Photochemistry of Cyclopropene Derivatives. Formation and Intramolecular Trapping Reactions of Vinylcarbenes[1]

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Received December 20, 1979

The intramolecular photocycloaddition reactions of a number of 3-allyl-substituted diphenylcyclopropenes have been studied. Photodimerization occurred when 1,2-diphenyl-3-allylcyclopropene was irradiated in benzene. The photodimerization reaction was shown to be derived from the triplet state since the photodimer could be quenched when the irradiation was carried out in the presence of piperylene. The major product formed under these conditions was 1,2-diphenylbicyclo[3.1.0]hex-2-ene. A similar cycloaddition occurred upon irradiation of 1,2-diphenyl-3-allyl-3-methylcyclopropene. The formation of the bicyclohexene ring can be rationalized in terms of a vinylcarbene intermediate which undergoes internal cycloaddition. The effect of substituents on the stereochemical course of the cycloaddition was probed by using (*E*)- and (*Z*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene. The results obtained indicate that the vinylcarbene intermediate cycloadds to the neighboring double bond in a nonstereospecific fashion. Support for the vinylcarbene intermediate was obtained by carrying out the irradiation of the cyclopropene in the presence of methanol. This resulted in the formation of a mixture of methoxy ethers. The addition of alcohol to the vinylcarbene was also found to occur intramolecularly. The vinylcarbenes generated from the photolysis of the isomeric 1,3-diphenyl-3-allylcyclopropene prefer to rearrange to a mixture of indenes rather than to undergo internal cycloaddition. The photoreactions observed on direct irradiation of these systems proceed through the singlet state since sensitization with thioxanthone gave rise to a tricyclo[2.2.0.0^{2,6}]hexane. This tricyclic structure arises by means of a novel intramolecular [2 + 2] cycloaddition reaction.

The chemistry of cyclopropene derivatives has attracted considerable interest mainly because of the high strain energy associated with the unsaturated three-membered ring.[1-5] The relief of ring strain combined with resonance stabilization of the corresponding ring-opened species accounts for the relatively facile ring-opening reaction of this system. The mechanism for the interconversion of the cyclopropene ring and the corresponding bond-cleaved species continues to be of both theoretical and experimental interest. Recent calculations predict that the thermal ring opening of cyclopropene should proceed to a diradical planar intermediate which may subsequently decay to a vinylcarbene.[6] The electronically excited singlet state of the cyclopropene, on the other hand, correlates directly with the lower lying vinylcarbene state.[6] The formation of the vinylcarbene in the direct irradiation experiments can be viewed as the result of heterolytic cleavage and simultaneous rotation of the disubstituted methylene carbon. Both electrons occupy an in-plane σ orbital with only two electrons in the conjugated π orbital. The vinylcarbene species can rotate back to the diradical state[7] or undergo reactions characteristic of a singlet or triplet methylene. These include intramolecular hydrogen abstraction,[8,9] insertion into a C–H bond,[10] alkyl group migration,[11] and electrocyclization.[12-19] Interestingly, none of the products previously reported correspond to addition of the carbene to a double bond.[20-22] When we initiated our studies dealing with the photochemistry of cyclopropene derivatives, it seemed to us that the intermediate vinylcarbene might undergo cycloaddition, provided an intramolecular trap was available. In order to establish the viability of this route, we studied the photochemical behavior of a series of 3-allyl-substituted cyclopropene derivatives.[23,24] We report here the results of this study which show that vinylcarbenes readily undergo intramolecular cycloaddition to give bicyclo[3.1.0]hex-2-enes in high yield.

Results and Discussion

1,2-Diphenyl-3-allylcyclopropene (**1**) was prepared in high yield by treating diphenylcyclopropenyl cation with allylmagnesium bromide according to the general proce-

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(20) 3,3-Dimethylcyclopropene, on pyrolysis in olefin solutions, gives a cyclopropane product which can be understood to have arisen by addition of (2-methylpropenyl)carbene to the olefin: Professor G. L. Closs, private communication, as cited in footnote 26 of ref 7.

(21) For a recent report of trapping a vinylcarbene with an olefin, see K. L. M. Stanley, J. Dingwall, J. T. Sharp, and T. W. Naisby, *J. Chem. Soc., Perkin Trans. 1*, 1433 (1979).

(22) Recent work by Franck-Newmann and co-workers has shown that thiovinylcarbenes can be trapped by olefins: M. Franck-Newmann and J. J. Lohmann, *Angew. Chem., Int. Ed. Engl.*, **16**, 323 (1977); M. Franck-Newmann and C. D. Buchecker, *Tetrahedron*, **34**, 2797 (1978); M. Franck-Newmann and J. J. Lohmann, *Tetrahedron Lett.*, 3729 (1978); 2075, 2397 (1979).

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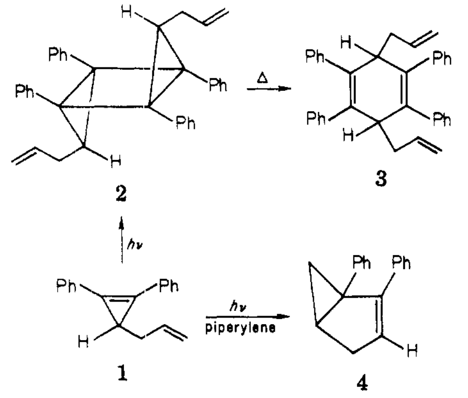
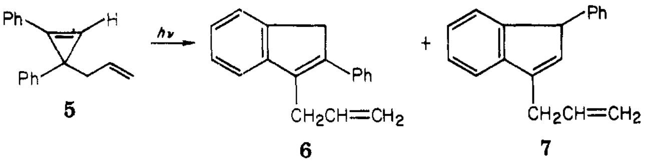
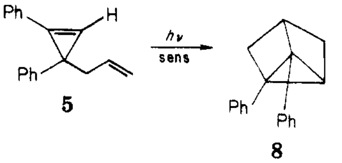
0022-3263/80/1945-2181$01.00/0 © 1980 American Chemical Society

dure of Breslow and Dowd.[25] Irradiation of **1** in benzene or hexane with Pyrex-filtered light resulted in dimerization and produced tricyclohexane **2** (mp 191–192 °C) in high yield. The assignment of structure **2** rests on its characteristic NMR, IR, and mass spectra, its elemental analysis, and its chemical behavior. Thus, photodimer **2** undergoes thermal rearrangement above 190 °C to an isomeric cyclohexadiene, **3**, mp 211–212 °C. Similar thermal rearrangements of related tricyclohexanes have been reported in the literature[26,27] and provide reasonable chemical analogy for this [2 + 2] retrogression reaction. The [2 + 2] photodimerization reaction of 1,2-diphenyl-substituted cyclopropenes has been independently studied by DeBoer[27] and Durr.[28] Photophysical studies including quantum yield measurements and isotope effects are consistent with the interpretation that the dimerization occurs exclusively from the triplet state and proceeds in a stepwise fashion via a diradical intermediate. Sensitization of **1** with benzophenone gave only **2**, in agreement with the involvement of a triplet state in the dimerization process.[27] When the photolysis of **1** was carried out in the presence of a triplet quencher (i.e., piperylene),[29] a new product was formed (75%) whose structure is assigned as 1,2-diphenylbicyclo[3.1.0]hex-2-ene (**4**) on the basis of its straightforward spectral properties: NMR (100 MHz) δ 0.54 (t, 1 H, J = 4.0 Hz), 1.51 (ddd, 1 H, J = 9.0, 6.0, and 4.0 Hz), 1.77 (dd, 1 H, J = 9.0 and 4.0 Hz), 2.39 (dd, 1 H, J = 17.0 and 2.0 Hz), 2.79 (ddd, 1 H, J = 17.0, 6.0, and 2.0 Hz), 5.67 (br s, 1 H), 7.0–7.3 (m, 10 H); UV (95% ethanol) λ_{max} 255 nm (ϵ 8000).

