shift was reported by Monti and Bertrand[42] and involved the thermal rearrangement of 3-acetyl-3-methylcyclopropene (**36**). More recently, Zimmerman and Hovey[39] found that the vinyl moiety present in cyclopropene **38** undergoes a 1,2 shift when subjected to irradiation. This rearrangement was rationalized in terms of π–π^* bridging of the excited cyclopropene to give diradical **39** which subsequently cleaves to produce the rearranged cyclopropene **40**. The bridging and cleavage steps are related to the first two steps of a di-π-methane rearrangement.[43]





Inspection of the data obtained from our studies reveals the following trends: (a) the 1,2 rearrangement occurs exclusively from the electronically excited singlet state; (b) increasing alkyl substitution on the allyl side chain progressively increases the importance of the side chain cleavage reaction; (c) the 1,2-rearrangement path appears to be regiospecific leading only to 1,3-diphenyl substituted cyclopropenes; (d) the substituent shift only occurs with the 1,2-diphenyl substituted cyclopropene systems; (e) in no case is a quantum yield above 0.33 obtained. In addition to these observations, we should point out that, in general, (f) photochemical reactions of tetrasubstituted cyclopropenes are quite clean and proceed in high chemical yield but with low quantum efficiency. We propose a mechanism analogous to that accepted for the type I reaction of ketones to account for the formation of the rearranged cyclopropenes. It should also be pointed out that other examples of photochemical 1,3-allylic migrations which proceed through a dissociation–reassociation path are known in the literature.[44]

The quantum efficiency for the 1,2-substituent shift reaction was found to increase with alkyl substitution on the side chain (i.e., $\Phi_1 = 0$ vs. $\Phi_4 = 0.06$ vs. $\Phi_7 = 0.10$ vs. $\Phi_{18} = 0.33$). This result is perfectly consistent with the proposition that the rearrangement occurs through a transition state which resembles a diradical intermediate. Introduction of methyl groups on the α or γ position of the allyl side chain stabilize the radical-pair

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(31) G. L. Closs, L. E. Closs, and W. A. Boll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).

(32) D. R. Arnold, J. A. Pincock, and R. Morchat, *J. Am. Chem. Soc.*, **95**, 7536 (1973).

(33) R. D. Streeper and P. D. Gardner, *Tetrahedron Lett.*, 767 (1973).

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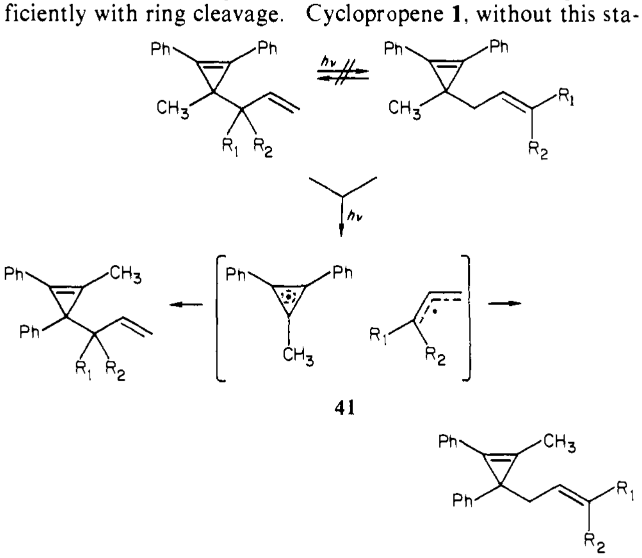
intermediate **41** enough to allow fragmentation to compete efficiently with ring cleavage. Cyclopropene **1**, without this stabilization, yields only ring-opened products. This same reasoning can explain the behavior of **18** (or **21**), where disubstitution prevents ring cleavage from competing with side-chain fragmentation. The fact that 3-*tert*-butylcyclopropene **22**, on irradiation in benzene, gives mostly products derived from cyclopropene ring opening ($\Phi = 0.07$) is not surprising since one would predict that the rate of side-chain cleavage would be relatively slow. The closely related 3-(β-phenethyl) substituted cyclopropene **27** does not give rise to vinylcarbene-type products, presumably because side-chain fragmentation ($\Phi = 0.31$) is too fast for ring opening to compete.

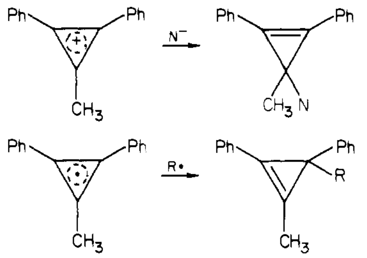


41

The 1,2-rearrangement path occurs with quantum efficiencies significantly less than unity. The low quantum yield observed for the singlet states can be attributed in part to a rapid return of the carbene intermediate to the cyclopropene ring. This reversibility could easily represent the major deactivation pathway for these systems. Still another possibility to account for the low quantum yield involves cage or noncage recombination of the initially formed radical pair. The role of radical-pair recombination in carbonyl-group photochemistry is well established and provides good analogy for this suggestion. For example, Yang[45] and Barltrop[46] have established the importance of cleavage-recombination for cycloalkanones which undergo photoepimerization at the α carbon as well as isomerization via a biradical intermediate. Possible cage reactions of the initially formed radical pair **41** include recombination to give ground-state cyclopropene and diffusion to give separated free radicals. Noncage radical reactions should include recombination and hydrogen abstraction from an appropriate hydrogen-atom donor. No effect on the quantum efficiency of rearrangement of cyclopropenes **18** and **21** was noted when the irradiations were carried out in the presence of 0.03 M 1-dodecanethiol. This would tend to suggest that noncage recombination of cyclopropenyl-allyl radical pairs from cyclopropenes **18** and **21** is not very important.

