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Photochemistry of Cyclopropene Derivatives. Synthesis of the Tricyclo[2.2.0.0^{2,6}]hexane Ring System via a Photosensitized [2 + 2] Cycloaddition Reaction[†1]

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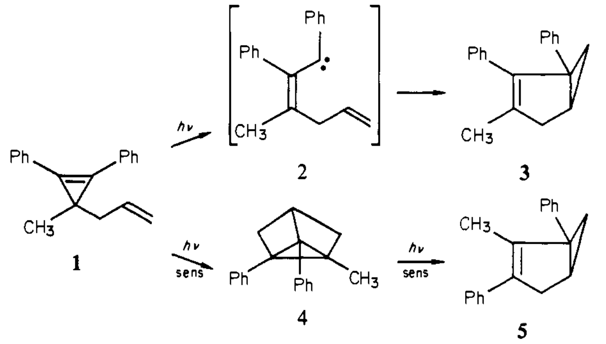
Abstract: The photosensitized triplet reactions of several 3-allyl-substituted diphenylcyclopropenes have been studied. The triplet-sensitized irradiations gave diphenyl-substituted tricyclo[2.2.0.0^{2,6}]hexanes in good yield by means of a novel intramolecular [2 + 2] cycloaddition. The sensitized cycloadditions proceed with total retention of stereochemistry about the olefinic π bond. Reasonable mechanistic options for the sensitized cycloaddition include a concerted pathway or a stepwise process involving a diradical intermediate. The data obtained indicate that these systems proceed through a boatlike conformation. On extended irradiation, the initially formed tricyclo[2.2.0.0^{2,6}]hexane ring system rearranged to a bicyclo[3.1.0]hex-2-ene. The mechanism proposed to account for the rearrangement involves a sequence consisting of sensitized ring opening of the tricyclohexane to a bicyclo[2.1.1]hexane diradical which subsequently undergoes a 1,2-methylene shift. The effect of substituents on the regio- and stereoselectivity of the sensitized rearrangement was studied in some detail.

Strained bicyclic and polycyclic compounds continue to play an important role in the understanding of many aspects of organic chemistry.[2-6] For this reason, synthetic efforts in this area have been extensive. One of the more common methods used to prepare such systems involves a photochemical [2 + 2] cycloaddition.[7-9] Intramolecular [2 + 2] photocycloadditions have also been used as the decisive reaction step in the synthesis of uncommon, highly strained hydrocarbons.[10,11] Strained polycyclics containing bicyclo[2.1.0]pentane and bicyclo[2.2.0]hexane units are readily prepared according to this principle.[12,13] As an integral part of a program directed toward the development of new strategies for the synthesis of strained small-ring hydrocarbons, we initiated a series of investigations to probe the feasibility of employing intramolecular [2 + 2] cycloaddition of cycloprene derivatives for the construction of novel polycyclic ring systems.[14-16]

The photochemistry of cyclopropene derivatives has attracted considerable interest over the past several years.[17] The photochemical behavior of this highly strained ring system has been shown to be remarkably dependent on the multiplicity of the excited state involved.[18,19] Singlet states react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinyl carbenes[20,21] while triplet states, generated by sensitization techniques, give high yield of cyclopropene dimers.[22-26] Attempts to obtain bimolecular 2+2-cycloadducts were unsuccessful, since the rate of reaction of the excited triplet cyclopropene with cyclopropene ground state is so rapid that observable cross-adduct formation is precluded.[27] When we initiated our studies dealing with the photochemistry of cyclopropene derivatives, it seemed to us that the cyclopropene ring might undergo [2 + 2] cycloaddition with π bonds, provided an intramolecular trap was available. In order to establish the viability of this route, we studied the photosensitized behavior of a series of 3-allyl-substituted cyclopropene derivatives.[28] We report here the results of this study which show that diaryl-substituted cyclopropenes readily undergo intramolecular [2 + 2] photoadditions to give tricyclo[2.2.0.0^{2,6}]hexanes in high yield.

Results

We have previously found that the direct irradiation of 3-allyl-3-methyl-1,2-diphenylcyclopropene (**1**) afforded 1,2-diphenyl-3-methylbicyclo[3.1.0]hex-2-ene (**3**) as the exclusive photoproduct.[29] The most reasonable explanation to account for the formation of **3** involves ring opening of the electronically excited singlet state of **1** to a vinylcarbene intermediate (**2**). Attack of the vinylcarbene carbon on the neighboring double bond generates the bicyclo[3.1.0]hexene skeleton. The photochemical reaction encountered on direct irradiation proceeds through the singlet manifold since irradiation of **1** in the presence of a triplet



[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

* John S. Simon Guggenheim Memorial Fellow, 1981-1982.

(1) Photochemical Transformations of Small Ring Compounds. 120. For part 119 see: Padwa, A.; Chou, C. S. *Tetrahedron* **1981**, 37, 3269.

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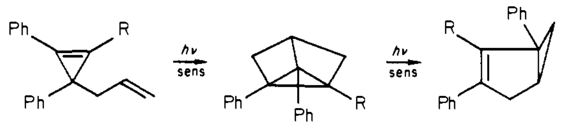
sensitizer gave rise to the isomeric bicyclohexene **5**. Subsequent studies showed that **5** is not a primary reaction product but is formed by a secondary photoreaction of tricyclohexane **4**. With short exposures, tricyclohexane **4** accounts for nearly all of the product produced. At longer exposures, owing to a secondary photoreaction of **4**, the amount of **5** increased. This was independently demonstrated by the conversion of **4** to **5** under triplet-sensitized conditions. The formation of tricyclohexane **4** can be attributed to a novel intramolecular [2 + 2] cycloaddition of the triplet state of cyclopropene **1**.

The sensitized conversion of 3-allyl-substituted cyclopropenes to bicyclo[3.1.0]hexenes was found to be a general reaction. Thus, irradiation of cyclopropenes **6–8** in the presence of thioxanthone afforded bicyclohexenes **12–14** in high yield. In each case, a tricyclo[2.2.0.$0^{2,6}$]hexane intermediate was initially formed which was then converted to the bicyclohexene ring system on extended irradiation.