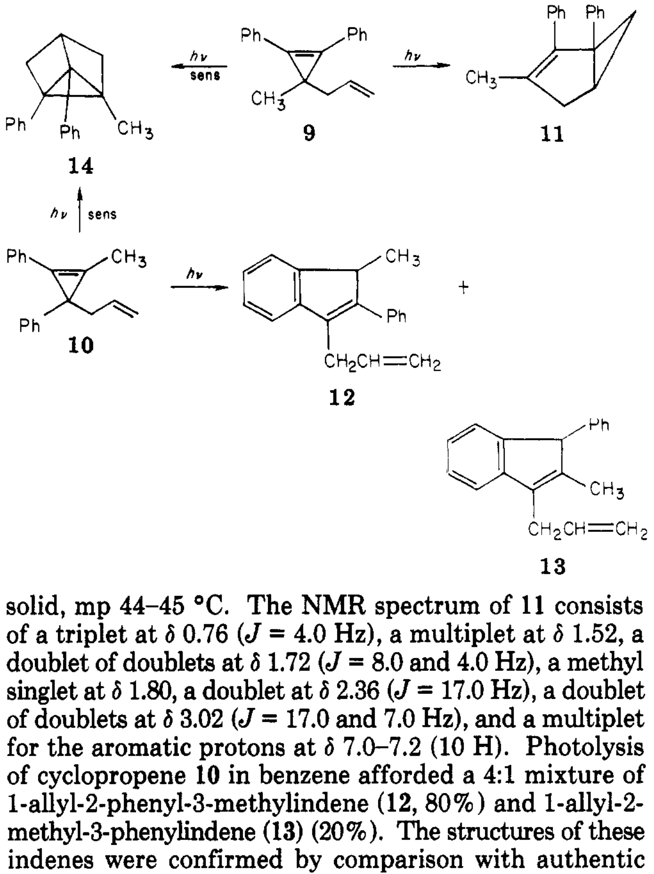


When the irradiation of the isomeric 1,3-diphenyl-3-allylcyclopropene (**5**) was carried out in benzene for 10 min, a 4:1 mixture of 2-phenyl-3-allylindene (**6**) and 1-phenyl-3-allylindene (**7**) was obtained. The structures of these indenes were confirmed by comparison with authentic samples.[16] In this case, rearrangement of the singlet state of the cyclopropene to the indene skeleton is preferred over bicyclohexene formation. The regiospecificity observed in the rearrangement of this unsymmetrical cyclopropene is similar to that encountered with related vinyl- and aryl-substituted cyclopropenes.[16,18] In contrast to the direct irradiation, the sensitized photolysis of **5** produced 1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**8**) as the exclusive photoproduct. This reaction formally corresponds to a [2 + 2] cycloaddition of the triplet excited state of the cyclopropene across the olefinic side chain.





The photoreactions of the closely related methyl- and allyl-substituted diphenylcyclopropenes **9** and **10** were also studied in order to further assess the excited-state behavior of these systems. Direct irradiation of **9** in benzene with Pyrex-filtered light afforded 1,2-diphenyl-3-methylbicyclo[3.1.0]hex-2-ene (**11**) in 65% yield as a crystalline solid, mp 44–45 °C. The NMR spectrum of **11** consists of a triplet at δ 0.76 (J = 4.0 Hz), a multiplet at δ 1.52, a doublet of doublets at δ 1.72 (J = 8.0 and 4.0 Hz), a methyl singlet at δ 1.80, a doublet at δ 2.36 (J = 17.0 Hz), a doublet of doublets at δ 3.02 (J = 17.0 and 7.0 Hz), and a multiplet for the aromatic protons at δ 7.0–7.2 (10 H). Photolysis of cyclopropene **10** in benzene afforded a 4:1 mixture of 1-allyl-2-phenyl-3-methylindene (**12**, 80%) and 1-allyl-2-methyl-3-phenylindene (**13**) (20%). The structures of these indenes were confirmed by comparison with authentic samples.[16]



The photochemical transformations encountered on direct irradiation of cyclopropenes **9** and **10** proceed through the singlet manifold since sensitization of both of these compounds with thioxanthone gave 1,2-diphenyl-6-methyltricyclo[2.2.0.0.^{2,6}]hexane (**14**) as the exclusive photoproduct [NMR (270 MHz) δ 1.33 (s, 3 H), 2.11 (d, 1 H, J = 8.0 Hz), 2.28 (d, 1 H, J = 8.0 Hz), 2.62 (dd, 1 H, J = 8.0 and 4.0 Hz), 2.79 (t, 1 H, J = 4.0 Hz), 2.83 (dd, 1 H, J = 8.0 and 4.0 Hz), 6.8–7.4 (m, 10 H)]. The formation of tricyclic structures **8** and **14** can be attributed to a novel intramolecular [2 + 2] cycloaddition. The implication of this observation is that there are severe steric constraints on the cyclopropene dimerization route. This is further indicated by the fact that related 1,2-diphenylcyclopropenes, where both 3-positions are substituted with groups larger than a hydrogen atom, do not dimerize.[27] As a consequence of this steric effect, the triplet states of tetrasubstituted cyclopropenes **9** and **10** prefer to undergo

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(25) R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).

(26) C. D. DeBoer and R. Breslow, *Tetrahedron Lett.*, 1033 (1967).

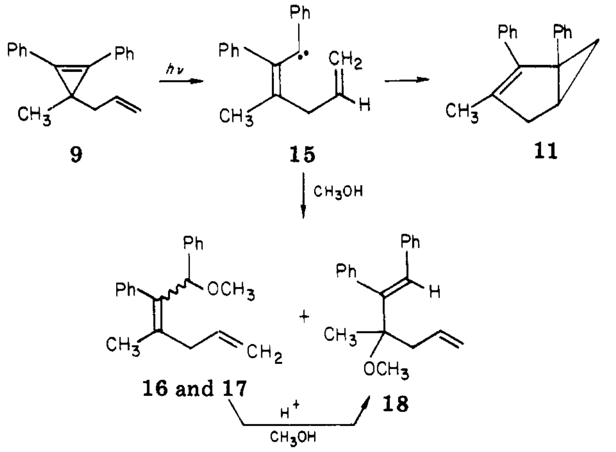
(27) C. D. DeBoer, D. H. Wadsworth, and W. C. Perkins, *J. Am. Chem. Soc.*, **95**, 861 (1973).

(28) H. Durr, *Tetrahedron Lett.*, 1649 (1967).

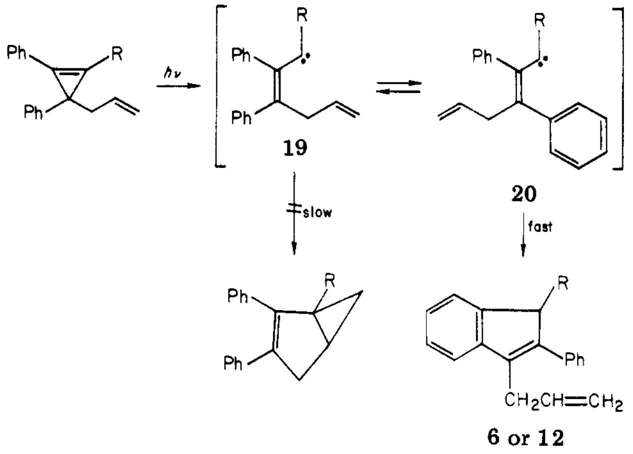
(29) It should be noted that the formation of **4** in the presence of piperylene has a much lower quantum yield than that for the formation of **2** in the direct irradiation of **1**.

intramolecular [2 + 2] addition rather than bimolecular dimerization. This is in dramatic contrast to the case of trisubstituted cyclopropene **1**, where dimerization of the triplet state is the only path followed. Our failure to detect reaction from the singlet state of cyclopropene **1** on direct irradiation can be reasonably attributed to a decrease in the rate of ring opening relative to intersystem crossing. Although the quantum yield for intersystem crossing of cyclopropenes is generally quite low,[8,27] it is nevertheless finite. Introduction of a methyl or phenyl substituent on the 3-position of the cyclopropene ring increases the rate of singlet ring opening relative to intersystem crossing. The low quantum efficiencies of both processes ($\Phi \approx 0.03$) are undoubtedly responsible for the manifestation of the substituent effect with these systems.[30]

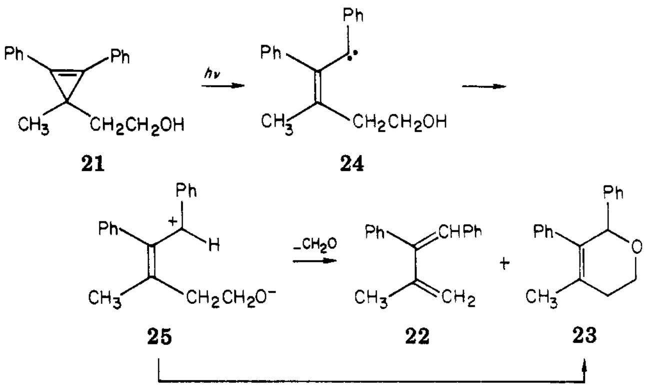
The most reasonable explanation to account for the formation of bicyclohexenes **4** and **11** involves a sequence consisting of ring opening of the electronically excited singlet state to a vinylcarbene intermediate (**15**). Attack of the carbene carbon on the neighboring double bond generates the bicyclo[3.1.0]hexene skeleton. Support for this postulate was obtained by carrying out the irradiation of **9** in a slightly basic methanol solution. With this solvent system, the major products obtained are the *E* and *Z* methoxy ethers **16** (25%) and **17** (34%) as well as (*E*)-3-methyl-3-methoxy-1,2-diphenyl-1,5-hexadiene (**18**, 25%). The identity of these compounds was established by comparison with independently synthesized samples. Methoxy ether **18** was prepared by treating 3,4-diphenyl-3-buten-2-one with allylmagnesium bromide followed by reaction with sodium hydride and methyl iodide. Treatment of ethers **16** and **17** with acidic methanol gave structure **18**. The formation of methoxy ethers **16**–**18** is perfectly consistent with the intervention of a vinylcarbene intermediate which is trapped by methanol prior to intramolecular cycloaddition.[31] It should also be noted that bicyclohexene **11** is stable toward irradiation in methanol and that the relative quantum yields for disappearance of **9** ($\Phi = 0.03$) are the same in methanol and benzene.