Several reports have appeared concerning the relative reactivity of the ends of delocalized radicals.[47,48] Cyclopropenes **18** and **21** provide an opportunity to determine the reactivity of a set of delocalized radicals with themselves. Three factors which may affect the distribution of the products are (1) relative spin density at the radical termini, (2) steric effects, and (3) product stability. On account of the exothermicity of radical recombination, little importance is attached to the latter effect. The product distribution on the allyl radical end reflects the greater steric hindrance to recombination of a tertiary site compared with a primary site.[49] The composition of the products derived from cyclopropene **18** (i.e., **19**:**20** = 1:1) differs substantially from that obtained from **21** (**19**:**20** = 1:3). This would suggest that recombination of the radical pair derived from **18** at the α carbon of the allyl group is faster than rotation; otherwise, one would expect the same product distribution from each cyclopropene. The formation of both **19** and **20** in these experiments rules out a concerted 1,2-sigmatropic allyl shift.

Turning now to the matter of regioselectivity, we note that the irradiation of cyclopropenes **18** and **21** gives only the 1,3-diphenyl substituted cyclopropenes. Moreover, cyclopropenes **18** and **21** were not interconverted under the photolytic conditions employed. The exclusive formation of the unsymmetrical cyclopropenes can nicely be accommodated by the dissociation-reassociation path. Breslow and co-workers had previously shown that alkyl groups stabilize cyclopropenyl cations more than phenyl groups.[50] This reversal of substituent effects was rationalized by assuming that the aromatic cyclopropenyl cation would not accept more electrons into its π system as required for assistance by a phenyl group. The cation can be stabilized by an inductive effect in which electron shifts occur within the σ bond. Such an effect is presumably responsible for the fact that nucleophilic attack on a diphenyl alkyl substituted cyclopropenyl cation occurs at the alkylated carbon atom.[51] Phenyl groups, on the other hand, will stabilize a radical located on a cyclopropene ring while alkyl groups will destabilize the radical center.[52] Thus, the preferential formation of cyclopropenes **19** and **20** from the irradiation of **18** or **21** is to be expected since the transition state of these systems prefers to localize the odd electron on the phenylated carbon.



One final point worth mentioning deals with the photochemistry of cyclopropene **29**. Irradiation of this compound in benzene gave products arising from both ring opening (i.e., **32** (85%)) and side-chain fragmentation (i.e., **33** (15%)). As was mentioned earlier, excitation of the charge-transfer complex between an electron-deficient olefin and cyclopropene ring serves to populate cyclopropene triplets. The absence of tricyclo[2.2.0.0^{2,6}]hexane **34** in the direct-irradiation experiments indicates that the triplet state of this system is not populated. This is probably due to the absence of any significant charge-transfer interaction between the unsaturated ester and cyclopropene portions of the molecule. The acrylate unit present in **29** possesses a much lower reduction potential than dimethyl fumarate thereby accounting for the absence of this absorption band in the UV spectrum.

Experimental Section[53]

Preparation of 2-Methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-propene (4) and 2-Methyl-3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-propene (6). A solution containing 2.5 g of methallylmagnesium

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(53) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer, using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz, using a Varian XL-100 and a Jeolco MH-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All irradiations were carried out by using a 450-W Hanovia medium-pressure mercury arc lamp.

chloride in 50 mL of anhydrous tetrahydrofuran was prepared according to the procedure of Rieke.[54] The entire solution was then added over a 10-min period at −78 °C to a stirred suspension containing 3.0 g of 3-methyl-1,2-diphenylcyclopropenylium perchlorate[50] in 100 mL of anhydrous ether. The reaction mixture was stirred for 1 h at −78 °C and let warm to 0 °C, where it was stirred for an additional 12 h. The reaction was quenched by the addition of a saturated ammonium chloride solution. The organic layer was washed with water and a saturated salt solution and dried over magnesium sulfate. The solvent was removed under reduced pressure, leaving behind a brown oil which was percolated through silica gel, using hexane as the eluent. Removal of the solvent left behind a light yellow oil which was chromatographed on a 1.5 × 100 cm silica gel column, using hexane as the eluent. The first component isolated from the column contained 0.92 g (35%) of a colorless oil identified as 2-methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-propene (**4**) on the basis of its physical and spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.45 (s, 3 H), 1.64 (s, 3 H), 2.56 (s, 2 H), 4.70 (s, 2 H), and 7.16–7.76 (m, 10 H); IR (neat) 3.26, 3.41, 5.50, 6.05, 6.24, 6.67, 6.88, 7.27, 9.28, 11.18, 13.18, and 14.5 μm; UV (95% ethanol) 337, 321, and 229 nm (ϵ 19 300, 26 800, and 19 100); *m/e* 260 (M^+), 245, and 205 (base).

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

The second component isolated from the column contained 0.60 g (23%) of a colorless oil identified as 2-methyl-3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-propene (**6**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.70 (s, 3 H), 2.36 (s, 3 H), 2.56 (d, J = 17 Hz, 1 H), 3.20 (d, J = 17 Hz, 1 H), 4.76 (s, 2 H), and 7.0–7.5 (m, 10 H); IR (neat) 3.39, 3.45, 5.40, 6.04, 6.24, 6.71, 6.92, 7.39, 9.30, 10.94, 11.22, 13.18, and 14.48 μm; UV (95% ethanol) 263 nm (ϵ 17 800); *m/e* 260 (M^+), 245, and 205 (base).

