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A New Photochemical Rearrangement. A Cyclopropyl-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry[1,2]

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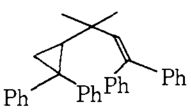
Abstract: The photochemistry of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene was investigated in order to ascertain the reactivity of a system having one π moiety and one cyclopropyl ring attached to a saturated carbon. Only the singlet excited state proved reactive. As photochemical products there were obtained 1,1-diphenylethylene, 2-methyl-1,1-diphenyl-1-propene, 1,1-diphenylbutadiene, 4-methyl-1,1-diphenyl-1,3-pentadiene, and 3-(2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane. The cyclobutane product was considered as a potential reaction intermediate in the formation of the other products, and its photochemistry was investigated. Irradiation of the cyclobutane was found to afford 2-methyl-1,1-diphenyl-1-propene and 1,1-diphenyl-1,3-butadiene but no diphenylethylene or 4-methyl-1,1-diphenyl-1,3-pentadiene. This evidence required that the diphenylethylene and the 4-methyl-1,1-diphenyl-1,3-pentadiene be primary photolysis products of the cyclopropylvinylmethane. Furthermore, extrapolation of the product distribution to zero time revealed an initial absence of 2-methyl-1,1-diphenyl-1-propene and diphenylbutadiene, thus showing these to be secondary photoproducts deriving from reaction of the cyclobutane. One a priori mechanism for formation of diphenylethylene and 4-methyl-1,1-diphenyl-1,3-pentadiene was carbene fragmentation followed by rearrangement. This was ruled out by independent study of the behavior of the carbene generated thermally and photochemically. A mechanism is postulated accounting both for formation of these products and the cyclobutane. This mechanism parallels that of the ubiquitous di-π-methane rearrangement but leads instead to the cyclobutane. Diversion of the reaction mechanism along the reaction coordinate leads to the fragmentation products.

Organic photochemistry is at a stage of development where its repertoire of established reactions consists of less than a score. Of these one is the di-π-methane rearrangement which has proved both extraordinarily general and synthetically useful.[3] It thus seemed worthwhile to investigate the possibility of effecting a parallel rearrangement in which one π moiety has been replaced by a three-membered ring, thus affording a cyclopropyl-π-methane or homo-di-π-methane rearrangement.

For this study, we selected 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene (**1**) because of its close structural relationship to the well-studied[3b,4] 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**2**).



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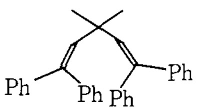

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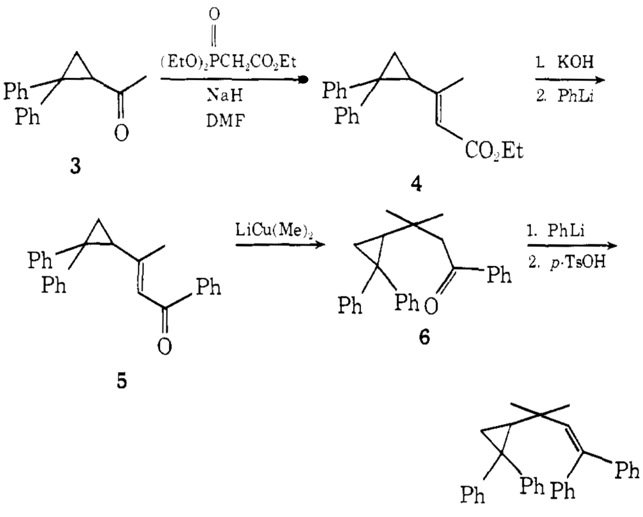
Results

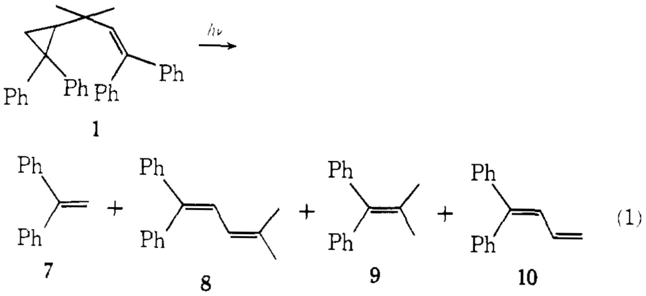
Synthesis of Reactant. The synthesis devised for cyclopropylvinylmethane **1** is outlined in Chart I. This route began with 2,2-diphenylcyclopropyl methyl ketone[5] (**3**) and its reaction with the conjugate base of triethyl phosphonoacetate. The phosphonate reaction[6] required somewhat more strenuous conditions than normal but proceeded in excellent yield. Otherwise the synthesis was unexceptional.

Exploratory Photochemistry of the Cyclopropylvinylmethane. Exploratory photolyses were run on a Rayonet[7] type of reactor consisting of 32 15-W low-pressure mercury lamps arranged in a cylindrical array surrounding a quartz vessel. It was observed that direct irradiation (sensitization led to no reaction) under these conditions led to five prod-

Chart I. Synthesis of 3-(2,2-Diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene

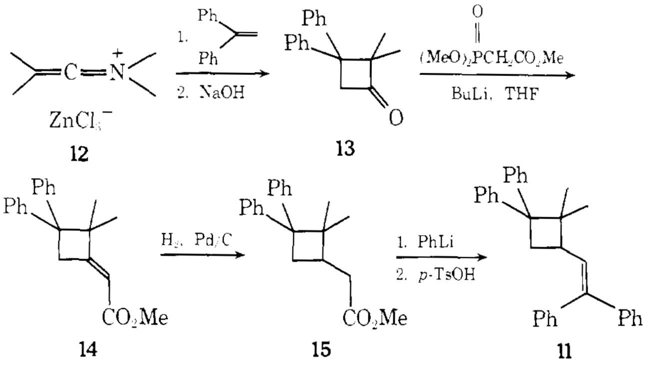


ucts. Four of these were isolated and identified by comparison with authentic samples as 1,1-diphenylethylene (**7**), 4-methyl-1,1-diphenyl-1,3-pentadiene (**8**), 2-methyl-1,1-diphenyl-1-propene (**9**), and 1,1-diphenyl-1,3-butadiene (**10**). Note eq 1. The fifth compound was present only in trace amounts and was not isolated. However, NMR evidence (see Experimental Section) and mechanistic reasoning suggested that the unknown product was 3-(2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane (**11**), and a synthesis of this compound was thus needed.

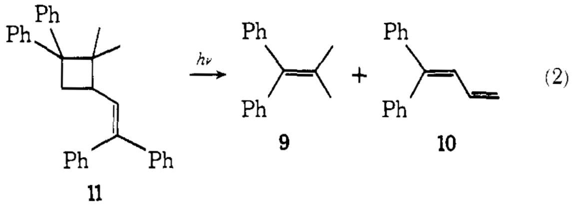


Synthesis of 3-(2,2-Diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane. This synthesis began with the reaction of the *N*,*N*-dimethyl-*N*-(2-methyl-1-propylidene)ammonium cation (**12**) with diphenylethylene in analogy to the recently reported^{8} reaction of this immonium compound with other olefins. The further steps proved routine and are outlined in Chart II. The NMR of this compound proved to match that for which evidence had been obtained in the photolysis of the cyclopropylvinylmethane **1** above.

Chart II. Synthesis of 3-(2,2-Diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane



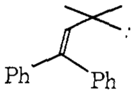
Exploratory Photolysis of 3-(2,2-Diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane. Because of the occurrence of this compound in the photolysis of the cyclopropyl-π-methane, its own photochemistry was of interest. It was observed that, on irradiation in the Rayonet type apparatus described above, it gave diphenylisobutylene **9** and diphenylbutadiene **10** but neither diphenylethylene **7** nor pentadiene **8**; note eq 2.



Thus it is clear that cyclobutane **11** was not a possible photochemical precursor to diphenylethylene **7** or pentadiene **8**, but was an a priori possibility in leading to diphenylisobutylene **9** and diphenylbutadiene **10**.

Of some interest was the observation that the sensitized photolysis of the cyclobutane gave the same products as the direct irradiation. Thus with the information in hand, one might conceive of the cyclobutane formed in the photolysis of the cyclopropyl-π-methane reacting further via either its singlet or its triplet.

Synthesis of Carbene Precursors. Our mechanistic reasoning, discussed below, led us to consider that diphenylethylene **7** and pentadiene **8** might be formed by way of 3,3-dimethyl-1,1-diphenyl-1-butenylidene (**16**). Literature analogy^{9} suggested that formation of this carbene in the photolysis of the cyclopropyl-π-methane was a possibility, so it was important to determine its behavior when generated independently.



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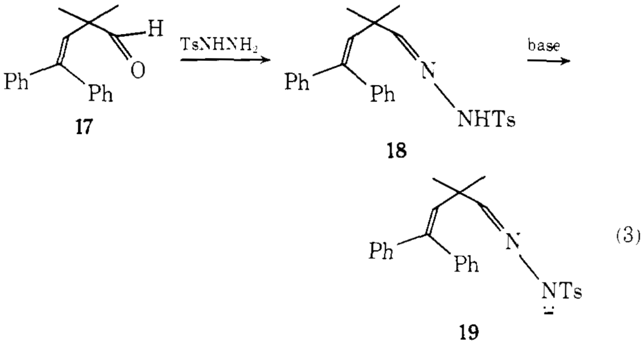
One approach involved the conjugate base **19** of the tosylhydrazone **18**, which was synthesized from the known aldehyde **17**^{10} as shown in eq 3.



Another approach utilized the diazocompound **26**. Its synthesis started from the known lactone **20**^{11} and involved as key steps the diazotization and Curtius rearrangement of acyl hydrazide **23** and base treatment of the nitrosourethane **25**. The synthesis is outlined in Chart III.

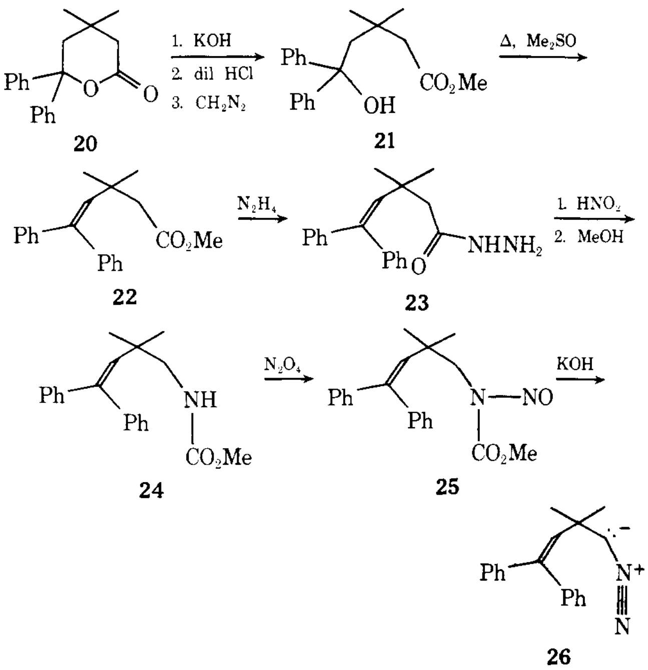
Thermal and Photochemical Generation of Carbene 16. The carbene was generated thermally from the diazocompound **26** by refluxing in pentane, when it gave 1-(2,2-diphenylvinyl)-1-methylcyclopropane (**27**), 1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (**28**), 1,8a-dihydro-1,1-dimethyl-3-phenylazulene (**29**), and 4-methyl-1,1-diphenyl-1,3-pentadiene (**8**), in the proportions qualitatively estimated in Table I. In contrast, photolysis of the diazo compound at 0°, at which temperature it was thermally stable for

Table I. Product Distribution from Carbene 16, Generated in Different Ways

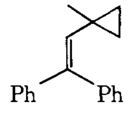
				Products			
Run	Reactant	Mode of reaction	T, °C	Cyclopropane 27	Dihydro-naphthalene 28	Dihydroazulene 29	Pentadiene 8
1	26	Thermal	35	Trace	Trace	Major	Minor
2	19	Thermal	180	Trace	Trace	Major	Minor
3	26	Photochemical	0	Major	*a*	*a*	Major
4	19	Photochemical	Ambient	Major	*a*	*a*	Major

[a] Not detectable.