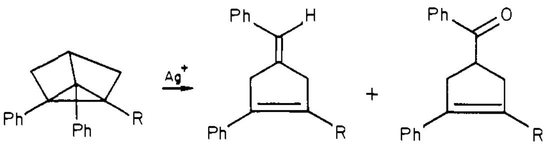


6, R = H
7, R = CH_3
8, R = Ph

9, R = H
10, R = CH_3
11, R = Ph

12, R = H
13, R = CH_3
14, R = Ph

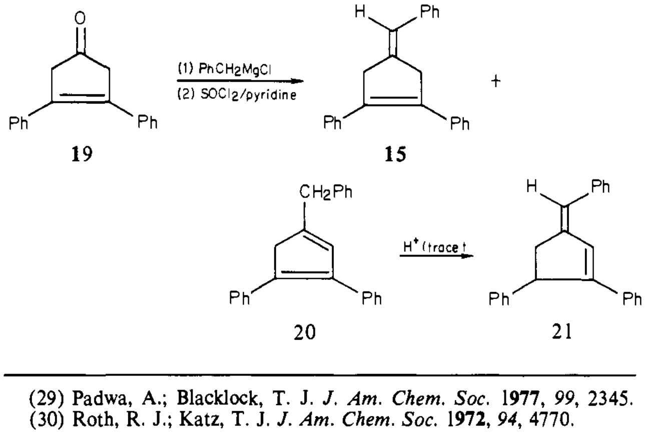
Prior to concerning ourselves with the molecular details of the reaction mechanism, two points are of interest. First, the conversion of the aryl-substituted tricyclo[2.2.0.$0^{2,6}$]hexanes to bicyclo[3.1.0]hexenes proceeds via the triplet state, since the photorearrangement of the tricyclohexane ring system could not be induced by direct irradiation. Secondly, it should be noted that Roth and Katz had previously demonstrated the rearrangement of tricyclo[2.2.0.$0^{2,6}$]hexane to bicyclo[3.1.0]hex-2-ene in the presence of silver ion.[30] We have found, however, that treatment of **11** with silver ion in benzene results in the formation of cyclopentenes **15** and **16**. Similar results were encountered with tricyclohexane **10**. The structure of cyclopentene **15** was confirmed by comparison with an authentic sample. 4-Benzylidene-1,2-diphenylcyclopent-1-ene (**15**) was prepared by treating 3,4-diphenylcyclopent-3-en-1-one (**19**) with benzylmagnesium chloride followed by dehydration with thionyl chloride in pyridine. In addition to **15**, a 32% yield of 4-benzyl-1,2-diphenyl-1,3-cyclopentadiene (**20**) was also isolated. Attempts to recrystallize **20** from ethanol gave rise to 3-benzylidene-1,5-diphenylcyclopent-1-ene (**21**) in high yield.



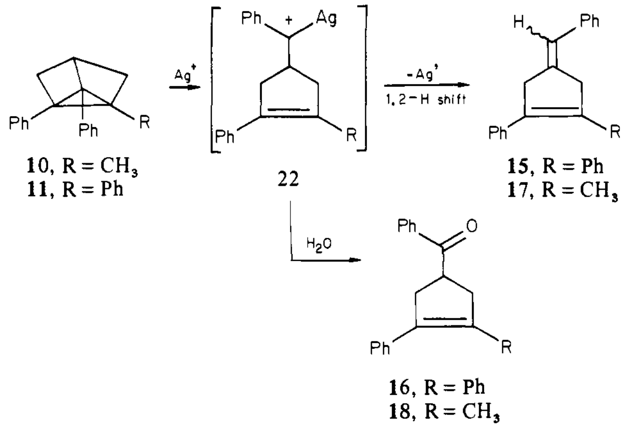
11, R = Ph
10, R = CH_3

15, R = Ph
17, R = CH_3

16, R = Ph
18, R = CH_3



The interaction of silver ion with strained carbocyclic compounds has been a subject of considerable interest in recent years.[31] Silver ion is known to catalyze a variety of rearrangements, the course of which depends both on the nature of the organic compound and the solvent employed.[31] In line with earlier evidence for the intermediacy of a metal-bonded carbonium ion metal-complexed carbene hybrid intermediate in the silver ion promoted rearrangement of strained-ring systems,[32,33] it is tempting to suggest the involvement of a related species in the silver-induced rearrangements of the above systems. Thus, we propose that silver ion behaves as a very specific Lewis acid which attacks the cyclopropene ring to yield argentocarbonium ion **22**. This reactive intermediate can either undergo a 1,2-hydrogen shift to give **15** (or **17**) or react with water to give **16** (or **18**). When the reaction of **10** or **11** with silver was carried out in aqueous methanol, benzoylcyclopentene **16** (or **18**) was the only product produced.



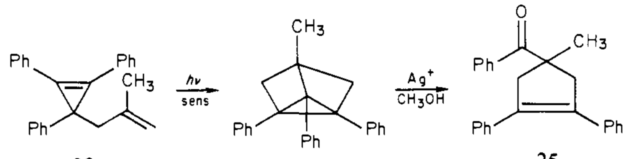
10, R = CH_3
11, R = Ph

22

15, R = Ph
17, R = CH_3

16, R = Ph
18, R = CH_3

Placement of a methyl group on the 4-position of the tricyclo[2.2.0.$0^{2,6}$]hexane ring causes a different mode of behavior to occur on exposure to silver ion. Tricyclohexane **24** was obtained from the sensitized irradiation of cyclopropene **23**. Treatment of **24** with silver ion in methanol afforded a single product in high yield. The structure of this material was identified as 4-benzoyl-4-methyl-1,2-diphenylcyclopent-1-ene (**25**) on the basis of its characteristic spectral properties (see Experimental Section). In this case, the initially formed argentocarbonium ion prefers to react with methanol than to undergo a 1,2-methyl shift.



23

24

25

In order to describe some measure of generality to the sensitized intramolecular [2 + 2] cycloaddition reaction, we studied a number of related systems. The thioxanthone sensitized reaction of cyclopropene **26** gave rise to tricyclohexane **28** in good yield. The same cycloadduct was also formed from the triplet-induced reaction of the prenyl-substituted isomer **27**. Control experiments showed that **26** and **27** were not interconverted under the sensitized conditions. Further irradiation of tricyclohexane **28** in the presence of thioxanthone afforded bicyclohexene **29** in high yield. Similar results were encountered with cyclopropenes **30** and **33**. With the above systems, the sensitized rearrangement of the tricyclohexane ring was found to be highly regiospecific producing 6,6-dimethyl-substituted bicyclohexenes **29** and **32** as the exclusive photoproducts.

At this stage of our studies we decided to investigate the stereochemical course of the intramolecular [2 + 2] cycloaddition reaction. In order to probe the stereochemical aspects of the

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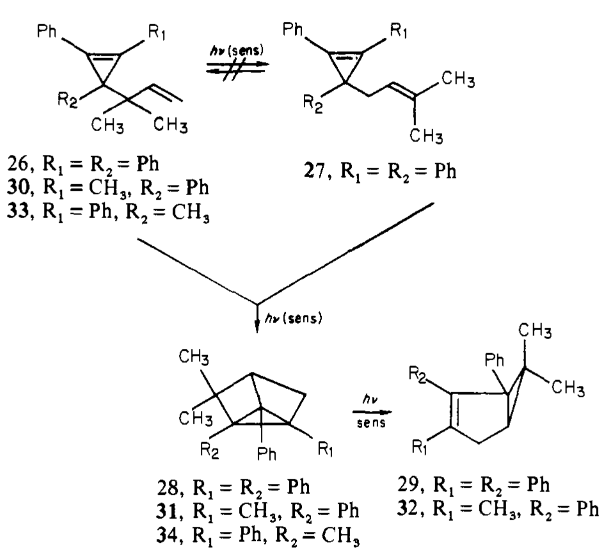