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

Direct Irradiation of 2-Methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-propene (4) in Benzene. A solution containing 330 mg of 2-methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-propene (**4**) in 250 mL of anhydrous benzene was irradiated for 45 min under an argon atmosphere. Removal of the solvent under reduced pressure left behind a yellow oil which was chromatographed on a 1.5 × 65 cm silica gel column, using hexane as the eluent. The major fraction isolated contained 232 mg (70%) of a colorless oil which was shown by NMR analysis to be a mixture of two compounds. The mixture was chromatographed on a 1.5 × 65 cm column containing silica gel impregnated with silver nitrate (10% w/w), using 5% ether in hexane as the eluent. The first component isolated contained 178 mg (80%) of a colorless oil identified as 3,5-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**5**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 0.83 (d, J = 4 Hz, 1 H), 0.94 (s, 3 H), 1.49 (d, J = 4 Hz, 1 H), 1.80 (s, 3 H), 2.49 (d, J = 17 Hz, 1 H), 2.78 (d, J = 17 Hz, 1 H), and 6.95–7.28 (m, 10 H); IR (neat) 3.26, 3.48, 6.24, 6.68, 6.92, 12.60, 13.15, and 14.32 μm; UV (95% ethanol) 256 nm (ϵ 9 330); *m/e* 260 (M^+) and 245 (base).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.03; H, 7.88.

The second component isolated contained 45 mg (20%) of a colorless oil identified as 2-methyl-3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-propene (**6**) by comparison with authentic material.

Preparation of 3-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (7) and 3-(2-Methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (8). To a stirred slurry containing 6.1 g of 1,2-diphenyl-3-methylcyclopropenylium perchlorate in 200 mL of anhydrous ether at −78 °C was added 150 mL of a 0.5 M solution of crotylmagnesium bromide in ether. The mixture was stirred for 2 h at −78 °C and allowed to warm up to room temperature, where it was stirred for an additional 4 h. The mixture was hydrolyzed with a saturated ammonium chloride solution. The ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which was chromatographed on a 2.5 × 65 cm silica gel column, using hexane as the eluent. The first component isolated contained 2.41 g (46%) of a colorless oil identified as 3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**7**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 0.93 (d, J = 8 Hz, 3 H), 1.46 (s, 3 H), 2.65 (dq, J = 8 and 8 Hz, 1 H), 4.87–5.05 (m, 2 H), 5.92 (ddd, J = 18, 10, and 8 Hz, 1 H), and 7.06–7.67 (m, 10 H); IR (neat) 3.28, 3.39, 3.50, 5.53, 6.69, 6.91, 7.28, 9.28, 9.68, 10.94, 13.20, and 14.03 μm; UV (95% ethanol) 338, 332, and 228 nm (ϵ 19 700, 27 000, and 17 900); *m/e* 260 (M^+), 245, 206, 205 (base), and 77.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.90.

The second component isolated contained 1.18 g (23%) of a colorless oil identified as a 1:1 diastereomeric mixture of 3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**8**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 0.91–1.06 (m, 3 H), 2.26 (s, 3 H), 3.08–3.48 (m, 1 H), 4.76–5.05 (m, 2 H), 5.52–6.01 (m, 1 H), and 6.84–7.48 (m, 10 H); IR (neat) 3.46, 5.37, 6.24, 6.68, 6.90, 9.26, 10.92, 13.08, 14.28, and 14.45 μm; UV (95% ethanol) 267 nm (ϵ 15 600); *m/e* 260 (M^+), 245, 206, and 205 (base).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.30; H, 8.05.

Direct Irradiation of 3-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (7) in Benzene. A solution containing 0.53 g of 3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**7**) in 450 mL of anhydrous benzene was irradiated with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve under an argon atmosphere for 2 h. Removal of the solvent under reduced pressure left behind a light yellow oil. The above procedure was repeated three additional times and the combined crude photolysate was chromatographed on a 2.5 × 100 cm silica gel column, using hexane as the eluent. Four major fractions were isolated. The first fraction was rechromatographed on a 1.5 × 100 cm silica gel column, using hexane as the eluent. The first component isolated contained 80 mg (3.8%) of a colorless oil which was not identified. The second component isolated contained 0.19 g (9.0%) of a colorless oil identified as (*E*)-4-methyl-3-methylene-1,2-diphenyl-1,5-hexadiene (**10a**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.20 (d, J = 8 Hz, 3 H), 3.13 (quintet, J = 8 Hz, 1 H), 4.84–5.15 (m, 4 H), 5.87 (ddd, J = 18, 10, and 6 Hz, 1 H), 6.68 (s, 1 H), and 6.78–7.33 (m, 10 H); IR (neat) 3.29, 3.40, 6.11, 6.24, 6.70, 6.92, 9.29, 9.70, 10.96, 12.83, 13.17, 14.22, and 14.42 μm; UV (95% ethanol) 285 and 226 nm (ϵ 16 000 and 14 300); *m/e* 260 (M^+), 206, 205 (base), 204, 203, 202, 169, 156, 141, 115, and 91.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.69.

The third component isolated contained 0.16 g (8%) of a colorless oil identified as (*Z*)-4-methyl-3-methylene-1,2-diphenyl-1,5-hexadiene (**10b**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.12 (d, J = 7 Hz, 3 H), 2.89 (quintet, J = 7 Hz, 1 H), 4.73–5.30 (m, 4 H), 5.83 (ddd, J = 16, 12, and 7 Hz, 1 H), 6.66 (s, 1 H), and 7.04–7.56 (m, 10 H); IR (neat) 3.30, 3.39, 6.12, 6.24, 6.72, 6.93, 9.30, 9.71, 10.0, 10.92, 13.13, and 14.28 μm; UV (95% ethanol) 288 and 223 nm (ϵ 14 200 and 15 500); *m/e* 260 (M^+), 206, 205 (base), 204, 203, 202, 156, 115, 91, and 77.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.26; H, 7.69.

The second fraction was also rechromatographed on a 1.5 × 100 cm silica gel column, using hexane as the eluent. The first component isolated contained 0.156 g (18%) of a colorless oil which solidified on standing, mp 65–66 °C (methanol), and which was identified as *exo*-3,4-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**11**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 0.71 (t, J = 4 Hz, 1 H), 1.20–1.33 (m, 5 H), 1.76 (s, 3 H), 2.51 (q, J = 7 Hz, 1 H), and 6.88–7.25 (m, 10 H); IR (KBr) 3.41, 5.17, 6.24, 6.73, 6.98, 8.93, 9.28, 9.79, 10.90, 11.91, 12.24, 13.10, 13.39, and 14.38 μm; UV (95% ethanol) 257 nm (ϵ 10 100); *m/e* 260 (M^+, base) 246, 245, 230, 215, 169, and 167.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.16; H, 7.81.