Chart III. Synthesis of 4-Diazo-3,3-dimethyl-1,1-diphenyl-1-butene



many hours, gave only vinylcyclopropane 27 and diene 8; see Table I. The structures of compounds 27, 28, and 29 were deduced from spectroscopic data and were proved by independent synthesis or degradation (see below).



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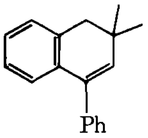

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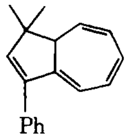


29

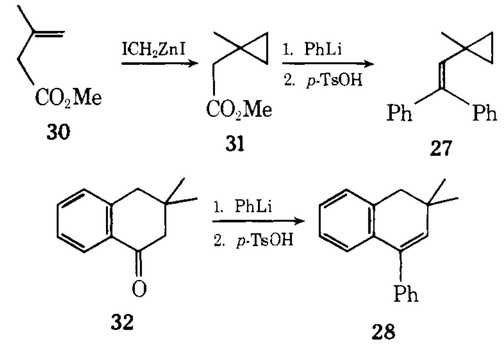
Interestingly, the same pattern of carbene products was observed starting from tosylhydrazone 18. The thermal reaction used the aprotic conditions of Freeman and Kuper.[12] Sodium methoxide was used to generate the conjugate base in diglyme solvent. For the photochemical reaction, Dauben's results[13] suggested that, for rigorous exclusion of a carbonium ion pathway, aprotic conditions should be used. In this work, Büchi's procedure[14] was slightly modified, using sodium hydride as the base and pentane containing 10% diglyme as solvent. These results are also indicated in Table I.

Elucidation of Structures of the Carbene Products. In the previous section, we described the reactivity of carbene 16 under a variety of conditions. However, we have not yet discussed the actual basis of the product structural assignments.

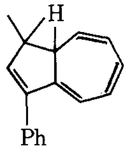
In each case, tentative structural assignments were made on a basis of the NMR data as detailed in the Experimental Section. Additionally, in the case of dihydroazulene 29, ultraviolet information proved invaluable. However, the first two carbene products were then unambiguously synthesized, and the dihydroazulene was degraded.

Thus, cyclopropane 27 was synthesized as depicted in Chart IV. Also included in Chart IV is the synthesis of dihydronaphthalene 28. The two syntheses are detailed in the Experimental Section.

Chart IV. Synthesis of 1-(2,2-Diphenylvinyl)-1-methylcyclopropane (27) and 1,2-Dihydro-2,2-dimethyl-4-phenylnaphthalene (28)



In the case of dihydroazulene 29, we found that treatment with palladium on carbon in refluxing triglyme afforded a mixture from which a blue azulene could be isolated by silicic acid chromatography. This azulene was shown to be 1,2-dimethyl-3-phenylazulene 33 by independent synthesis. The key step in the synthesis is the cyclization of the ketocarbene derived from diazoketone 36 by loss of nitrogen. This has recently been suggested as a general synthesis of azulenes.[15] Both the degradation and the synthesis are given in Chart V. With the azulene structure established, there were still two reasonable structures to be considered for the dihydroazulene, namely 29 and 34. The NMR spectrum really did not distinguish between these possibilities since the observed methine multiplet at τ 7.55 would be anticipated in either case. Also, the styryl vinyl hydrogen singlet at τ 4.07 fits either structure. However, the ultraviolet spectrum showed a maximum at 315 nm (ϵ 4000). The literature revealed that cycloheptatrienes absorb[16] at ca. 270–275 nm with none above 280 nm, thus excluding 34 as a possibility. The formation of azulene 33 with methyl migration on Pd/C treatment has precedent in the literature.[17] Thus, at this point, structures had been established for the products of reaction of carbene 16.



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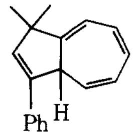

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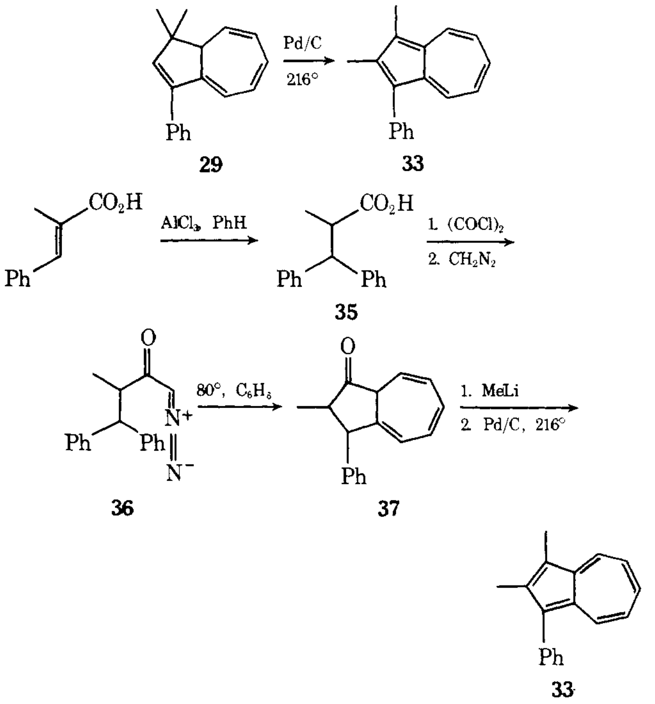
Quantum Yields and Other Quantitative Aspects of the Photochemistry of Cyclopropylvinylmethane 1. The quantum yields of formation of diphenylethylene 7, pentadiene 8, diphenylisobutylene 9, and diphenylbutadiene 10 were determined using the Black Box apparatus[18] with solution filters having a maximum transmission at 250 nm to minimize product light absorption. Low conversions were needed to avoid errors arising from product light absorption and due to two-photon processes involving formation and reac-

Table II. Quantum Yield Determinations

Run	Reactant	Added reagents	λ_{irrad}	% conv	Diphenylethylene **7**	Pentadiene **8**	Diphenylisobutylene **9**	Diphenylbutadiene **10**
1	**1**		250	1.8	0.018[a] (0.018)	0.017[a] (0.017)	0.0003	0.0003
2	**1**		250	4.3	0.019[a] (0.018)	0.019[a] (0.018)	0.0010	0.0009
3	**1**		250	8.4	0.018[a] (0.017)	0.017[a] (0.016)	0.0019	0.0016
4	**11**		250	1.8	$<10^{-4}$[b]	$<10^{-4}$[b]	0.056	0.054
5	**11**		250	4.9	$<10^{-4}$[b]	$<10^{-4}$[b]	0.060	0.058
6	**11**	*m*-Methoxyacetophenone (4.4×10^{-3} *M*)	325	0.4	$<10^{-5}$[c]	$<10^{-5}$[c]	0.0011	0.0010

[a] Corrected for light absorbed by cyclobutane. Uncorrected values are given in parentheses. [b] Below the limits of detection. [c] Estimated value.

Chart V. Structure Proof for 1,8a-Dihydro-1,1-dimethyl-3-phenylazulene



tion of cyclobutane **11**. Evidence is presented below that diphenylisobutylene **9** and diphenylbutadiene **10** are secondary products. Thus, the measured quantities of these compounds, coupled with the measured (vide infra) quantum yield with which cyclobutane **11** gave these two, allowed calculation of light absorbed by cyclobutane intermediate; this correction, however, was minor. The results are shown in Table II. It is noted that the quantum yields for diphenylethylene **7** and pentadiene **8** remain constant with increasing conversion, showing these to be primary products.

Additionally, evidence was available bearing on the ratio of diphenylisobutylene **9** and diphenylbutadiene **10** to diphenylethylene **7** and pentadiene **8**. This is seen in Table II wherein runs 1, 2, and 3 have been made to 1.8, 4.3, and 8.4% conversions, respectively. The ratio of **7**:**8** is essentially invariant, whereas the ratio of **9** and **10** to **7** and **8** increases with conversion. This is in accord with the idea that diphenylisobutylene **9** and diphenylbutadiene **10** are secondary photoproducts.

Also, to check this point further, another run was made with GC monitoring after various times of irradiation. Again, it was found that the ratio of peak heights for diphenylethylene **7** and pentadiene **8** was independent of the extent of conversion, whereas the relative peak heights for diphenylisobutylene **9** and diphenylbutadiene **10** increased with increasing conversion.

One other piece of information which promised to be useful was the ratio of secondary to primary photoproducts at higher conversions. To the extent that cyclobutane **11** is the source of these secondary photoproducts, this ratio could allow determination of the quantum yield of formation of cyclobutane. Gas chromatographic analysis showed this ratio to be $(\mathbf{9} + \mathbf{10})/(\mathbf{7} + \mathbf{8}) = 0.25$. Details are given in the Experimental Section.

Single Photon Counting Determination of Low-Temperature Singlet Lifetime and Magic Multiplier Extrapolation to Room Temperature. Derived Rates for Cyclopropylvinylmethane 1. The low-temperature (77 K) lifetime of cyclopropylvinyl methane **1** proved readily accessible by our method of on-line single photon counting with reiterative convolution.[4] These runs were made in triplicate at three different wavelengths (300, 310, and 320 nm), giving a mean lifetime of 6.3 ± 0.3 nsec. Note the Experimental Section.

However, the room-temperature lifetime proved too rapid for easy direct single photon measurement, and we turned to the method of magic multipliers[4] to amplify our rate capabilities. Thus the room-temperature rate is given by eq 4.

$$k_{dt}^{RT} = k_{dt}^{77}M \tag{4a}$$

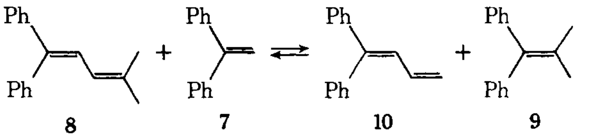
where

$$(\phi_t^{77}/\phi_t^{RT}) = M \tag{4b}$$

A value of 243 was obtained for M. This, together with the value determined for k_{dt}^{77} (i.e., $1/\tau^{77}$) of 1.59×10^8 sec^{-1}, gave $k_{dt}^{RT} = 3.9 \times 10^{10}$ sec^{-1} and $\tau^{RT} = 26$ psec. These values could be used (vide infra) to determine the various singlet excited state rate constants.

Quantum Yield of Cyclobutane 11 Reaction. With cyclobutane **11** as reactant, the quantum yields in Table II were determined. These runs were made, again, with the Black Box[18] apparatus. Details are given in the Experimental Section.

Control Experiments. Since evidence was found for cyclobutane **11** formation, it was necessary to ascertain whether this compound arises at all from 2 + 2 reaction of diene and monoene components. Such a reaction would not only lead to complications in the quantum yield determination but also could lead to interconversion of the photoproducts of the type indicated in eq 5.



(5)

However irradiation of a mixture of diphenylethylene **7** and pentadiene **8** was shown not to cause reaction. Similarly, irradiation of a mixture of diphenylisobutylene **9** and diphenylbutadiene **10** resulted in no change.

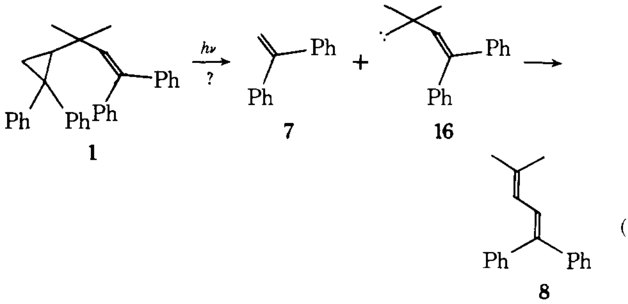
Another possible concern was that vinylcyclopropane **27**, encountered in the independent generation of carbene **16**, might be formed in the photolysis of cyclopropylvinylmethane **1** and, being photochemically labile, might react further to afford pentadiene **8**. Thus, the control experiment, in which vinylcyclopropane **27** was irradiated, was carried out. This, however, gave no pentadiene **8**. The details are in the Experimental Section.

Finally, the possibility had to be considered that different products were observed in the photochemical and thermal approaches to carbene **16** because of further photolysis of a primary product in the photochemical experiment. Thus, dihydroazulene **29** could be formed photochemically but then undergo further photochemical reaction to give vinylcyclopropane **27** or pentadiene **8**. Accordingly, dihydroazulene **29** was photolyzed, but it did not give either of these products, showing them to be primary products from the photochemically generated carbene. Details are given in the Experimental Section.