All attempts to isolate a bicyclohexene from the irradiation of the unsymmetrical 1,3-diphenyl-3-allyl-substituted cyclopropenes failed. The only products formed were substituted indenes. It would seem as though the initially generated vinylcarbene prefers to rearrange to an indene rather than to undergo internal cycloaddition. Also complicating matters here is the possibility of forming *cis*- and *trans*-vinylcarbenes. The *trans*-vinylcarbene **20** apparently undergoes cyclization to indene at a faster rate than the addition of the *cis*-vinylcarbene **19** onto the neighboring double bond. Earlier work by Padwa[16,17] and Zimmerman[18,19] has shown that an unusual substituent effect operates in the photorearrangement of a series of unsymmetrically substituted cyclopropenes. The major product obtained (ca. 80%) from the irradiation of a 1,3-diphenyl-2-methyl-substituted cyclopropene was always found to correspond to preferential cleavage of the cyclopropene bond which is methyl rather than phenyl substituted. This unusual regioselectivity was attributed to a funneling of the excited state of the cyclopropene to the energy surface of the higher lying carbene state.[16] Thus the formation of indene **6** (or **12**) as the major photoproduct obtained from the irradiation of **5** (or **10**) is perfectly compatible with the earlier observations.



As was mentioned previously, the vinylcarbene generated from irradiation of the 1,2-diphenyl-substituted cyclopropene could be trapped by an external alcohol. As a continuation of our investigations in this area, we were particularly interested in determining whether the addition reaction would also occur when the alcohol and the cyclopropene ring were constrained to be within the same molecule. In order to probe this possibility, we carried out a study dealing with the photochemistry of hydroxy-substituted cyclopropenes. The first compound investigated was 1-methyl-2,3-diphenyl-2-cyclopropene-2-ethanol (**21**). This material was prepared by the lithium aluminum hydride reduction of *tert*-butyl 1-methyl-2,3-diphenyl-2-cyclopropene-1-acetate. Irradiation of **21** in benzene led to a mixture of *cis*- and *trans*-1,2-diphenyl-3-methylbutadiene (**22**, 38%) as well as 5,6-dihydro-4-methyl-2,3-diphenyl-2*H*-pyran (**23**, 26%). The structure of **23** was readily established by examination of its characteristic NMR spectrum ($CDCl_3$, 60 MHz): δ 1.67 (d, $J = 1$ Hz, 3 H), 2.13 (m, 2 H), 3.85 (m, 2 H), 5.30 (q, $J = 1$ Hz, 1 H),



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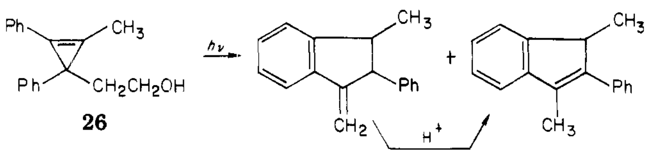
(30) For a related substituent effect in ketone photochemistry, see P. S. Engel, M. A. Schexnayder, J. Ziffer, and J. I. Seeman, *J. Am. Chem. Soc.*, **96**, 924 (1974).

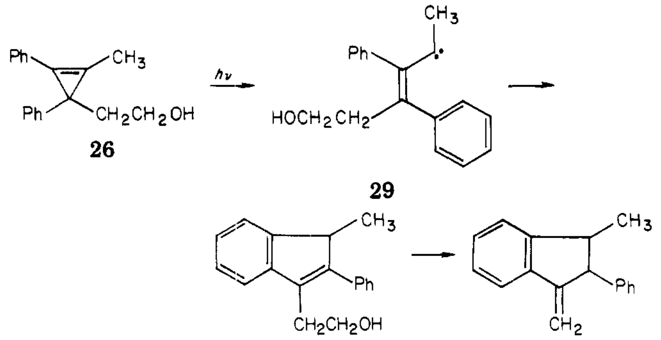
(31) An alternate mechanism involving protonation of the excited cyclopropene double bond followed by a cyclopropyl-allyl cation rearrangement and methanol trapping cannot necessarily be eliminated at this time.

6.75–7.30 (m, 10 H). The formation of diene **22** and dihydropyran **23** is perfectly consistent with a vinylcarbene intermediate (**24**). This reactive species inserts into the neighboring OH bond to give zwitterion **25** which either collapses to dihydropyran **23** or undergoes loss of formaldehyde and formation of the cis and trans dienes **22**.

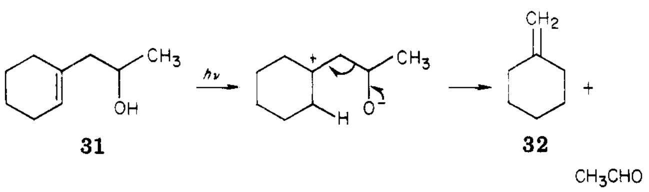
Attention was next turned to the photochemical behavior of the isomeric 2-methyl-1,3-diphenyl-2-cyclopropene-2-ethanol (**26**) system. Irradiation of **26** in benzene gave a mixture of two compounds in a 2:1 ratio. The major product obtained was identified as 1-methyl-3-methylene-2-phenylindan (**27**) on the basis of its characteristic NMR spectrum which showed a doublet at δ 1.39 (3 H, J = 7.0 Hz), a doublet of quartets at δ 3.26 (1 H, J = 7.0 Hz), a multiplet at δ 3.55 (1 H), a doublet at δ 4.71 (1 H, J = 3.0 Hz), a doublet at δ 5.62 (1 H, J = 3.0 Hz), and a multiplet at δ 7.32 (9 H). The minor compound was identified as 1,3-dimethyl-2-phenylindene (**28**) by comparison with an authentic sample. Under slightly acidic conditions indan **27** was quantitatively isomerized to **28**. The most reasonable mechanism to account for the formation of **27** and **28** involves an initial ring opening reaction to a vinylcarbene (**29**) which cyclizes to give indene **30** as a transient species. Loss of formaldehyde from **30** gives rise to indan **27** which then partially isomerizes to indene **28** under the reaction conditions. The regiospecificity observed in this reaction is similar to that encountered with cyclopropenes **5** and **10**. The presumed photofragmentation of **30** to **27** formally corresponds to a retro-Prins reaction and has analogy in the photochemical conversion of α-methyl-1-cyclohexeneethanol (**31**) to methylenecyclohexane (**32**).[32] This reaction is thought to proceed via a mechanism involving an initial photoprotonation followed by collapse of the resulting intermediate.



26 **27** **28**

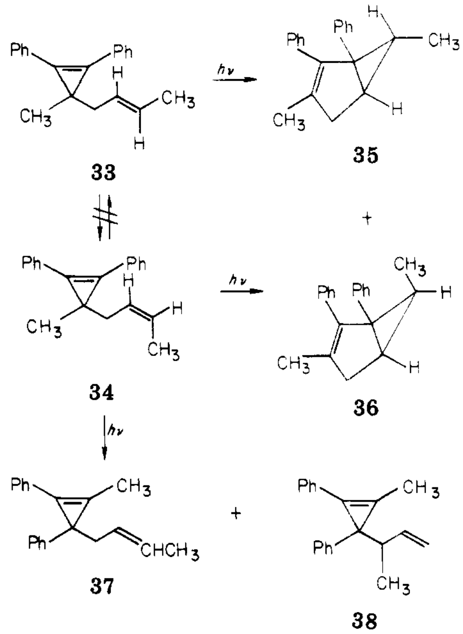


26 **29** **30** **27**



31 **32**

At this stage of our studies we decided to investigate the stereochemical couse of the intramolecular vinylcarbene cycloaddition reaction. Extended Hückel calculations carried out on the parent vinylcarbene system suggest a triplet diradical-type structure for the ground state of this system.[33-36] Recent ESR experiments by Arnold and co-workers support this conclusion.[37] 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. Since the photochemical ring-opening reaction does not occur from the triplet state, it seems likely that the initial intermediate produced in the ring cleavage is the singlet rather than the more stable triplet vinylcarbene. Singlet carbenes normally produce cyclopropanes stereospecifically from alkenes whereas the triplet addition of carbenes to olefins gives rise to a mixture of nonstereospecific products.[38] In order to probe the stereochemical course of the internal cycloaddition reaction, we have studied the photochemical behavior of (E)-**33** and (Z)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**34**).