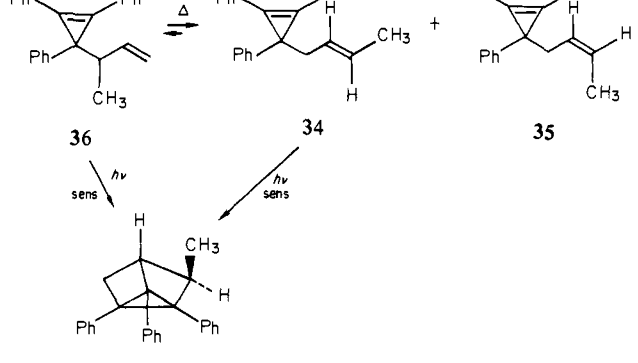
26, $R_1 = R_2 = Ph$
30, $R_1 = CH_3$, $R_2 = Ph$
33, $R_1 = Ph$, $R_2 = CH_3$

27, $R_1 = R_2 = Ph$

28, $R_1 = R_2 = Ph$
31, $R_1 = CH_3$, $R_2 = Ph$
34, $R_1 = Ph$, $R_2 = CH_3$

29, $R_1 = R_2 = Ph$
32, $R_1 = CH_3$, $R_2 = Ph$

cycloaddition, we studied the sensitized behavior of (*E*)-**34** and (*Z*)-1-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-butene (**35**). These compounds were prepared by heating 3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-butene (**36**). Previous work from our laboratory has shown that heating a 3-(1-methylallyl)-substituted cycloproprene results in a novel Cope rearrangement, giving rise to the thermodynamically more stable 2-butenyl substituted isomer as the major product.[34] In agreement with our earlier findings, thermolysis of **36** at 175 °C for 14 h produced a mixture of **34** (55%) and **35** (22%) which could be separated by column chromatography. Extended heating of **34** and **35** did not produce any detectable quantities of **36**, thereby suggesting that the equilibrium lies far to the right.

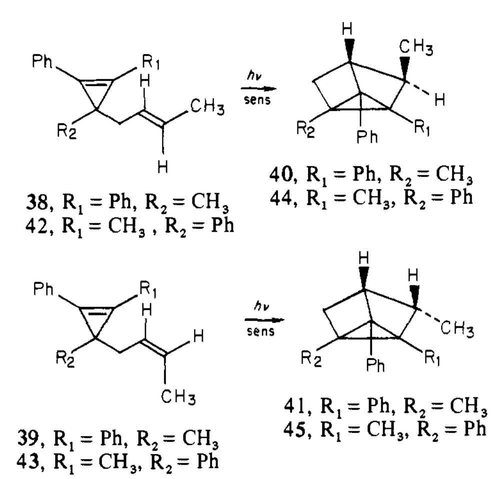


36 34 35

37

The photosensitized cycloaddition reaction of **34** afforded a cycloadduct (i.e., **37**) where complete retention of stereochemistry about the π bond has occurred. The same tricyclohexane was produced from the thioxanthone sensitized reaction of cyclopropene **36**. The structure of **37** was easily assigned on the basis of its characteristic NMR spectrum. The absence of coupling between protons H_3 and H_4 fixes the C_3-methyl group in the exo position. This is to be expected since molecular models show that the dihedral angle for this set of protons is ~90°. Unfortunately, the sensitized irradiation of the *Z*-substituted cyclopropene **35** gave rise to a complex mixture of photoproducts which prevented analysis of the stereochemical course of the cycloaddition reaction.

In order to provide additional evidence for the stereochemical course of the cycloaddition reaction, we examined the sensitized behavior of the closely related (*E*)-**38** and (*Z*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**39**) system. The sensitized irradiation of **38** produced tricyclohexane **40** as the exclusive cycloadduct. Subjection of **39** to similar photolysis conditions gave the endo-substituted tricyclohexane **41** as the sole photoproduct.



38, $R_1 = Ph$, $R_2 = CH_3$
42, $R_1 = CH_3$, $R_2 = Ph$

40, $R_1 = Ph$, $R_2 = CH_3$
44, $R_1 = CH_3$, $R_2 = Ph$

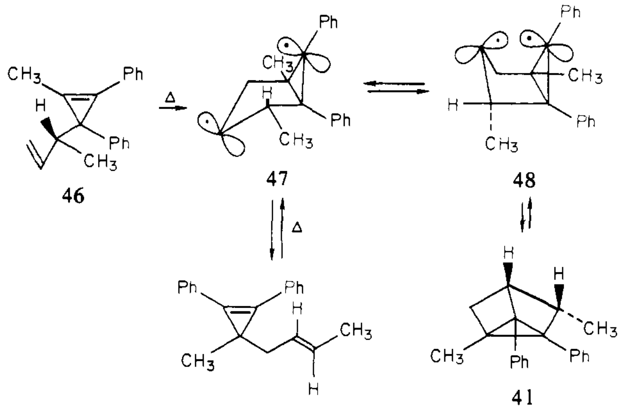
39, $R_1 = Ph$, $R_2 = CH_3$
43, $R_1 = CH_3$, $R_2 = Ph$

41, $R_1 = Ph$, $R_2 = CH_3$
45, $R_1 = CH_3$, $R_2 = Ph$

Spin decoupling experiments indicate that protons H_3 and H_4 in the endo-substituted isomer are coupled by 4.5 Hz.[35] Similar results were found in the triplet-sensitized irradiation of (*E*)-**42** and (*Z*)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**43**). With these compounds, the sensitized cycloaddition was found to be highly stereospecific producing *exo*-(**44**) and *endo*-(**45**) tricyclohexanes, respectively. The most significant finding here is that the *sensitized intramolecular [2 + 2] cycloaddition proceeds with complete retention of stereochemistry about the π bond.*

Discussion

The thermal [2 + 2] cycloaddition of untwisted ethylenes to form cyclobutanes is a rare phenomenon.[36-41] The constraints imposed upon such reactions by orbital symmetry factors[42] make them of more than usual mechanistic interest. We have previously reported that the thermolysis of 3-allyl-substituted cyclopropenes results in a novel intramolecular [2 + 2] cycloaddition.[34] For example, heating a sample of cyclopropene **46** results in both a Cope rearrangement and tricyclo[2.2.0.0^{2,6}]hexane formation.[34] The mechanism which has been proposed to account for the stereochemical results encountered on thermolysis of **46** involves the initial formation of a biradical intermediate (**47**) in a conformation which is analogous to the chair conformation of cyclohexane. Subsequent fragmentation of this species affords the Cope rearrangement product **38**. Ring inversion of the initially formed chair intermediate **47** generates the boat biradical **48** which



