On the Problem of Regioselectivity in the Photochemical Ring-Opening Reaction of 3-Phenyl- and 3-Vinyl-Substituted Cyclopropenes to Indenes and 1,3-Cyclopentadienes[1]

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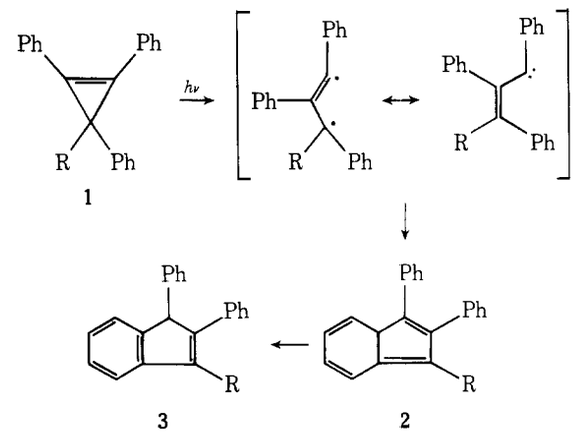
The photochemical rearrangement of several 3-phenyl- and 3-vinyl-substituted cyclopropenes to indenes and 1,3-cyclopentadienes has been studied. The rearrangements were shown to be derived from the π,π^* singlet state since triplet sensitization led to no reaction or else resulted in a 2 + 2 dimerization reaction. When an unsymmetrical cyclopropene such as 1,3-diphenyl-2-methyl-3-benzylcyclopropene (**9**) was used, a mixture of 1-methyl-2-phenyl-3-benzylindene (**10**; 80%) and 1-phenyl-2-methyl-3-benzylindene (**11**; 20%) was obtained. Irradiation of 1,3-diphenyl-2-methyl-3-vinylcyclopropene (**32**) produced a mixture of 3-methyl-1,2-diphenyl- (**27**), 1-methyl-2,3-diphenyl- (**28**), and 2-methyl-1,3-diphenyl-1,3-cyclopentadiene (**33**) as well as 1-methyl-2-phenyl-3-vinylindene (**34**) in good yield. The major products formed correspond to cleavage of the cyclopropene bond attached to the methyl group. Two fundamentally different mechanisms seem plausible. One path involves cyclopropene ring opening to give a 1,3-diradical intermediate which subsequently decays to a vinylcarbene. An alternate path involves π–π^* bridging in the excited singlet state to give a bicyclo[2.1.0]pentane diradical, which then undergoes a subsequent fragmentation. Some support for the carbene mechanism was obtained from the irradiation of 1-phenyl-2,3,3-trimethylcyclopropene (**52**). The distribution of methoxy ethers obtained from the irradiation of this compound in methanol also corresponds to cleavage of the cyclopropene bond attached to the methyl group.

The thermal and photochemical reactions of strained, small ring molecules have been extensively studied.[2] Cyclopropene is one of the simplest of such molecules in terms of chemical composition and at the same time perhaps the most strained of the compounds hitherto known, if strain energy is calculated per carbon atom.[3] Vinylcarbenes have frequently been proposed as intermediates in the thermal and photochemical reactions of cyclopropenes.[4–24] The mechanism for the interconversion of the cyclopropene ring and the corresponding bond-cleaved species continues to be of both theoretical and experimental interest. Extended Hückel calculations carried out on the parent vinylcarbene system suggest a triplet diradical type structure for the ground state of this system.[25–28] Recent ESR experiments by Arnold and coworkers[11] support this conclusion. These workers found that the irradiation of vinyldiazo compounds generates vinylcarbenes as stable triplet species. The temperature dependence of the ESR signal indicates that the triplet is the ground state and that the singlet state is not thermally populated within the temperature range (5–30 K) examined. More recent calculations by Davis, Goddard, and Bergman predict that the thermal ring-opening reaction of cyclopropene first proceeds to a diradical planar intermediate, which subsequently decays to a carbene.[23]

During the last few years the photochemistry of cyclopropene derivatives has attracted considerable interest. The photochemical behavior of this small ring system was shown to be markedly dependent on the multiplicity of the excited state involved.[11] Singlet states react by σ-bond cleavage to give products which can be attributed to vinylcarbenes.[9,10] In contrast, triplet states generated by sensitization techniques give 2 + 2 dimers.[29–32] The cyclopropene singlet is known to have a very inefficient ($<10^{-3}$) intersystem crossing efficiency,[32] which accounts for the absence of 2 + 2 dimers from direct irradiation experiments. One of the more frequently encountered photochemical reactions of 3-aryl-substituted cyclopropenes involves rearrangement to indenes.[7,8] Formally analogous to the vinylcyclopropane–cyclopentene isomerization, this rearrangement can also be effected by acid,[33] transition metals,[34–36] or heat.[5]

The reaction has been proposed to proceed via an isoindene intermediate (**2**) which subsequently undergoes a thermally allowed [1,5] sigmatropic shift to give the aromatic indene **3**.[5]



While several examples of this transformation have been reported, the photochemistry of unsymmetrically substituted cyclopropenes has remained uninvestigated.[37–39] We have therefore undertaken a careful study of the products and mechanism of the photolysis of several unsymmetrical 3-aryl- and 3-vinyl-substituted cyclopropenes. During the course of our investigation we encountered an unusual substituent effect on the mode of ring opening of these systems. In this paper we report our observations which, when taken together, present a consistent and satisfying mechanistic rationale for the ring-opening reaction.

Results

3-Phenyl-substituted cyclopropenes were prepared by treating variously substituted cyclopropenyl cations with Grignard reagents according to the general procedure of Breslow and co-workers.[40] In all the cases studied, nucleophilic attack by the Grignard reagent on the cyclopropenyl cation afforded the 1,2-diphenyl-substituted cyclopropene (**5**) as the major product. This is consistent with Breslow's previous observations in that nucleophilic attack occurs preferentially on the carbon atom of the cyclopropenyl cation which is best able to localize the positive charge.[40,41] The mixture of isomers could readily be separated by silica gel chromatography.

Irradiation of 3-methyl-1,2,3-triphenylcyclopropene (**7**) in benzene for relatively short periods of time provided 1,2-diphenyl-3-methylindene (**8**) in 75% isolated yield. The

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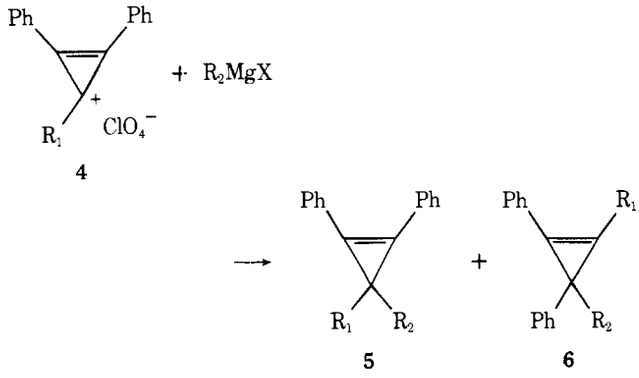
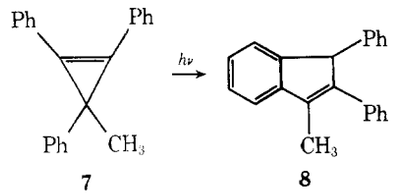
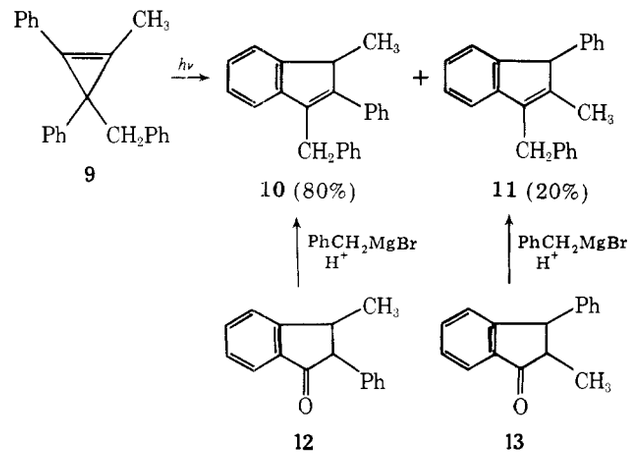


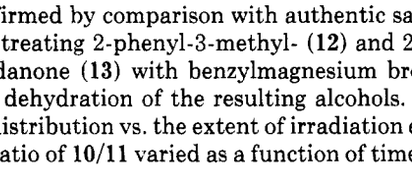
structure of this product was unambiguously established by comparison with an authentic sample.



When the irradiation of an unsymmetrical cyclopropene such as 1,3-diphenyl-2-methyl-3-benzylcyclopropene (**9**) was carried out in benzene for 1 h, a 4:1 mixture of 1-methyl-2-phenyl-3-benzylindene (**10**) and 1-phenyl-2-methyl-3-benzylindene (**11**) was obtained. The structures of these indenes

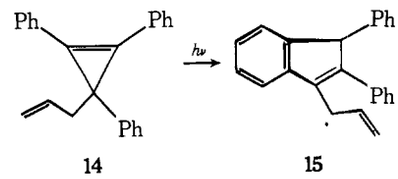


were confirmed by comparison with authentic samples prepared by treating 2-phenyl-3-methyl- (**12**) and 2-methyl-3-phenylindanone (**13**) with benzylmagnesium bromide, followed by dehydration of the resulting alcohols. A study of product distribution vs. the extent of irradiation established that the ratio of **10**/**11** varied as a function of time. At longer exposures, owing to a secondary photoreaction of **11**, the amount of **10** increased (ratio **10**/**11**, 10:1). This was independently demonstrated by the quantitative conversion of **11** to **10** in benzene under comparable photolytic conversions. The observed rearrangement represents an exchange of the indene 1 and 2 carbon atoms and is analogous to the process recently described by Morrison and Palensky[42] for related substituted indenes, except that in their case, the presence of an alkyl group at the 3 position completely quenched the photoreaction. The above rearrangement proceeds exclusively in one direction since the irradiation of indene **10** resulted in recovered starting material, even under lengthy photolytic conditions. It should be noted, however, that when the irradiation of cyclopropene **9** was carried out for short periods of time (10 min, <10% conversion) the ratio of indenes (**10**/**11**) was 4:1. This result clearly indicates that **10** is the predominant primary photoproduct and is not formed from **11** under the kinetic conditions employed. It is also important to note that the thermolysis of cyclopropene **9** gave indene **11** as the exclusive product. Thus, the excited-state and ground-state behavior of this small ring system are quite distinct.

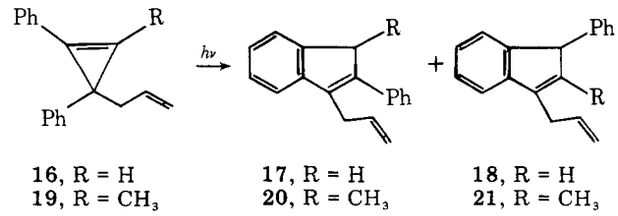


In order to help elucidate the correct mechanism for indene formation, the photochemistry of **9** was carried out in methanol. Under these conditions, no detectable quantities of indenes **10** and **11** were present in the crude photolysate. Unfortunately, all attempts to separate the complex mixture of photoproducts were unsuccessful. Nevertheless, examination of the NMR spectrum of the crude photolysate clearly showed the presence of several methoxy ethers and a number of triphenyl-substituted pentadienes. It should be noted that the indene skeleton is retained on irradiation in methanol and that the relative quantum yields for the disappearance of **9** are the same in methanol and benzene.