Interpretative Discussion

The Mechanism of Formation of Diphenylethylene 7 and Pentadiene 8. In considering a priori mechanisms for formation of these products, two possibilities come to mind. One is a carbene fission, and the other is a cyclopropyl-π-methane rearrangement; these are considered in this order.

The carbene mechanism has considerable analogy in the literature, primarily because of the investigations of Griffin and coworkers.[9] Thus, the present reaction would be formulated as in eq 6.



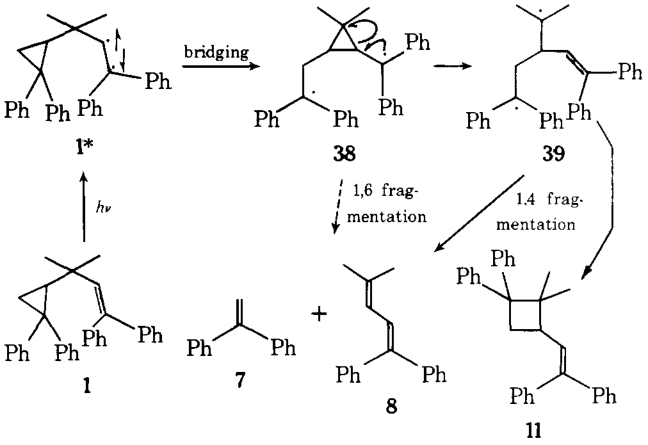
(6)

One suggestive feature of the reaction which gave evidence against this pathway was the observed regiospecificity. Thus, Griffin has commented[19] that, in general, the most stable carbene is generated in three ring fragmentations. On this basis, one would expect diphenylcarbene-disengagement to be preferred. This was, in fact, observed in the recent elegant studies of Hixson[20] with a *gem*-diphenyl cyclopropane.

However, the strongest evidence comes from comparison of the present products with those arising from carbene **16** when generated independently. Thus, while carbene **16** produced thermally led to dihydroazulene **29** as the major product, this was not observed as a photoproduct from cyclopropylvinylmethane **1**. Similarly, while photochemical generation of carbene **16** did afford one of the products from cyclopropylvinylmethane photolysis, namely pentadiene **8**, it also led to an equal amount of the methyl insertion product **27**, which was not observed in the photochemistry of cyclopropylvinylmethane **1**. (Note Table I which summarizes the thermal and photochemical behavior of independently generated carbene **16**.) The formation of different products from carbene **16** when generated thermally and photochemically is of independent interest but is presently not relevant.[21] However, we can conclude that two different electronic states of carbene **16** are involved in the thermal and photochemical experiments. These are most reasonably the lowest triplet and the lowest singlet. With the reactivity of the carbene **16** thus being defined and being different from the photochemistry encountered in the cyclopropylvinylmethane study, we can conclude that carbene **16** is not involved in the cyclopropyl-π-methane reaction.

The second mechanism considered is in precise analogy to the well-known di-π-methane rearrangement, differing only in replacement of one of the π bonds by a cyclopropyl ring. This mechanism is outlined in Chart VI. Thus, the excited state of cyclopropylvinylmethane **1** (i.e., **1***) bridges to give biradical **38** with subsequent unzipping to biradical **39**. This last species may fragment to give diphenylethylene **7** and pentadiene **8**. Alternatively one can envisage a direct 1,6 fragmentation of biradical **38** to give **7** and **8**. As in the di-π-methane mechanism, the biradical species drawn do not necessarily represent energy minima but are convenient structures to allow one to envisage the reacting species involved in the mechanism.

Chart VI. Mechanism for Formation of Fragmentation Products 7 and 8 and Cyclobutane 11



Finally, in regard to the formation of diphenylethylene **7** and pentadiene **8**, the lack of reactivity on sensitization rules out a triplet mechanism. Preference for a singlet process parallels the behavior of acyclic di-π-methanes.[3b,c]

Formation and Reactivity of Cyclobutane 11. The first point to be noted is that the mechanism presented in Chart VI, accounting for the olefinic fragmentation products, also nicely accommodates formation of cyclobutane **11**. This arises from simple cyclization of diradical **39**.[24] Furthermore, the mechanism is then directly analogous to that postulated by us much earlier for our di-π-methane rearrangement.[3a]

The next aspect of interest is that cyclobutane **11** exhibits the reactivity required to understand formation of diphenylisobutylene **9** and diphenylbutadiene **10** in the cyclopropylvinylmethane photochemistry. The direct irradiation quantum yields for this fragmentation of cyclobutane **11** are given in Table II. Interestingly, some reactivity is observed from cyclobutane **11** on *m*-methoxyacetophenone sensitization, but this is low as seen from the quantum yield given in Table II. This low triplet reactivity relative to the singlet is reasonably ascribed to intervention of free rotor energy dissipation.[2b,28] However, evidence on the free rotor effect as a function of multiplicity[29] indicates that triplet free rotor effects are less rapid than singlet free rotor energy wastage. Normally, singlet reaction rates are much more rapid than triplet ones, and the triplet free rotor is much more able to intervene and inhibit reaction. Presently, concerted reverse 2s + 2s singlet fission must be sufficiently more rapid than the triplet fission to allow the triplet free rotor largely to eliminate reaction.

A final point of interest is that the data available allow determination of the quantum yield of formation of cyclobutane **11** from cyclopropylvinylmethane **1.** The primary assumption employed is that, at high conversion, the secondary products (diphenylisobutylene **9** and diphenylbutadiene **10**) are present in much larger amounts than the small amounts of cyclobutane, and the amounts of these represent a very good measure of how much cyclobutane **11** had been formed cumulatively in the reaction. This justifies the substitution in the second expression in eq 7, where $\phi^{\square}{}_{\rm prim}$ = quantum yield of formation of cyclobutane **11,** $\phi^{=}{}_{\rm prim}$ = (quantum yield of formation of primary olefins **7** and **8,** and $\phi^{=}{}_{\rm app}$ = apparent quantum yield for secondary olefins **9** and **10.**

$$\phi^{\square}{}_{\rm prim}/\phi^{=}{}_{\rm prim} = \phi^{=}{}_{\rm app}/\phi^{=}{}_{\rm prim} \approx \text{(ratio of secondary products 9 and 10 to primary products 7 and 8)} \quad (7)$$

With the ratio of the two types of products isolated at high conversion known, and with $\phi^{=}{}_{prim}$ determined (vide supra), we can utilize eq 7 to solve for $\phi^{\square}{}_{\rm prim}$. Thus the quantum yield of formation of cyclobutane **11** is found to be 0.0045.

Importantly, the relatively high quantum yield of cyclobutane consumption ($\phi^{\square}{}_{\rm cons}$ = 0.057) compared with its quantum yield of formation ($\phi^{\square}{}_{\rm prim}$ = 0.0045), combined with its extinction coefficient at 254 nm of 17,000 compared with that of cyclopropylvinylmethane **1** (14,400), accounts for the relatively small amounts of cyclobutane **11** present during the photolysis of cyclopropylvinylmethane **1.** These figures predict a maximum ratio of cyclobutane **11**/cyclopropylvinylmethane **1** = 6.6%.

Reaction Rates and Efficiencies. From the room temperature quantum yields ($\phi^{=}_{\rm prim}$ = 0.018; $\phi^{\square}_{\rm prim}$ = 0.0045) and $k_{dt}{}^{\rm RT} = 3.9 \times 10^{10}$ sec^{-1}, one obtains from eq 8 the corresponding excited singlet rates.

$$k^{=}{}_{\rm prim} = \phi^{=}{}_{\rm prim}k_{\rm dt} = 7.0 \times 10^{8}\ \text{sec}^{-1} \quad (8a)$$

$$k^{\square}{}_{\rm prim} = \phi^{\square}{}_{\rm prim}k_{dt} = 1.7 \times 10^{8}\ \text{sec}^{-1} \quad (8b)$$

$$k_{r,\rm total} = \phi_r k_{dt} = 8.7 \times 10^{8}\ \text{sec}^{-1} \quad (8c)$$

These results allow us to interpret the reaction quantum yield which is much lower than the ϕ = 0.080 value found for the ordinary di-π-methane rearrangement of tetraphenyldiene **2.** Thus the lower quantum yield presently (ϕ_r = 0.022) is in spite of the longer lifetime of the excited singlet of cyclopropylvinylmethane **1** (τ = 26 psec) compared with 0.55 psec[4] for tetraphenyldiene **2.** The much lower efficiency is seen to derive from the lower inherent rate of excited singlet reaction, presently 8.7×10^{8} sec^{-1} compared with 1.4×10^{11} sec^{-1} found[4] for S_1 of tetraphenyldiene **2.**

This reveals that excited state vinyl-vinyl bridging is more facile than cyclopropyl-vinyl bridging. This accords with our finding that σ plus π processes are relatively sluggish compared with the di-π-methane rearrangement.[30]

General Observations

Considering the dramatic emergence of the di-π-methane rearrangement over the last 8 years as a broadly synthetically useful and general photochemical reaction, the appearance of the first example of the cyclopropyl-π-methane rearrangement offers hope for a still further useful rearrangement. Thus, photochemistry is still in its infancy relative to ground-state organic chemistry both in terms of its synthetic utility and regarding its level of mechanistic sophistication.

Experimental Section[31]

Chromatographic Monitoring. Gravity chromatography was run in Vycor or Quartz columns using adsorbent admixed with ca. 1% of phosphor (Sylvania calcium silicate doped with manganese and lead). This allowed monitoring of bands by quenching of the red luminescence upon observation using an ultraviolet lamp with filter.

Gas Chromatography. Column A: 5% QF-1 on Varaport 30, 100-120 mesh, 0.25 in. × 5 ft, at 130°, flow rate 20 ml/min. Column B: 3% Carbowax 20M on Varaport 30, 100-120 mesh, 0.25 in. × 5 ft, at 160°, flow rate 20 ml/min.

Ethyl *cis*- and *trans*-3-(2,2-Diphenylcyclopropyl)-2-butenoate. To a stirred suspension of 2.213 g (49.8 mmol) of sodium hydride (54% dispersion in mineral oil) in 100 ml of anhydrous dimethylformamide, under nitrogen, was added a solution of 11.21 g (50.0 mmol) of triethyl phosphonoacetate[6] in 25 ml of anhydrous dimethylformamide. After stirring for 0.5 hr, evolution of hydrogen had ceased, and 9.47 g (40.1 mmol) of 2,2-diphenylcyclopropyl methyl ketone[5] in 25 ml of anhydrous dimethylformamide was added. The stirred mixture was heated at 135° for 12 hr, cooled, diluted with ether, water washed, dried, and concentrated in vacuo to afford an oil which was chromatographed on a 135 × 4.3 cm column, slurry packed with silica gel (Davidson, grade 62) in hexane. Elution with 1% ether in hexane afforded as the first band 2.46 g (19.2%) of cis ester (pure by NMR) which was recrystallized from methanol, mp 66-67°. Elution with 2% ether in hexane afforded as the second band 5.86 g (46.1%) of trans ester (pure by NMR) and with 5% ether in hexane afforded 2.79 g (29.4%) of recovered starting ketone (pure by NMR). The total yield of esters based on unrecovered starting material was 93%.

The spectral data for the cis ester were: ir ($CHCl_3$) 3.27, 3.30, 3.32, 3.35, 5.90, 6.17, 6.25, 6.70, 6.92, 7.28, 7.91, 8.20, 8.63, 8.82, 9.15, 9.41, 9.61, 10.35, 11.75, 14.40 μ; NMR (CCl_4) τ 2.9 (m, 10 H, arom), 4.29 (s, 1 H, vinyl), 5.87 (q, 2 H, J = 7 Hz, $-CH_2CH_3$), 6.20 (d of d, 1 H, J = 7.0, 8.0 Hz, allylic), 8.19 (d of d, 1 H, J = 5.0, 7.0 Hz, cyclopropyl), 8.63 (d of d, 1 H, J = 5.0, 8.0 Hz, cyclopropyl), 8.76 (t, 3 H, J = 7 Hz, $-CH_2CH_3$), 8.92 (s, 3 H, $-CH_3$).