46 47 48

38 41

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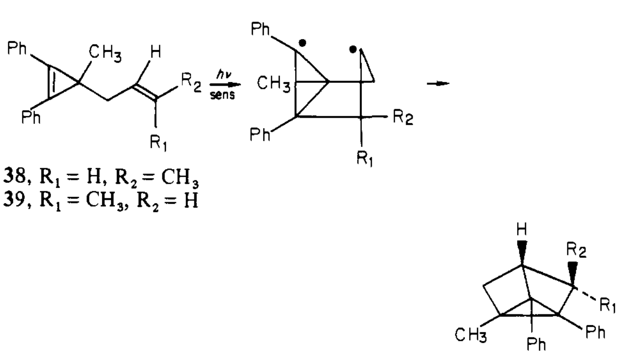
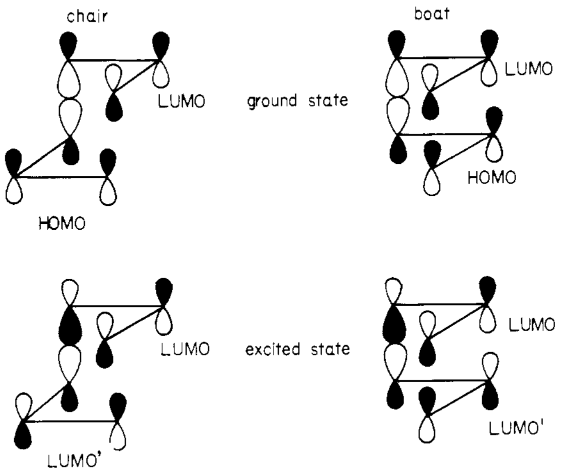


38, $R_1 = H$, $R_2 = CH_3$
39, $R_1 = CH_3$, $R_2 = H$

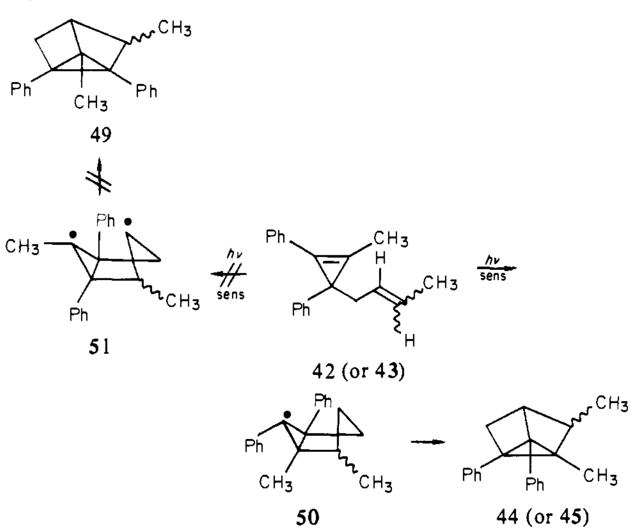
40, $R_1 = H$, $R_2 = CH_3$
41 $R_1 = CH_3$, $R_2 = H$

cyclizes to the tricyclo[2.2.0.0^{2,6}]hexane ring system. Tricyclohexane **41** was also formed from the thermolysis of cyclopropene **38** via intermediates **47** and **48**. The overall inversion of stereochemistry in the thermal [2 + 2] cycloaddition reaction of **38** can be attributed to the fact the thermal reaction proceeds through a four-center, chairlike conformation. The ring flip of the initially formed chair intermediate **47** to the boat diradical **48** is the major factor responsible for the overall inversion of stereochemistry of the thermal cycloaddition.

In marked contrast to the thermal results, we have found that the triplet-sensitized cycloaddition reaction of allyl-substituted cyclopropenes produces tricyclo[2.2.0.0^{2,6}]hexanes in which retention of stereochemistry has occurred. Our data indicate that there is a major difference in the stereochemical course of the thermal and triplet-induced [2 + 2] cycloaddition reactions of these allyl-substituted cyclopropenes. Reasonable mechanistic options for the sensitized cycloaddition reaction include a concerted pathway[43] or a stepwise process involving a diradical intermediate. It is tempting to suggest that the triplet-induced reaction proceeds through a boatlike conformation. Overlap of the frontier orbitals involved in the [2 + 2] cycloaddition reaction should favor the boatlike arrangement in the excited state and disfavor it in the ground state. It is well-known that the chairlike transition state is preferred to a boatlike one for ground-state Cope rearrangements.[44] This has been attributed to the antibonding interaction which exists between the lobes on the C_2 and C_5 atoms in the boatlike orientation.[45] In the excited state, however, this secondary interaction is favorable and will therefore stabilize the boatlike arrangement.



An additional point worth mentioning concerns the regiochemistry associated with the [2 + 2]-sensitized cycloaddition of an unsymmetrically substituted cyclopropene. For example, the triplet-sensitized irradiation of cyclopropene **42** (or **43**) gave rise to the 5,6-dimethyl-substituted tricyclohexane ring (i.e., **44** or **45**). No signs of the isomeric 1,3-dimethyl-substituted isomer **49** could be detected in the crude photolysate. The regioselectivity exhibited by cyclopropene **42** (or **43**) can be readily rationalized in terms of the formation of diradical intermediate **50**. Alternatively, if the system stays on the triplet surface until cycloaddition is complete and the triplet product then collapses to its ground-state singlet, the pathway to the observed product **44** will be a [$_{\pi}2_s$ + $_{\pi}2_s$] "allowed" excited-state reaction. Even if collapse to the ground state occurs along the cycloaddition pathway, the [$_{\pi}2_s$ + $_{\pi}2_s$] path will still be substantially favored over the other possible mode of cycloaddition (i.e., [$_{\pi}2_s$ + $_{\pi}2_a$]).[43,46] Of the two possible orientations, **42a** and **42b** (which is rotated by 120° for clarity), the former would lead to a more stable transition state for concerted cycloaddition than the latter, in which there would be steric repulsion between the methyl and phenyl substituents. Thus, the fact that tricyclohexane **44** is formed rather than the alternative isomer **49** is also understandable in terms of a concerted cycloaddition.



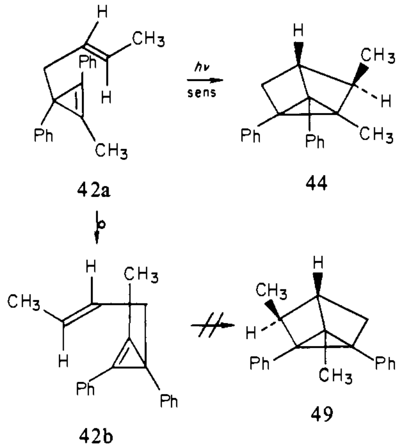
49

51

42 (or **43**)

50

44 (or **45**)



42a

44

42b

49

The mechanism by which the substituted tricyclo[2.2.0.0^{2,6}]hexanes undergo rearrangement to bicyclo[3.1.0]hex-2-enes also requires some comment. A reasonable route to account for the formation of the bicyclo[3.1.0]hexene system involves a sequence consisting of sensitized ring opening of the tricyclohexane to a bicyclo[2.1.1]hexane diradical **52** which subsequently undergoes a 1,2-methylene shift. Fragmentation of the tricyclohexane ring to the alternate bicyclo[2.2.0]hexane diradical **53** should have produced bicyclohexanes **54** or **55**. Neither of these compounds were observed with any of the tricyclohexanes studied.