The second component contained 0.154 g of a colorless oil which was shown by NMR spectroscopy to be a 1.4:1 mixture of 3,4-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**11**) and an isomeric material identified as 1,2-dimethyl-3,4-diphenylbicyclo[3.1.0]hex-2-ene (**12**, 4%) on the basis of its NMR spectra ($CDCl_3$, 100 MHz): δ 0.22 (t, J = 4 Hz, 1 H), 0.84 (dd, J = 8 and 4 Hz, 1 H), 1.38 (br s, 4 H), 1.89 (d, J = 2 Hz, 3 H), 3.93 (br s, 1 H), and 6.88–7.30 (m, 10 H). This mixture was not separable by repetitive chromatography.

The third and fourth fractions were combined and rechromatographed on a 1.5 × 65 cm column containing silica gel impregnated with silver nitrate (10% w/w), using 10% ether in hexane as the eluent. The first component isolated contained 0.45 g (27%) of a colorless oil identified as a 1:1 mixture of (*E*)- and (*Z*)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**9**) by comparison with authentic material.[55] The second component isolated contained 0.55 g (33%) of a colorless oil which was shown to be a 1:1 diastereomeric mixture of 3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**8**) by comparison with authentic material.

Triplet-Sensitized Irradiation of 3-(1-Methyl-2,3-Diphenyl-2-cyclopropen-1-yl)-1-butene (7). A solution containing 200 mg of **7** and 70 mg of thioxanthen-9-one in 200 mL of anhydrous benzene was irradiated for 45 min under an argon atmosphere, using a 450-W Hanovia lamp equipped with a uranium glass filter sleeve. The solution was concentrated under reduced pressure and the resulting residue was chromato-

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(54) R. D. Rieke and S. E. Bales, *J. Am. Chem. Soc.*, **96**, 1775 (1974).

graphed on a thick layer plate. The two major products obtained were identified as *endo*- and *exo*-5,6-dimethyl-1,2-diphenyltricyclo$[2.2.0.0^{2,6}]$hexane (**15**) by comparison with authentic samples.[55]

Reaction of Prenylmagnesium Chloride with 1,2-Diphenyl-3-methylcyclopropenylium Perchlorate. To a stirred suspension containing 9.1 g of 1,2-diphenyl-3-methylcyclopropenylium perchlorate in 200 mL of anhydrous either at −78 °C was added 250 mL of a 0.4 M solution of prenylmagnesium chloride in ether. The mixture was allowed to warm to 0 °C and stirred for an additional 8 h. The reaction mixture was hydrolyzed with a saturated ammonium chloride solution. The ethereal layer was washed with water and a saturated sodium chloride solution, then dried over anhydrous magnesium sulfate. Removal of the ether under reduced pressure left behind a dark yellow oil which was chromatographed on a 1.5 × 100 cm column, using hexane as the eluent. The first fraction isolated contained 3.17 g (38%) of a colorless oil which was identified as 3-methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**18**) on the basis of its physical and spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.05 (s, 6 H), 1.40 (s, 3 H), 4.80–5.08 (m, 2 H), 6.05 (dd, *J* = 16 and 10 Hz, 1 H), and 7.12–7.68 (m, 10 H); IR (neat) 3.40, 5.53, 6.24, 6.09, 6.91, 7.28, 9.04, 10.96, 13.23, and 14.56 μm; UV (95% ethanol) 341 nm (ε 18 200), 323 (25 800), and 230 (18 000); *m/e* 274 (M^+), 259, and 205 (base).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.86; H, 8.11.

The second fraction isolated contained 0.45 g (6%) of 3-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**21**) which was identified on the basis of its physical and spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.46 (s, 3 H), 1.52 (s, 3 H), 1.66 (s, 3 H), 2.46 (d, *J* = 8.0 Hz, 2 H), 5.33 (t, *J* = 8.0 Hz, 1 H), and 7.20–7.69 (m, 10 H); IR (neat) 3.39, 3.45, 5.50, 6.24, 6.70, 6.93, 13.24, and 14.55 μm; UV (95% ethanol) 338 nm (ε 19000), 321 (25 300), 238 (19000), 321 (25 300), 238 (14 000), and 230 (17 000); *m/e* 274 (M^+), 260, and 259 (base).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.75; H, 8.25.

The third fraction isolated contained 1.89 g (23%) of a colorless oil which was identified as 3-methyl-3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**19**) on the basis of its physical and spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.04 (s, 3 H), 1.08 (s, 3 H), 2.39 (s, 3 H), 4.73–5.00 (m, 2 H), 6.07 (dd, *J* = 16 and 11 Hz, 1 H), and 7.00–7.64 (m, 10 H); IR (neat) 3.44, 5.47, 6.24, 6.75, 6.98, 9.32, 9.95, 11.00, 13.20, 14.44, and 14.51 μm; UV (95% ethanol) 275 nm (ε 14 200), 268 (14 100), and 263 (13 400); *m/e* 274 (M^+), 259, and 205 (base).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.79; H, 8.10.

Thermolysis of a sample of cyclopropene **19** at 175 °C for 1 h gave cyclopropene **21** as the exclusive product in 93% isolated yield. The last fraction isolated contained 0.18 g (2%) of a colorless oil which was identified as 3-methyl-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**20**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.54 (s, 3 H), 1.61 (s, 3 H), 2.21 (s, 3 H), 2.81 (d, *J* = 7 Hz, 2 H), 5.20 (t, *J* = 7 Hz, 1 H), and 7.03–7.52 (m, 10 H); IR (neat) 3.32, 3.39, 3.44, 5.49, 6.24, 6.81, 6.92, 9.28, 13.18, and 14.43 μm; UV (95% ethanol) 264 nm (ε 15 300); *m/e* 274 (M^+), 206, and 205 (base).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.84; H, 8.10.