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.31; H, 7.24. Found: C, 82.40; H, 7.28.

The spectral data for the trans ester were: ir ($CHCl_3$) 3.22, 3.25, 3.27, 3.31, 3.33, 3.35, 3.39, 5.87, 6.09, 6.24, 6.69, 6.90, 7.15, 7.20, 7.30, 7.50, 7.77, 8.08, 8.63, 8.80, 9.00, 9.11, 9.40, 9.60, 10.16, 11.54, and 14.37 μ; NMR (CCl_4) τ 2.82 (br s, 10 H, arom), 4.43 (s, 1 H, vinyl), 6.02 (q, 2 H, J = 7 Hz, $-CH_2CH_3$), 7.63 (t, 1 H, J = 7.5 Hz, allylic), 8.61 (s obscuring d of d, 4 H, $-CH_3$ and cyclopropyl), 8.78 (d of d, 1 H, J = 5.5, 7.5 Hz, cyclopropyl), 8.86 (t, 3 H, J = 7 Hz, $-CH_2CH_3$).

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.31; H, 7.24. Found: C, 82.19; H, 7.25.

***cis*- and *trans*-3-(2,2-Diphenylcyclopropyl)-1-phenyl-2-buten-1-one.** A mixture of 3.69 g (12.0 mmol) of ethyl *cis*- and *trans*-3-(2,2-diphenylcyclopropyl)-2-butenoate and 2.81 g (50.0 mmol) of potassium hydroxide in 50 ml of methanol was refluxed for 4 hr. The solvent was removed in vacuo and the residue dissolved in water, ether washed, acidified, and ether extracted. The organic extract was dried and concentrated in vacuo to give an oil which was dissolved in anhydrous ether and treated with excess phenyllithium in ether (TLC monitoring of reactant consumption). The ether solution was quenched with water, water washed, dried, and concentrated in vacuo to afford an oil which was chromatographed on a 90 × 2.5 cm column slurry packed with silica gel in hexane. Elution with 2% ether in hexane afforded cis enone which was recrystallized from methanol, mp 122-124°, yield 0.537 g (13.3%). Elution with 3% ether in hexane afforded trans enone which was recrystallized from methanol, mp 103.5-104°, yield 0.872 g (21.6%).

The spectral data for the cis enone were: ir ($CHCl_3$) 3.23, 3.29, 6.07, 6.29, 6.68, 6.90, 7.16, 7.26, 7.60, 8.06, 8.49, 8.63, 8.81, 9.29, 9.56, 9.78, 9.98, 10.07, 10.28, 10.87, 11.76, and 14.50 μ; NMR (CCl_4) τ 1.9-3.0 (m, 15 H, arom), 3.13 (q, 1 H, J = 1.3 Hz, vinyl), 6.19 (d of d, 1 H, J = 7.0, 8.0 Hz, allylic), 8.09 (d of d, 1 H,

J = 5.0, 7.0 Hz, cyclopropyl), 8.58 (d of d, 1 H, J = 5.0, 8.0 Hz, cyclopropyl), 8.74 (d, 3 H, J = 1.3 Hz, $-CH_3$).

Anal. Calcd for $C_{25}H_{22}O$: C, 88.71; H, 6.56. Found: C, 88.60; H, 6.59.

The spectral data for the trans enone were: ir ($CHCl_3$) 3.25, 3.32, 6.04, 6.26, 6.70, 6.91, 7.13, 7.29, 7.46, 8.04, 8.50, 8.83, 9.11, 9.29, 9.40, 9.80, 10.39, 10.68, 11.71, 12.10, and 14.42 μ; NMR (CCl_4) τ 2.5–2.9 (m, 15 H, arom), 3.76 (s, 1 H, vinyl), 7.56 (d of d, 1 H, J = 6.5, 7.5 Hz, allylic), 7.94 (s, 3 H, $-CH_3$), 8.02 (d of d, 1 H, J = 5.5, 6.5 Hz, cyclopropyl), 8.42 (d of d, 1 H, J = 5.5, 7.5 Hz, cyclopropyl).

Anal. Calcd for $C_{25}H_{22}O$: C, 88.71; H, 6.56. Found: C, 88.68; H, 6.64.

3-(2,2-Diphenylcyclopropyl)-3-methyl-1-phenyl-1-butanone. To lithium dimethylcuprate formed from 3.09 g (16.2 mmol) of cuprous iodide, 100 ml of anhydrous ether, and 15.5 ml of methyllithium (1.82 *M* in ether, 28.2 mmol) stirred under nitrogen at −22° was added 3.35 g (9.90 mmol) of *trans*-3-(2,2-diphenylcyclopropyl)-1-phenyl-2-buten-1-one in 75 ml of anhydrous ether. The mixture was stirred in an ice bath for 3 hr, poured into saturated aqueous ammonium chloride, separated, water washed, dried and concentrated in vacuo to afford an oil which was chromatographed on a 100 × 2.5 cm column of silica gel slurry packed in hexane. Elution with 2.5% ether in hexane using scanning uv monitoring afforded 3.43 g (97.9%) of ketone as a single peak, which was pure by NMR. Subjection of 1.32 g (6.95 mmol) of cis enone to similar conditions gave 1.42 g (86.4%) of the same ketone product.

The spectral data were: ir ($CHCl_3$) 3.25, 3.36, 3.40, 3.47, 5.99, 6.25, 6.34, 6.70, 6.81, 6.92, 7.23, 7.31, 7.39, 7.58, 7.70, 8.10, 8.27, 8.51, 8.69, 9.02, 9.31, 9.58, 9.84, 9.93, 10.97, 11.91, and 14.56 μ; NMR (CCl_4) τ 2.1–3.1 (m, 15 H, arom), 7.21 (br s, 2 H, $-CH_2-$), 8.03 (d of d, 1 H, J = 7.5, 9.5 Hz, cyclopropyl), 8.46, (d of d, 1 H, J = 5.0, 7.5 Hz, cyclopropyl), 9.13 (s obscuring d of d, 7 H, J = 5.0, 9.5 Hz, cyclopropyl and CH_3); mass spectrum *m/e* (calcd for $C_{26}H_{26}O$, 354.1982) 354.1978.

3-(2,2-Diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene. To a solution of 4.80 g (13.6 mmol) of 3-(2,2-diphenylcyclopropyl)-3-methyl-1-phenyl-1-butanone in 50 ml of anhydrous ether under nitrogen was added, with stirring, excess ethereal phenyllithium (TLC monitoring of reactant consumption). The reaction was stirred for 0.5 hr and quenched with water and the organic phase water washed, dried, and concentrated in vacuo to yield an oil which was dissolved in 100 ml of benzene. *p*-Toluenesulfonic acid (50 mg) was added, and the solution was refluxed for 1 hr, cooled, concentrated in vacuo, and chromatographed on a 2.5 × 100 cm column of silica gel slurry packed in hexane. Elution with 0.5% ether in hexane afforded an oil which crystallized from ethanol-chloroform, mp 100–102°, yield 4.53 g (80.5%). Recrystallization from methanol-chloroform raised the melting point to 102.9–103.1°.

The spectral data were: ir ($CHCl_3$) 3.25, 3.30, 3.35, 6.25, 6.70, 6.81, 6.91, 7.32, 8.48, 8.59, 9.31, 9.71, and 14.38 μ; NMR (CCl_4) τ 2.9 (m, 20 H, arom), 4.09 (s, 1 H, vinyl), 8.25 (d of d, 1 H, J = 7, 9 Hz, cyclopropyl), 8.40 (d of d, 1 H, J = 4, 7 Hz, cyclopropyl), 8.96 (d of d, 1 H, J = 4, 9 Hz, cyclopropyl), 9.16 (s, 3 H, $-CH_3$), 9.34 (s, 3 H, $-CH_3$); uv λ_{max} (EtOH) 250 (15,000).

Anal. Calcd for $C_{32}H_{30}$: C, 92.70; H, 7.30. Found: C, 92.67; H, 7.30.

2,2-Dimethyl-3,3-diphenylcyclobutanone. *N,N*-Dimethylisobutyramide (22.8 g, 0.20 mol), 18.3 ml (0.2 mol) of phosphorus oxychloride, and 150 ml of anhydrous ether were refluxed under nitrogen for 22 hr to give a two-phase system. Triethylamine (27.8 ml, 0.20 mol) and then 100 ml of pentane was added. The upper phase was decanted into a distillation flask and the solvent removed by distillation to give crude 1-chloro-1-dimethylamino-2-methylpropane,[8,32] which was dissolved in 150 ml of methylene chloride. 1,1-Diphenylethylene (25.0 g, 0.139 mol) and 23.5 g (0.172 mol) of freshly fused, powdered, anhydrous zinc chloride were added, the mixture was refluxed for 4 hr, extracted with 400 ml of 1 *M* aqueous sodium hydroxide, water washed, dried, and concentrated in vacuo to give a red oil which was chromatographed on a 93 × 2.5 cm column of silica gel slurry packed in hexane. Elution with hexane gave 15.3 g (61.2%) of recovered diphenylethylene as a first band and with 1% ether in hexane gave the cyclobutanone as the second band. This crystallized from methanol to give 5.471 g (43.0% based on unrecovered diphenylethylene), mp 58.5–60°. Recrystallization from methanol gave mp 59–60°.

The spectral data were: ir ($CHCl_3$) 3.25, 3.31, 3.35, 3.40, 3.48, 5.64, 6.24, 6.70, 6.83, 6.91, 7.13, 7.21, 8.20, 8.71, 9.30, 9.69, 9.98, 10.18, 10.49, 10.83, 11.40, and 14.32 μ; NMR (CCl_4) τ 2.8 (m, 10 H, arom), 6.30 (s, 2 H, $-CH_2-$), 8.92 (s, 6 H, $-CH_3$).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.22; H, 7.27.

***cis*- and *trans*-3-Methoxycarbonylmethylene-2,2-dimethyl-1,1-diphenylcyclobutane.** To a solution of 2.73 g (15.0 mmol) of trimethyl phosphonacetate[6] in 60 ml of anhydrous tetrahydrofuran, under nitrogen, was added with stirring, 6.2 ml of butyllithium (2.4 *M* in hexane, 14.9 mmol). After stirring 0.5 hr, 3.34 g (13.4 mmol) of 2,2-dimethyl-3,3-diphenylcyclobutanone in 20 ml of anhydrous tetrahydrofuran was added, and stirring was continued for 14 hr. The reaction was quenched with water, the solvent was removed in vacuo, and the residue was taken up in ether, water washed, dried, and concentrated in vacuo to yield an oil which was chromatographed on a 95 × 2.5 cm column slurry packed with silica gel in hexane. Elution with 1% ether in hexane gave first 0.213 g (5.2%) of cis ester (pure by NMR) which was recrystallized from methanol, mp 99–100°, then 2.75 g (67.3%) of trans ester (pure by NMR) which was recrystallized from methanol, mp 62–63°.

The spectral data for the cis isomer were: ir ($CHCl_3$) 3.26, 3.31, 3.36, 3.38, 3.41, 5.85, 6.00, 6.24, 6.20, 6.92, 6.97, 7.41, 7.81, 8.07, 8.22, 8.49, 8.74, 9.11, 9.64, 9.77, 9.83, 10.11, 10.32, 10.72, 10.97, 11.77, and 14.34 μ; NMR (CCl_4) τ 2.8 (m, 10 H, arom), 4.27 (t, 1 H, J = 2.0 Hz, vinyl), 6.37 (s, 3 H, $-O-CH_3$), 6.57 (d, 2 H, J = 2.0 Hz, $-CH_2$), 8.75 (s, 6 H, $-CH_3$).

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.31; H, 7.24. Found: C, 82.48; H, 7.42.

The spectral data for the trans isomer were: ir ($CHCl_3$) 3.25, 3.29, 3.31, 3.37, 3.41, 3.49, 5.88, 5.99, 6.24, 6.70, 6.94, 7.22, 7.42, 7.82, 7.94, 8.50, 9.41, 9.79, 9.95, 11.73, and 14.32 μ; NMR (CCl_4) τ 2.78 (br s, 10 H, arom), 4.31 (t, 1 H, J = 2.3 Hz, vinyl), 6.11 (d, 2 H, J = 2.3 Hz, $-CH_2-$), 6.28 (s, 3 H, $-OCH_3$), 8.89 (s, 6 H, $-CH_3$).