33 **35** **34** **36** **37** **38**

These compounds were prepared by treating 1-methyl-2,3-diphenyl-2-cyclopropene-1-acetaldehyde with ethylidenetriphenylphosphorane followed by separation of the cis and trans isomers on a silver nitrate impregnated silica gel column. Irradiation of a sample of the pure E isomer (**33**) in benzene gave rise to a mixture of *endo*-**35** (30%) and *exo*-3,6-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**36**, 31%). In addition to the bicyclohexenes, a 1:1 mixture of (E)- and (Z)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butenes (**37**) and a 1:1 diastereomeric mixture of 3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butenes (**38**) were also obtained. Similar results were obtained on irradiation of the Z isomer **34** although, in this case, the bicyclohexenes **35** and **36** were present in a 1:2.5

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[32] P. J. Kropp and H. J. Krauss, *J. Am. Chem. Soc.*, **91**, 7466 (1969).

[33] S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, **14**, 305 (1969).

[34] R. Hoffmann, G. D. Zeiss, and G. W. VanDine, *J. Am. Chem. Soc.*, **90**, 1485 (1968).

[35] R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968).

[36] L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

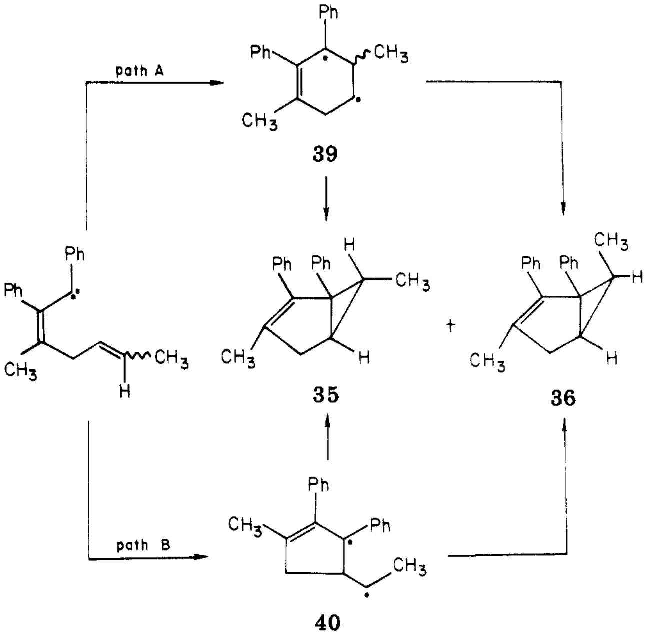
[37] D. R. Arnold, R. W. Humphreys, W. J. Leigh, and G. E. Palmer, *J. Am. Chem. Soc.*, **98**, 6225 (1976).

[38] P. P. Gaspar and G. S. Hammond, "Carbenes", Vol II, R. A. Moss and M. Jones, Jr., Eds., Wiley, New York, 1975, Chapter 6.

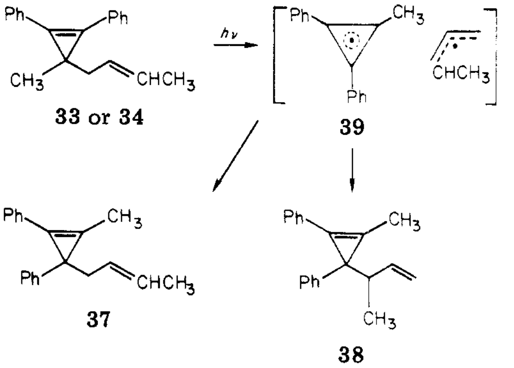
ratio. Appropriate control experiments established that no cis–trans isomerization of either the starting materials (i.e., between **33** and **34**) or the products (i.e., between **35** and **36**) was operative under the reaction conditions. The structures of the *endo*-methyl- and *exo*-methyl-substituted bicyclo[3.1.0]hex-2-enes were easily assigned on the basis of their characteristic NMR spectra. Spin-decoupling experiments indicate that protons H_5 and H_6 in the exo-substituted isomer **35** are coupled by 3.7 Hz whereas the coupling with the endo isomer **36** is 8.5 Hz. The identities of cyclopropenes **37** and **38** were verified by comparison with independently synthesized samples.

The above experimental observations clearly indicate that the intramolecular cycloaddition reactions of cyclopropenes **33** and **34** are not stereospecific. It should be noted, however, that the reaction does show a slight degree of stereoselectivity. Thus, cyclopropene **34** affords a larger amount of bicyclohexene **36** than **35**. This corresponds to the preferential retention of stereochemistry in the cycloaddition reaction. The results are somewhat surprising since singlet carbene additions to olefins are generally thought to proceed with complete retention of configuration.[39] A number of explanations can account for the above results. One possibility is that cycloaddition occurs from the lower lying triplet vinylcarbene. This would require that the photochemically generated singlet vinylcarbene decay to the triplet before cycloaddition occurs. A second mechanistic scenario is that the initially formed singlet vinylcarbene is in equilibrium with a triplet which reacts with the double bond to form a diradical. The triplet diradical then undergoes nonstereospecific ring closure. In a third conceivable mechanism, both bicyclohexenes could be formed from a common singlet vinylcarbene intermediate which reacts in a stepwise fashion with the neighboring double bond. The lack of stereospecificity in the cycloaddition may be due to the geometric constraints placed on the transition state by the developing bicyclohexene which makes a concerted addition extremely difficult. Two stepwise pathways are possible. One path (path A, Scheme I) involves initial cyclization via a six-membered ring to produce intermediate **39** which subsequently closes to give either bicyclohexene **35** or **36**. The alternate possibility (path B) involves cyclization through a five-membered transition state to produce intermediate **40** which undergoes a subsequent ring closure. Molecular models show that there are no steric constraints for either pathway. Baldwin's rules[40] suggest that both the 6-endo-trig (path A) and 5-exo-trig (path B) are allowed processes. It should be pointed out that over the past few years several reports of stepwise addition of singlet carbenes have crept up in the literature, thereby providing reasonable analogy for the above suggestion.[41-47] At the current time the available data do not distinguish between the various possibilities for intramolecular cycloaddition.

Scheme I



Finally, the formation of cyclopropenes **37** and **38** from the irradiation of **33** or **34** merits some comment. A mechanism analogous to that accepted for the type I reaction of ketones[48] can readily account for the formation of the rearranged cyclopropenes. Introduction of a methyl group on the γ-position of the allyl side chain apparently stabilizes the radical pair intermediate **39** enough to allow fragmentation to compete efficiently with ring cleavage. Cyclopropenes **1** and **9**, without this stabilization, yield only ring-opened products. It should be pointed out that the formation of **37** and **38** from the radical pair **39** is to be expected since the transition state prefers to localize the odd electron on a phenylated carbon.[49] The above reaction corresponds to a rare example of a singlet-state reaction of a cyclopropene in which the three-membered ring has been retained.[50]



The results obtained from this investigation allow the following generalizations to be made regarding the photochemistry of allyl-substituted cyclopropene derivatives. (1) Excited cyclopropene singlets give products consistent with σ-bond cleavage to vinylcarbenes whereas triplet states undergo intramolecular [2 + 2] cycloadditions. (2) A sensitive competition between ring opening of the singlet state of the cyclopropene and intersystem crossing to the

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triplet exists and is influenced by the substituent groups on the 3-position of the ring. (3) Photochemically generated vinylcarbenes can be readily trapped with alcohols. (4) Vinylcarbenes cycloadd to the neighboring double bond in a nonstereospecific fashion to give bicyclo[3.1.0]hex-2-enes. (5) Vinylcarbene intermediates generated from 3-allyl-3-aryl-substituted cyclopropenes prefer to rearrange to indenes rather than undergo internal cycloaddition. (6) Side-chain fragmentation can compete with ring cleavage as a primary process when stable radicals are produced.