Attention was next turned to the photochemical behavior of 2-allyl-1,2,3-triphenylcyclopropene (**14**). We hoped that with this system the initially generated vinylcarbene would undergo internal cycloaddition to give a bicyclo[3.1.0]hex-2-ene. We had previously reported the successful utilization of such a process in proving the intermediacy of a vinylcarbene in the photolysis of 1,2-diphenyl-3-methyl-3-allylcyclopropene.[38] Irradiation of **14** in benzene, however, gave 3-allyl-1,2-diphenylindene (**15**), mp 79–81 °C, as the exclusive photoproduct. It would seem that if a vinylcarbene intermediate is involved in this reaction, the rate of cycloaddition of the intermediate with the neighboring double bond is not rapid enough to afford bicyclohexene in competition with indene formation. Also complicating matters here is the possibility of forming isomeric *cis*- and *trans*-vinylcarbenes.

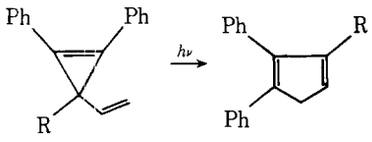


Additional examples of indene formation are provided by the photolysis of 3-allyl-1,3-diphenylcyclopropene (**16**) and 3-allyl-3-methyl-1,3-diphenylcyclopropene (**19**). The structures of the resulting photoproducts were verified by comparison with independently synthesized samples. In both of these cases, the major indene (**17** or **20**) formed (80%) was derived from cleavage of the cyclopropene bond attached to the R substituent. In neither case were we able to detect the presence of a bicyclo[3.1.0]hex-2-ene.



During our studies with the above 2-arylcyclopropenes, it occurred to us that a similar photoreaction should take place with the closely related 3-vinylcyclopropene system. In order

to establish this possibility, a number of 3-vinyl-substituted diarylcyclopropenes were prepared by treating variously substituted cyclopropenyl cations with vinyl Grignard reagents and separating the mixture of isomers formed by column chromatography. Although indenes are generally formed from the irradiation of 3-aryl-substituted cyclopropenes, the photolysis of 1,2,3-triphenyl-3-vinylcyclopropene (**22**) resulted

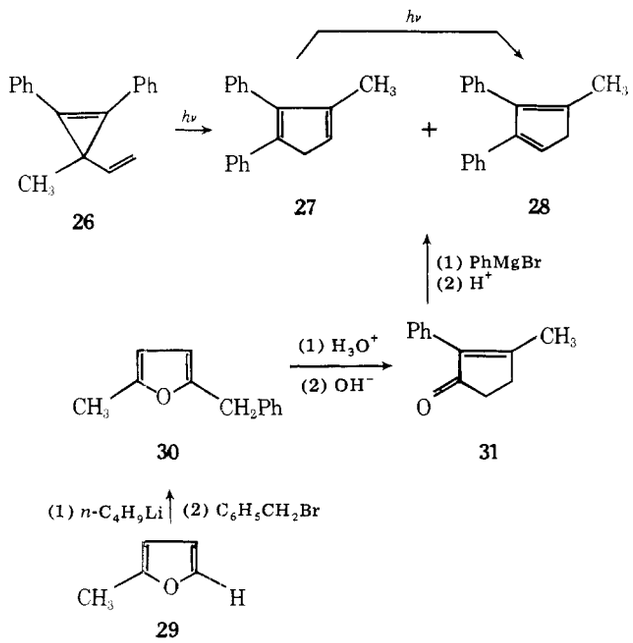


22, R = Ph
24, R = H
26, R = CH_3

23, R = Ph
25, R = H
27, R = CH_3

in the exclusive formation of 1,2,3-triphenyl-1,3-cyclopentadiene (**23**). Similar rearrangements were also found to occur with cyclopropenes **24** and **26**. The photolysis of these systems was sufficiently free of byproducts that the reaction can be considered to be of general synthetic utility for the construction of substituted 1,3-cyclopentadienes. The structures of the 1,3-cyclopentadienes were established by comparison with authentic samples (see Experimental Section).

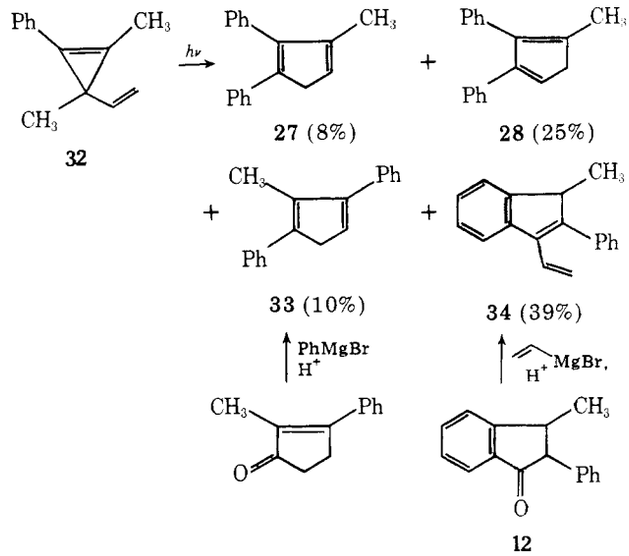
In the studies involving the photochemistry of cyclopropene **26**, considerable difficulty was experienced in isolating a pure sample of cyclopentadiene **27**. In addition to **27** (75%), a sig-



nificant quantity (ca. 25%) of the isomeric 1-methyl-2,3-diphenylcyclopentadiene (**28**) was present in the crude photolysate. The structures of both products were established by comparison with independently synthesized samples. The synthesis of 2-methyl-3-phenylcyclopentenone (**31**) involved the metalation of 2-methylfuran with butyllithium to give 2-lithio-5-methylfuran,[43] which was condensed with benzyl bromide. The resulting 2,5-disubstituted furan (**30**) was hydrolyzed to the corresponding diketone, which was subsequently subjected to a base-induced cyclization to afford cyclopentenone **31**. Treatment of this material with phenyl Grignard reagent followed by an acid-induced dehydration afforded a 1:3 mixture of cyclopentadienes **27** and **28**.

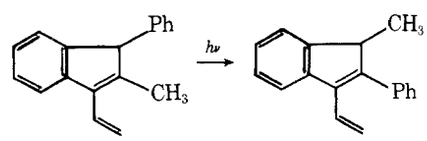
At first glance it would seem as though the formation of **28** is derived by means of a [1,5]sigmatropic hydrogen shift from cyclopentadiene **27**. McLean[44-46] and others[47,48] have shown that equilibration of 1,3-cyclopentadienes can be established through a purely thermal 1,5 migration of a hydrogen atom. This process is so facile that in certain systems it takes place at an appreciable rate even at room temperature.[45] If the above two cyclopentadienes were rapidly equilibrating at room temperature, then the ratio of **27**/**28** should be the same regardless of the method of generation. We note, however, that a different distribution of cyclopentadienes was obtained from the photolysis of **26** than from the acid-catalyzed dehydration of the benzylic alcohol derived from **31**. Furthermore, the ratio of the two cyclopentadienes derived from the photolysis of cyclopropene **26** varied as a function of time. With short exposures, cyclopentadiene **27** accounts for nearly all of the product produced. At longer exposures, owing to a secondary photoreaction of **27**, the amount of **28** increased. Thus, the presence of **28** in the crude photolysate derived from **26** can be attributed to a subsequent photoreaction of **27** rather than to a thermally induced 1,5-hydrogen shift.

We next turned our attention to the photochemistry of the isomeric 2-methyl-1,3-diphenyl-3-vinylcyclopropene (**32**) system in order to assess the regioselectivity of the bond cleavage reaction. Subjection of **32** to conditions similar to that used with **26** gave a mixture of 1-methyl-2,3-diphenyl- (**28**), 1,2-diphenyl-3-methyl- (**27**) and 2-methyl-1,3-diphenyl-



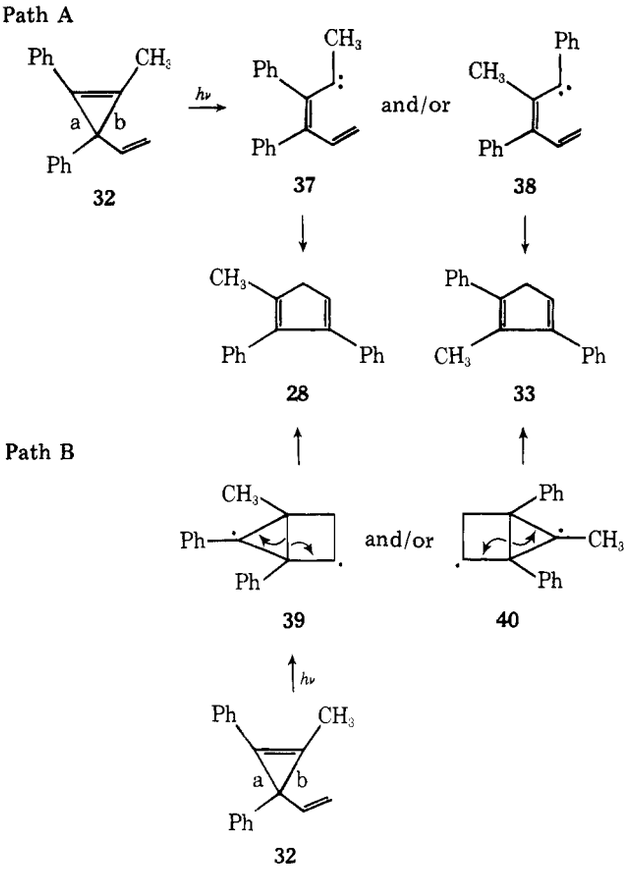
1,3-cyclopentadiene (**33**) as well as 1-methyl-2-phenyl-3-vinylindene (**34**) in good yield. The structures of **33** and **34** were based on their spectroscopic and analytical properties and were further confirmed by comparison with authentic samples.

The small amount (ca. 8%) of **27** present in the crude reaction mixture can be attributed to a thermally induced 1,5-hydrogen shift of the initially produced cyclopentadiene **28**. This contention stems from the fact that the photolysis of an enriched sample of **28** (containing **27** as the contaminant) does not produce additional quantities of **27**. It should also be noted that the isomeric 1-phenyl-2-methyl-3-vinylindene (**36**) was



not present in the crude photolysate. What complicates the problem here is that when an authentic sample of **36** was independently synthesized and subjected to irradiation, it quantitatively rearranged to indene **34**. This reaction is analogous to that previously described with the related ben-

Scheme I



zyl-substituted indene system (i.e., 11 → 12). As a consequence of this, the determination of the regioselectivity of bond cleavage of cyclopropene **32** is made more difficult. Nevertheless, examination of the crude photolysate by NMR spectroscopy at low conversions of **32** showed that no significant quantities of **36** were present. Thus, the major products obtained from **32** correspond to the preferential cleavage of the cyclopropene bond attached to the methyl group (ratio (**27** + **28** + **34**)/**33** 7:1).