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.31; H, 7.24. Found: C, 82.53; H, 7.37.

Methyl 2,2-Dimethyl-3,3-diphenylcyclobutaneacetate. A solution of 2.33 g (7.60 mmol) of 3-methoxycarbonylmethylene-2,2-dimethyl-1,1-diphenylcyclobutane in 60 ml of methanol was hydrogenated over 0.498 g of 10% palladium on charcoal at atmospheric pressure for 20 hr. The catalyst was removed by filtration, and the solvent *in vacuo*, to give 2.32 g (98.9%) of the ester (pure by NMR) which was recrystallized from methanol, mp 91.5–92.5°.

The spectral data were: ir ($CHCl_3$) 3.22, 3.26, 3.36, 5.80, 6.24, 6.21, 6.86, 6.97, 7.22, 7.31, 7.55, 7.83, 8.37, 8.51, 8.69, 9.54, 9.73, 10.66, 10.94, and 14.38 μ; NMR (CCl_4) τ 2.7 (m, 10 H, arom), 6.40 (s, 3 H, $-OCH_3$), 6.85 (d of d, 1 H, J = 6.0, 10.6 Hz, one of $-CH_2CO_2-$), 7.3–7.9 (m, 4 H), 8.92 (s, 3 H, $-CH_3$), 9.12 (s, 3 H, $-CH_3$).

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.80; H, 7.83.

3-(2,2-Diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane. To excess phenyllithium in ether was added 2.23 g (7.24 mmol) of methyl 2,2-dimethyl-3,3-diphenylcyclobutaneacetate in 20 ml of anhydrous ether. After stirring for 1 hr, the reaction was quenched with water and the organic phase water washed, dried, and concentrated in vacuo to give an oil which was dissolved in 50 ml of benzene. *p*-Toluenesulfonic acid (100 mg) was added, and the solution was refluxed for 1 hr, cooled, concentrated in vacuo, and chromatographed on a 95 × 2.5 cm column slurry packed with silica gel in hexane. Elution with 0.5% ether in hexane gave 2.20 g (73.6%) of the vinylcyclobutane (pure by NMR) as the first band.

The spectral data were: ir ($CHCl_3$) 3.23, 3.25, 3.31, 3.37, 3.48, 6.25, 6.70, 6.85, 6.92, 7.21, 7.30, 8.49, 8.73, 8.98, 9.20, 9.32, 9.74, 14.38, and 15.02 μ; NMR (CCl_4) τ 2.8 (m, 20 H, arom), 3.90 (d, 1 H, J = 8.5 Hz, vinyl), 6.97 (m, 2 H, cyclobutyl), 7.47 (d of d, 1 H, J = 10.5, 14.0 Hz, cyclobutyl), 8.74 (s, 3 H, $-CH_3$), 9.26 (s, 3 H, $-CH_3$); uv λ_{max} (EtOH) 258 (17,800).

Anal. Calcd for $C_{32}H_{30}$: C, 92.70; H, 7.30. Found: C, 92.63; H, 7.40.

Methyl 3,3-Dimethyl-5,5-diphenyl-5-hydroxypentanoate. 3,3-Dimethyl-5,5-diphenyl-5-hydroxypentanoic acid lactone[11] (18.85 g, 66.1 mmol), and 10.5 g (0.188 mol) of potassium hydroxide in

300 ml of 95% ethanol, and 50 ml of water were refluxed for 0.5 hr. The solvent was removed in vacuo and the residue taken up in water, ether washed, acidified to methyl orange, and ether extracted. The extract was dried, concentrated in vacuo to ca. 100 ml, and added slowly to excess ethereal diazomethane. After stirring 7 hr, excess diazomethane was blown off in a stream of nitrogen, and the ethereal residue was dried and concentrated in vacuo to yield an oil which crystallized from hexane, mp 70–70.5°, yield 13.32 g (63.4%).

The spectral data were: ir ($CHCl_3$) 2.91, 3.21, 3.25, 3.31, 3.37, 3.48, 5.86, 6.25, 6.71, 6.91, 7.18, 7.30, 7.41, 7.50, 7.72, 8.28, 8.69, 8.83, 9.40, 9.63, 9.72, 9.97, 10.22, 10.82, 11.29, 11.71, 14.34, and 15.39 μ; NMR ($CDCl_3$) τ 2.42–2.93 (m, 10 H, arom), 5.97 (s, 1 H, -OH), 6.42 (s, 3 H, $-OCH_3$), 7.48 (s, 2 H, $-CH_2-$), 7.54 (s, 2 H, $-CH_2$), 9.22 (s, 6 H, $-CH_3$).

Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.90; H, 7.74. Found: C, 77.06; H, 7.82.

Methyl 3,3-Dimethyl-5,5-diphenyl-4-pentenoate. A solution of 4.78 g (15.2 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-5-hydroxypentanoate in 22 ml of anhydrous dimethyl sulfoxide[33] was heated at 175–180° for 2 hr. After cooling, the solution was diluted with ether, water washed, dried, and concentrated in vacuo to yield an oil which was chromatographed on a 93 × 2.5 cm column slurry packed with silica gel in hexane. Elution with 5% ether in hexane gave as the first band 4.06 g (90.3%) of ester pure by NMR.

The spectral data were: ir ($CHCl_3$) 3.22, 3.24, 3.27, 3.31, 3.36, 3.46, 5.79, 6.25, 6.35, 6.69, 6.93, 7.30, 7.40, 7.52, 8.32, 8.60, 8.90, 9.30, 9.72, 9.89, 10.98, 11.30, 14.40, and 15.59 μ; NMR (CCl_4) τ 2.68–2.90 (m, 10 H, arom), 3.90 (s, 1 H, vinyl), 6.42 (s, 3 H, $-OCH_3$), 7.78 (s, 2 H, $-CH_2-$), 8.97 (s, 6 H, $-CH_3$).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.49; H, 7.40.

3,3-Dimethyl-5,5-diphenyl-4-pentenoic Acid Hydrazide. Methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate (3.013 g, 10.2 mmol), 5 ml (103 mmol) of hydrazine hydrate, and 30 ml of 1-butanol were refluxed for 24 hr, concentrated in vacuo, taken up in ether, water washed, dried, and concentrated in vacuo to yield an oil which was chromatographed on a 95 × 2.5 cm column slurry packed with silica gel in methylene chloride. Elution with methylene chloride gave recovered ester as the first band and with 2% methanol in methylene chloride gave the hydrazide as an oil (pure by NMR), as the second 2.205 g (73.2%).

The spectral data were: ir (neat liquid) 3.02, 3.22, 3.26, 3.29, 3.36, 3.40, 3.47, 6.08, 6.58, 6.69, 6.80, 6.92, 7.33, 7.98, 8.50, 8.68, 9.02, 9.35, 9.91, 13.20, and 14.38 μ; NMR (CCl_4) τ 2.84 (m, 10 H, arom), 3.90 (s, 1 H, vinyl), 5.0–6.5 (br s, 3 H, -NH), 7.93 (s, 2 H, $-CH_2-$), 9.06 (s, 6 H, $-CH_3$); mass spectrum *m/e* (calcd for $C_{19}H_{22}N_2O$, 294.1731) 294.1732.

Methyl 2,2-Dimethyl-4,4-diphenyl-3-butenylcarbamate. A two-phase mixture of 17.45 g (59.4 mmol) of 3,3-dimethyl-5,5-diphenyl-4-pentenoic acid hydrazide, 200 ml of ether, 50 ml of water, and 6.08 g (88.1 mmol) of sodium nitrite was stirred in an ice bath, while 30 ml (0.3 mol) of concentrated hydrochloric acid was added in portions directly into the lower phase, over the course of 15 min. Stirring was continued for 10 min, the phases were separated, the organic phase was water washed and dried over calcium chloride. Methanol (300 ml) was added and the solution distilled slowly to dryness, leaving a yellow oil which was chromatographed on a 4.2 × 83 cm column slurry packed with silica gel in hexane. Elution with 20% ether in hexane gave as the first band 10.17 g of product (pure by NMR). Elution with ether gave as the second band 3.95 g of recovered starting material. Yield based on unrecovered starting material was 71.7% (pure by NMR). The product was recrystallized from pentane, mp 58.5–59.5°.

The spectral data were: ir ($CHCl_3$) 2.89, 3.27, 3.32, 3.38, 3.48, 5.82, 6.25, 6.61, 6.82, 6.92, 7.30, 7.70, 8.10, 8.70, 9.33, 9.60, 9.70, 9.90, and 14.31 μ; NMR (CCl_4) τ 2.8 (m, 10 H, arom), 4.06 (s, 1 H, vinyl), 5.18 (br s, 1 H, -NH), 6.45 (s, 3 H, $-OCH_3$), 6.97, 7.03 (s, s, 2 H, $-CH_2-$), 9.12 (s, 6 H, $-CH_3$).

Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.84; H, 7.53; N, 4.41.

Methyl 2,2-Dimethyl-4,4-diphenyl-3-butenylnitrosocarbamate. A suspension of 3.02 g (36.9 mmol) of anhydrous sodium acetate in 20 ml of carbon tetrachloride and 1.50 g (4.84 mmol) of methyl 2,2-dimethyl-4,4-diphenyl-3-butenylcarbamate was stirred in an ice bath during the dropwise addition of a solution of nitrogen dioxide in carbon tetrachloride (ca. 0.75 *M*).[34] When the NMR of an aliquot showed the yield to be optimized, addition was discontinued, and the solution was washed with aqueous potassium carbonate, dried, concentrated in vacuo, and chromatographed on two 20 × 20 cm thick layer plates. Elution with 20% ether in hexane gave from the fastest running band (R_f 0.6), the product (pure by NMR) as a yellow oil (0.777 g, 47.5%).

The spectral data were: ir (neat liquid) 3.26, 3.29, 3.37, 3.47, 5.69, 6.25, 6.60, 6.70, 6.93, 7.08, 7.32, 7.66, 8.34, 8.84, 9.50, 9.60, 11.58, 12.06, 13.20, 13.79, and 14.30 μ; NMR (CCl_4) τ 2.8 (m, 10 H, arom), 4.10 (s, 1 H, vinyl), 6.01 (s, 3 H, $-OCH_3$), 6.29 (s, 2 H, $-CH_2-$), 9.24 (s, 6 H, $-CH_3$); mass spectrum *m/e* (calcd for $C_{20}H_{22}N_2O_3$, 338.1629) 338.1622.

4-Diazo-3,3-dimethyl-1,1-diphenyl-1-butene. A two-phase mixture of 25 ml of pentane and 15 ml of 3 *M* potassium hydroxide in methanol was stirred in an ice bath shielded from direct light. Methyl 2,2-dimethyl-4,4-diphenyl-3-butenylnitrosocarbamate (0.783 g, 2.32 mmol) in 10 ml of pentane was added over 5 min. Stirring was continued for 10 min, and 25 ml of iced water was added. After a further 10 min of stirring, the reaction was worked up using only chilled apparatus and solvents and avoiding intense light. The phases were separated, the organic phase was water washed, dried over potassium hydroxide pellets, and concentrated in vacuo to yield 0.601 g (98%) of an unstable orange oil, shown by NMR to be almost pure diazo compound (>90%).

The spectral data were: ir (neat liquid) 3.24, 3.29, 3.36, 3.40, 3.49, 4.85, 6.25, 6.70, 6.92, 7.33, 7.82, 7.99, 8.91, 9.33, 9.70, 11.49, 12.75, 13.20, and 14.31 μ; NMR (CCl_4) τ 2.7 (m, 10 H, arom), 3.93 (s, 1 H, vinyl), 6.89 (s, 1 H, $-CHN_2$), 8.82 (s, 6 H, $-CH_3$).