Experimental Section(51)

Irradiation of 3-Allyl-1,2-diphenylcyclopropene (1) in Benzene. A solution containing 100 mg of 3-allyl-1,2-diphenylcyclopropene (1)[16] in 150 mL of anhydrous benzene was irradiated for 1 h under an argon atmosphere with a 550-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve. The solvent was removed under reduced pressure, and the remaining semisolid was triturated with pentane to remove unreacted starting material. The resulting solid (67 mg, 67%, mp 191–192 °C) was assigned as (1α,2β,3β,4β,5α,6α)-3,6-diallyl-1,2,4,5-tetraphenyltricyclo[3.1.0.0^{2,4}]hexane (2) on the basis of its spectral properties: IR (KBr) 3.27, 3.37, 6.11, 6.24, 6.70, 6.94, 9.62, 9.70, 10,0, 10.91, 12.65, 13.15, 13.65, 14.1, 14.35 μm; NMR (CDCl$_3$, 100 MHz) δ 2.15 (dd, 2 H, J = 8.0 and 2.0 Hz), 2.76 (t, 1 H, J = 2.0 Hz), 4.87 (d, 1 H, J = 17.0 Hz), 4.92 (d, 1 H, J = 9.0 Hz), 5.48–5.96 (m, 1 H), 7.30 (s, 20 H); UV (acetonitrile) 230 nm (ϵ 28160); mass spectrum, *m/e* 424, 423 (base), 383, 382, 167, 91.

Anal. Calcd for C$_{36}$H$_{32}$: C, 93.06; H, 6.94. Found: C, 92.92; H, 7.04.

A 136-mg (0.29 mmol) sample of (1α,2β,3β,4β,5α,6α)-3,6-diallyl-1,2,4,5-tetraphenyltricyclo[3.1.0.0^{2,4}]hexane (2) was heated neat at 210 °C under an argon atmosphere for a period of 10 min. The reaction mixture was then crystallized from ethyl acetate to give 120 mg (88%) of a white granular solid (mp 206–207 °C) which was identified as *trans*-2,5-diallyl-1,3,4,6-tetraphenyl-1,4-cyclohexadiene (3) on the basis of its spectral properties: IR (KBr) 3.26, 3.31, 3.44, 3.50, 6.07, 6.24, 6.71, 6.95, 7.06, 8.93, 9.34, 9.87, 10.04, 10.75, 10.85, 10.97, 11.15, 12.90, 13.80, 14.25 μm; NMR (CDCl$_3$, 100 MHz) δ 1.88 (br d, 4 H, J = 7 Hz), 4.04 (br s, 2 H), 4.72 (dd, 2 H, J = 18 and 2 Hz), 5.04 (dd, 2 H, J = 10 and 2 Hz), 5.64–6.12 (m, 2 H), 7.07.3 (m, 20 H); UV (95% ethanol) 245 nm (ϵ 8360); mass spectrum, *m/e* 423 (base), 382, 218, 204, 91.

Anal. Calcd for C$_{36}$H$_{32}$: C, 93.06; H, 6.94. Found: C, 92.95; H, 6.99.

The irradiation of cyclopropene 1 was also carried out in the presence of piperylene. A solution containing 390 mg of 3-allyl-1,2-diphenylcyclopropene (1) and 1 g of *trans*-piperylene in 200 mL of anhydrous benzene was irradiated for 12 h under an argon atmosphere with a Hanovia 450-W medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left a semicrystalline material which was triturated with pentane to afford 70 mg of dimer 2. The remaining oil was then chromatographed on a 1.5 × 100 cm column of silica gel with hexane as the eluent. The major fraction eluted contained 120 mg of a colorless oil which was further chromatographed on a 20 × 20 × 0.1 cm preparative-layer silica gel plate impregnated with silver nitrate with a 10% ether in hexane mixture as the eluent. The only fraction isolated contained 100 mg (26%) of a crystalline solid, mp 94.5–95.5 °C (methanol), which was identified as 1,2-diphenylbicyclo[3.1.0]hex-2-ene (4) on the basis of its spectral properties: IR (neat) 3.30, 3.49, 3.52, 6.24, 6.70, 6.93, 9.09, 9.67, 10.29, 10.90, 12.35, 13.26, 14.4 μm; NMR (CDCl$_3$, 100 MHz) δ 0.54 (t, 1 H, J = 4.5 Hz), 1.40–1.64 (m, 1 H), 1.77 (dd, 1 H, J = 8.0 and 4.5 Hz), 2.49 (dd, 1 H, J = 17 and 2.5 Hz), 2.79 (ddd, 1 H, J = 17, 6.5, 2.5 Hz), 5.67 (m, 1 H), 7.0–7.3 (m, 10 H); UV (95% ethanol) 255 nm (ϵ 8000); mass spectrum, *m/e* 232 (M$^+$, base), 217, 215, 141, 91.

Anal. Calcd for C$_{18}$H$_{16}$: C, 93.06; H, 6.94. Found: C, 92.98; H, 6.97.

When the irradiation was carried out under high dilution (50 mg of cyclopropene 1 and 2.5 g of *trans*-piperylene in 500 mL of anhydrous benzene) it was shown by high-pressure reverse-phase liquid chromatography that the dimerization process was completely suppressed and that the reaction mixture contained 1,2-diphenylbicyclo[3.1.0]hex-2-ene (4) as the exclusive component.

Triplet-Sensitized Irradiation of 3-Allyl-1,2-diphenylcyclopropene (1). A solution containing 180 mg of 3-allyl-1,2-diphenylcyclopropene (1), 90 mg of thioxanthen-9-one, and 1 mL of pyridine in 150 mg of benzene was irradiated for 45 min under an argon atmosphere with a 450-W Hanovia lamp equipped with a uranium-glass filter sleeve. The reaction mixture was concentrated under reduced pressure to a volume of approximately 5 mL and passed through a 1.5 × 5 cm column of silica gel, eluting with 200 mL of hexane. Removal of the solvent under reduced pressure produced 125 mg (71%) of a colorless oil which was identified as 1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (8) on the basis of its spectral properties: IR (neat) 3.30, 3.41, 3.50, 6.24, 6.67, 6.90, 7.95, 8.12, 9.28, 9.21, 11.25, 12.85, 13.17, 14.45 μm; UV (95% ethanol) 257 nm (ϵ 11000); mass spectrum, *m/e* 232 (M$^+$, base), 230, 191, 141, 128, 115, 91, 77; NMR (CDCl$_3$, 270 MHz) δ 1.99 (d, 1 H, J = 7.5 Hz), 2.16 (d, 1 H, J = 7.5 Hz), 2.66 (dd, 1 H, J = 4.6 and 3.0 Hz), 2.76–2.87 (m, 1 H), 3.01 (ddd, 1 H, J = 7.5, 4.5, and 2.4 Hz), 6.90–7.33 (m, 10 H). External irradiation of the doublet at δ 2.16 collapsed the signal at δ 3.01 into a doublet of doublets (J = 4.5 and 2.4 Hz). Irradiation of the multiplet at δ 2.76–2.87 collapsed the doublet at δ 1.99 into a singlet, the doublet of doublets at δ 2.66 into a singlet, and the signal at δ 3.01 into a doublet (J = 7.5 Hz).

Anal. Calcd for C$_{18}$H$_{16}$: C, 93.06; H, 6.94. Found: C, 92.90; H, 7.00.

Direct Irradiation of 3-Allyl-3-methyl-1,2-diphenylcyclopropene (9) in Benzene. A solution containing 100 mg of 3-allyl-3-methyl-1,2-diphenylcyclopropene (9)[16] in 150 mL of anhydrous benzene was irradiated for 55 min under an argon atmosphere with a 550-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left 93 mg of a clear oil which was shown to contain one major component (65%) by NMR spectroscopy. Chromatography on a 1.5 × 60 cm column of silica gel impregnated with silver nitrate (10%) and eluted with a 5% ether/hexane mixture produced 65 mg (65%) of a crystalline solid, mp 44–45 °C, whose structure was identified as 3-methyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (11) on the basis of its spectral properties: IR (KBr) 3.28, 3.46, 6.68, 6.93, 9.80, 13.16, 13.32, 14.35 μm; NMR (CDCl$_3$, 100 MHz) δ 0.76 (t, 1 H, J = 4.0 Hz), 1.39–1.68 (m, 1 H), 1.72 (dd, 1 H, J = 8.0 and 4.0 Hz), 1.80 (s, 3 H), 2.36 (d, 1 H, J = 17.0 Hz), 3.02 (dd, 1 H, J = 17.0 and 7.0 Hz), 7.0–7.2 (m, 10 H); UV (95% ethanol) 256 (ϵ 11000); mass spectrum, *m/e* 248 (M$^+$, base), 230, 215, 214, 154, 114.

Anal. Calcd for C$_{19}$H$_{18}$: C, 92.63; H, 7.37. Found: C, 92.47; H, 7.37.