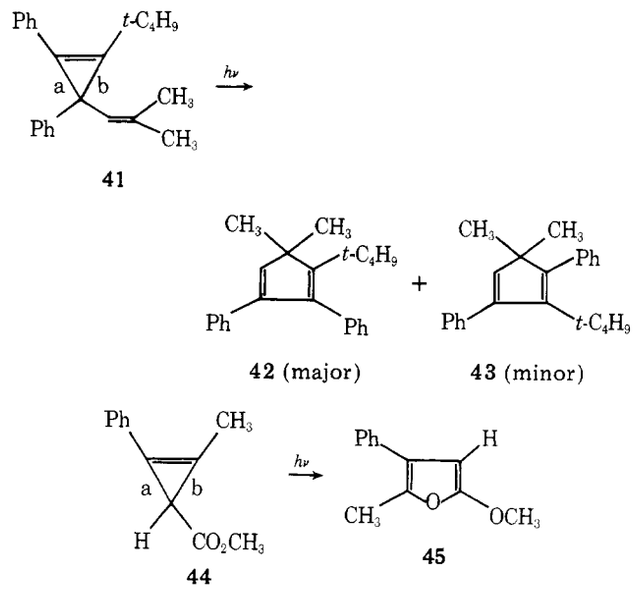
The excited state responsible for the photorearrangement of the 3-aryl- and 3-vinyl-substituted cyclopropenes is a π–π^* singlet since sensitization with thioxanthone led to no reaction with cyclopropenes **7**, **9**, **22**, and **26** and gave a 2 + 2 dimer with **24**. This is consistent with DeBoer's earlier observation that the intersystem crossing efficiencies of aryl-substituted cyclopropenes are close to 0.[32] Thus, it can be concluded that both the 1,3-cyclopentadienes and indenes arise from the singlet excited state of the cyclopropene and that the corresponding triplet does not undergo a ring-opening reaction. Recent experimental results by Pincock and Moutsokapas[49] with an optically active cyclopropene also support the argument that the cyclopropene triplet does not ring open. There seems to be a barrier on the cyclopropene–vinylcarbene triplet surface which does not exist on the singlet surface and which accounts for the difference in photobehavior of the singlet and triplet states.[50]

Quantum yield studies were carried out on a merry-go-round apparatus equipped with a series of 3000-Å lamps. The quantum efficiencies for product formation from cyclopropenes **22**, **24**, and **26** were 0.027, 0.031, and 0.022. Although the reaction efficiency of the rearrangement was quite low, the photolysis was free of byproducts, and the isolated yields of cyclopentadienes were high. The low quantum efficiencies will be discussed below in connection with the reaction mechanism.

Discussion

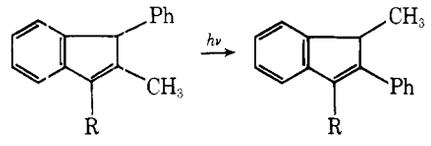
The mechanism by which these substituted cyclopropenes undergo rearrangement is of considerable interest. Two fundamentally different mechanisms seem possible and are presented in Scheme I. Path A involves cyclopropene ring opening to give a butadienylcarbene followed by electrocyclic ring closure. In the case of the 3-aryl-substituted cyclopropene system, the initially formed isoindene (i.e., **2**) would be expected to undergo a rapid 1,5-hydrogen shift to give an indene derivative (i.e., **3**). The above route bears a strong similarity to mechanisms previously suggested to rationalize the products derived from substituted cyclopropenes on electronic excitation.[4–23,38] The alternate path (B) involves π–π bridging of the excited cyclopropene to give a diradical intermediate which subsequently cleaves to produce either the isoindene or 1,3-cyclopentadiene ring system. The bridging and cleavage steps are related to the first two formal steps of a di-π-methane rearrangement.[51] The two mechanistic possibilities illustrated in Scheme I make use of the unsymmetrical 3-vinyl-substituted cyclopropene ring system **32**. Analogous pathways can also be drawn for indene formation from the irradiation of the 3-aryl-substituted cyclopropenes.

The most dramatic result requiring discussion is the unusual substituent effect on the mode of ring opening of the unsymmetrical diarylcyclopropenes. In all the cases studied, the major product (indene or cyclopentadiene) formed was derived from cleavage of the cyclopropene bond attached to the methyl group (bond b). Similar findings have recently been made by others in related systems. Thus, Zimmerman and Aasen report that cyclopentadiene **42** is the major cyclopentadiene produced from the direct irradiation of cyclopropene **41**.[39] Similarly, Pincock and Moutsokapas have shown that methyl 1-methyl-2-phenylcyclopropen-3-carboxylate (**44**) is converted exclusively to 2-methoxy-5-methyl-4-phenylfuran (**45**) on direct irradiation.[49] The formation of this furan occurs by cleavage of the cyclopropene single bond which is methyl- rather than phenyl-substituted.

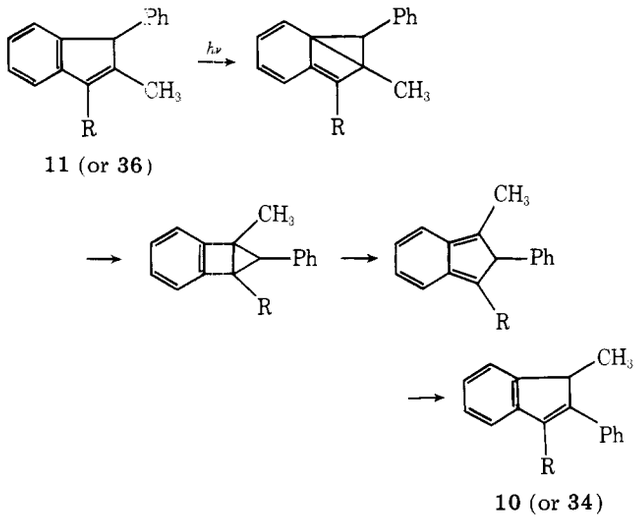


The molecular forces controlling this regioselectivity require comment. It is well-known that phenyl substituents stabilize free radicals, and thereby lower carbon–carbon bond energies in saturated three-membered rings.[52,53] Were this effect to operate in the cyclopropene system, methylphenylcyclopropene **32** should undergo preferential cleavage of bond a. We note, however, that the major cyclopentadiene (or indene) produced corresponds to cleavage of bond b. In the Results

it has been pointed out that this selectivity is a result of a kinetic preference and not to either interconversion of products or selective destruction of the indene corresponding to bond a cleavage. It should be noted, however, that on extended irradiation, indene 11 (and/or **36**) quantitatively rearranges to the corresponding isomer **10** (and/or **34**). This photorearrangement may be depicted as proceeding via the following steps: (1) an electrocyclic ring closure, (2) a [1,3]sigmatropic shift, (3) ring opening to an isoindene, and (4) a [1,5]sigmatropic hydrogen shift. The above process is analogous to that recently described by Morrison and Palensky for related substituted indenes.[42] Careful monitoring of the arylcyclopropene photolyses for short periods of time (<10% conversion) clearly shows that the ratio of the initially observed indenes is not affected by this subsequent interconversion.



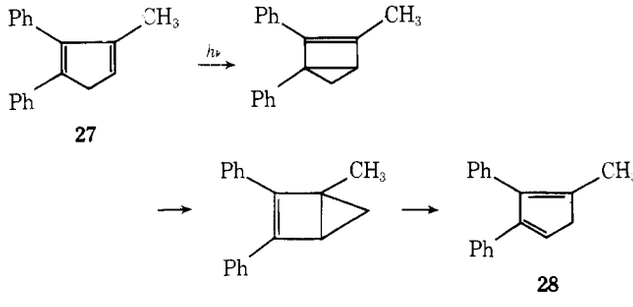
11, R = $CH_2C_6H_5$ **10**, R = $CH_2C_6H_5$
36, R = $CH{=}CH_2$ **34**, R = $CH{=}CH_2$



11 (or 36)

10 (or 34)

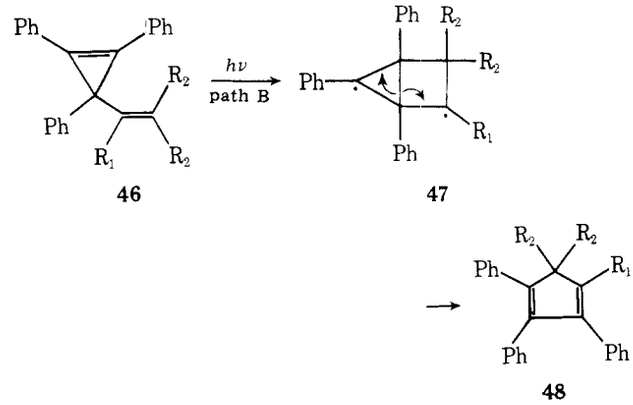
A mechanism similar to that outlined above could also account for the formation of cyclopentadiene **28** from **27**. As was pointed out in the Results, the presence of **28** in the crude photolysate from cyclopropene **26** is due to a secondary photoreaction of the initially generated cyclopentadiene **27** rather than to a thermally induced [1,5]sigmatropic hydrogen shift. This rearrangement may be proceeding by two consecutive 1,3-hydrogen shifts. Alternatively, the rearrangement may be envisioned as occurring by (1) a ring closure, (2) a [1,3]sigmatropic shift, and (3) a subsequent ring-opening reaction. The first and last steps of the above sequence are well-documented reactions.[54-58] In fact, Baldwin and Andrews[59] have recently reported a photochemical carbon skeleton rearrangement of cyclopentadiene which proceeds by a photochemical 1,3-carbon migration of a transient bicyclo[2.1.0]-pent-2-ene valence isomer, thus providing an excellent analogy for this pathway.



27

28

Turning now to the matter of regioselectivity of the cyclopropene ring opening, we note that the predominant scission of bond b can be nicely accommodated by path B (see Scheme I). According to this mechanism π–π bridging would be expected to give the most stable diradical (**39**) and thus lead to the preferential formation of 1-methyl-2,3-diphenyl-1,3-cyclopentadiene (**28**). A similar explanation would also account for the regioselectivity observed for indene formation with cyclopropenes **9**, **16**, and **19**. Zimmerman and Aasen[39] have noted that the quantum yield for the rearrangement of cyclopropene **46b** is twice as large as that for **46a**. This is a reasonable corollary of path B since π–π bridging of **46b** to give a housane diradical (i.e., **47b**) would be expected to be facilitated over **47a** as a result of the phenyl group being located at a center bearing odd electron density. These workers have also found that cyclopropene **46c** reacts with a lower direct irradiation efficiency than **46a**. This also fits the diradical mechanism (path B) since the isopropylidene group must approach the excited cyclopropene π bond, and steric hindrance should make this process more difficult. As was pointed out by other investigators,[60,61] quantum yields are not necessarily directly related to excited-state rate constants. Nevertheless, the above data does suggest that path B is a very reasonable possibility.



46 47 48

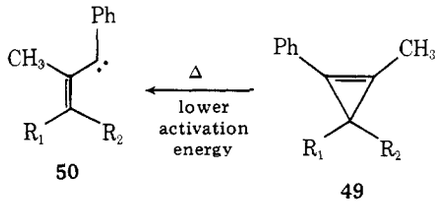
a, $R_1 = R_2 = H$; b, $R_1 = Ph$, $R_2 = H$; c, $R_1 = H$, $R_2 = CH_3$

According to the carbene mechanism for cyclopentadiene or indene formation (path A, Scheme I), preferential formation of the more stabilized carbene **38** (phenyl-substituted) might be expected. This is not the case. It should be pointed out that theory predicts[28] that it is the 1,3-diradical singlet state which results on thermal opening of the cyclopropene ring. This may also be the case for the electronically excited singlet state. The initially produced 1,3 diradical may then decay to the carbene, which could undergo subsequent reactions characteristic of a singlet vinylcarbene. Thus, one possibility to account for the preferential bond b cleavage (carbene route) is that the initially generated vinyl radical is inductively destabilized by the attached phenyl group. A great deal of evidence can be cited to support the thesis that vinyl-free radicals possess sp^2 hybridization and a low inversion barrier for radical equilibration.[62-65] Conjugation of a radical center in an sp^2-hybridized orbital with an adjacent phenyl group may not be significant as a result of the high degree of strain that would be generated by radical delocalization into the phenyl ring. On the other hand, a vinyl radical containing an attached alkyl group could be stabilized by a favorable nonconjugative interaction, which is of course what is implied in the term "inductive effect".[66]