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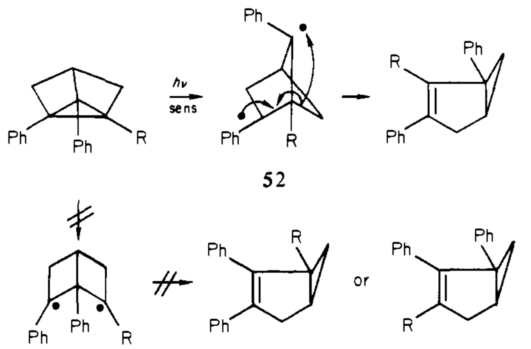
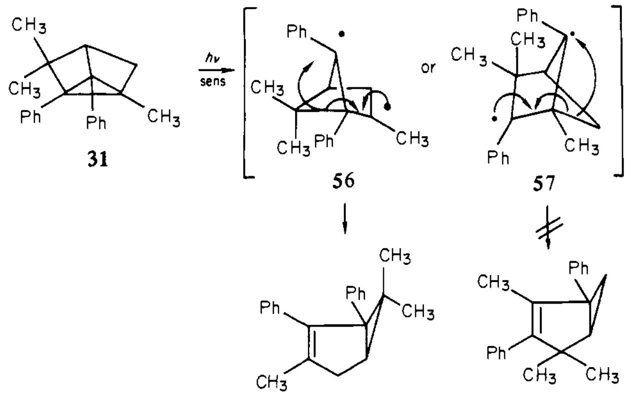
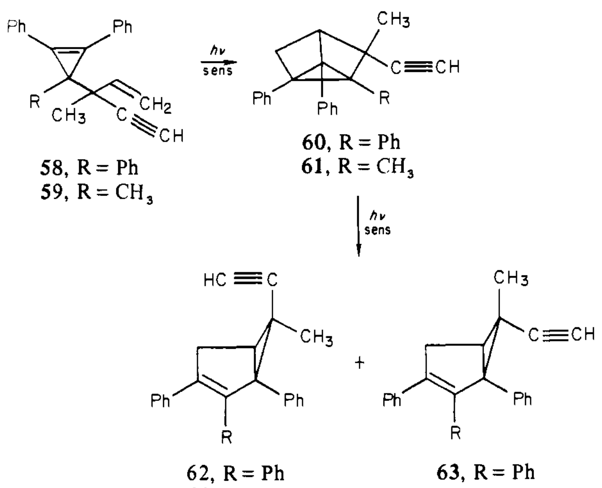


It is also of interest to note that the 3,3,6-trimethyl-substituted tricyclohexane **31** produced the 3,6,6-trimethyl-substituted bicyclohexene **32** as the exclusive photoproduct. According to the mechanism outlined above, two possible diradicals could be formed. The preferential formation of bicyclohexene **32** is probably a result of the development of radical character on the tertiary carbon in the transition state for the C–C bond shift. Migration of the methylene bond in **57** would have resulted in a less stable primary radical on the migrating carbon. It seems that the stability of the radical center on the migrating carbon is more important than the stability of the initial ring-opened intermediate.

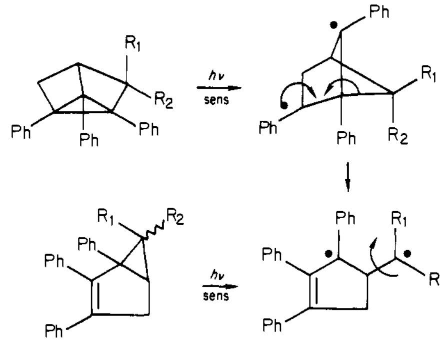


In order to probe the stereochemical features of the above rearrangement, we examined the sensitized irradiation of a tricyclohexane bearing two different substituent groups on the 3-position of the ring. This was accomplished by studying the triplet-sensitized irradiation of tricyclohexanes **60** and **61**. These compounds were formed in high yield by irradiating cyclopropenes **58** and **59** in the presence of thioxanthone. A similar rearrangement was also found to occur with tricyclohexane **61**. The stereochemical assignments for the exo and endo bicyclohexenes were made on the basis of their characteristic NMR spectra. The location of the endo-methyl group of compound **63** at higher chemical field (δ 1.18) relative to the exo isomer **62** (δ 1.50) is consistent with the expected anisotropic shielding effect of the bicyclohexene ring.[47,48] Our results with tricyclohexane **60** indicates that the sensitized rearrangement of the tricyclohexane ring proceeds in a nonstereospecific manner. The stereorandomness associated with the bond migration step can be accounted for in terms of a diradical intermediate (i.e., **65**) which is long enough lived to undergo rotation about the single bond prior to radical coupling.



62, R = Ph
64, R = CH_3

63, R = Ph



65

Further studies on the scope of the intramolecular [2 + 2] cycloaddition reaction of cyclopropene derivatives are in progress and will be reported in due course.

Experimental Section[49]

Triplet-Sensitized Irradiation of 3-Allyl-3-methyl-1,2-diphenylcyclopropene (1). A solution containing either 100 mg of 3-allyl-3-methyl-1,2-diphenylcyclopropene (**1**)[50] or 3-allyl-1,3-diphenyl-2-methylcyclopropene (**7**)[50] and 100 mg of thioxanthone in 150 mL of benzene was irradiated under an argon atmosphere for 1 h by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. The reaction mixture was concentrated under reduced pressure, and the residue was chromatographed on a silica gel column by using hexane as the eluant. The major component isolated contained 70 mg (70%) of 6-methyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**4**).[51] A minor component was also isolated. The yield of this material increased when the irradiation of **1** or **7** was carried out for 12 h or when tricyclohexane **4** was photolyzed in the presence of thioxanthone for 10 h. Chromatography of the crude reaction mixture on a silica gel thick layer plate impregnated with a 10% silver nitrate solution gave 2-methyl-1,3-diphenylbicyclo[3.1.0]hex-2-ene (**5**) as a white crystalline solid, mp 43–44 °C, whose structure was assigned on the basis of the following spectral data: IR (KBr) 3.26, 3.32, 3.43, 3.50, 6.19, 6.67, 6.89, 7.19, 9.13, 9.66, 13.24, 14.27 μm; NMR ($CDCl_3$, 100 MHz) δ 0.77 (t, 1 H, J = 4.0 Hz), 1.48 (dd, 1 H, J = 8.0 and 4.0 Hz), 1.60–1.84 (m, 1 H), 1.70 (t, 3 H, J = 2.0 Hz), 2.76 (br d, 1 H, J = 17.5 Hz), 3.24 (br ddd, 1 H, J = 17.5, 8.0, and 2.0 Hz), 7.2–7.4 (m, 10 H); UV (95% ethanol) 261 nm (ε 14 430); m/e 246 (M^+, base) and 231. Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.58; H, 7.24.