Direct Irradiation of 3-Methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (18). A solution containing 250 mg of cyclopropene **18** in 250 mL of anhydrous benzene was irradiated for 30 min, using a 550-W Hanovia lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a 1.5 × 15 cm column of silica gel, using hexane as the eluent. Removal of the solvent afforded 200 mg (80%) of a colorless oil, which was shown by NMR and LC analysis to contain 3-methyl-3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**19**) and 3-methyl-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**20**) in a 1:1 ratio.

Irradiation of 3-Methyl-1-(1-methyl-2,3-cyclopropen-1-yl)-2-butene (21). A solution containing 200 mg of cyclopropene **21** in 250 mL of anhydrous benzene was irradiated for 30 min, using a 550-W Hanovia lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a 1.5 × 15 cm column of silica gel, using hexane as the eluent. Removal of the solvent afforded 160 mg (80%) of a colorless oil, which was shown by NMR and LC analysis to contain 3-methyl-3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**19**) and 3-methyl-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**20**) in a 1:3 ratio.

Preparation of 3-*tert*-Butyl-3-methyl-1,2-diphenyl- (22) and 2-*tert*-Butyl-3-methyl-1,3-diphenylcyclopropene (26). A solution containing 1.58 g of *tert*-butylphenylacetylene[56] and 1.83 g of phenylchlorodiazirine[57] in 100 mL of dry benzene was refluxed for 4 h. The benzene was removed under reduced pressure, leaving behind a yellow oil which was taken up in 100 mL of methanol. To the methanol solution was added 2.0 g of sodium borohydride in small portions at 0 °C. The mixture was stirred for 30 min and the solution was concentrated under reduced pressure and extracted with ether. The ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which was percolated through silica gel, using hexane as the eluent. Removal of the solvent left behind a light yellow oil which solidified on standing. Recrystallization from methanol afforded 1.2 g (48%) of a white, crystalline material identified as 3-*tert*-butyl-1,2-diphenylcyclopropene on the basis of its spectral properties: mp 65.5–66 °C; NMR ($CDCl_3$, 100 MHz) δ 1.01 (s, 9 H), 2.14 (s, 1 H), and 7.13–7.76 (m, 10 H); IR (neat) 3.28, 3.41, 3.53, 5.56, 6.24, 6.70, 6.93, 7.19, 7.35, 7.48, 7.96, 8.29, 9.30, 9.50, 10.84, 13.06, 13.37, and 14.38 μm; UV (95% ethanol) 340, 322, 313, 238, and 230 nm (ε 19 100, 27 100, 24 200, 14 400, and 18 000); *m/e* 248 (M^+), 192, and 191 (base).

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.83; H, 8.12.

To a stirred solution containing 1.0 g of 3-*tert*-butyl-1,2-diphenylcyclopropene in 25 mL of acetonitrile was added 1.32 g of trityl perchlorate[58] in small portions. The mixture was stirred for an additional 30 min and then 200 mL of anhydrous ether was added. The resultant white precipitate was filtered to give 1.1 g (80%) of a white, amorphous solid which was identified as 3-*tert*-butyl-1,2-diphenylcyclopropenylium perchlorate, mp 197 °C dec, on the basis of its physical properties and subsequent chemical behavior.

To a stirred suspension containing 1.64 g of the above perchlorate in 150 mL of anhydrous ether at −78 °C was added 2.5 mL of a 3.0 M solution of methylmagnesium bromide in ether. The mixture was stirred at −78 °C and then allowed to warm to 4 °C and stirred for an additional 12 h. The mixture was hydrolyzed with a saturated ammonium chloride solution. The organic layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the ether under reduced pressure left behind a yellow oil which was chromatographed on a 1.5 × 100 cm silica gel column, using hexane as the eluent. The first component isolated contained 0.56 g (45%) of a colorless oil identified as 3-*tert*-butyl-3-methyl-1,2-diphenylcyclopropene (**22**) on the basis of its spectral properties: NMR δ 1.07 (s, 9 H), 1.46 (s, 3 H), and 7.20–7.94 (m, 10 H); IR (neat) 3.31, 3.40, 5.57, 6.24, 6.21, 6.96, 7.30, 7.38, 9.03, 9.32, 9.71, 10.98, 13.10, and 14.53 μm; UV (95% ethanol) 341, 323, 315, 239, and 230 nm (ε 18 900, 26 600, 23 200, 12 900, and 16 700); *m/e* 206, 205 (base), 158, 143, and 128.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.54; H, 8.44.

The second component isolated contained 0.34 g (27%) of a colorless oil identified as 2-*tert*-butyl-3-methyl-1,3-diphenyl-3-methylcyclopropene (**26**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.25 (s, 9 H), 1.75 (s, 3 H), and 7.00–7.52 (m, 10 H); IR (neat) 3.40, 5.43, 6.24, 6.71, 6.92, 7.35, 9.71, 12.94, 13.14, 14.38, and 14.48 μm; UV (95% ethanol) 264 nm (ε 17 500); *m/e* 262 (M^+), 247, 232, 207, 206, 205 (base), 204, 203, 202, 191, 189, 128, 127, 91, 77, and 57.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.41; H, 8.47.