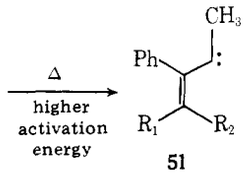
Alkyl-substituted cyclopropenes are known to decompose with activation energies in the range of 30–40 kcal/mol. For example, Bergman and co-workers have studied the thermal racemization of optically active 1,3-diethylcyclopropene.[12] These workers have suggested that ring cleavage and rotation occur simultaneously in this system, leading to a vinylcarbene intermediate. The activation energy for racemization was found to be 32.6 kcal/mol. Although a racemization experiment on an appropriately 1,2-diaryl-substituted cyclopropene was not carried out, Battiste and co-workers have examined the products formed on pyrolysis of a number of tetraaryl-substituted cyclopropenes.[5] These molecules rearrange to indenes by a process much like the one we have been discussing with an activation energy of 40 kcal/mol. This 7-kcal difference in the ring-opening step suggests that phenyl groups can affect the C–C single bond energies in cyclopropenes in a strikingly different manner than that encountered with the related cyclopropane ring system.[52,53]

If the "inductive destabilization" rationale for bond cleavage were correct, one might expect that the thermal ring opening of an unsymmetrical cyclopropene would follow the same general pattern as that encountered photochemically. This was not the case. Thus, thermolysis of cyclopropene **9** afforded indene **11** (bond a cleavage) as the exclusive product. It would appear, therefore, that inductive destabilization of the initially generated vinyl radical by the attached phenyl ring can not account for the regioselectivity of bond cleavage in the excited state since this argument demands similar behavior on thermolysis. Recent MO calculations by Pincock and Boyd[50] suggest a reasonable interpretation of the thermal results. These workers have found that the presence of a vinyl and phenyl group on the cyclopropene double bond opposite the σ bond which is breaking results in a substantial increase (ca. 8 kcal/mol) in the activation barrier for bond cleavage. Their results suggest that cross conjugated carbenes such as **51** are less stable than linearly conjugated systems like **50**. This explanation also accounts for the very high activation energy (40 kcal/mol) observed in the tetraphenylcyclopropene pyrolysis.[5]

An alternate explanation which could account for the observed photochemical regioselectivity (carbene route) involves reversible cyclopropene ring opening followed by rate-limiting cyclopentadiene formation. The fact that vinylcarbene intermediates generated from the decomposition of vinyldiazo



50 49



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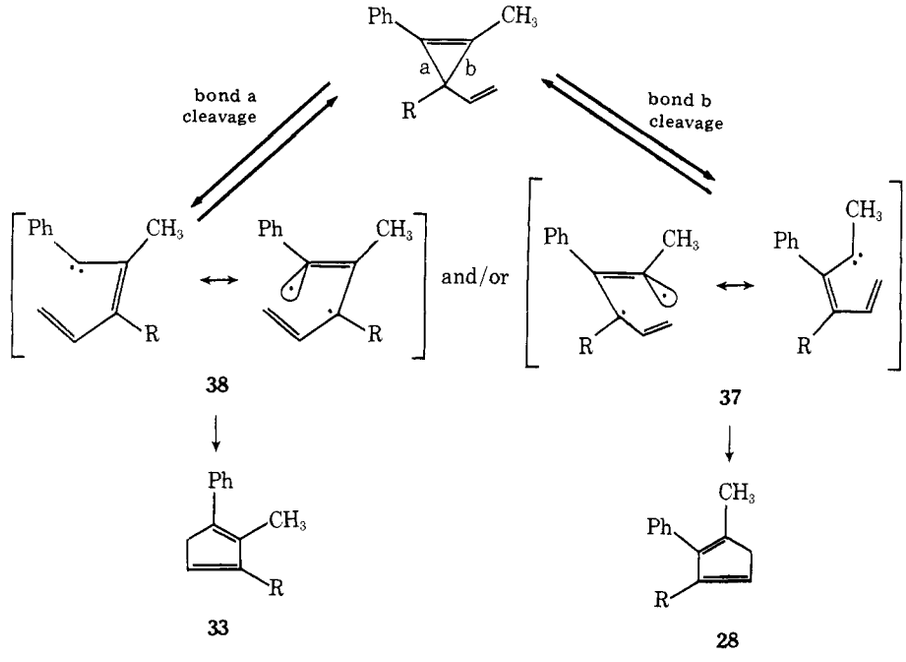
compounds[67,68] give predominantly cyclopropene products provides some support for this suggestion. In fact, the ring closure of vinylcarbenes is the basis of the synthetic procedures used for the preparation of cyclopropenes.[67–77] Bergman and co-workers have also found that the vinylcarbene intermediate generated from the pyrolysis of 1,3-diethylcyclopropene undergoes ring closure nine times faster than it goes on to product.[12] Moreover, recent results with the optically active cyclopropene ester **44** have shown that photochemical racemization occurs 2.5 times as fast as conversion to furan **45**.[49] The low quantum efficiency observed for the singlet states of the 3-aryl- and 3-vinylcyclopropenes (Φ ca. 0.02) can also be attributed to a rapid return of the carbene intermediate to the cyclopropene ring. This reversibility could easily represent the major deactivation pathway for these systems. Thus, the possibility exists that the distribution of cyclopentadienes (or indenes) is a result of the greater reactivity of the methyl-substituted carbene **37** over the phenyl-substituted isomer **38**. Since the quantum yields are so low, it may be possible that the observed regioselectivity is the result of some rate constant other than ring opening. The effects noted only correspond to fractions of kilocalories in pathway energy differences.

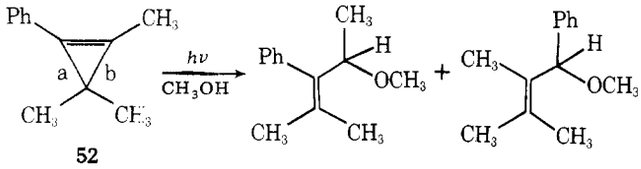
Still another possibility to account for the observed regioselectivity involves the close approach of the excited singlet surface of cyclopropene **49** with the ground-state surfaces of vinylcarbenes **50** and **51**. The preferential cleavage of the cyclopropene bond attached to the methyl group agrees well with the "funnel theory" of excited-state to ground-state conver-



sions as outlined principally by Michl.[78] Close approach of the two surfaces greatly enhances internal conversion and therefore gives a route for excited singlet cyclopropene to open to vinylcarbene and then either return to ground-state cyclopropene or rearrange to the 1,3-cyclopentadiene or indene. Since the carbene derived from bond b cleavage (i.e., **37**) is higher lying than that derived from bond a cleavage (i.e., **38**), it could be more easily funneled into from the excited singlet surface of the cyclopropene.

In order to help distinguish between paths A and B (see Scheme I), the photochemistry of a representative 3-aryl- (**9**) and 3-vinylcyclopropene (**24**) was carried out in methanol. The complete suppression of indene formation with cyclopropene **9** is consistent with the formation of a vinylcarbene intermediate which is trapped by protonation in methanol to give an allyl cation.[79] Subsequent loss of a proton or nucleophilic attack by methanol could, in principle, afford four different methoxy ethers and numerous *cis*- and *trans*-pentadiene isomers. The methanol results with cyclopropene **9**, while not very clean, are highly suggestive of the involvement of a vinylcarbene in the formation of the indene skeleton. The trapping experiment was unsuccessful with the 3-vinylcyclopropene system. The only product isolated here was 1,2-diphenyl-1,3-cyclopentadiene (**25**). Failure to trap a carbene intermediate derived from **24** does not necessarily eliminate this species as a reaction intermediate. The absence of methanol insertion products with this system may be due to the facile intramolecular cyclization path available to the butadienyl carbene. The probability of trapping a vinylcarbene derived from the 3-arylcyclopropene ring would be expected to be greater than that for the 3-vinyl system since the cyclization step with the former would involve a loss of aromaticity and therefore should proceed at a slower rate. Alternatively, the vinyl-substituted cyclopropene system may rearrange to the 1,3-cyclopentadiene via path B, whereas a vinylcarbene intermediate (path A) may operate in indene formation.

Some additional support for the carbene mechanism was obtained from the irradiation of 1-phenyl-2,3,3-trimethylcyclopropene (**52**). The only products obtained from the irradiation of **52** in methanol are methoxy ethers **53** (78%) and



52 53 54

54 (9%). The identity of these compounds was established by comparison with independently synthesized samples (see Experimental Section). It is particularly worthy to note that the distribution of the methoxy ethers obtained corresponds to preferential bond b cleavage (78%) and is closely related to the results encountered with the 3-aryl- and vinyl-substituted cyclopropenes. In all of these cases, the major product is derived from cleavage of the cyclopropene bond attached to the methyl group. Even though cyclopropene **39** does not contain a π bond at the the 3 position, it still prefers to undergo bond b fragmentation. The quantum yield for ether formation is identical ($\Phi = 0.03$) to that for cyclopentadiene ($\Phi = 0.03$) or indene ($\Phi = 0.03$) formation. We conclude therefore that the bulk of the evidence is compatible with the involvement of a vinylcarbene intermediate in the formation of the indene ring system. By analogy, one could argue that the same mechanism also holds with the vinylcyclopropenes, especially since the distribution of products obtained from the irradiation of the unsymmetrical system (i.e., **32**) is similar to that obtained from the photolysis of cyclopropene **52**. It should be pointed out, however, that a fortuitous distribution of products could be occurring here. Since it was not possible to trap a carbene with any of the vinylcyclopropenes, the rearrangement of this system may be proceeding by a different pathway (i.e., path B). Further work is necessary to establish this point.

Experimental Section[80]

Irradiation of 3-Methyl-1,2,3-triphenylcyclopropene (7) in Benzene. A solution containing 100 mg of 3-methyl-1,2,3-triphenylcyclopropene[81] (**7**) in 150 mL of benzene was irradiated for 1 h under an argon atmosphere with a 550-W Hanovia lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left a pale yellow solid which was recrystallized from acetic acid to give 75 mg (75%) of 1,2-diphenyl-3-methylindene (**8**): mp 90–91 °C; IR (KBr) 3.30, 3.34, 6.24, 6.71, 6.82, 6.90, 6.96, 7.28, 9.31, 12.73, 13.18, 13.35, 13.49, 13,85, 14.37 μm; UV (95% ethanol) 295 nm (ε 16 700), 230 (15 800); NMR ($CDCl_3$, 100 MHz) τ 7.68 (d, 3 H, J = 2.0 Hz), 5.09 (q, 1 H, J = 2.0 Hz), 2.6–3.10 (m, 14 H); *m/e* 280 (M^+, base), 267.

Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.21; H, 6.61.

The structure of this material was further established by comparison with an authentic sample prepared according to the procedure of Koelsch and Johnson.[82]

Preparation of 1,3-Diphenyl-2-methyl-3-benzylcyclopropene (9). To a stirred slurry containing 12 g of 1,2-diphenyl-3-methylcyclopropenyl perchlorate[83] in 250 mL of anhydrous tetrahydrofuran at −78 °C was added 50 mL of a 1.0-M solution of benzylmagnesium chloride in ether. The mixture was stirred at 4 °C for 4 h and at room temperature for 12 h. After quenching the solution with a saturated ammonium chloride solution, the organic layer was washed with water and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was chromatographed over silica gel using a 15% benzene–hexane mixture as the eluent. The first fraction isolated from the column contained 3.05 g of 1,2-diphenyl-3-benzyl-3-methylcyclopropene (27%): mp 58–59 °C; IR (neat) 3.29, 3.43, 5.50, 6.24, 6.69, 6.91, 7.29, 9.32, 13.18, 13.45, 14.24, 14.58 μm; NMR ($CDCl_3$, 100 MHz) τ 8.59 (s, 3 H), 7.06 (s, 2 H), 2.56–3.05 (m, 15 H); UV (95% ethanol) 339 nm (ε 18 700), 322 (24 700), 230 (18 900); *m/e* 296 (M^+), 281, 205 (base), 178

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 92.86; H, 6.94.