Triplet-Sensitized Irradiation of 3-Allyl-1,3-diphenylcyclopropene (6) in Benzene. A solution containing 180 mg of **6**[50] and 90 mg thioxanthen-9-one in 150 mL of benzene was irradiated for 45 min under an argon atmosphere by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. The reaction

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(47) Dauben, W. G.; Wipke, W. T. *J. Org. Chem.* **1967**, *32*, 2976.

(48) Schneider, M.; Crawford, R. J. *Can. J. Chem.* **1970**, *48*, 628.

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

(50) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481.

(51) Padwa, A.; Blacklock, T. J.; Loza, R.; Polniaszek, R. *J. Org. Chem.* **1980**, *45*, 2181.

mixture was concentrated under reduced pressure, and the residue was chromatographed on a silica gel column by using hexane as the eluant. The first component isolated was identified as 1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**9**) on the basis of its spectral properties.[51] Irradiation of cyclopropene **6** for a period of 4 h produced a mixture of two compounds which were separated by chromatography over a 10% silver nitrate silica gel column by using a 10% ether-hexane mixtures as the eluant. The first band contained 5% of tricyclohexane **9**. The second band isolated consisted of a crystalline solid, mp 48–49 °C, whose structure was assigned as 1,3-diphenylbicyclo[3.1.0]hex-2-ene (**12**) on the basis of its characteristic spectral properties: IR (KBr) 3.30, 3.44, 3.52, 6.21, 6.68, 6.90, 7.21, 9.00, 9.28, 9.65, 10.72, 11.68, 13.23, 14.42 μm; NMR ($CDCl_3$, 100 MHz) δ 0.76 (t, 1 H, J = 4.0 Hz), 1.61 (dd, 1 H, J = 8.0 and 17.5 Hz), 3.24 (ddd, 1 H, J = 17.5, 7.0, and 2.0 Hz), 6.68 (br s, 1 H), 7.1–7.6 (m, 10 H); UV (95% ethanol) 268 and 218 nm (ϵ 16 510 and 17 480); *m/e* 232 (M^+, base), 217, 215, 203, 141, 91.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.05; H, 6.89.

Triplet-Sensitized Irradiation of 1,2,6-Triphenyltricyclo[2.2.0.0^{2,6}]hexane (11). A solution containing 200 mg of tricyclohexane **11**[34] and 80 mg of thioxanthone in 150 mL of benzene was irradiated for 4 h. Removal of the solvent under reduced pressure followed by silica gel chromatography using hexane as the eluant gave a crystalline solid in 85% yield, mp 121–122 °C, whose structure was assigned as 1,2,3-triphenylbicyclo[3.1.0]hex-2-ene (**14**) on the basis of its spectral properties: IR (KBr) 3.29, 3.32, 3.37, 3.46, 3.55, 6.29, 6.39, 6.73, 6.97, 8.70, 9.03, 9.30, 9.80, 10.00, 11.00, 12.99, 13.51, 14.60 μm; NMR ($CDCl_3$, 100 MHz) δ 0.88 (t, 1 H, J = 4.0 Hz), 1.58–1.96 (m, 2 H), 2.75 (d, 1 H, J = 17 Hz), 3.59 (dd, 1 H, J = 17 and 6.0 Hz), 7.0–7.3 (m, 15 H); UV (95% ethanol) 287 and 226 nm (ϵ 10 200 and 21 190); *m/e* 308 (M^+, base), 217, 215, 115, 91.

Anal. Calcd for $C_{24}H_{20}$: C, 93.43; H, 6.54. Found: C, 93.39; H, 6.56.

Silver(I)-Induced Rearrangement of 1,2,6-Triphenyltricyclo[2.2.0.0^{2,6}]hexane (11) in Benzene. A solution containing 120 mg of 1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (**11**)[34] and 200 mg of silver(I) perchlorate in 20 mL of benzene was heated at 40 °C for 1 h in the dark. The mixture was diluted with ether, and the organic layer was washed with a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which was chromatographed on a 1.5 × 65 cm silica gel column by using a 10% ether–hexane mixture as the eluant. The first component isolated contained 70 mg (58%) of a colorless oil which solidified on standing. Recrystallization from ethanol gave a white crystalline solid, mp 85–86 °C, whose structure was assigned as 4-benzylidene-1,2-diphenylcyclopent-1-ene (**15**) on the basis of its spectra data: NMR ($CDCl_3$, 100 MHz) δ 3.84–3.98 (m, 4 H), 6.51 (*t*, J = 2 Hz, 1 H), 7.02–7.60 (*m*, 15 H); IR (KBr) 3.43, 6.24, 6.74, 7.95, 9.36, 10.98, 11.69, 13.1, 14.5 μm; UV (ethanol) 293, 253, 242 nm (ϵ 8270, 30 600, 27 800); *m/e* 308 (M^+) 307, 306 (base), 229, 228, 219, 217, 215, 91, 77.

Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.44; H, 6.53.

The second component isolated contained 49 mg (39%) of a colorless oil which solidified on standing. Recrystallization from ethanol gave a white crystalline solid, mp 120–121 °C, which was identified as 4-benzoyl-1,2-diphenylcyclopent-1-ene (**16**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 3.10–3.22 (m, 4 H), 4.28 (quint, J = 8 Hz, 1 H), 7.20 (brs, 10 H), 7.44–7.60 (m, 3 H), 8.00–8.14 (m, 2 H); IR (KBr) 3.30, 3.43, 5.95, 6.24, 6.91, 7.37, 7.86, 8.17, 9.85, 11.09, 13.04, 14.28 μm; UV (95% ethanol) 271 and 236 nm (ϵ 11 700 and 24 000); *m/e* 324 (M^+), 309, 306, 220, 219 (base), 105, 91, 77.

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.90; H, 6.28.

Treatment of tricyclohexane **11** with silver ion in the presence of methanol gave 4-benzoyl-1,2-diphenylcyclopent-1-ene (**16**) in over 90% yield.

Further support for the structure of 4-benzylidene-1,2-diphenylcyclopent-1-ene (**15**) was obtained by comparison with an independently synthesized sample. It should be pointed out tricyclohexanes **10** and **11** do not rearrange when subjected to silica gel thick layer chromatography.