2,2-Dimethyl-4,4-diphenyl-3-butenal 4-Toluenesulfonylhydrazone. 2,2-Dimethyl-4,4-diphenyl-3-butenal[10] (2.013 g, 8.06 mmol), 1.50 g (8.08 mmol) of *p*-toluenesulfonylhydrazide, and 0.2 ml of acetic acid were refluxed in 20 ml of methanol for 4 hr. On standing in the freezer, a white solid appeared, which was recrystallized from methanol in the cold to yield a colorless solid, mp 110.5–111.5°, yield 2.347 g (69.8%).

The spectral data were: ir ($CHCl_3$) 3.05, 3.29, 3.32, 3.35, 3.40, 3.47, 3.51, 6.24, 6.70, 6.95, 7.16, 7.34, 7.62, 8.58, 9.16, 9.31, 9.87, 11.05, 14.35, and 15.24 μ; NMR ($CDCl_3$) τ 2.21 (d, 2 H, J = 8.4 Hz, tosyl), 2.70 (d, 2 H, J = 8.4 Hz, tosyl), 3.0 (m, 10 H, arom), 3.44 (s, 1 H, aldehydic), 4.05 (s, 1 H, vinyl), 7.58 (s, 3 H, $p-CH_3$), 8.44 (s, 1 H, -NH), 8.69 (s, 6 H, *gem*-dimethyl); mass spectrum *m/e* (calcd for $C_{25}H_{26}N_2SO_2$, 418.1714) 418.1711.

Methyl 1-Methylcyclopropaneacetate. Zinc-copper couple[35] (7.0 g, 0.107 mol), 15 ml of anhydrous ether, 5.7 ml (70.7 mmol) of methylene iodide, and 4.53 g (39.7 mmol) of methyl 3-methyl-3-butenoate were refluxed for 22 hr. All volatile material was removed by distillation and the distillate redistilled to give the methyl methylcyclopropaneacetate as a colorless liquid, bp 136–137° (atmospheric pressure), yield 3.733 g (73.5%).

The spectral data were: ir (neat liquid) 3.21, 3.30, 3.36, 5.76, 6.96, 7.37, 7.74, 8.00, 8.66, 9.15, 9.88, 10.76, 11.10, 11.92, 13.00, 13.60, and 14.37 μ; NMR (CCl_4) τ 6.38 (s, 3 H, $-OCH_3$), 7.86 (s, 2 H, $-CH_2-$), 8.88 (s, 3 H, $-CH_3$), 9.63 (ABq, 4 H, J = 7 Hz, cyclopropyl).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.56; H, 9.29.

1-(2,2-Diphenylvinyl)-1-methylcyclopropane. Methyl 1-methylcyclopropaneacetate (3.521 g, 27.5 mmol) was added dropwise, with stirring to 0.12 mol of ethereal phenylmagnesium bromide. The mixture was refluxed for 1 hr and quenched with saturated aqueous ammonium chloride. The organic phase was water washed, dried, and concentrated in vacuo to afford an oil which was dissolved in 50 ml of benzene. *p*-Toluenesulfonic acid (0.10 g) was added, and the solution was refluxed for 2 hr and concentrated in vacuo to give an oil which was chromatographed on a 93 × 2.5 cm column of silica gel slurry packed in hexane. Elution with hexane gave as the first band crude product which was distilled through a 5-cm Vigreux column to give 2.034 g (31.3%) of the vinylcyclopropane, bp 145–147° (1.3 mm).

The spectral data were: ir ($CHCl_3$) 3.24, 3.31, 3.36, 3.47, 6.16, 6.25, 6.35, 6.69, 6.91, 7.25, 7.32, 7.61, 7.81, 8.66, 9.17, 9.31, 9.54, 9.72, 9.85, 10.06, 10.40, 10.72, 10.97, 11.17, 11.38, 11.86, 14.45, and 15.85 μ; NMR (CCl_4) τ 2.8 (brd, 10 H, arom), 3.99 (s, 1 H, vinyl), 8.72 (s, 3 H, $-CH_3$), 9.61 (d, 4 H, cyclopropyl).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.67.

1,2-Dihydro-2,2-dimethyl-4-phenylnaphthalene. To a solution of 1.62 g (9.29 mmol) of 3,4-dihydro-3,3-dimethyl-1(2*H*)-naphthalenone[36] in 20 ml of anhydrous ether under nitrogen was added, with stirring, excess ethereal phenyllithium (TLC monitoring of reactant consumption). After stirring 0.5 hr, the reaction was quenched with water. The organic phase was water washed, dried, concentrated in vacuo, and dissolved in 50 ml of benzene. *p*-Toluenesulfonic acid (100 mg) was added and the solution refluxed for 2 hr, cooled, and concentrated in vacuo to give an oil which was chromatographed on a 92 × 2.5 cm column slurry packed with silica gel in hexane. Elution with hexane gave the product which crystallized from methanol, yield 1.97 g (89.9%, pure by NMR). Recrystallization from methanol gave mp 85–85.5°.

The spectral data were: ir ($CHCl_3$) 3.32, 3.29, 3.37, 3.39, 3.46, 6.24, 6.71, 6.90, 7.19, 7.32, 7.39, 7.48, 7.72, 7.80, 8.60, 8.85, 9.30, 9.58, 10.22, 10.45, 11.76, and 14.30 μ; NMR (CCl_4) τ 2.69 (s, 5 H, arom), 2.9 (m, 4 H, arom), 4.24 (s, 1 H, vinyl), 7.25 (s, 2 H, $-CH_2-$), 8.89 (s, 6 H, $-CH_3$).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.35; H, 7.73.

2-Methyl-3,3-diphenylpropionic Acid. Following the general procedure of Eijkman,[37] 20.0 g (0.15 mol) of anhydrous aluminum chloride was added portionwise to a stirred solution of 14.1 g (0.087 mol) of α-methylcinnamic acid in 100 ml of anhydrous benzene. Stirring was continued for 40 hr, when the mixture was poured into iced concentrated hydrochloric acid. The phases were separated, and the organic phase was washed with dilute hydrochloric acid, dried, and concentrated in vacuo to give a colorless crystalline solid which was washed with hexane to give 2-methyl-3,3-diphenylpropionic acid (20.0 g, 95.8%), mp 158–162° (lit.[37] 161°).

The spectral data were: ir ($CHCl_3$) 2.8–4.0 (broad, unresolved), 5.86, 6.25, 6.70, 6.89, 7.08, 7.74, 8.49, 8.97, 9.27, 9.69, 10.80, 10.99, 14.30, and 15.05 μ; NMR ($CDCl_3$) τ 0.4 (broad, s, 1 H, $-OH$), 2.71 (broad s, 10 H, arom), 5.92 (d, 1 H, $J = 12$ Hz, Ph_2CH-), 6.68 (d of q, 1 H, $J = 12, 7$ Hz, CH_3CH-), 8.89 (d, 3 H, $J = 7$ Hz, CH_3-).

4-Diazo-2-methyl-1,1-diphenyl-3-butanone. Oxalyl chloride (8.5 ml, 12.55 g, 99.0 mmol) was added dropwise to a stirred solution of 12.03 g (50.2 mmol) of 2-methyl-3,3-diphenylpropionic acid and 0.1 ml of dimethylformamide in 100 ml of anhydrous benzene under nitrogen. Stirring was continued 3 hr, the solvent and excess reagent were removed in vacuo, and the residue was dissolved in anhydrous ether and added to excess ethereal diazomethane with stirring. After 1 hr, excess diazomethane was removed in a stream of nitrogen, and the solution was concentrated in vacuo to leave a yellow oil which crystallized on trituration with ether, yield 12.97 g (98.2%), mp 91–95°.

The spectral data were: ir ($CHCl_3$) 3.20, 3.22, 3.25, 3.31, 3.35, 3.40, 3.47, 4.74, 6.10, 6.70, 6.90, 7.25, 7.32, 7.61, 8.76, 9.03, 9.28, 9.71, 9.99, 10.14, 10.63, 10.98, 14.35, and 15.09 μ; NMR (CCl_4) τ 2.79 (m, 10 H, arom), 5.09 (s, 1 H, CHN_2-), 5.93 (d, 1 H, $J = 12$ Hz, Ph_2CH-), 6.87 (d of q, 1 H, $J = 7, 12$ Hz, CH_3CH-), 8.97 (d, 3 H, $J = 7$ Hz, $-CH_3$).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.21; H, 6.06; N, 10.59.

3,8a-Dihydro-2-methyl-3-phenyl-1(2*H*)-azulenone. Benzene (150 ml), 1.49 g of cuprous chloride, and 3.57 g (13.5 mmol) of 4-diazo-2-methyl-1,1-diphenyl-3-butanone were stirred under reflux for 10 min,[15] filtered, and concentrated in vacuo to yield 3.07 g (96.3%) of an almost colorless oil shown by NMR to be essentially pure (>90%) 3,8a-dihydro-2-methyl-3-phenyl-1(2*H*)-azulenone. Further purification was unnecessary and was not attempted since the compound was unstable to silica gel chromatography.

The spectral data were: ir (neat liquid) 3.22, 3.26, 3.29, 3.35, 3.40, 3.48, 5.71, 6.24, 6.67, 6.74, 6.87, 7.25, 7.47, 7.57, 7.79, 8.55, 9.25, 9.39, 9.71, 10.69, 10.90, 11.18, 11.63, 11.88, 12.84, 13.12, 14.29, and 14.71 μ; NMR (CCl_4) τ 2.73 (m, 5 H, arom), 3.59 (m, 2 H, vinyl), 3.76 (m, 1 H, vinyl), 4.09 (m, 1 H, vinyl), 4.85 (d of d, 1 H, $J = 4.0, 9.6$ Hz, terminal vinyl), 6.39 (d, 1 H, $J = 11.6$ Hz, $PhCH-$), 7.12 (m, 1 H, $-COCH-$), 7.54 (d of q, 1 H, $J = 11.6, 7.0$ Hz, CH_3CH-), 8.89 (d, 3 H, $J = 7.0$ Hz, $-CH_3$); mass spectrum m/e (calcd for $C_{17}H_{16}O$, 236.1201) 236.1202.

1,2-Dimethyl-3-phenylazulene. To a solution of 3.28 g (13.9 mmol) of 3,8a-dihydro-2-methyl-3-phenyl-1(2*H*)-azulenone in 50 ml of anhydrous ether was added with stirring 10.0 ml of ethereal methyllithium (1.9 *M*, 19.0 mmol). After stirring for 10 min, saturated aqueous ammonium chloride was added. The phases were separated, and the organic was water washed, dried, and concentrated in vacuo to give an oil which was dissolved in 20 ml of triglyme. 10% palladium on charcoal (0.950 g) was added, and the mixture was refluxed 1 hr, cooled, diluted with hexane, filtered, concentrated in vacuo, and chromatographed on a 56 × 2 cm column slurry packed with silica gel in hexane. Elution with hexane gave a blue band which crystallized on standing, mp 75–78°, yield 1.667 g (51.9%). Recrystallization from methanol raised the melting point to 80–81°.

The spectral data were: ir ($CHCl_3$) 3.28, 3.32, 3.36, 3.43, 3.50, 6.25, 6.38, 6.41, 6.70, 6.82, 6.99, 7.21, 7.75, 9.33, 9.85, 14.24, and 15.21 μ; NMR (CCl_4) τ 1.96 (d, 1 H, $J = 9$ Hz, H_4 or H_8), 2.12 (d, 1 H, $J = 9$ Hz, H_4 or H_8), 2.67 (m, 6 H, arom and H_6), 3.12 (6 line m, 2 H, H_5 and H_7), 7.44 (s, 3 H, $-CH_3$), 7.53 (s, 3 H, $-CH_3$).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.00; H, 7.02.

Exploratory Photolysis of 3-(2,2-Diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene. A solution of 0.409 g of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene (1.41×10^{-3} *M*) in 700 ml of *tert*-butyl alcohol under deoxygenerated nitrogen was irradiated for 4.0 hr at the center of a circular array of 32 15-W low-pressure mercury lamps. The *tert*-butyl alcohol was removed in vacuo, and the resulting oil was chromatographed on a 30 × 1.0 cm column slurry packed with silica gel in hexane. Elution with hexane gave two fractions. Fraction 2 contained 239 mg (58.5%) of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene. Fraction 1 (186 mg, 45.5%) was rechromatographed on a 135 × 4.3 cm column slurry packed with a mixture of silicic acid and Celatom (3:1, v/v) in hexane. Elution with hexane gave, in addition to overlap fractions, fractions containing, in order, 1,1-diphenylethylene, 2-methyl-1,1-diphenyl-1-propene, 1,1-diphenyl-1,3-butadiene, and 4-methyl-1,1-diphenyl-1,3-pentadiene. Each compound was spectroscopically identical with authentic material.