The second component isolated from the chromatography column contained 6.58 g of a white crystalline solid, mp 47–48 °C, whose structure was assigned as 1,3-diphenyl-2-methyl-3-benzylcyclopropene (**9**) on the basis of the following data: IR (KBr) 3.32, 5.40, 6.24, 6.73, 6.95, 9.31, 13.20, 14.43 μm; NMR ($CDCl_3$, 100 MHz) τ 7.84 (s, 3 H), 6.66 (d, 1 H, J = 13.0 Hz), 6.58 (d, 1 H, J = 13.0 Hz), 2.7–3.2 (m, 15 H); UV (95% ethanol) 264 nm (ε 10 550); *m/e* 296 (M^+), 205 (base), 91.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 92.90; H, 7.01.

Irradiation of 1,3-Diphenyl-2-methyl-3-benzylcyclopropene (9). A solution containing 113 mg of **9** in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which was shown to contain two components in a 4:1 ratio by NMR analysis. Chromatography of the mixture over silica gel resulted in the separation of the two products. The major component (80%) of the reaction mixture was identified as 1-methyl-2-phenyl-3-benzylindene (**10**), mp 74–75 °C, on the basis of its spectroscopic properties: IR (neat) 3.30, 6.24, 6.71, 6.83, 6.89, 12.28, 14.32 μm; NMR ($CDCl_3$, 100 MHz) τ 8.78 (d, 3 H, J = 8.0 Hz), 6.12 (q, 1 H, J = 8.0 Hz), 6.02 (s, 2 H), 2.6–3.1 (m, 15 H); UV (95% ethanol) 296 nm (ε 16 800), 229 (15 200); *m/e* 296 (M^+), 205 (base), 204, 190, 177, 164, 91. Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.33; H, 6.79.

The structure of this material was unambiguously verified by comparison with an authentic sample. A 1.8-g sample of 2-phenyl-3-methylindanone (**12**)[82] was treated with 12 mL of a 1.0-M solution of benzylmagnesium chloride in ether at 0 °C followed by heating at reflux for 1.5 h. The reaction mixture was hydrolyzed with a saturated ammonium chloride solution, and the ether layer was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude residue was added to 9 mL of glacial acetic acid, 1 mL of concentrated sulfuric acid, and 0.4 mL of water. The mixture was stirred for 15 min at room temperature and then poured onto ice water and extracted with ether. The ethereal layer was washed with a saturated sodium bicarbonate solution and water, and then dried over magnesium sulfate. The solvent was re-

moved under reduced pressure, and the crude residue was purified by silica gel chromatography using a 5% ether–hexane mixture as the eluent. The major component isolated was identical in every detail with a sample of 1-methyl-2-phenyl-3-benzylindene (**10**) obtained from the irradiation of **9**.

The minor component isolated from the crude photolysate obtained from the irradiation of **9** was identified as 1-phenyl-2-methyl-3-benzylindene (**11**) on the basis of its characteristic data: mp 103–104 °C; IR (KBr) 6.25, 6.72, 8.43, 9.31, 9.72, 10.60, 13.26, 13.80, 14.54 μm; NMR ($CDCl_3$, 100 MHz) τ 8.12 (s, 3 H), 6.12 (s, 2 H), 5.70 (s, 1 H), 2.68–3.2 (m, 14 H); UV (95% ethanol) 265 nm (ε 9400); *m/e* 296 (M^+), 206, 205 (base), 91.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.34; H, 6.49.

The structure of this material was further verified by comparison with an authentic sample. To a 2.4-g sample of 2-methyl-3-phenylindanone (**13**)[84] dissolved in 100 mL of ether was added 16 mL of a 1.0-M solution of benzylmagnesium chloride in ether. The mixture was stirred for 2 h at 25 °C and then hydrolyzed with a saturated ammonium chloride solution. The ethereal layer was separated, washed with water, and dried over magnesium sulfate. Removal of the solvent left a crude oil which was taken up in 45 mL of glacial acetic acid which contained 5 mL of concentrated sulfuric acid and 2 mL of water. The mixture was stirred at room temperature for 30 min, poured onto ice water, and extracted with ether. The ether layer was washed with a saturated sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent left a yellow oil which solidified on standing. Recrystallization of this material from ethanol gave 1.2 g (37%) of 1-phenyl-2-methyl-3-benzylindene (**11**), mp 103–104 °C, which was identical in every detail with the minor component isolated from the photolysis of cyclopropene **9**.

When the irradiation of 1,3-diphenyl-2-methyl-3-benzylcyclopropene (**9**) was carried out for 2.5 h, the only product present in the crude photolysate was 1-methyl-2-phenyl-3-benzylindene (**10**). Further studies showed that 1-phenyl-2-methyl-3-benzylidene (**11**) was quantitatively converted to 1-methyl-2-phenyl-3-benzylindene (**10**) on irradiation. Thus, a 91-mg sample of **11** in 250 mL of benzene was irradiated for 2.5 h. Removal of the solvent under reduced pressure followed by thick-layer chromatography gave a pure sample of 1-methyl-2-phenyl-3-benzylindene (**10**) as the only isolable product.

Preparation of 3-Allyl-1,2,3-triphenylcyclopropene (14). To a stirred slurry containing 0.5 g of triphenylcyclopropenyl bromide[85] in 40 mL of anhydrous tetrahydrofuran at −78 °C was added 5 mL of a 0.67-N allylmagnesium bromide solution in ether. The mixture was stirred for 2 h and then allowed to warm to room temperature. After quenching the solution with a saturated ammonium chloride solution, the organic layer was washed with water and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was chromatographed on a thick-layer plate to give 0.31 g (70%) of 3-allyl-1,2,3-triphenylcyclopropene (**14**) as a crystalline solid: mp 64–65 °C; IR (KBr) 3.49, 3.64, 5.67, 6.26, 6.43, 6.89, 7.02, 9.52, 10.19, 11.09, 13.34, 14.64 μm; UV (95% ethanol) 333 nm (ε 22 000), 316 (26 600), 228 (28 700); NMR ($CDCl_3$, 60 MHz) τ 6.80 (d, 2 H, *J* = 7.5 Hz), 5.05 (d, 1 H, *J* = 17.0 Hz), 4.95 (d, 1 H, *J* = 7.5 Hz), 4.50–3.80 (m, 1 H), 2.20–3.00 (m, 15 H); *m/e* 308 (M^+), 306, 267 (base).

Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.16; H, 6.66.

Irradiation of 3-Allyl-1,2,3-triphenylcyclopropene (14) in Benzene. A solution containing 100 mg of **14** in 150 mL of benzene was irradiated for 1 h under an argon atmosphere with a 550-W Hanovia lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which slowly crystallized on standing to give 83 mg (83%) of 3-allyl-1,2-diphenylindene (**15**): mp 83–85 °C; IR (KBr) 3.28, 3.30, 6.10, 6.24, 6.69, 6.80, 6.89, 9.30, 9.71, 10.05, 10.95, 13.23, 14.30 μm; UV (95% ethanol) 295 nm (ε 19 300), 228 (20 500); NMR ($CDCl_3$, 100 MHz) τ 6.54 (dd, 2 H, *J* = 5.0, 2.0 Hz), 5.09 (t, 1 H, *J* = 2.0 Hz), 4.87 (dd, 1 H, *J* = 8.0, 1.5 Hz), 5.19 (dd, 1 H, *J* = 17.0, 1.5 Hz), 3.6–4.1 (m, 1 H), 2.6–3.1 (m, 18 H); *m/e* 308 (M^+), 268, 267 (base), 265.

The structure of this material was unambiguously verified by comparison with an independently synthesized sample. To a solution containing 2.6 g of 2,3-diphenylindanone[86] in 75 mL of ether and 25 mL of benzene was added 5 mL of a 2.37-M solution of allylmagnesium chloride in tetrahydrofuran. The reaction mixture was stirred for 1 h at 25 °C, and then a saturated ammonium chloride solution was added. The organic layer was separated, washed with water, and dried over magnesium sulfate. Removal of the solvent left 2.9 g of a yellow oil which was added to a mixture containing 17 mL of acetic acid, 2 mL of sulfuric acid, and 1 mL of water. The resulting mixture was stirred for 5 min at 25 °C and then diluted with water and neutralized with sodium bicarbonate. The aqueous mixture was extracted with ether and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 2.5 g of 3-allyl-1,2-diphenylindene (**15**), which was identical in every detail with the material obtained from the irradiation of **14**.

Preparation of 3-Allyl-1,3-diphenylcyclopropene (16). To a stirred suspension containing 6.0 g of 1,2-diphenylcyclopropenyl perchlorate[87] in 200 mL of anhydrous tetarhydrofuran at −78 °C was added 50 mL of a 0.67-M allylmagnesium bromide solution in ether. The mixture was stirred for 4 h at −78 °C and then allowed to warm to room temperature. At the end of this time a saturated ammonium chloride solution was added, and the organic layer was separated, washed with water, and dried over magnesium sulfate. Removal of the solvent left a clear yellow oil which was chromatographed on a silica gel column using hexane as the eluent. The first component isolated contained 1.7 g (41%) of a clear oil whose structure was assigned as 3-allyl-1,2-diphenylcyclopropene on the basis of the following data: IR (neat) 3.29, 3.46, 5.52, 5.99, 6.24, 6.70, 6.92, 9.32, 9.72, 10.92, 13.24, 14.52 μm; UV (95% ethanol) 336 nm (ε 20 800), 318 (27 900), 310 (23 800), 228 (18 900), 225 (18 200); NMR ($CDCl_3$, 100 MHz) τ 7.48–7.88 (m, 3 H), 4.99 (d, 1 H, *J* = 9.0 Hz), 4.92 (c, 1 H, *J* = 18.0 Hz), 3.72–4.20 (m, 1 H), 2.20–2.80 (m, 10 H); *m/e* 232 (M^+), 191, 178 (base), 91.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.69; H, 7.09.

The second component isolated from the column contained 0.8 g (20%) of a clear oil whose structure was assigned as 3-allyl-1,3-diphenylcyclopropene (**16**) on the basis of its spectral data:[88] IR (neat) 3.48, 3.63, 5.88, 6.28, 6.43, 6.92, 7.12, 9.48, 10.18, 11.08, 13.18, 14.48 μm; UV (95% ethanol) 260 nm (ε 12 400); NMR ($CDCl_3$, 100 MHz) τ 7.09 (d, 2 H, *J* = 5.5 Hz), 4.95–5.20 (m, 2 H), 3.8–4.6 (m, 1 H), 2.4–3.0 (m, 11 H); *m/e* 232 (M^+), 192, 191 (base), 91.

Irradiation of 3-Allyl-1,3-diphenylcyclopropene (16). A solution containing 100 mg of **16** in 150 mL of hexane was irradiated for 10 min under an argon atmosphere with a 550-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure left a light yellow oil which contained two components. The major component (80%) could be obtained in pure form by column chromatography and was identified as 2-phenyl-3-allylindene (**17**) on the basis of its spectral properties and by comparison with an independently synthesized sample: IR (neat) 3.20, 3.63, 6.25, 6.39, 6.87, 7.01, 7.11, 7.14, 7.34, 9.84, 10.19, 11.04, 13.29, 13.59, 14.54 μm; UV (95% ethanol) 293 nm (ε 18 700), 227 (11 900); NMR ($CDCl_3$, 100 MHz) τ 6.52 (dt, 2 H, *J* = 6.0, 1.5 Hz), 6.25 (s, 2 H), 4.68–5.02 (m, 2 H), 3.68–4.09 (m, 1 H), 2.40–2.90 (m, 9 H); *m/e* 232 (M^+), 191 (base).