Direct Irradiation of 3-*tert*-Butyl-3-methyl-1,2-diphenylcyclopropene (22) in Benzene. A solution containing 750 mg of 3-*tert*-butyl-3-methyl-1,2-diphenylcyclopropene (**22**) in 450 mL of anhydrous benzene was irradiated for 2 h under an argon atmosphere with a 550-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve. Removal of the benzene under reduced pressure left behind a light yellow oil which was chromatographed on a 1.5 × 100 cm silica gel column, using hexane as the eluent. The first fraction isolated contained 240 mg (32%) of a colorless oil which was identified as (*E*)-3-*tert*-butyl-1,2-diphenyl-1,3-butadiene (**23**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 0.95 (s, 3 H), 5.08 (d, *J* = 2 Hz, 1 H), 5.16 (d, *J* = 2 Hz, 1 H), 6.48, (s, 1 H), 6.90–7.16 (m, 5 H), and 7.22 (s, 5 H); IR 3.40, 6.24, 6.70, 6.92, 8.72, 9.24, 10.98, 12.77, and 14.32 μm; UV (95% ethanol) 277 and 228 nm (ε 11 500 and 19 300); *m/e* 262 (M^+), 206, 205 (base), 143, and 91.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.41; H, 8.55.

The second component isolated contained 242 mg (32%) of a colorless oil which was identified as (*Z*)-3-*tert*-butyl-1,2-diphenyl-1,3-butadiene

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(**24**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 0.98 (s, 9 H), 5.17 (d, J = 2 Hz, 1 H), 5.47 (d, J = 2 Hz, 1 H), 6.61 (s, 1 H), and 7.08–7.68 (m, 10 H); IR (neat) 3.41, 6.24, 6.72, 6.93, 8.72, 10.94, 13.06, 14.36, and 14.46 μm; UV (95% ethanol) 282 and 218 nm (ε 17400 and 13800); *m/e* 262 (M^+), 206, 205 (base), 143, and 91.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.41; H, 8.55.

The third component isolated contained 31 mg (4%) of a colorless oil identified as 3-*tert*-butyl-2-methyl-1,3-diphenylcyclopropene (**26**) by comparison with authentic material. The fourth component isolated contained 131 mg (17%) of a colorless oil which solidified on standing. Recrystallization from methanol gave a white solid which was identified as 2,3,3-trimethyl-1,5-diphenylcyclopent-1-ene (**25**) on the basis of its physical and spectral properties: mp 65–66 °C; NMR ($CDCl_3$, 100 MHz) δ 1.12 (s, 3 H), 1.18 (s, 3 H), 1.67 (dd, J = 12.6 and 8.4 Hz, 1 H), 1.79 (d, J = 2.2 Hz, 3 H), 2.34 (dd, J = 12.6 and 8.1 Hz, 1 H), 4.20 (dd, J = 8 and 2.2 Hz, 1 H), and 6.99–7.24 (m, 10 H); IR (neat) 3.36, 3.44, 3.55, 6.24, 6.71, 6.86, 6.91, 7.40, 8.69, 9.31, 9.70, 12.82, 13.30, and 14.21 μm; UV (95% ethanol) 248 nm (ε 11600); *m/e* 262 (M^+), 148, 147 (base), and 91.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.42; H, 8.57.

Preparation and Irradiation of (*E*)-3-*tert*-Butyl-1,2-diphenyl-1,3-butadiene (23). To 8 mL of a 1.9 M solution of *tert*-butyllithium in pentane at −78 °C was added dropwise a solution containing 3.3 g of (*E*)-3,4-diphenyl-3-buten-2-one[59] in 100 mL of hexane. The reaction mixture was allowed to warm up to room temperature and quenched with water. The organic layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a light yellow oil which dissolved in 75 mL of glacial acetic acid. To this solution at 0 °C were added 15 mL of concentrated sulfuric acid and 1 mL of water. After being stirred for an additional 45 min at 0 °C the mixture was poured into iced water. The mixture was extracted with ether. The ethereal layer was washed several times with water, a saturated sodium bicarbonate solution, and a saturated salt solution. Drying of the organic layer over magnesium sulfate followed by removal of the solvent under reduced pressure left behind a yellow oil which was percolated through silica gel, using hexane. Removal of the solvent left behind a light yellow oil which was chromatographed on a 1.5 × 100 cm silica gel column, using hexane as the eluent. The major component isolated contained 0.26 g (7%) of (*E*)-3-*tert*-butyl-1,2-diphenyl-1,3-butadiene (**23**) which was identical in every detail with the material isolated from the direct irradiation of 3-*tert*-butyl-3-methyl-1,2-diphenylcyclopropene (**22**).

A solution containing 166 mg of **23** in 250 mL of dry benzene was irradiated under an argon atmosphere for 1 h, using a 550-W Hanovia medium pressure mercury arc lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left behind a clear oil which was shown by NMR analysis to contain a 1:1 mixture of (*E*)- and (*Z*)-3-*tert*-butyl-1,2-diphenyl-1,3-butadiene (**23** and **24**). Chromatography on silica gel, using hexane as the eluent, confirmed the NMR analysis.

Synthesis of 3-Methyl-3-(β-phenethyl)-1,2-diphenylcyclopropene (27). A solution containing 1.98 g of β-phenethylmagnesium chloride in 50 mL of anhydrous tetrahydrofuran was prepared according to the procedure of Rieke.[54] The entire solution was then added over a 10-min period at −78 °C to a stirred suspension containing 3.0 g of 3-methyl-1,2-diphenylcyclopropenylium perchlorate in 150 mL of anhydrous tetrahydrofuran. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to 0 °C where it was stirred for an additional 4 h. The reaction was quenched by the addition of a saturated ammonium chloride solution and the mixture then diluted with ether. The organic layer was washed with water and a saturated salt solution and dried over magnesium sulfate. The solvent was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a 1.5 × 100 cm silica gel column, using a 15% benzene–hexane mixture as the eluent. The first component isolated contained 0.33 g (11%) of a colorless oil which was identified as 3-methyl-3-(β-phenethyl)-1,2-diphenylcyclopropene (**27**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.20 (d, J = 7 Hz, 3 H), 1.37 (s, 3 H), 3.19 (q, J = 7 Hz, 1 H), and 7.01–7.56 (m, 15 H); IR (neat) 3.41, 3.49, 5.52, 6.24, 6.69, 6.91, 7.28, 9.30, 9.69, 10.93, 12.68, 13.24, 14.21, and 14.54 μm; UV (95% ethanol) 341, 323, and 230 nm (ε 16800, 23900, and 20600); *m/e* 310 (M^+), 295, 206, and 205 (base).