Preparation of 4-Benzylidene-1,2-diphenylcyclopent-1-ene (**15**). To a solution containing 1.0 g of 3,4-diphenylcyclopent-3-en-1-one[52] (**19**) in 100 mL of anhydrous ether was added 20 mL of a 0.5 M solution of benzylmagnesium chloride in ether. The reaction mixture was stirred for an additional 4 h and then quenched 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 50 mL of anhydrous benzene which contained 3 mL of pyridine. To this solution was added a solution containing 1.0 g of thionyl chloride in 25 mL of benzene. The mixture was stirred at room temperature for 30 min and then poured into ice water. The organic layer was washed with water, a 10% aqueous hydrochloric acid solution, water, and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a yellow oil which was chromatographed on a 1.5 × 65 cm silica gel column by using hexane as the eluant. The first component isolated contained 140 mg (11%) of a colorless oil which solidified when treated with cold ethanol. Recrystallization from ethanol afforded 4-benzylidene-1,2-diphenylcyclopent-1-ene (**15**) which was in every detail identical with the previously isolated material. The second component isolated contained 420 mg (32%) of a colorless oil identified as 4-benzyl-1,2-diphenyl-1,3-cyclopentadiene (**20**) on the basis of its characteristics spectral properties: NMR ($CDCl_3$, 100 MHz) δ 3.36 (s, 2 H), 3.76 (br s, 2 H), 6.27 (br s, 1 H), 7.03–7.16 (m, 15 H); UV (95% ethanol) 320 and 235 nm (ϵ 9600 and 20 500); *m/e* 308 (M^+), 306, 218, 217 (base), 215, 181, 91. These data were in good agreement with the spectral properties published by Rio and Charifi for 4-methyl-1,2-diphenyl-1,3-cyclopentadiene.[53] This oil solidified on treatment with cold ethanol. Recrystallization from ethanol afforded a white crystalline solid, mp 169–170 °C, whose spectral properties differed greatly from those of the oil. The solid was identified as 3-benzylidene-1,5-diphenylcyclopent-1-ene (**21**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 2.83 (br d, J = 16 Hz, 1 H), 4.49 (br d, J = 8 Hz, 1 H), 6.47 (br s, 1 H), 6.91 (br s, 1 H), 7.00–7.34 (m, 15 H); IR (KBr) 3.37, 6.74, 6.97, 9.30, 11.10, 13.00, 13.23, 14.25, 14.66 μm; UV (95% ethanol) 346, 333, 235 nm (ϵ 37 400, 42 000, 10 600); *m/e* 309, 308 (M^+, base), 218 and 217, 91.

Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.40; H, 6.58.

Silver(I)-Induced Rearrangement of 6-Methyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (10) in Benzene. A solution containing 100 mg of 6-methyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**10**)[34] and 210 mg of silver(I) perchlorate in 10 mL of benzene was stirred under a nitrogen atmosphere for 5 h in the dark. The reaction mixture was diluted with ether and the organic layer was washed with a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which was chromatographed on a preparative thick layer plate by using a 5% acetone–hexane mixture as the eluant. The first component isolated contained 46 mg (46%) of a light yellow oil which was identified as 4-benzylidene-2-methyl-1-phenylcyclopent-1-ene (**17**) on the basis of its characteristic NMR spectrum ($CDCl_3$, 100 MHz): δ 1.87 (br s, 3 H), 3.44 (br s, 2 H), 3.67 (br s, 2 H), 6.37 (br s, 1 H), 6.96–7.44 (m, 10 H).

The second component isolated contained 35 mg (33%) of a colorless oil identified as 4-benzoyl-1-methyl-2-phenylcyclopent-1-ene (**18**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.80 (br s, 3 H), 2.72–3.20 (m, 4 H), 4.05 (tt, J = 9.5 and 7.5 Hz, 1 H), 7.06–7.29 (m, 5 H), 7.31–7.48 (m, 3 H), 7.84–8.00 (m, 2 H); IR (neat) 3.34, 3.48, 3.57, 5.95, 6.32, 6.66, 6.73, 6.95, 7.44, 8.19, 9.91, 13.09, 14.37 μm; UV (95% ethanol) 245 nm (ϵ 22 600); *m/e* 262 (M^+), 158, 157 (base), 156, 105, 77.

Anal. Calcd for $C_{19}H_{18}O$: P^+, 262.13567. Found: P^+, 262.13444.

Treatment of a sample of tricyclohexane **10** with silver ion in methanol produced 4-benzoyl-1-methyl-2-phenylcyclopent-1-ene (**18**) as the exclusive product which could be isolated in 93% yield.

Triplet-Sensitized Irradiation of 2-Methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-propene (23) in Benzene. A solution containing 269 mg of 2-methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-propene (**23**)[34] and 100 mg of thioxanthen-9-one in 250 mL of benzene was irradiated under an argon atmosphere for 1 h by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. Concentration of the solvent to ca. 5 mL followed by chromatography of the residue on a 2.5 × 4 cm silica gel column using a 10% hexane–benzene mixture gave a light yellow oil which solidified on standing. Recrystallization from ethanol afforded 250 mg (93%) of a white crystalline solid, mp 70–71 °C, identified as 4-methyl-1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (**24**) on the basis of its characteristic spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.19 (s, 3 H), 2.57 (d, J = 8 Hz, 2 H), 6.8–7.6 (m, 15 H): IR (KBr) 3.21, 3.45, 3.53, 6.24, 6.69, 6.95, 7.24, 8.38, 8.65, 9.23, 9.32, 9.70, 9.80, 12.6, 12.9, 13.1, 13.2, 14.4 μ; m/e 322 (M^+), 321, 306, 267, 266 (base), 264, 251, 232, 214, 105, 91.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12, H, 6.88. Found: C, 93.01; H, 6.92.

Silver(I)-Induced Rearrangement of 4-Methyl-1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (24) in Methanol. A solution containing 130 mg of 4-methyl-1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (**24**) and 210 mg of

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(52) Corey, E. J.; Uda, H. *J. Am. Chem. Soc.* **1963**, *85*, 1788.

(53) Rio, G.; Charifi, M. *Bull. Soc. Chim. Fr.* **1970**, 3585.

silver(I) perchlorate in 20 mL of methanol was stirred at room temperature for 12 h in the dark. The mixture was extracted with ether, and the ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the ether under reduced pressure left a yellow oil which solidified on standing. Recrystallization from ethanol afforded 117 mg (86%) of white needles, mp 97–98 °C, whose structure was assigned as 4-benzoyl-4-methyl-1,2-diphenylcyclopent-1-ene (**25**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.60 (s, 3 H), 2.87 (br d, J = 16 Hz, 2 H), 3.73 (br d, J = 16 Hz, 2 H), 7.04–7.31 (m, 13 H), 7.88–8.06 (m, 2 H); IR (KBr) 3.46, 5.98, 6.24, 6.95, 7.86, 8.07, 10.36, 12.45, 12.95, 14.00, 14.37 μm; UV (95% ethanol) 269 and 229 nm (ϵ 11 000 and 22 800); *m/e* 338 (M^+), 323, 245, 233, 219, 205, 180, 179, 178, 165, 129, 115, 105, 91 (base), 83, 77.

Anal. Calcd for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 88.81; H, 6.28.

Under identical experimental conditions using benzene as the solvent, only unreacted starting material was recovered.