The structure of this material was further verified by comparison with an authentic sample. To a solution containing 4.16 g of 2-phenylindanone in 100 mL of ether was added 40 mL of a 0.67-M allylmagnesium bromide solution in ether. After stirring for 1 h at room temperature, a saturated ammonium chloride solution was added. The organic phase was separated, washed with water, and dried over magnesium sulfate. Removal of the solvent left 4.9 g of 1-allyl-2-phenyl-1-indanol: NMR ($CDCl_3$, 100 MHz) τ 8.39 (s, 1 H), 7.33 (broad t, 2 H, *J* = 6.0 Hz), 6.70 (broad d, 2 H, *J* = 8.0 Hz), 6.36 (broad t, 1 H, *J* = 8.0 Hz), 4.76 (d, 1 H, *J* = 10.0 Hz), 4.72 (d, 1 H, *J* = 18.0 Hz), 3.80–4.25 (m, 1 H), 2.44–2.68 (m, 9 H).

This material was used in the next step without further purification. To 1.1 g of the crude indanol was added 5 mL of a mixture containing 0.5 mL of sulfuric acid, 4.25 mL of glacial acetic acid, and 0.25 mL of water. The solution was stirred for 5 min at 25 °C and then diluted with water. The solution was neutralized with sodium bicarbonate and extracted with ether. The ether extracts were washed with water and dried over magnesium sulfate. Removal of the solvent left 0.94 g (92%) of 3-allyl-2-phenylindene (**17**) as a colorless oil which was identical in every detail with the major component isolated from the photolysis of cyclopropene **16**.

The minor component present in the crude photolysate derived from the photolysis of **16** was assigned the structure of 1-phenyl-3-allylindene (**18**) on the basis of its NMR spectrum ($CDCl_3$, 100 MHz): τ 6.71 (dt, 2 H, *J* = 6.0, 1.5 Hz), 5.45 (broad s, 1 H), 6.64–6.94 (m, 2 H), 3.70–4.15 (m, 1 H), 3.70 (d, 1 H, *J* = 1.5 Hz), 2.40–2.90 (m, 9 H). It was not possible to completely separate this isomer from indene **17** even by extensive chromatography.

Preparation of 1,3-Diphenyl-2-methyl-3-allylcyclopropene (19). To a suspension containing 5 g of 3-methyl-1,2-diphenylcyclopropenyl perchlorate[83] in 500 mL of tetrahydrofuran at −78 °C was added 100 mL of a 0.67-M allylmagnesium bromide solution in ether. The mixture was stirred at −78 °C for 4 h and then allowed to warm

to room temperature. The mixture was quenched with a saturated ammonium chloride solution and extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a clear oil which was chromatographed on silica using hexane as the eluent. The first component isolated contained 2.3 g (55%) of 3-allyl-3-methyl-1,2-diphenylcyclopropene: bp 70–71 °C (0.01 mm); IR (neat) 3.38, 3.47, 5.52, 6.08, 6.26, 6.70, 6.94, 7.31, 8.64, 9.33, 9.73, 10.95, 13.25, 14.55 μm; UV (95% ethanol) 338 nm (ε 21 400), 320 (28 600), 229 (18 200); NMR ($CDCl_3$, 100 MHz) τ 8.54 (s, 3 H), 7.44 (d, 2 H, J = 7.5 Hz), 5.05 (d, 1 H, J = 9.5 Hz), 5.01 (d, 1 H, J = 17.0 Hz), 3.84–4.32 (m, 1 H), 2.24–2.92 (m, 10 H); m/e 246 (M^+), 231, 206, 205 (base), 77.

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.59; H, 7.35.

The second component isolated from the thick-layer plate contained 1.3 g (31%) of a clear liquid whose structure is assigned as 1,3-diphenyl-2-methyl-3-allylcyclopropene (**19**) on the basis of its spectral data: bp 80–81 °C (0.01 mm); IR (neat) 3.27, 3.44, 5.39, 6.25, 6.69, 6.93, 9.33, 10.02, 10.94, 13.14, 14.40 μm; UV (95% ethanol) 262 nm (ε 16 900); NMR ($CDCl_3$, 100 MHz) τ 7.74 (s. 1 H), 7.10 (d, 2 H, J = 8.0 Hz), 5.10 (d, 1 H, J = 8.0 Hz), 4.99 (d, 1 H, J = 14.0 Hz), 3.96–4.44 (m, 1 H), 2.48–3.16 (m, 10 H); m/e 246 (M^+), 231, 205 (base), 77.

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.55; H, 7.37.

Irradiation of 1,3-Diphenyl-2-methyl-3-allylcyclopropene (19). A solution containing 150 mg of **19** in 200 mL of benzene was irradiated for 50 min with a 550-W Hanovia lamp equipped with a Pyrex filter sleeve. Removal of the solvent followed by thick-layer chromatography gave two products. The major component in the reaction mixture (58%) was a colorless oil whose structure was assigned as 1-methyl-2-phenyl-3-allylindene (**20**) on the basis of its characteristic spectral properties: IR (KBr) 3.30, 3.33, 3.40, 3.45, 6.15, 6.24, 6.82, 6.90, 9.30, 9.70, 10.95, 13.60, 14.70 μm; UV (95% ethanol) 294 nm (ε 11 900), 230 (11 600), 226 (10 800); NMR ($CDCl_3$, 100 MHz) τ 8.80 (d, 3 H, J = 7.0 Hz), 6.62 (d, 2 H, J = 5.0 Hz), 6.14 (q, 1 H, J = 7.0 Hz), 4.95 (d, 1 H, J = 10.0 Hz), 4.90 (d, 1 H, J = 15.0 Hz), 3.72–4.16 (m, 1 H), 2.48–2.98 (m, 9 H); m/e 246 (M^+), 206, 205 (base), 77.

The structure of this material was unambiguously verified by comparison with an authentic sample. To a stirred solution containing 1.0 g of 2-phenyl-3-methylindanone (**12**) in 25 mL of ether was added 7.5 mL of a 0.67-M allylmagnesium bromide solution in ether. The mixture was stirred for 1 h at room temperature and then quenched by a saturated ammonium chloride solution. The aqueous layer was extracted with ether, and the ethereal solution was washed with water and dried over magnesium sulfate. Removal of the solvent left a clear oil which was taken up in a mixture containing 9 mL of acetic acid, 1 mL of concentrated sulfuric acid, and 10 drops of water. The reaction mixture was stirred for 5 min and extracted with ether. The ethereal solution was neutralized with a 5% sodium bicarbonate solution, washed with water, and dried over magnesium sulfate. Removal of the solvent left 0.8 g of a yellow oil which was purified by thick-layer chromatography to give 0.65 g (63%) of 1-methyl-2-phenyl-3-allylindene (**20**), identical to the major photoproduct obtained from the photolysis of **19**.

The minor component (5%) present in the photolysis mixture derived from **19** was identified as 1-phenyl-2-methyl-3-allylindene (**21**) on the basis of its characteristic spectral data: IR (neat) 3.32, 3.45, 6.12, 6.24, 6.71, 6.90, 9.75, 10.05, 10.90, 12.85, 13.30, 13.65, 14.35 μm; UV (95% ethanol) 263 nm (ε 6900), 220 (17 800); NMR ($CDCl_3$, 100 MHz) τ 8.16 (s, 3 H), 6.68 (d, 2 H, J = 5.5 Hz), 5.72 (s, 1 H), 4.80–5.24 (m, 2 H), 3.82–4.28 (m, 1 H), 2.64–3.10 (m, 9 H); m/e 246 (M^+), 206, 205 (base), 108, 77.

The structure of this material was further verified by comparison with an independently synthesized sample. To a stirred solution containing 1.0 g of 2-methyl-3-phenyl-1-indanone (**13**) in 25 mL of ether was added 7.5 mL of a 0.67-M allylmagnesium bromide solution in ether. The reaction mixture was stirred for 1 h at 25 °C followed by the addition of a saturated ammonium chloride solution. Extraction of the mixture with ether followed by washing with water and drying over magnesium sulfate gave 1.0 g of a pale yellow oil on removal of the solvent. This material was taken up in a mixture containing 9 mL of acetic acid, 1 mL of concentrated sulfuric acid, and 10 drops of water. The solution was stirred for 5 min and extracted with ether. The ethereal layer was washed with a 5% sodium bicarbonate solution followed by water. After drying over magnesium sulfate, the solvent was removed under reduced pressure to give 0.76 g of a yellow oil. This material was purified by thick-layer chromatography to give 0.6 g (65%) of 1-phenyl-2-methyl-3-allylindene (**21**) which was identical to the minor component obtained from the photolysis of **19**.

Preparation of 1,2,3-Triphenyl-3-vinylcyclopropene (22). A 0.7-M solution of vinylmagnesium bromide in 100 mL of tetrahydrofuran was slowly added to a suspension of triphenylcyclopropenyl perchlorate[85] in 250 mL of tetrahydrofuran at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 4 h. After quenching with a saturated ammonium chloride solution, the organic layer was diluted with ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure to give a yellow oil which recrystallized from methanol to give 3.0 g (75%) of 1,2,3-triphenyl-3-vinylcyclopropene (**22**) as a crystalline solid: mp 87–88 °C; IR ($CHCl_3$) 3.34, 5.49, 6.17, 6.73, 6.95, 7.14, 9.33, 9.74, 10.05, 10.95 μm; NMR ($CDCl_3$, 60 MHz) τ 4.92 (dd, 1 H, J = 11.0, 1.0 Hz), 4.86 (dd, 1 H, J = 16.0, 1.0 Hz), 3.38 (dd, 1 H, J = 16.0, 11.0 Hz), 2.2–2.9 (m, 15 H); UV (95% ethanol) 330 nm (ε 21 000), 314 (23 600), 227 (29 500); m/e 294 (M^+), 218, 217, 215, 202, 115, 91.

Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.99; H, 6.42.

Irradiation of 1,2,3-Triphenyl-3-vinylcyclopropene (22). A solution containing 354 mg of **22** in 400 mL of benzene was irradiated with a 550-W Hanovia lamp equipped with a Pyrex filter sleeve for 5 h. Removal of the solvent followed by thick-layer chromatography gave 250 mg (70%) of a crystalline solid, mp 157–158 °C, whose structure was assigned as 1,2,3-triphenylcyclopentadiene (**23**): IR (KBr) 3.10, 6.25, 6.68, 6.95, 7.28, 8.25, 9.34, 9.73, 10.24, 10.84, 10.95, 11.28, 11.44, 12.95, 13.16, 13.56, 14.41 μm; UV (95% ethanol) 305 nm (ε 11 000), 246 (30 200); NMR ($CDCl_3$, 60 MHz) τ 6.40 (d, 2 H, J = 2.0 Hz), 3.48 (t, 1 H, J = 2.0 Hz), 2.70–3.0 (m, 15 H).

The structure of this material was further confirmed by comparison with an authentic sample prepared according to the procedure of Pauson and Williams.[89]

Preparation of 1,2-Diphenyl-3-vinylcyclopropene (24). A 0.86-M solution of vinylmagnesium bromide in tetrahydrofuran was slowly added to a suspension of 5.0 g of diphenylcyclopropenyl perchlorate[87] in 300 mL of tetrahydrofuran at −78 °C. The reaction mixture was allowed to warm to 25 °C and was stirred at this temperature for 4 h. At the end of this time the solution was quenched with a saturated ammonium chloride solution. The organic layer was diluted with ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left 2.8 g of a yellow oil which was sublimed at 35 °C (0.03 mm) to give 2.4 g (65%) of 1,2-diphenyl-3-vinylcyclopropene (**24**) as a crystalline solid: mp 31–32 °C; IR (neat) 3.34, 3.53, 5.53, 6.22, 6.33, 6.77, 7.02, 7.72, 7.88, 8.62, 9.42, 9.83, 11.23, 13.33, 14.63 μm; NMR ($CDCl_3$, 60 MHz) τ 7.23 (d, 1 H, J = 7.0 Hz), 5.08 (dd, 1 H, J = 10.0, 3.0 Hz), 4.74 (dd, 1 H, J = 17.0, 3.0 Hz), 4.28 (ddd, 1 H, J = 17.0, 10.0, 7.0 Hz), 2.2–2.8 (m, 10 H); UV (95% ethanol) 332 nm (ε 26 300), 315 (32 100) 236 (21 400), 227 (27 700); m/e 218 (M^+), 217, 216, 215, 203, 202, 115, 77.