NMR Detection of 3-(2,2-Diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane in the Photolysate from 3-(2,2-Diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene. A solution of 92 mg of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene in 700 ml of *tert*-butyl alcohol under deoxygenated nitrogen was irradiated for 20 min using the Rayonet type apparatus described above. The solvent was removed in vacuo and the resulting oil chromatographed on a 1 × 30 cm column slurry packed in hexane. Elution with hexane gave fraction 1, and 0.5% ether in hexane gave fraction 2. Analysis of this second fraction using a 270-MHz NMR with signal averaging over 250 transients showed, in addition to peaks attributable to starting material and trace impurities, all nonaromatic signals appropriate to 3-(2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane. Approximate integration of the vinyl doublet at τ 3.90 due to cyclobutane relative to the vinyl singlet at τ 4.09 due to starting cyclopropylvinylmethane showed that the cyclobutane was present to the extent of about 7%.

Sensitized Photolysis of 3-(2,2-Diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene. A solution of 0.200 g of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene (3.86×10^{-3} *M*) and 61 mg of 3-methoxyacetophenone in 125 ml of *tert*-butyl alcohol was purged with deoxygenated nitrogen for 1.5 hr prior to and during the photolysis. Irradiation for 4 hr using a 450-W Hanovia lamp equipped with a Pyrex glass filter afforded, after concentration in vacuo, an oil which was chromatographed on a 20 × 20 cm thick layer plate. Elution with 5% ether in hexane gave only two uv-active bands. Band 1 contained 0.198 g (98%) of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene. Band 2 contained 52 mg of 3′-methoxyacetophenone.

Exploratory Photolysis of 3-(2,2-Diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane. A solution of 0.150 g of 3-(2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane (0.52×10^{-3} *M*) in 700 ml of *tert*-butyl alcohol under deoxygenated nitrogen was irradiated for 17 min using the Rayonet type apparatus described above. The *tert*-butyl alcohol was removed in vacuo, and the resulting oil was chromatographed on a 20 × 20 cm thick layer plate. Elution with hexane (3×) gave two bands. Band 2 contained 73 mg (48.7%) of 3-(2,2-diphenyl)-2,2-dimethyl-1,1-diphenylcyclobutane. Band 1 (68 mg, 45.4%) was rechromatographed on a 135 × 4.3 cm column slurry packed with a mixture of silicic acid and Celatom (3:1, v/v) in hexane. Elution with hexane gave, in addition to overlap fractions, fractions containing 2-methyl-1,1-diphenyl-1-propene and 1,1-diphenyl-1,3-butadiene. Gas chromatographic analysis (column A) of the material in band 1 showed the absence of 1,1-diphenylethylene and 4-methyl-1,1-diphenyl-1,3-pentadiene with a detectability level of 0.1%.

Sensitized Photolysis of 3-(2,2-Diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane. A solution of 0.214 g of 3-(2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane (4.1×10^{-3} *M*) and 74 mg of 3-methoxyacetophenone (3.9×10^{-3} *M*) in 125 ml of *tert*-butyl alcohol was purged with deoxygenated nitrogen for 1 hr prior to and during the photolysis. Irradiation for 4 hr using a 450-W Hanovia lamp equipped with a Pyrex glass filter afforded, after concentration in vacuo, an oil which was chromatographed on a 1 × 30 cm column slurry packed with silica gel in hexane. Elution with hexane gave fraction 1 which contained 23 mg (11%) of 2-methyl-1,1-diphenyl-1-propene and 1,1-diphenyl-1,3-butadiene. Elution with 1% ether in hexane gave 157 mg (74%) of 3-(2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane. Elution with 5% ether in hexane gave 58 mg (79%) of 3′-methoxyacetophenone. Gas chromatographic analysis (column A) of fraction 1 showed, in addition to compounds mentioned, peaks having appropriate retention times for 1,1-diphenylethylene and 4-methyl-1,1-diphenyl-1,3-butadiene, but amounting to less than 1% of the mixture.

Photolysis of 1,1-Diphenylethylene and 4-Methyl-1,1-diphenyl-1,3-pentadiene. A solution of 0.114 g (0.55 mmol) of 4-methyl-1,1-diphenyl-1,3-pentadiene in 125 ml of *tert*-butyl alcohol under deoxygenated nitrogen was irradiated for 3 hr using a 450-W Hanovia medium-pressure mercury lamp equipped with a 1-mm Corex glass filter. Examination of the crude photolysate by gas chromatography (column A) and NMR showed the absence of 2-methyl-1,1-diphenyl-1-propene and 1,1-diphenyl-1,3-butadiene with a detectability level of 0.5%.

Photolysis of 2-Methyl-1,1-diphenyl-1-propene and 1,1-Diphenyl-1,3-butadiene. Similar irradiation and analysis of 0.093 g (0.45 mmol) of 2-methyl-1,1-diphenyl-1-propene and 0.102 g (0.43 mmol) of 1,1-diphenyl-1,3-butadiene in 125 ml of *tert*-butyl alcohol showed the absence of 1,1-diphenylethylene and 4-methyl-1,1-diphenyl-1,3-pentadiene.

Thermal Decomposition of 4-Diazo-3,3-dimethyl-1,1-diphenyl-1-butene. Methyl 2,2-dimethyl-4,4-diphenyl-3-butenylnitrosocarbamate (0.674 g, 1.99 mmol) was converted to the diazo compound as described above. The orange oil was dissolved in 50 ml of pentane and the solution refluxed for 24 hr in the absence of intense light. The solution was concentrated in vacuo and chromatographed on a 135 × 4.3 cm column slurry packed with a mixture of silicic acid and Celatom (3:1, v/v) in hexane. Elution with hexane gave, in addition to overlap fractions and traces of unidentified material, fractions containing, in order of elution, 1-(2,2-diphenylvinyl)-1-methylcyclopropane (trace), 1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (trace), 1,8a-dihydro-1,1-dimethyl-3-phenylazulene (major product), and 4-methyl-1,1-diphenyl-1,3-pentadiene (minor product). The total yield of hydrocarbons was 0.385 g (75.0%).

The spectral data for 1,8a-dihydro-1,1-dimethyl-3-phenylazulene were: ir (neat liquid) 3.29, 3.37, 3.48, 6.23, 6.52, 6.70, 6.81, 6.91, 7.23, 7.33, 8.98, 9.31, 9.72, 10.35, 10.72, 10.95, 11.56, 11.80, 12.71, 13.13, and 14.32 μ; NMR (CCl_4) τ 2.72 (m, 5 H, arom), 3.46–4.04 (m, 4 H, vinyl), 4.07 (s, 1 H, styryl), 4.69 (d of d, 1 H, J = 4.5, 9.5 Hz, terminal vinyl), 7.55 (five-line pattern, 1 H, allylic), 8.68 (s, 3 H, $-CH_3$), 8.74 (s, 3 H, $-CH_3$); uv λ_{max} (EtOH) 315 (4,800); mass spectrum m/e (calcd for $C_{18}H_{18}$, 234.1408) 234.1402.

The other compounds were spectroscopically identical with authentic material.

Photochemical Decomposition of 4-Diazo-3,3-dimethyl-1,1-diphenyl-1-butene. Methyl 2,2-dimethyl-4,4-diphenyl-3-butenylnitrosocarbamate (0.783 g, 2.32 mmol) was converted to the diazo compound as described above. The orange oil was transferred to an immersion-well photolysis apparatus containing pentane (125 ml) and cooled in an ice bath. The solution was irradiated for 3 hr using a Hanovia 450-W lamp equipped with a Pyrex glass filter, when the ir spectrum of an aliquot showed disappearance of the diazo band at 4.85 μ. The solution was concentrated in vacuo and chromatographed on a 135 × 4.3 cm column slurry packed with a mixture of silicic acid and Celatom (3:1, v/v) in hexane. Elution with hexane gave, in addition to overlap fractions and traces of unidentified material, fractions containing 1-(2,2-diphenylvinyl)-1-methylcyclopropane (major product) and 4-methyl-1,1-diphenyl-1,3-pentadiene (major product). Both were spectroscopically identical with authentic material. The total yield of hydrocarbons was 0.272 g (49.7%).

Thermal Carbene Generation from 2,2-Dimethyl-4,4-diphenyl-3-butenal 4-Toluenesulfonylhydrazone. To a stirred solution of 0.902 g (2.16 mmol) of 2,2-dimethyl-4,4-diphenyl-3-butenal 4-toluenesulfonylhydrazone in 60 ml of diglyme using nitrogen was added 0.565 g (10.5 mmol) of sodium methoxide. The mixture was placed in a preheated oil bath at 170° and stirred at this temperature for 12 min. The reaction mixture was cooled rapidly, diluted with pentane, water washed, dried, concentrated in vacuo, and chromatographed on a 135 × 4.3 cm column slurry packed in hexane with silicic acid and Celatom (3:1, v/v). Elution with hexane gave, in addition to overlap fractions and traces of unidentified material, fractions containing, in order of elution, 1-(2,2-diphenylvinyl)-1-methylcyclopropane, 1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene, and 1,8a-dihydro-1,1-dimethyl-3-phenylazulene. The total yield of hydrocarbons was 0.353 g, 69.9%.

Photochemical Carbene Generation from 2,2-Dimethyl-4,4-diphenyl-3-butenal 4-Toluenesulfonylhydrazone. To a 200-ml immersion-well photochemical reactor were added successively, under nitrogen, a solution of 0.695 g (1.66 mmol) of 2,2-dimethyl-4,4-diphenyl-3-butenal 4-toluenesulfonylhydrazone in 20 ml of anhydrous diglyme, 180 ml of anhydrous pentane, and ca. 54 mg (ca. 2 mmol) of oil-free sodium hydride. The mixture was stirred and agitated with bubbling nitrogen for 20 min prior to and during the photolysis. The mixture was irradiated for 1.5 hr using a 450-W medium-pressure mercury lamp equipped with a Pyrex glass filter. The photolysate was water washed, dried, concentrated in vacuo, and chromatographed on a 96 × 4 cm column slurry packed in hexane with silicic acid and Celatom (3:1, v/v). Elution with hexane gave, in addition to overlap fractions and traces of unidentified material, fractions containing 1-(2,2-diphenylvinyl)-1-methylcyclopropane and 4-methyl-1,1-diphenyl-1,3-pentadiene. The total yield of hydrocarbons was 0.281 g (72.1%).

Photolysis of 1,8a-Dihydro-1,1-dimethyl-3-phenylazulene. A solution of 0.152 g of 1,8a-dihydro-1,1-dimethyl-3-phenylazulene (5.3×10^{-3} *M*) in 120 ml of pentane, under deoxygenated nitrogen, was irradiated for 1 hr using a 450-W medium-pressure mercury lamp equipped with a 1-mm Pyrex glass filter. Examination of the crude photolysate by gas chromatography (column B) and NMR showed the presence of at least one new compound but showed that 1-(2,2-diphenylvinyl)-1-methylcyclopropane and 4-methyl-1,1-diphenyl-1,3-pentadiene had not been produced.

Aromatization of 1,8a-Dihydro-1,1-dimethyl-3-phenylazulene. 1,8a-Dihydro-1,1-dimethyl-3-phenylazulene (2.452 g, 10.5 mmol) and 1.006 g of 10% palladium on charcoal were refluxed 1 hr in 13 ml of triglyme. The mixture was cooled, diluted with hexane, water washed, dried, concentrated in vacuo, and chromatographed on a 87 × 2.5 cm column slurry packed with silica gel in hexane. Elution with hexane gave a blue band which was rechromatographed on a 135 × 4.3 cm column slurry packed with silicic acid and Celatom (3:1, v/v) in hexane. Elution with hexane gave a blue band which contained 0.025 g (1.0%) of 1,2-dimethyl-3-phenylazulene, spectroscopically identical with authentic material.