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 93.01; H, 7.23.

The second component isolated contained 2.4 g (77%) of a light yellow oil which was identified as a 1:1 diastereomeric mixture of 3-methyl-3-(β-phenethyl)-1,2-diphenylcyclopropene (**27**) on the basis of its spectral properties: NMR δ 1.27 (d, J = 7 Hz, 3 H), 2.30 (s, 3 H), 3.84 (q, J = 7 Hz, 1 H), 6.88–7.44 (m, 15 H), 1.20 (d, J = 7 Hz, 3 H), 2.90 (s, 3 H), 4.01 (q, J = 7 Hz, 1 H), 6.88–7.44 (m, 15 H); IR (neat) 3.32, 3.48, 5.41, 6.24, 6.72, 6.93, 12.62, 12.70, 13.20, and 14.44 μm; UV (95% ethanol) 268 nm (ε 12700); *m/e* 310 (M^+), 206, 205 (base), 203, 202, and 105.

Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.76; H, 7.18.

Direct Irradiation of 3-Methyl-3-(β-phenethyl)-1,2-diphenylcyclopropene (27). A solution containing 120 mg of 3-methyl-3-(β-phenethyl)-1,2-diphenylcyclopropene (**27**) in 200 mL of benzene was irradiated for 30 min under an argon atmosphere, using a 550-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left behind a yellow oil which was chromatographed on a preparative thick layer plate, using a 15% benzene–hexane mixture as the eluent. The major component isolated contained 87 mg (73%) of a colorless oil identified as 2-methyl-3-(β-phenethyl)-1,3-diphenylcyclopropene (**28**) by comparison with authentic material.

Preparation of Methyl 4-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butenoate (29). To a solution containing 1.36 g of 1-methyl-2,3-diphenyl-2-cyclopropene-1-acetaldehyde[55] in 150 mL of methylene chloride was added 1.8 g of carbomethoxymethylenetriphenylphosphorane.[60] The mixture was heated at reflux for 12 h and the solvent was removed under reduced pressure. The resulting oil was triturated with ether to remove the precipitated triphenylphosphine oxide. After filtration, the solution was concentrated under reduced pressure and the resulting oil was chromatographed on a 3.5 × 60 cm silica gel column, using 10% ether–hexane as the eluent. The major fraction collected contained 1.0 g (60%) of a clear oil whose structure was assigned as methyl 4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butenoate (**29**): IR (neat) 3.36, 5.55, 5.80, 6.10, 6.30, 6.72, 6.98, 7.05, 7.31, 7.62, 7.90, 8.41, 8.64, 9.42, 10.28, 13.40, and 14.91 μm; NMR ($CDCl_3$, 100 MHz) δ 1.50 (s, 3 H), 2.62 (dd, 2 H, J = 9.0 and 1.0 Hz), 3.63 (s, 3 H), 5.92 (td, 1 H, J = 18.0 and 1.0 Hz), 6.80–7.60 (m, 11 H); UV (95% ethanol) 336, 318, and 223 nm (ε 21000, 27300, and 23400); *m/e* 304 (M^+), 289, 205.

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.88; H, 6.82.

Direct Irradiation of Methyl 4-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butenoate (29). A solution containing 300 mg of **29** in 250 mL of benzene was irradiated for 7 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a uranium glass filter sleeve under an argon atmosphere. The benzene was removed under reduced pressure, leaving behind a light yellow oil which was chromatographed on a thick layer plate, using a 10% ether–hexane mixture as the eluent. The first component isolated from the plate contained 255 mg (85%) of a colorless oil which was identified as 1,2-diphenyl-3-methyl-6-*exo*-carbomethoxybicyclo[3.1.0]hex-2-ene (**32**) on the basis of its characteristic spectral properties: IR (neat) 3.30, 3.41, 5.82, 6.25, 6.75, 6.99, 7.20, 7.61, 7.90, 8.63, 9.52, 11.10, 13.52, and 14.86 μm; UV (95% ethanol) 250 nm (ε 9000); NMR ($CDCl_3$, 100 MHz) δ 1.68 (s, 3 H), 1.92 (d, 1 H, J = 5.0 Hz), 2.56 (d, 1 H, J = 18.0 Hz), 2.60 (dd, 1 H, J = 7.0 and 5.0 Hz), 3.16 (dd, 1 H, J = 18.0 and 7.0 Hz), 3.50 (s, 3 H), 7.0–7.6 (m, 10 H).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 83.86; H, 6.62. Found: C, 82.74; H, 6.53.

The second fraction isolated from the thick layer plate contained 45 mg (15%) of a pale yellow oil whose structure was assigned as methyl 4-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butenoate (**33**) on the basis of its spectral properties: IR (neat) 3.35, 5.40, 5.80, 6.02, 6.25, 6.70, 6.91, 7.50, 7.92, 8.31, 8.60, 9.32, 9.70, 11.05, 13.24, and 14.50 μm; NMR ($CDCl_3$, 90 MHz) δ 2.28 (s, 3 H), 3.0 (m, 2 H), 3.62 (s, 3 H), 5.80 (d, 1 H, J = 16.0 Hz), 6.8–7.5 (m, 11 H); UV (95% ethanol) 260 nm (ε 17300); *m/e* 304 (M^+), 205, and 100 (base).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.65; H, 6.66.