Anal. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 93.18; H, 6.58.

Irradiation of 1,2-Diphenyl-3-vinylcyclopropene (24). A solution containing 105 mg of **24** in 150 mL of benzene was irradiated with a 550-W Hanovia lamp equipped with a Pyrex filter sleeve for 75 min. Removal of the solvent left a pale yellow oil which contained a single product as judged from NMR analysis. Purification of this product was accomplished by preparative thick-layer chromatography. The only material isolated from the thick-layer plate was a crystalline solid, mp 68–70 °C, whose structure was identified as 1,2-diphenylcyclopentadiene (**25**) (67% isolated yield) on the basis of its characteristic spectral data: IR (KBr) 3.29, 6.24, 6.72, 6.95, 7.35, 8.19, 9.40, 9.73, 10.36 10.79, 11.03, 11.19, 12.83, 13.03, 13.30, 14.28 μm; UV (95% ethanol) 308 nm (ε 9200), 233 (20 000); NMR ($CDCl_3$, 60 MHz) τ 6.55 (t, 1 H, J = 1.5 Hz), 3.58 (td, 1 H, J = 5.0, 1.5 Hz), 3.36 (td, 1 H, J = 5.0, 1.5 Hz), 2.6–3.0 (m, 10 H).

The structure of this material was unambiguously established by comparison with an authentic sample prepared according to the procedure of Rio and Charafi.[90]

Preparation of 1,2-Diphenyl-3-methyl-3-vinyl- (26) and 1-Methyl-2,3-diphenyl-3-vinylcyclopropene (32). To a suspension of 4.0 g of 3-methyl-1,2-diphenylcyclopropenyl perchlorate in 100 mL of tetrahydrofuran at −78 °C was added 100 mL of a 0.67-M vinylmagnesium bromide solution in tetrahydrofuran. The reaction mixture was allowed to warm to 25 °C and was stirred for 4 h at this temperature. The excess Grignard reagent was destroyed by the addition of a saturated ammonium chloride solution. The organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was subjected to silica gel chromatography using hexane as the eluent. The first component isolated from the column contained 1.98 g (65%) of 1,2-diphenyl-3-methyl-3-vinylcyclopropene (**26**): mp 34–35 °C; IR (neat)

3.32, 3.48, 5.52, 6.23, 6.30, 6.77, 6.99, 7.36, 9.38, 9.76, 10.07, 11.19, 13.30, 14.63 μm; NMR ($CDCl_3$, 100 MHz) τ 8.44 (s, 3 H), 5.03 (d, 1 H, J = 9.5 Hz), 4.93 (d, 1 H, J = 17.5 Hz), 4.25 (dd, 1 H, J = 17.5, 9.5 Hz), 2.42–2.82 (m, 10 H); UV (95% ethanol) 332 nm (ε 26 100), 315 (31 000), 227 (21 800); m/e 232 (M^+, base), 217, 215.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.04; H, 7.13.

The second component isolated from the chromatography column contained 0.27 g (9%) of a clear oil which crystallized on standing and whose structure was assigned as 1-methyl-2,3-diphenyl-3-vinylcyclopropene (**32**): mp 38–39 °C; IR (neat) 3.33, 3.47, 5.28, 6.17, 6.26, 6.71, 6.93, 7.12, 9.31, 10.06, 11.02, 13.16, 14.32, 14.49 μm; NMR ($CDCl_3$, 100 MHz) τ 7.70 (s, 3 H), 5.14 (d, 1 H, J = 10.0 Hz), 4.91 (d, 1 H, J = 17.0 Hz), 3.60 (dd, 1 H, J = 17.0, 10.0 Hz), 2.5–2.9 (m, 10 H); UV (95% ethanol) 260 nm (ε 15 900); m/e 232 (M^+, base), 217, 215.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.68; H, 7.05.

Since the yield of **32** was so low (i.e., 9%), an alternate synthetic procedure was used to prepare larger quantities of this material. To a solution containing 2.0 g of bis(1,2-diphenyl)cyclopropenyl ether[87] in 200 mL of benzene at 25 °C was added 35 mL of a 1.1-M vinylmagnesium bromide solution in tetrahydrofuran. The mixture was stirred at 35 °C for 3.5 h and subsequently quenched with a saturated ammonium chloride solution. The organic layer was extracted with water and dried over magnesium sulfate. Removal of the solvent left a colorless oil whose NMR spectrum showed that it contained mostly 3-vinyl-1,3-diphenylcyclopropene: NMR ($CDCl_3$, 100 MHz) τ 5.02 (dd, 1 H, J = 17.0, 1.5 Hz), 4.96 (dd, 1 H, J = 10.0, 1.5 Hz), 3.54 (dd, 1 H, J = 17.0, 10.0 Hz), 2.2–3.0 (m, 1 H).

The above sample was taken up in 100 mL of tetrahydrofuran and cooled to −78 °C. To this solution was added 30 mL of a 1.7-M methyllithium solution in ether. The mixture was allowed to warm to 25 °C for 30 min and then cooled to −78 °C. To this solution was added 1.1 g of methyl iodide in 50 mL of tetrahydrofuran. After the addition was complete, the solution was stirred at room temperature for 1 h and then quenched with a saturated ammonium chloride solution. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give a yellow oil. This material was chromatographed on a silica gel column using hexane as the eluent to give a pure sample (80%) of 1-methyl-3-vinyl-2,3-diphenylcyclopropene (**32**), which was identical to the minor component obtained from the reaction of 1,2-diphenyl-3-methylcyclopropenyl perchlorate with vinylmagnesium bromide.

Irradiation of 1,2-Diphenyl-3-methyl-3-vinylcyclopropene (26). A solution containing 114 mg of **26** in 125 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 4 h. Removal of the solvent followed by thick-layer chromatography gave 74 mg (65%) of a colorless oil whose structure was assigned as 1,2-diphenyl-3-methylcyclopentadiene (**27**) on the basis of its spectral data: IR (neat) 3.28, 3.43, 5.67, 6.24, 6.71, 6.95, 7.26, 9.32, 9.68, 10.50, 10.93, 13.18, 14.34 μm; UV (95% ethanol) 298 nm (ε 8400), 220 (14 300); NMR ($CDCl_3$, 100 MHz) τ 8.20 (broad s, 3 H), 6.66 (broad s, 2 H), 3.88 (broad s, 1 H), 2.5–3.0 (m, 10 H); m/e 232 (M^+, base), 217, 215, 154, 105, 91, 77.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.97; H, 7.07.

Continued irradiation of a sample of cyclopentadiene **27** resulted in its equilibration with 1-methyl-2,3-diphenylcyclopentadiene (**28**). In fact, small quantities of **28** were present in the crude photolysate derived from the irradiation of cyclopropene **26**. All attempts to separate the isomeric 1,3-cyclopentadienes failed. The structure of **28** was assigned on the basis of its NMR spectrum and by an independent synthesis.

A solution containing 8.2 g of 2-methylfuran in 50 mL of tetrahydrofuran was added to a mixture containing 50 mL of a 2.4-M n-butyllithium solution in hexane and 50 mL of tetrahydrofuran at −35 °C. The solution was allowed to warm to −10 °C and was kept at this temperature for 4 h. At the end of this time, 17 g of benzyl bromide in 50 mL of tetrahydrofuran was added, and the mixture was warmed to 25 °C and allowed to stand for 12 h at this temperature. The mixture was poured over water, extracted with ether, and dried. Removal of the solvent left 11.6 g of a yellow oil which was taken up in a mixture containing 20 mL of acetic acid, 10 mL of water, and 1 mL of a 10% sulfuric acid solution. The resulting solution was heated at reflux for 4 h, and then poured onto ice and extracted with ether. The ethereal solution was washed with 5% sodium bicarbonate solution and water, and dried over magnesium sulfate. Removal of the solvent left 10.5 g of a yellow oil which was used in the next step without purification.

A solution containing 5.0 g of the above oil and 2.5 g of potassium hydroxide in 50 mL of methanol was heated at reflux for 5 h. The mixture was poured onto water, extracted with ether, washed with water, and dried over magnesium sulfate. Removal of the solvent followed by distillation of the crude residue at 94 °C (0.01 mm) gave a clear oil which solidified on standing. Recrystallization of this material gave 2.7 g of 2-phenyl-3-methylcyclopentenone (**31**): mp 60–61 °C; IR (KBr) 3.29, 3.44, 5.92, 6.11, 6.25, 6.70, 6.98, 7.27, 8.84, 10.63, 13.09, 14.30 μm; UV (95% ethanol) 248 nm (ε 8300), 221 (14 100); NMR ($CDCl_3$, 100 MHz) τ 7.88 (s, 3 H), 7.31–7.61 (m, 4 H), 2.53–2.91 (m, 5 H); m/e 172 (M^+, base), 129, 115, 77.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.65; H, 7.18.

To a solution containing 106 mg of **31** in 50 mL of ether was added 1.5 mL of a 2.0-M phenyllithium solution at 0 °C. After stirring at 0 °C for 1 h, the solution was poured onto water and extracted with ether. The ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent left a clear oil which was dissolved in 5 mL of ethanol containing 0.5 mL of acetic acid. The solution was heated at reflux for 30 min, cooled, and poured onto ice water. The mixture was extracted with ether, washed with a 5% sodium bicarbonate solution and water, and dried over magnesium sulfate. Removal of the solvent left a clear oil whose NMR spectrum indicated it to be a 1:3 mixture of 1,2-diphenyl-3-methyl- (**27**) and 1-methyl-2,3-diphenylcyclopentadiene (**28**). The NMR, IR, and mass spectra of this mixture were identical to that obtained from the photolysis of cyclopropene **26**. The mixture of isomeric cyclopentadienes could not be separated by extensive column chromatography. The NMR spectrum of 1-methyl-2,3-diphenylcyclopentadiene (**28**) was obtained from the crude reaction mixture and showed signals at τ 7.96 (s, 3 H), 6.88 (d, 2 H, J = 2.0 Hz), 3.76 (t, 1 H, J = 2.0 Hz), and 2.5–3.0 (m, 10 H).

Irradiation of 1-Methyl-2,3-diphenyl-3-vinylcyclopropene (32). A solution containing 132 mg of **32** in 125 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 2 h. Removal of the solvent under reduced pressure left a pale yellow oil which was shown to contain four major components by NMR analysis. The major fraction (39%) present in the crude photolysate was identified as 1-methyl-2-phenyl-3-vinylindene (**34**) on the basis of its spectral data and by comparison with an independently synthesized sample: IR (neat) 3.25, 3.32, 6.20, 6.66, 6.81, 8.60, 8.85, 9.28, 9.94, 10.90, 13.00, 13.38, 14.29 μm; UV (95% ethanol) 303 nm (ε 16 000), 232 (18 300); NMR ($CDCl_3$, 100 MHz) τ 8.77 (d, 3 H, J = 5.0 Hz), 6.10 (q, 1 H, J = 5.0 Hz), 4.51 (d, 1 H, J = 11.5 Hz), 4.12 (d, 1 H, J = 18.0 Hz), 3.21 (dd, 1 H, J = 18.0, 11.5 Hz), 2.55–2.79 (m, 10 H); m/e 232 (M^+), 217 (base), 215, 208, 205, 193, 178, 130, 115, 91, 77.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.97; H, 7.27.