Photolysis of 1-(2,2-Diphenylvinyl)-1-methylcyclopropane. A solution of 0.108 g of 1-(2,2-diphenylvinyl)-1-methylcyclopropane in 125 ml of *tert*-butyl alcohol, under deoxygenated nitrogen, was irradiated for 3 hr using a 450-W medium-pressure mercury lamp equipped with a Corex glass filter. Analysis of the crude photolysate by GC (column B) and NMR showed, in addition to starting material, at least nine components, but not including 4-methyl-1,1-diphenyl-1,3-butadiene.

Photolysis Equipment and Quantum Yield Determinations. Quantum yield irradiations were performed on the "Black Box" apparatus previously described.[18] Light output was monitored by ferrioxalate actinometry, and the light absorbed in the reaction cell was determined by the splitting ratio technique.

For direct irradiations, the solution filters used were: filter A, (a) 2 *M* nickel sulfate in 5% sulfuric acid; (b) 0.25 *M* cobalt sulfate in 5% sulfuric acid; (c) 9×10^{-3} *M* 2,7-dimethyl-3,6-diaza-1,6-cycloheptadiene perchlorate[38] in water. This combination (2.4-cm thickness for each of three cells) gave a transmission maximum at 251 nm (40% transmission) and was opaque above 268 and below 232 nm. After 2-3 hr irradiation, the transmission had fallen by 10-20% because of decomposition of solution c so that solution was replaced every 2-3 hr. The other solutions were shown to be stable. For sensitized irradiation, the solution filters used were: filter B, (a) 1 *M* nickel sulfate in 5% sulfuric acid; (b) 1 *M* cobalt sulfate in 5% sulfuric acid; (c) 0.015 *M* stannous chloride in 10% hydrochloric acid. This combination gave a transmission maximum at 327 nm (37% transmission) and was opaque above 360 and below 302 nm.

Analysis involved a preliminary chromatography on a 1 × 30 cm column (or for the sensitized run nos. 5, 2.5 × 40 cm) slurry packed with silica gel in hexane. Elution with hexane gave, as the first uv-absorbing fraction, a mixture of the fragmentation products to which a weighed amount of internal standard, triphenylmethane, was added. The mixture was analyzed by gas chromatography (column A), using a calibrating mixture. The retention times were: 1,1-diphenylethylene, 3.2 min; 2-methyl-1,1-diphenyl-1-propene, 4.1 min; 1,1-diphenyl-1,3-butadiene, 6.3 min; 4-methyl-1,1-diphenyl-1,3-pentadiene, 13.5 min; triphenylmethane, 20.9 min.

Run 1. Filter combination A. Starting cyclopropylvinylmethane, 0.732 mmol; 0.753 mEinsteins absorbed; mmol of product formed—diphenylethylene, 0.0139 (ϕ = 0.0185); diphenylisobutylene, 0.00025 (ϕ = 0.0003); diphenylbutadiene, 0.00026 (ϕ = 0.0003); pentadiene 0.0127 (ϕ = 0.0168). Light absorbed by cyclobutane, 0.004 mEinstein. Corrected quantum yields: diphenylethylene, 0.0185; pentadiene, 0.0169; 1.8% conversion.

Run 2. Filter combination A. Starting cyclopropylvinylmethane, 0.486 mmol; 1.071 mEinsteins absorbed; mmol of product formed—diphenylethylene, 0.01919 (ϕ = 0.0179); diphenylisobutylene, 0.00109 (ϕ = 0.0010); diphenylbutadiene, 0.00102 (ϕ = 0.0009); pentadiene, 0.01986 (ϕ = 0.0186). Light absorbed by cyclobutane, 0.037 mEinstein. Corrected quantum yields: diphenylethylene, 0.0186; pentadiene, 0.0192; 4.3% conversion.

Run 3. Filter combination A. Starting cyclopropylvinylmethane, 0.244 mmol; 1.128 mEinsteins absorbed; mmol of product formed—diphenylethylene, 0.0190 (ϕ = 0.0174); diphenylisobutylene, 0.0021 (ϕ = 0.0019); diphenylbutadiene, 0.0017 (ϕ = 0.0016); pentadiene, 0.0184 (ϕ = 0.0164). Light absorbed by cyclobutane, 0.033 mEinstein. Corrected quantum yields: diphenylethylene, 0.0179; pentadiene, 0.0169; 8.4% conversion.

Run 4. Filter combination A. Starting cyclobutane, 1.00 mmol; 0.325 mEinsteins absorbed; mmol of product formed—diphenylisobutylene, 0.0185 (ϕ = 0.056); diphenylbutadiene, 0.0178 (ϕ = 0.054); 1.8% conversion.

Run 5. Filter combination A. Starting cyclobutane, 0.490 mmol; 0.518 mEinsteins absorbed; mmol of product formed—0.0314 (ϕ = 0.060); diphenylbutadiene, 0.0302 (ϕ = 0.058); 6.1% conversion.

Run 6. Filter combination B. Starting cyclobutane, 1.59 mmol; sensitizer, *m*-methoxyacetophenone, 3.33 mmol; 6.41 mEinsteins absorbed; mmol of product formed—diphenylisobutylene, 6.96×10^{-3} (ϕ = 0.00108); diphenylbutadiene, 6.18×10^{-3} (ϕ = 0.00096); 0.4% conversion.

Low-Conversion Product Distribution from 3-(2,2-Diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene. To check the time dependence of the product ratios on extent of irradiation, the ratio of product peak heights as a function of irradiation time was measured. A solution of 0.281 g of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene in 700 ml of *tert*-butyl alcohol was irradiated in the Rayonet type apparatus described above. Aliquots (ca. 3 ml) were removed at intervals, concentrated in vacuo, and chromatographed on 2.5 × 7 cm thin layer plates. The fastest running band was eluted and analyzed by gas chromatography (column A) measuring peak heights. The following gives irradiation time, ratio of diphenylethylene to pentadiene, ratio of diphenylisobutylene to pentadiene, and ratio of diphenylbutadiene to pentadiene: 15 min, 2.4, 0.33, 0.23; 30 min, 2.6, 0.53, 0.34; 60 min, 2.5, 0.63, 0.46; 120 min, 2.2, 0.87, 0.52.

High-Conversion Product Distribution from 3-(2,2-Diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene. Solutions containing ca. 100 mg of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene in 700 ml of *tert*-butyl alcohol were irradiated in the Rayonet apparatus described above. Analysis was performed in the same manner as for the quantum yield determinations (vide supra).

Run 1. Starting cyclopropylvinylmethane used, 0.251 mmol; diphenylethylene formed, 7.64×10^{-2} mmol; pentadiene, 8.04×10^{-2} mmol; diphenylisobutylene, 2.29×10^{-2} mmol; diphenylbutadiene, 1.76×10^{-2} mmol; 39% conversion; ratio 0.258.

Run 2. Starting cyclopropylvinylmethane used, 0.222 mmol; diphenylethylene formed, 6.03×10^{-2} mmol; pentadiene, 1.53×10^{-2} mmol; diphenylisobutylene, 1.40×10^{-2} mmol; diphenylbutadiene, 1.40×10^{-2} mmol; 34% conversion; ratio 0.243.

Single Photon Counting. Determination of the Rate of Excited Singlet State Rearrangement of 3-(2,2-Diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene. Samples of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene were crystallized five times from hexane and then at least twice from fluorescence pure methylcyclohexane prior to making solutions of the compound in 4:1 methylcyclohexane:isopentane. All samples were degassed using at least four alternate freeze-thaw cycles; liquid nitrogen was used for freezing the samples.

Magic Multiplier. The fluorescence spectrum was recorded at 298° and 77 K under otherwise identical conditions using an Aminco-Kiers spectrofluorometer with a Hanovia 901C-1 150-W Xenon lamp. Concentrations were adjusted to give an optical density in the range of 0.8-1.5 to minimize scatter.

The magic multiplier was obtained for two separate samples by integrating the emission intensities obtained at 77° and 298 K. The values thus obtained were 267 and 219, mean value 243.

Single Photon Counting Procedure. Excitation and emission monochromators were employed. To avoid counting double photon pulses, the monochromator slits were narrowed to the point at which the rate of photon counting was less than $\frac{1}{20}$th of the lamp frequency,[39] which was maintained at 20-30 kHz in these runs. Collection was continued until the maximum number of counts per channel was 1700-2000. The lamp flash was obtained from a run using a Ludox scattering solution in the sample cell. A lamp flash run was made contiguous in time with each experimental run.

Summary of Single Photon Counting Data. For each run, the following are given in order: solution emission wavelength, time resolution in sec/channel, lifetime after time axis shifting,[4] "*A* value". The *A* value is defined as the percent variation of areas of the emission curve and the convoluted curve obtained using the determined decay function. All runs were made at 77 K, with excitation wavelength set at 250 nm.

Run 1: A, 300 nm, 9.81×10^{-11}, 6.16 nsec, 4.9%. **Run 2:** A, 310 nm, 9.81×10^{-11}, 6.03 nsec, 4.5%. **Run 3:** A, 320 nm, 9.81×10^{-11}, 6.05 nsec, 4.5%. **Run 4:** B, 310 nm, 9.40×10^{-11}, 6.41 nsec, 4.5%. **Run 5:** B, 320 nm, 9.40×10^{-11}, 6.59 nsec, 4.6%. **Run 6:** C, 300 nm, 9.58×10^{-11}, 6.61 nsec, 4.5%. **Run 7:** C, 310 nm, 9.58×10^{-11}, 6.53 nsec, 4.6%. **Run 8:** C, 320 nm, 9.58×10^{-11}, 6.30 nsec, 4.3%

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Experimental Proof That the Diels–Alder Reaction of Tetracyanoethylene with 9,10-Dimethylanthracene Passes through Formation of a Complex between the Reactants

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Abstract: Up to the present, it has been considered impossible to determine kinetically whether the complex often formed between diene and dienophile is a true intermediate in the Diels–Alder reaction. A method based on the effect of temperature on the reaction rates has been tested and found successful in proving that the complex formed by tetracyanoethylene and 9,10-dimethylanthracene is indeed a true intermediate in the Diels–Alder reaction of those molecules.

For nearly 50 years, the Diels–Alder reaction (DAR) has been employed as an important method of synthesis of carbocyclic and heterocyclic compounds. In the last 2 decades, the mechanism of the reaction has been given considerable attention.[2-5] The influence of substituents both in the diene and in the dienophile[6] and the nature of the effects of solvents,[7,8] pressure,[9] catalysts,[3,4] and other factors have been investigated.

Experiment and theory indicate that the transition state in the DAR comes about by a closely concerted and symmetric interaction of the π-electron systems of the reactants.[2-5] Nevertheless, the interpretations of the experimental kinetic parameters are often complicated by remarkably strong interactions between the reactants and the solvent, the transition state and the solvent, and even between the reactants themselves. The latter interaction often results in an electron donor-acceptor molecular complex (MC) as shown by a charge-transfer band in the ultraviolet spectrum[10] before reaction.

The effect of such complex formation on the DAR was first treated by Andrews and Keefer.[11-13] For the two possible pathways from reactants A and B to adduct P:

$$\mathrm{A + B \rightleftarrows MC \xrightarrow{k_1} P} \tag{1}$$

$$\mathrm{MC \rightleftarrows A + B \xrightarrow{k_2} P} \tag{2}$$

it was shown that the experimental rate constant, k_{exp}, is related to k_1 and k_2 as follows:

$$k_{\mathrm{exp}} = k_1K/(1 + K[\mathrm{B}]) \tag{3}$$

$$k_{\mathrm{exp}} = k_2/(1 + K[\mathrm{B}]) \tag{4}$$

where K is the equilibrium constant for the formation of MC and $[\mathrm{B}] \gg [\mathrm{A}]$. The observed decrease of k_{exp} with increase of [B] in the DAR of anthracene and 9,10-dimethylanthracene with maleic anhydride and some of its derivatives was in agreement with eq 3 and 4. Furthermore, the value of K for the complex formed by 9,10-dimethylanthracene and maleic anhydride obtained by those equations from the rate data agreed well with the value obtained directly from the zero-time optical densities by the usual spectroscopic procedure. Although their data could not distinguish between pathways 1 and 2, they showed that the principal effect of the concentration change of the reactants