Triplet-Sensitized Irradiation of 3-Allyl-3-methyl-1,2-diphenylcyclopropene (9). A solution containing 100 mg of 9 and 100 mg of thioxanthen-9-one in 150 mL of benzene was irradiated under an argon atmosphere for 1 h with a 450-W Hanovia arc lamp equipped with a uranium-glass filter sleeve. The reaction mixture was concentrated under reduced pressure to a volume of approximately 10 mL and chromatographed through a 2.5 × 5 column of silica gel, eluting with 200 mL of hexane. Removal of the solvent under reduced pressure left 70 mg (70%) of a colorless oil which was identified at 6-methyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (14) on the basis of its spectral properties: IR (neat) 3.29, 3.42, 3.51, 6.24, 6.67, 6.92, 7.22, 10.10, 14.30 μm; UV (95% ethanol) 240 nm (ϵ 10800); mass spectrum, *m/e* 246 (M$^+$), 231, 155, 154 (base), 115, 91, 77; NMR (CDCl$_3$, 270 MHz) δ 1.33 (s, 3 H), 2.11 (d, 1 H, J = 8.0 Hz), 2.29 (d, 1 H, J = 8.0 Hz), 2.62 (dd, 1 H, J = 8.0 and 4.0 Hz), 2.77–2.85 (m, 2 H), 6.80–7.40 (m, 10 H). External irradiation of the doublet

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

at δ 2.11 resulted in the collapse of the doublet of doublets at δ 2.62 into a doublet (*J* = 4.0 Hz). Irradiation of the doublet at δ 2.29 collapsed the multiplet at δ 2.77–2.85 into a doublet (*J* = 4.0 Hz) and a triplet (*J* = 4.0 Hz). Irradiation of the doublet of doublets at δ 2.62 collapsed the doublet at δ 2.11 into a singlet and the multiplet at δ 2.77–2.85 into a six-peak signal. Irradiation of the multiplet at δ 2.77–2.85 resulted in the collapse of the doublet at δ 2.29 into a singlet and the collapse of the doublet of doublets at δ 2.62 into a doublet (*J* = 8.0 Hz).

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.60; H, 7.36.

Direct Irradiation of 3-Allyl-3-methyl-1,2-diphenylcyclopropene (9) in Methanol. A solution containing 200 mg of 3-allyl-3-methyl-1,2-diphenylcyclopropene (9)[16] in 200 mL of anhydrous methanol was irradiated for 1 h under an argon atmosphere with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure produced a clear yellow oil which was chromatographed on a 1.5 × 100 cm column of silica gel with a 3% ether in hexane mixture as the eluent. The first fraction eluted contained 25 mg (13%) of a crystalline solid, mp 44–45 °C, which was identified as 3-methyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (11). The second fraction contained 118 mg (59%) of a colorless oil which was shown by high-pressure reverse-phase liquid chromatography to consist of two components. These were identified by NMR spectroscopy as a mixture of (*E*)- and (*Z*)-4-methyl-6-methoxy-5,6-diphenyl-1,4-hexadienes (16 and 17) in a 1.4:1 ratio, respectively: NMR ($CDCl_3$, 100 MHz) δ 1.52 (s, 3 H), 2.04 (s, 3 H), 2.58 (d, 2 H, *J* = 7.5 Hz), 3.20 (d, 2 H, *J* = 7.5 Hz), 3.40 (s, 3 H), 3.42 (s, 3 H), 4.79–5.28 (m, 4 H), 5.40 (s, 1 H), 5.43 (s, 1 H), 5.45–6.05 (m, 2 H), 6.60–6.79 (m, 4 H), 6.90–7.25 (m, 16 H); mass spectrum, *m/e* 278, 262, 246, 205 (base), 155, 91, 78, 77.

Anal. Calcd for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.18; H, 7.99.

The presence of methoxy dienes 16 and 17 was further substantiated by their conversion to (*E*)-3-methyl-3-methoxy-1,2-diphenyl-1,5-hexadiene (18) upon treatment with acidic methanol. The third fraction eluted from the column contained 50 mg (25%) of a colorless oil which was identified as (*E*)-3-methyl-3-methoxy-1,2-diphenyl-1,5-hexadiene (18) on the basis of its spectral properties and by comparison with an independently synthesized sample: IR (neat) 3.24, 3.35, 3.40, 3.51, 6.03, 6.20, 6.67, 6.90, 7.29, 7.85, 8.55, 9.25, 9.64, 9.91, 10.85, 12.90, 13.14, 13.86, 14.19, 14.38 μm; NMR ($CDCl_3$, 100 MHz) δ 1.47 (s, 3 H), 2.44–2.64 (m, 2 H), 3.50 (s, 3 H), 5.19 (d, 1 H, *J* = 18 Hz), 5.21 (d, 1 H, *J* = 10 Hz), 5.80–6.24 (m, 1 H), 6.86 (s, 1 H), 6.86–7.68 (m, 10 H); UV (95% ethanol) 256 nm (ε 14150); mass spectrum, *m/e* 246, 231, 205, 155, 116 (base), 94.

Anal. Calcd for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.49; H, 8.02.

Preparation of (*E*)-3-Methyl-3-methoxy-1,2-diphenyl-1,5-hexadiene (18). To a solution containing 1.1 g of (*E*)-1,2-diphenylbut-1-en-3-one[52] in 25 mL of anhydrous ether was added 9 mL of a 0.67 N allylmagnesium bromide solution in ether at 0 °C. The reaction mixture was stirred for 1 h and allowed to warm to room temperature. A saturated ammonium chloride solution was then added, and the reaction mixture was stirred until both phases became clear. The organic layer was removed, washed with a saturated sodium chloride solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure produced 1.1 g (99%) of a crystalline solid, mp 50.5–51.5 °C, which was identified as (*E*)-1,2-diphenyl-3-hydroxy-3-methyl-1,5-hexadiene on the basis of its spectral properties: IR (KBr) 2.82, 2.90, 3.29, 3.39, 3.42, 6.08, 6.24, 6.70, 6.91, 7.30, 7.49, 7.82, 8.60, 9.05, 9.27, 9.68, 9.95, 10.85, 11.50, 12.82, 13.20, and 14.3 μm; NMR ($CDCl_3$, 100 MHz) δ 1.41 (s, 3 H), 2.06 (s, 1 H), 2.26 (dd, 1 H, *J* = 15.0 and 8.0 Hz), 2.52 (dd, 1 H, *J* = 15.0 and 6.0 Hz), 5.12 (d, 1 H, *J* = 16.0 Hz), 5.16 (d, 1 H, *J* = 10.0 Hz), 5.68–6.25 (m, 1 H), 6.68–7.40 (m, 11 H); UV (methanol) 255 nm (ε 15040); mass spectrum, *m/e* 246 (M^+), 231, 222, 179 (base), 178.

Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.26; H, 7.65.

To a stirred solution containing 264 mg of the above compound and 700 mg of iodomethane in 5 mL of anhydrous tetrahydrofuran at room temperature was added 36 mg of sodium hydride. After 24 h, the reaction mixture was diluted with 50 mL of ether, washed twice with water and once with a saturated salt solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a 1.5 × 60 cm column of silica gel, eluting with a 5% ether in hexane mixture. The first fraction eluted contained 218 mg (79%) of a colorless oil which was identical in every respect with a sample of (*E*)-3-methyl-3-methoxy-1,2-diphenyl-1,5-hexadiene (18) isolated from the direct irradiation of 3-allyl-3-methyl-1,2-diphenylcyclopropene (9) in methanol.

Acid-Catalyzed Isomerization of a Mixture of (*E*)- and (*Z*)-4-Methyl-6-methoxy-5,6-diphenyl-1,4-hexadienes (16) and (17) in Methanol. To a stirred solution containing 118 mg of a 1.4:1 mixture of methoxy dienes 16 and 17 in 25 mL of methanol was added 1 mL of a 0.1 N solution of hydrochloric acid. The reaction mixture was stirred at room temperature for 48 h and was then neutralized with aqueous sodium carbonate. The reaction mixture was then taken up in 100 mL of ether, washed six times with equal volumes of water and once with a saturated salt solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded a colorless oil which was chromatographed on a 20 × 20 × 0.1 cm silica gel preparative-layer plate with a 3% ether in hexane mixture as the eluent. The fastest moving band contained 64 mg (54%) of a colorless oil which was identified as recovered starting material by its characteristic NMR spectrum. The next band eluted contained 54 mg (46%) of a colorless oil which was identified as (*E*)-3-methyl-3-methoxy-1,2-diphenyl-1,5-hexadiene (18) by comparison with an authentic sample.