The structure of this material was further verified by comparison with an independently synthesized sample prepared by treating 2-phenyl-3-methyl-1-indanone (**12**) with vinylmagnesium bromide followed by an acid-catalyzed dehydration by a procedure similar to that used for the synthesis of the related allyl- and benzylindenes.

The minor component (10%) present in the crude photolysate was identified as 1,3-diphenyl-2-methylcyclopentadiene (**33**) on the basis of its spectral data and by comparison with an independently synthesized sample: mp 130–132 °C; IR (KBr) 3.34, 3.45, 6.28, 6.74, 6.97, 7.26, 8.47, 9.31, 9.74, 10.18, 10.39, 11.26, 12.80, 13.11, 13.55, 14.32 μm; UV (95% ethanol) 288 nm (ε 8300), 237 (14 500); NMR ($CDCl_3$, 100 MHz) τ 7.88 (t, 2 H, J = 1.0 Hz), 6.62 (q, 2 H, J = 1.0 Hz), 3.64 (broad s, 1 H), 2.5–2.9 (m, 10 H); m/e 232 (M^+, base), 217, 215, 154.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.74; H, 6.77.

The structure of this material was further established by comparison with an independently synthesized sample. A solution containing 11.6 g of 2-phenylfuran[91] in 50 mL of tetrahydrofuran was added to a mixture containing 40 mL of a 2.4-M n-butyllithium solution in hexane and 50 mL of tetrahydrofuran at −30 °C. The solution was stirred for 2 h at −10 °C, and then 9 g of ethyl bromide in 50 mL of tetrahydrofuran was added at −30 °C. The solution was kept at −30 °C for 1 h and was then allowed to warm to room temperature. After stirring for 12 h at 25 °C, the mixture was poured onto water and extracted with ether. The ether layer was dried over magnesium sulfate and concentrated under reduced pressure to give 11.5 g of a yellow oil. An 8.1-g sample of oil was taken up in a mixture containing 30 mL of acetic acid and 15 mL of a 20% sulfuric acid solution. The resulting mixture was heated at reflux for 4 days, poured onto water, extracted with ether, washed with a 5% sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent left a dark oil which was dissolved in 50 mL of methanol which contained 2.5 g of potas-

sium hydroxide. The solution was heated at reflux for 3 h, poured onto water, and extracted with ether. The ether layer was dried over magnesium sulfate and concentrated under reduced pressure to give a yellow oil which was subjected to Florisil column chromatography. Elution of the column with benzene gave a 6.2-g sample of 2-methyl-3-phenylcyclopentenone (**35**): mp 52–53 °C (lit.[92] mp 53–55 °C); IR (KBr) 3.51, 5.88, 6.14, 6.67, 6.90, 7.23, 7.43, 8.11, 9.07, 9.26, 9.41, 11.79, 13.08, 14.37 μm; NMR ($CDCl_3$, 100 MHz) τ 8.06 (t, 3 H, J = 2.0 Hz), 7.36–7.56 (m, 2 H), 6.98–7.19 (m, 2 H), 2.40–2.66 (m, 5 H).

To a solution containing 250 mg of the above cyclopentenone in 25 mL of ether was added 3.0 mL of a 2.0-M phenyllithium solution. After stirring at 0 °C for 1 h, the solution was poured onto water and extracted with ether. The ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent left 230 mg of a clear oil which was dissolved in 5 mL of ethanol containing 0.5 mL of acetic acid. After refluxing for 30 min, the mixture was poured over ice, extracted with ether, washed with a 5% sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent left 190 mg of a crystalline solid, mp 130–132 °C, which was identical to a sample of 1,3-diphenyl-2-methylcyclopentadiene (**33**) isolated from the irradiation of cyclopropene **32**.

The middle band isolated from the thick-layer separation of the crude photolysate derived from cyclopropene **32** contained 40 mg (30%) of a clear oil whose NMR spectrum indicated it to be a 1:3 mixture of 1,2-diphenyl-3-methyl- (**27**) and 1-methyl-2,3-diphenylcyclopentadiene (**28**).

Preparation and Irradiation of 1-Phenyl-2-methyl-3-vinylindene (36). To a stirred solution containing 1.15 g of 2-methyl-3-phenylindanone (**13**) in 25 mL of ether was added 8.5 mL of a 0.67-M vinylmagnesium bromide solution in ether. The reaction mixture was stirred for 1 h at room temperature followed by the addition of a saturated ammonium chloride solution. The solution was extracted with ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left a pale yellow oil which was taken up in 9 mL of acetic acid which contained 1 mL of sulfuric acid and 1 mL of water. After stirring for 15 min at 25 °C, the mixture was poured onto ice and extracted with ether. The ethereal solution was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a pale yellow oil which crystallized on standing. The structure of this material was assigned as 1-phenyl-2-methyl-3-vinylindene (**36**): mp 70–71 °C; IR (KBr) 3.44, 6.12, 6.26, 6.72, 6.91, 7.26, 8.46, 9.33, 9.72, 10.08, 10.93, 13.15, 13.47, 14.30 μm; UV (95% ethanol) 270 nm (ε 7300); NMR ($CDCl_3$, 100 MHz) τ 8.06 (s, 3 H), 5.66 (s, 1 H), 4.48 (d, 1 H, J = 12.0 Hz), 4.14 (d, 1 H, J = 17.0 Hz), 3.14 (dd, 1 H, J = 17.0, 12.0 Hz), 2.38–3.0 (m, 9 H); m/e 232 (M^+), 217 (base), 215, 202, 115.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.02; H, 7.22.

A solution containing 50 mg of **36** in 125 mL of benzene was irradiated with a 450 W-Hanovia lamp equipped with a Corex filter sleeve for 1 h. Removal of the solvent left a pale yellow oil which consisted mostly of 1-methyl-2-phenyl-3-vinylindene (**34**) as evidenced by NMR analysis. Thick-layer chromatography of the crude photolysate gave a pure sample of **34**.

Irradiation of 1-Phenyl-2,3,3-trimethylcyclopropene (52) in Methanol. A solution containing 130 mg of 1-phenyl-2,3,3-trimethylcyclopropene[93] (**52**) in 150 mL of methanol was irradiated with a 450-W Hanovia lamp equipped with a Vycor filter sleeve for 1 h. Removal of the solvent under reduced pressure left a crude yellow oil which was shown to contain two major products as judged by NMR analysis. Thick-layer chromatography of the mixture resulted in the separation of these two components. The major product isolated from the thick-layer plate was a colorless oil whose structure was assigned as 2-methoxy-3-phenyl-4-methylpent-3-ene (**53**; 78%) on the basis of its characteristic spectral data: IR (neat) 3.37, 3.46, 6.24, 6.73, 6.96, 7.34, 7.54, 7.76, 8.32, 9.10, 9.26, 9.36, 10.54, 11.90, 13.05, 14.27 μm; NMR ($CDCl_3$, 60 MHz) τ 8.95 (d, 3 H, J = 6.0 Hz), 8.51 (s, 3 H), 8.18 (s, 3 H), 6.71 (s, 3 H), 5.61 (q, 1 H, J = 6.0 Hz), 2.6–3.1 (m, 5 H); m/e 190 (M^+), 175, 159, 144, 143 (base), 142, 141, 129, 115, 91.

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.38; H, 9.88.

The structure of this material was further confirmed by comparison with an authentic sample. To a solution containing 0.81 g of 3-phenyl-4-methyl-3-penten-2-ol[94] and 1 mL of methyl iodide in 10 mL of tetrahydrofuran was added 0.24 g of sodium hydride. The mixture was stirred at 25 °C for 24 h, quenched with water, and extracted with ether. The ether layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting residue was purified by thick-layer chromatography, and the major component isolated was identical in every detail with a sample of **53** obtained from the photolysis of **52**.

The minor product (9%) obtained from the irradiation of 1-phenyl-2,3,3-trimethylcyclopropene (**52**) was identified as 1-methoxy-1-phenyl-2,3-dimethyl-2-butene (**54**) on the basis of its characteristic spectral data: IR (neat) 3.44, 6.24, 6.70, 6.91, 7.29, 7.49, 7.66, 8.40, 8.68, 8.87, 9.18, 9.69, 10.29, 10.90, 11.23, 12.87, 13.78, 14.38 μm; NMR ($CDCl_3$, 60 MHz) τ 8.59 (broad s, 3 H), 8.36 (broad s, 3 H), 8.18 (broad s, 3 H), 6.87 (s, 3 H), 4.79 (s, 1 H), 2.6–3.0 (m, 5 H); m/e 190 (M^+), 175, 158, 143 (base), 129, 115, 105, 91, 77.

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.19; H, 9.91.

The structure of this material was unambiguously confirmed by comparison with an authentic sample. To a solution containing 1.0 g of 2,3-dimethyl-1-phenylbut-2-en-1-one[95] in 75 mL of dioxane and 25 mL of water was added 2.2 g of sodium borohydride. The mixture was stirred at 25 °C for 24 h and was then added to 75 mL of water and extracted with ether. The ether layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 0.92 g of a pale oil. This material was taken up in 15 mL of tetrahydrofuran which contained 1 mL of methyl iodide. A 0.32-g sample of sodium hydride was added, and the mixture was stirred at room temperature for 24 h. At the end of this time, the solution was quenched with water and extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 0.83 g of 1-methoxy-1-phenyl-2,3-dimethyl-2-butene (**54**), which was identical in every detail with the minor component isolated from the irradiation of **52**.

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.[96] Reliably reproducible output rates of 1.73×10^{17} quanta/s were recorded. After the irradiation the degree of reaction was determined by quantitative NMR. The conversions were run to 15% or less. The mass balances in these runs were generally better than 95%.

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Registry No.—**7,** 58310-19-3; **8,** 62747-73-3; **9,** 65086-13-7; **10,** 65086-14-8; **11,** 65086-15-9; **12,** 62907-55-5; **13,** 52957-74-1; **14,** 65086-16-0; **15,** 65086-17-1; **16,** 65086-18-2; **17,** 65086-19-3; **18,** 65086-20-6; **19,** 62907-51-1; **20,** 62907-53-3; **21,** 62907-54-4; **22,** 62747-62-0; **23,** 4982-35-8; **24,** 62937-82-0; **25,** 24102-68-9; **26,** 62937-83-1; **27,** 65086-21-7; **28,** 62937-86-4; **31,** 50397-92-7; **32,** 62937-85-3; **33,** 62937-87-5; **34,** 62937-88-6; **35,** 26029-34-5; **36,** 65103-88-0; **52,** 50902-98-2; **53,** 65103-89-1; **54,** 65103-90-4; 1,2-diphenyl-3-methylcyclopropenyl perchlorate, 65103-91-5; benzyl chloride, 100-44-7; 1,2-diphenyl-3-benzyl-3-methylcyclopropene, 65103-92-6; triphenylcyclopropenyl bromide, 23147-72-0; allyl bromide, 106-95-6; 2,3-diphenylindanone, 7474-64-8; 1,2-diphenylcyclopropenyl perchlorate, 65103-93-7; 3-allyl-1,2-diphenylcyclopropene, 62907-47-5; 2-phenylindanone, 16619-12-8; 1-allyl-2-phenyl-1-indanol, 65103-94-8; 3-allyl-3-methyl-1,2-diphenylcyclopropene, 62907-50-0; vinyl bromide, 593-60-2; triphenylcyclopropenyl perchlorate, 65103-95-9; bis(1,2-diphenylcyclopropenyl) ether, 65103-96-0; 3-vinyl-1,3-diphenylcyclopropene, 65103-97-1; 2-methylfuran, 534-22-5; benzyl bromide, 100-39-0; 2-phenylfuran, 17113-33-6; ethyl bromide, 74-96-4; 3-phenyl-4-methyl-3-penten-2-ol, 53546-24-0; 2,3-dimethyl-1-phenylbut-2-en-1-one, 52776-41-7.

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