The structure of this material was unambiguously verified by comparison with an authentic sample. A solution containing 300 mg of 2-methyl-1,3-diphenyl-2-cyclopropene-1-acetaldehyde[55] and 450 mg of carbomethoxymethylenetriphenylphosphorane in 50 mL of methylene chloride was heated at reflux for 12 h under a nitrogen atmosphere. The solvent was removed under reduced pressure and the resulting oil was chromatographed through a neutral alumina column to remove the tri-

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phenylphosphine oxide. The resulting oil was rechromatographed on a thick layer plate to give 300 mg (73%) of a pale yellow oil which was identical in all respects with a sample of methyl 4-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butenoate (**33**) isolated from the photolysis of cyclopropene **29**.

Triplet-Sensitized Irradiation of Methyl 4-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butenoate (29). A solution containing 200 mg of **29** and 100 mg of thioxanthen-9-one in 500 mL of benzene was irradiated for 2.5 h under an argon atmosphere, using a 450-W Hanovia lamp equipped with a uranium glass filter sleeve. The solution was concentrated under reduced pressure and the resulting residue was chromatographed on a thick layer plate, using a 9% ether–hexane mixture as the eluent. The major component from the reaction mixture contained 150 mg (75%) of a crystalline solid, mp 67–68 °C, whose structure was assigned as *exo*-6-carbomethoxy-3-methyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**34**) on the basis of its spectral properties: IR (KBr) 3.40, 5.81, 6.50, 6.71, 6.90, 7.03, 7.32, 7.56, 8.31, 8.50, 8.62, 13.48, 13.83, 14.26, and 14.44 μm; NMR ($CDCl_3$, 100 MHz) δ 1.35 (s, 3 H), 2.20 (d, 1 H, $J = 9.0$ Hz), 2.76 (dd, 1 H, $J = 9.0$ and 5.0 Hz), 3.05 (d, 1 H, $J = 5.0$ Hz), 3.52 (s, 1 H), 3.66 (s, 3 H), and 7.0–7.6 (m, 10 H); UV (95% ethanol) 238 nm (ε 13 000); *m/e* 304 (M^+), 289, 245, 205, and 77.

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.65; H, 6.70.

Quantum-Yield Determinations. All quantitative measurements were made on a rotating assembly at room temperature, using a Rayonet reactor equipped with 3000-Å lamps. Samples were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum-yield determinations.[61] Reliably reproducible output rates of 1.73×10^{17} quanta/s were recorded. After the irradiation the degree of reaction was determined by quantitative LC analysis. An Altex 3.2 × 250 mm Lichrosorb 5-m C-18 reverse phase column with aqueous methanol was used for the analyses. The conversions were run to 15% or less. The mass balances in these runs were generally better than 95%.

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Charge-Transfer Mechanism for Quenching of the Lowest ^{3}n,π* State of Vapor-Phase Carbonyl-Containing Compounds by O_2

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Abstract: Rate constants, ranging between 0.20 and 6.9×10^9 M^{-1} s^{-1}, for quenching of the lowest ^{3}n,π* state of several carbonyl-containing compounds by oxygen in the vapor phase have been measured with a flash sensitization technique. In general, the rate constants increase with increasing energy of the ^{3}n,π* state, have small negative activation energies, and increase as the difference in energy between the ionization potential and triplet state energy of the carbonyl-containing compounds decreases. This is in accordance with coupling of the initially formed complex to a charge-transfer state. Spectroscopic evidence was obtained for the existence of a complex between acetone and oxygen.

Introduction

Oxygen has two excited electronic singlet states at energies less than the triplet-state energy of most organic molecules,[1] which allows oxygen to quench these triplet states by both intermolecular transfer of electronic energy and enhancement of intersystem crossing. Both processes are expected to occur through the formation of a complex with allowed singlet, triplet, or quintet spin multiplicity. However, spin selection rules allow the transfer of energy to occur only through the singlet-state complex and disallow relaxation of the quintet-state complex. Hence processes 1 and 2 are expected to be most important.

$$T + O_2 \underset{k_{-c}}{\overset{1/9k_c}{\rightleftarrows}} {}^1(T\cdots O_2)^* \xrightarrow{k_{et}} S_0 + O_2^* \tag{1}$$

$$T + O_2 \underset{k_{-c}}{\overset{1/3k_c}{\rightleftarrows}} {}^3(T\cdots O_2)^* \xrightarrow{k_{isc}} S_0 + O_2 \tag{2}$$

$$T + O_2 \underset{k_{-c}}{\overset{5/9k_c}{\rightleftarrows}} {}^5(T\cdots O_2)^* \tag{3}$$

T and S_0 are the triplet state and ground state of the organic molecule, respectively. The collision partners in reactions 1, 2, and 3 collide with rates given by $^1/_9k_c$, $^1/_3k_c$, and $^5/_9k_c$, respectively, where k_c is the hard sphere collisional rate constant and $^1/_9$, $^1/_3$, and $^5/_9$ are the statistical probabilities for formation of a complex with singlet, triplet, and quintet spin multiplicity, respectively. The collision complex dissociates with a rate constant k_{-c} to form reactants.

Extensive studies of the quenching of triplet-state aromatic hydrocarbons by oxygen in dilute solution have yielded quenching constants, k_q, which are less than $^1/_9k_d$ (where k_d is the rate constant for diffusional contact), indicating the predominance of process 1.[2,3] Exceptions, for which k_q approaches $^1/_3k_d$, include several stilbene derivatives for which it has been suggested that the small energy difference between the lowest excited singlet and triplet states in "twisted" geometries facilitates quenching through the formation of triplet-state complexes (process 2).[4] In ref 2 and 3 it was found that k_q decreases with increasing triplet energy of the aromatic. This was attributed to control of quenching by Franck–Condon factors associated with C–H stretching modes, and Siebrand's expressions for radiationless decay rates[5] were used to explain the results.[6]

The mechanism for quenching of ^{3}n,π* states seems to be less well understood. Merkel and Kearns have reported that the

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