Preparation of 1-Methyl-2,3-diphenyl-2-cyclopropene-2-ethanol (21) and 2-Methyl-1,3-diphenyl-2-cyclopropene-2-ethanol (26). To a stirred suspension containing 0.69 g of lithium aluminum hydride in 200 mL of anhydrous ether at 0 °C was added dropwise a solution containing 5.8 g of a 4:1 mixture of *tert*-butyl 1-methyl-2,3-diphenyl-2-cyclopropene-1-acetate[53] and *tert*-butyl 2-methyl-1,3-diphenyl-2-cyclopropene-1-acetate[53] in 50 mL of ether. After the addition was complete the mixture was stirred at 0 °C for an additional 3 h. To this mixture was added in succession 1 mL of water, 1 mL of a 0.1 M sodium hydroxide solution, and 3 mL of water. The mixture was filtered through Celite, and the ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a thick yellow oil which was chromatographed on a 2.5 × 100 cm silica gel column with 15% acetone in hexane as the eluent. The first component isolated contained 3.1 g (69%) of a clear oil identified as 1-methyl-2,3-diphenyl-2-cyclopropene-2-ethanol (21) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.45 (s, 3 H), 1.75 (br s, 1 H), 2.10 (t, *J* = 6 Hz, 2 H), 3.59 (t, *J* = 6 Hz, 2 H), 7.2–7.8 (m, 10 H); IR (neat) 2.95, 3.20, 3.46, 5.52, 6.24, 6.71, 6.93, 7.30, 9.31, 9.50, 9.75, 10.9, 12.7, 13.3, 14.6 μm; UV (95% ethanol) 337, 319, 238, 228 nm (ε 20300, 27100, 12300, 16000); mass spectrum, *m/e* 250 (M^+), 248, 235, 220, 205 (base), 191, 105.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.06; H, 7.19.

The second component isolated contained 0.81 g (18%) of a colorless oil identified as 2-methyl-1,3-diphenyl-2-cyclopropene-2-ethanol (26): NMR ($CDCl_3$, 100 MHz) δ 1.63 (br s, 1 H), 2.28 (s, 3 H), 2.39 (t, *J* = 7 Hz, 2 H), 3.61 (t, *J* = 7 Hz, 2 H), 6.96–7.50 (m, 10 H); IR (neat) 2.96, 3.40, 5.38, 6.24, 6.68, 6.90, 9.30, 9.68, 13.12, 14.38 μm; UV (95% ethanol) 263 nm (ε 15400); mass spectrum, *m/e* 250 (M^+), 248, 235, 220, 219, 206, 205 (base), 204, 203, 202, 191, 178, 173, 129, 128, 127, 115, 105, 101, 91, 77.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.06; H, 7.19.

Irradiation of 1-Methyl-2,3-diphenyl-2-cyclopropene-2-ethanol (21) in Benzene. A solution containing 200 mg of 1-methyl-2,3-diphenyl-2-cyclopropene-2-ethanol (21) in 250 mL of benzene was irradiated for 4 h with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve

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under an argon atmosphere. The benzene was removed under reduced pressure, leaving behind a light yellow oil which was chromatographed on a preparative thick-layer plate with a 10% ether–hexane mixture as the eluent. The first component isolated contained 66 mg (38%) of a colorless oil which was identified as a 55:45 mixture of *cis-* and *trans*-1,2-diphenyl-3-methylbutadiene (**22**) on the basis of their characteristic NMR spectra ($CDCl_3$, 60 MHz): cis isomer, δ 2.06 (br s, 3 H), 4.66 (m, 1 H), 5.03 (m, 1 H), 6.64 (br s, 1 H), 6.7–7.3 (m, 10 H); trans isomer, δ 1.90 (br s, 3 H), 4.97 (m, 1 H), 5.20 (m, 1 H), 6.64 (br s, 1 H), 6.7–7.3 (m, 10 H). The chemical shifts and couplings for these compounds were identical with those reported by Arnold.[8] The second component isolated contained 51 mg (26%) of a colorless oil which was identified as 5,6-dihydro-4-methyl-2,3-diphenyl-2*H*-pyran (**23**) on the basis of its spectral properties: NMR ($CDCl_3$, 60 MHz) δ 1.67 (d, *J* = 1 Hz, 3 H), 2.13–2.14 (m, 2 H), 3.52–4.18 (m, 2 H), 5.30 (q, *J* = 1 Hz, 1 H), 6.75–7.30 (m, 10 H); IR 3.26, 3.29, 3.37, 3.39, 3.48, 6.24, 6.71, 6.86, 7.03, 7.91, 8.90, 9.28, 10.94, 13.2, 13.6, and 14.2 μm; UV (95% ethanol) 235 nm (ε 6630); mass spectrum, *m/e* 250 (M^+), 235 (base), 205, 173, 129, 115, 105, 77.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.36; H, 7.29.

Irradiation of 2-Methyl-1,3-diphenyl-2-cyclopropene-2-ethanol (26). A solution containing 110 mg of 2-methyl-1,3-diphenyl-2-cyclopropene-2-ethanol (**26**) in 200 mL of benzene was irradiated for 40 min under an argon atmosphere with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left behind a dark brown oil which was percolated through a 1.0 × 10 cm silica gel column with hexane as the eluent. The major component isolated contained 36 mg (36%) of a light yellow oil which was shown by NMR spectroscopy and VPC analysis, using a $^1/_4$ in. × 5 ft SE-30 on Chromosorb W column, to be a mixture of two components in a 2:1 ratio. Preparative VPC resulted in the separation of the two components. The major product isolated was identified as 1-methyl-3-methylene-2-phenylindan (**27**) on the basis of its characteristic NMR spectrum ($CDCl_3$, 100 MHz): δ 1.39 (d, *J* = 7 Hz, 3 H), 3.26 (q, *J* = 7 and 7 Hz, 1 H), 3.44–3.66 (m, 1 H), 4.71 (d, *J* = 3 Hz, 1 H), 5.62 (d, *J* = 3 Hz, 1 H), 7.04–7.61 (m, 9 H). The minor component was identified as 1,3-dimethyl-2-phenylindene (**28**) by comparison of its NMR spectrum with that of an independently synthesized sample. Additional support for the structural assignment of **27** was gained from treatment of a 25-mg sample of the mixture with a catalytic amount of 48% tetrafluoroboric acid in 25 mL of benzene for 24 h at room temperature. The benzene solution was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind 21 mg of a light yellow oil which solidified on standing. Recrystallization from ethanol afforded a white crystalline material (mp 72–73 °C) identified as 1,3-dimethyl-2-phenylindene (**28**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.15 (d, *J* = 7 Hz, 3 H), 2.21 (d, *J* = 3 Hz, 3 H), 3.65–4.00 (m, 1 H), 7.08–7.52 (m, 9 H); IR (KBr) 3.54, 6.24, 7.05, 13.23, 3.50, 14.45 μm; UV (95% ethanol) 292 nm (ε 25 800), 228 (15 200); mass spectrum, *m/e* 220 (M^+, base), 205.

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.40; H, 7.57.

The structure of this material was unambiguously verified by comparison with an authentic sample. A 440-mg sample of 3-methyl-2-phenylindanone[54] was taken up in 50 mL of anhydrous ether. To this solution was added dropwise 0.8 mL of a 3 M solution of methylmagnesium bromide in ether under a nitrogen atmosphere. The mixture was refluxed for 4 h and was then hydrolyzed with a saturated ammonium chloride solution. The ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which was taken up in 20 mL of glacial acetic acid. To this stirred solution were added 0.5 mL of water and 5 mL of concentrated sulfuric acid. The mixture was stirred for 30 min and then poured into iced water. The mixture was extracted with ether. The ethereal layer was washed with water, a saturated sodium bicarbonate solution, and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which solidified on standing. Recrystallization from ethanol afforded 250 mg (57%) of 1,3-dimethyl-2-phenylindene (**28**) as a white crystalline solid (mp 72–73 °C) which was identical in all respects with the material isolated from the photolysis.

Direct Irradiation of (*E*)-1-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (33) in Benzene. A solution containing 115 mg of (*E*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene[53] (**33**) in 250 mL of anhydrous benzene was irradiated for 30 min under an argon atmosphere with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve. The solvent was removed under reduced pressure, and the clear yellow oil obtained was chromatographed on a 1.5 × 65 cm column of silica gel impregnated with 10% silver nitrate (w/w) by using a 10% ether in hexane mixture as the eluent. The first fraction eluted contained 70 mg of a colorless oil which was shown by high-pressure liquid chromatography to consist of two components in a 1:1 ratio. This mixture was then subjected to silica chromatography using a 1.5 × 100 cm column with hexane as the eluent. The first fraction eluted contained 36 mg (31%) of a white crystalline solid, mp 52–53 °C (methanol), which was identified as *exo*-3,6-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**35**) on the basis of its spectral properties: IR (CCl_4) 3.33, 3.48, 6.24, 6.70, 6.92, 8.00, 9.92, 10.21, 12.3, 12.9, 13.6, 14.8 μm; UV (95% ethanol) 252 nm (ε 6510); mass spectrum, *m/e* 260 (M^+, base) 245, 230, 215, 167, 115, 91; NMR ($CDCl_3$, 270 MHz) δ 0.97–1.00 (m, 4 H), 1.42 (dd, *J* = 6.6 and 3.7 Hz, 1 H), 1.63 (s, 3 H), 2.47 (d, *J* = 18 Hz, 1 H), 2.98 (dd, *J* = 18 and 6.6 Hz), 6.97–7.19 (m, 10 H). External irradiation of the doublet of doublets at δ 1.42 caused the doublet of doublets at δ 2.98 to collapse to a doublet (*J* = 18 Hz).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.34; H, 7.62.

The second component eluted from the column contained 35 mg (30%) of a colorless oil whose structure was assigned as *endo*-3,6-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**36**) on the basis of its spectral properties: IR (CCl_4) 3.38, 3.50, 6.24, 6.71, 6.95, 8.01, 8.80, 9.28, 9.70, 10.0, 12.4 and 14.4 μm; UV (95% ethanol) 256 nm (ε 9670); mass spectrum, *m/e* 260 (M^+, base), 245, 230, 215, 167, 115, 91; NMR ($CDCl_3$, 270 MHz) δ 1.05 (d, *J* = 5.9 Hz, 3 H), 1.52 (dd, *J* = 8.8 and 8.5 Hz, 1 H), 1.89–1.94 (m, 1 H), 2.15 (d, *J* = 18 Hz, 1 H), 2.93 (dd, *J* = 18 and 8.8 Hz, 1 H), 7.00–7.22 (m, 10 H). External irradiation of the doublet at δ 1.05 caused the multiplet at δ 1.89–1.94 to collapse to a doublet (*J* = 8.5 Hz). Irradiation of the multiplet at δ 1.89–1.94 caused the doublet at δ 1.05 to collapse to a singlet. External irradiation of the signal at δ 2.93 caused the doublet at δ 2.15 to collapse to a singlet and the doublet of doublets at δ 1.52 to collapse to a doublet (*J* = 8.5 Hz).

Anal. Calcd for $C_{20}H_{20}$: *m/e* 260.1566 (P^+). Found: *m/e* 260.1572 (P^+).

The second fraction obtained from the silver nitrate column contained 20 mg (17%) of a colorless oil which was identified as a 1:1 mixture of (*E*)- and (*Z*)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butenes (**37**) by comparison with independently prepared samples.[53] The third fraction eluted from the column contained 12 mg (10%) of a colorless oil which was identified as a 1:1 mixture of diastereomeric 3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butenes (**38**) by comparison with authentic samples.[53]

Direct Irradiation of (*Z*)-1-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (34) in Benzene. A solution containing 110 mg of (*Z*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene[53] (**34**) in 250 mL of anhydrous benzene was irradiated for 30 min under an argon atmosphere with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a 1.5 × 65 cm column of silica gel impregnated with 10% silver nitrate (w/w) by using 10% ether in hexane as the eluent. The first fraction eluted contained 50 mg (45%) of a colorless oil which was shown by NMR spectroscopy to consist of a mixture of *exo*-3,6-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**35**) and *endo*-3,6-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**36**) in a 1:2 ratio. The identity of these isomers was confirmed by com-

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parison with authentic samples. The second and third fractions contained 25 mg (23%) of a colorless oil which was unidentified. The fourth fraction contained 17 mg (15%) of a colorless oil which was identified as a 1:1 mixture of (*E*)- and (*Z*)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butenes (**37**) by comparison with authentic samples.[53] The fifth fraction contained 10 mg (10%) of a colorless oil which was identified as a 1:1 mixture of diastereomeric 3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butenes (**38**) by comparison with authentic samples.[53]

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.

Registry No. **1**, 62907-47-5; **2**, 62955-52-6; **3**, 73377-53-4; **4**, 62907-49-7; **5**, 65086-18-2; **8**, 71956-73-5; **9**, 62907-50-0; **10**, 62907-51-1; **11**, 62907-52-2; **12**, 62907-53-3; **13**, 62907-54-4; **14**, 66221-08-7; **16**, 73377-54-5; **17**, 73377-55-6; **18**, 73377-56-7; **21**, 73377-57-8; (*E*)-**22**, 50555-64-1; (*Z*)-**22**, 50555-63-0; **23**, 73377-58-9; **26**, 73377-59-0; **27**, 73377-60-3; **28**, 58310-20-6; **33**, 66221-12-3; **34**, 66221-10-1; **35**, 73377-61-4; **36**, 73464-49-0; (*E*)-**37**, 66221-09-8; (*Z*)-**37**, 70840-44-7; **38**, isomer 1, 66221-07-6; **38**, isomer 2, 66221-06-5; (*E*)-1,2-diphenylbut-1-en-3-one, 38661-88-0; allyl bromide, 106-95-6; (*E*)-1,2-diphenyl-3-hydroxy-3-methyl-1,5-hexadiene, 73377-62-5; *tert*-butyl 1-methyl-2,3-diphenyl-2-cyclopropene-1-acetate, 73377-63-6; *tert*-butyl 2-methyl-1,3-diphenyl-2-cyclopropene-1-acetate, 73377-64-7; 3-methyl-2-phenylindanone, 62907-55-5; methyl bromide, 74-83-9.

Photochemical Reactions of Bicyclo[2.2.2]octadienones

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Received August 7, 1979

A series of spirooxirano-substituted bicyclo[2.2.2]octadienones have been prepared by Diels–Alder addition of dimethyl acetylenedicarboxylate to 2,4-cyclohexadienones, and their photochemistry was investigated. Upon direct excitation, they were found to aromatize by elimination of 2-carbonyloxirane which was trapped by ethanol to give ethyl glycidate. The acetophenone-sensitized reaction of bicyclooctadienones gave tricyclic isomers whose formation by regiospecific di-π-methane rearrangement is discussed.

Substituted bicyclo[2.2.2]octadienones **3a–i** are conveniently accessible by reaction of dimethyl acetylenedicarboxylate with 2,4-cyclohexadienones **2** which, unless stabilized by bulky substituents,[1] can be generated by thermal dissociation of their Diels–Alder dimers **1**.[2] Consideration of bicyclooctadienones both as β,γ-unsaturated ketones and as homoconjugated dienes indicates that they may conceivably undergo a variety of photochemical reactions. Photochemical fragmentation of **3a** or **3f**, as known[3] for related bicyclooctadienones, gives **4** or **5** and the correspondingly substituted dimethyl phthalates **6**. Photochemical isomerization by skeletal rearrangement of **3** formally could lead to ten products. **7** and **8** are the two possible 1,3-acyl-migration products of **3**, and **9–12** may derive from oxa-di-π-methane rearrangements (see Scheme I) for which precedence exists in the triplet-sensitized reaction of benzobicyclo[2.2.2]octadienone.[4,5] The formation of **13-16** may be rationalized by conceivable di-π-methane rearrangements of **3** as outlined in Scheme II.[6] Moreover, intramolecular cycloaddition of **3**, analogous to that of norbornadiene, would give products of tetracyclane structure.[7]

Challenged by the multitude of formally conceivable excited-state reactions mentioned above, we have prepared bicyclooctadienones **3a–i** and studied their photochemistry.[8]

Results and Discussion

Structure and Spectral Properties of Bicyclooctadienones 3. The Diels–Alder reaction of acetylenedicarboxylate with 2,4-cyclohexadienones **2** afforded in one case, namely, that of 4-*tert*-butyl-2,4-cyclohexadienone, a mixture of the two possible diastereomers **3b** and **3c**, differing in the configuration of the substituents R^4 and R^5. In all other cases, only one isomer was isolated whose structural assignment rests on the ^{1}H NMR spectral data listed in Table I and the following evidence. For **3f–h**, structure was established by determining the configuration of the substituents R^4 and R^5 by chemical means as outlined in Scheme III. As for **3i**, its structure has been confirmed by X-ray analysis.[9] Thus, for all the established structures of bicyclooctadienones, R^5 is either a methylene or methyl group. In apparent analogy to the formation of Diels–Alder dimers **1**, the attack of 2,4-cyclohexadienones **2** by acetylenedicarboxylate is governed by steric factors; in the transition complex involved in the formation of **3**, the sterically less demanding substituent at the disubstituted sp^3 carbon of **2** is oriented towards the dienophile.

The ultraviolet spectral properties of bicyclooctadienones **3** are typical of β,γ-unsaturated ketones.[5] Thus, the UV spectra are characterized by an enhanced n-π* absorption (ε ~400) at about 310 nm (see Table II). Unfortunately, we have not been able to separate the two

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