Triplet-Sensitized Irradiation of 3-Methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-butene (26) in Benzene. A mixture containing 100 mg of 3-methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-butene (**26**)[34] and 100 mg of thioxanthen-9-one in 150 mL of benzene was irradiated under an argon atmosphere for 1 h by using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium glass filter sleeve. The solution was concentrated to about 20 mL and the thioxanthen-9-one was removed on a 2 × 3 cm column of silica gel eluting with 200 mL of a 20% benzene in hexane mixture. Removal of the solvent under reduced pressure left 90 mg of colorless oil which was chromatographed on a 1.5 × 60 cm column of silica gel by using hexane as the eluant. The first component isolated contained 30 mg (30%) of a solid which was identified as 3,3-dimethyl-1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (**28**), mp 69–70 °C, on the basis of its spectral properties: IR (KBr) 3.31, 3.40, 3.49, 6.24, 6.68, 6.90, 7.21, 7.32, 9.26, 9.68, 12.95, 13.16, 14.35 μm; NMR ($CDCl_3$, 100 MHz) δ 1.04 (s, 3 H), 1.32 (s, 3 H), 2.34 (d, 1 H, J = 4.0 Hz), 2.59 (d, 1 H, J = 6.0 Hz), 2.88 (dd, 1 H, J = 6.0 and 4.0 Hz), 6.6–7.2 (m, 15 H); *m/e* 336 (M^+), 321 (base), 294, 105.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.71; H, 7.21.

The second fraction isolated contained 60 mg (60%) of a white solid which was identified as 6,6-dimethyl-1,2,3-triphenylbicyclo[3.1.0]hexane (**29**), mp 83–84 °C, on the basis of its spectral properties: IR (KBr) 3.31, 3.48, 6.24, 6.71, 6.95, 7.23, 9.31, 9.68, 12.39, 13.20, 13.40, 14.40 μm; NMR ($CDCl_3$, 100 MHz) δ 0.99 (s, 3 H), 1.31 (s, 3 H), 1.67 (d, 1 H, J = 8.0 Hz), 2.71 (d, 1 H, J = 17.0 Hz), 3.19 (dd, 1 H, J = 17 and 8.0 Hz), 6.70–7.20 (m, 15 H); UV (absolute ethanol) 280 nm (ϵ 12 190); *m/e* 336 (M^+, base), 321, 294.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.68; H, 7.20.

The same two products were also formed from the triplet-sensitized irradiation of 2-methyl-4-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-butene (**27**)[34] in benzene. Control experiments demonstrated that tricyclohexane **28** was smoothly converted to bicyclohexene **29** on triplet sensitization in benzene.

Sensitized Irradiation of 3-Methyl-3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (30). A solution containing 250 mg of cyclopropene (**30**)[51] and 100 mg of thioxanthen-9-one in 250 mL of anhydrous benzene was irradiated for 10 min by using a 450-W Hanovia lamp equipped with a Uranium filter sleeve. The benzene solution was concentrated to ca. 5 mL and chromatographed on a 1.5 × 15 cm column of silica gel by using hexane as the eluant. Removal of the solvent left behind a yellow oil which was chromatographed on silica gel (1.5 × 100 cm) column with hexane as the eluant. The major component isolated contained 175 mg (70%) of a colorless oil which was identified as 3,3,6-trimethyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**31**) on the basis of its characteristic spectral data: NMR ($CDCl_3$, 100 MHz) δ 0.95 (s, 3 H), 1.21 (s, 6 H), 2.22 (d, J = 8 Hz, 1 H), 2.37 (dd, J = 8 and 4 Hz, 1 H), 2.47 (d, J = 4 Hz, 1 H), 6.72–7.32 (*m*, 10 H); IR (neat) 3.40, 6.24, 6.66, 6.92, 12.16, 13.08, 14.33 μm; UV (95% ethanol) 246 nm (ϵ 14 600); *m/e* 274 (M^+), 259 (base), 244, 229, 215, 115, 91.

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.74; H, 8.08.

Sensitized Irradiation of 3,3,6-Trimethyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane. A solution containing 250 mg of tricyclohexane **31** and 100 mg of thioxanthen-9-one in 250 mL of anhydrous benzene was irradiated for 45 min with a 450-W Hanovia lamp equipped with a Uranium filter sleeve. The benzene solution was concentrated to ca. 5 mL and chromatographed on a 1.5 × 15 cm column of silica gel by using hexane as the eluant. Removal of the solvent under reduced pressure left behind a yellow oil which was chromatographed on silica gel (1.5 × 100 cm column) by using hexane as the eluant. The major component isolated contained 170 mg (68%) of a colorless oil which was identified as 3,6,6-trimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**32**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 0.97 (s, 3 H), 1.17 (s, 3 H), 1.49 (d, J = 7 Hz, 1 H), 1.63 (s, 3 H), 2.22 (d, J = 18 Hz, 1 H), 2.92 (dd, J = 18 and 8 Hz, 1 H), 6.88–7.26 (m, 10 H); IR (neat) 3.32, 3.46, 6.24, 6.69, 6.92, 9.27, 13.15, 14.30 μm; UV (95% ethanol) 250 nm (ϵ 6080); *m/e* 274 (M^+) and 259 (base).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.92; H, 8.04.

Sensitized Irradiation of 3-Methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (33). A solution containing 250 mg of cyclopropene **33**[51] and 150 mg of thioxanthen-9-one in 250 mL of anhydrous benzene was irradiated for 30 min by using a 450-W Hanovia lamp equipped with a Uranium filter sleeve. The benzene solution was concentrated to ca. 5 mL and chromatographed on a 1.5 × 15 cm column of silica gel by using hexane as the eluant. Removal of the solvent left behind a yellow oil which was chromatographed on silica gel (1.5 × 100 cm column) by using hexane as the eluant. The major component isolated contained 170 mg (68%) of a colorless oil which solidified on standing. Recrystallization from methanol gave a white crystalline material identified as 2,3,3-trimethyl-1,6-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**34**) on the basis of its physical and spectral properties: mp 31–32 °C; NMR ($CDCl_3$, 100 MHz) δ 1.02 (s, 3 H), 1.20 (s, 3 H), 1.31 (s, 3 H), 2.35 (d, J = 8 Hz, 1 H), 2.45 (d, J = 4 Hz, 1 H), 2.67 (*dd*, J = 8 and 4 Hz, 1 H), 6.87–7.36 (m, 10 H); IR (neat) 3.41, 6.24, 6.68, 6.93, 7.24, 7.33, 8.13, 9.30, 13.16, 14.26; UV (95% ethanol) 245 nm (ϵ 13 300); *m/e* 274 (M^+), 260, 259 (base), 244, 232, 231, 229, 215, 91.

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.96; H, 8.01.

Preparation and Triplet-Sensitized Irradiation of 3-(1,2,3-Triphenyl-2-cyclopropen-1-yl)-1-butene (36). To a stirred suspension containing 3.0 g of 1,2,3-triphenylcyclopropenylium perchlorate in 250 mL of tetrahydrofuran was added 25 mL of a 0.5 M crotylmagnesium bromide solution in ether. The reaction was stirred for 3 h, and then a saturated ammonium chloride solution was added and the reaction mixture was stirred until both phases became clear. The organic phase was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was chromatographed on a silica gel column by using a 15% benzene–hexane mixture as the eluant. The major component isolated contained 2.0 g (70%) of a crystalline solid, mp 80–90 °C, whose structure was assigned as 3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-butene (**36**) on the basis of its spectra properties: IR (KBr) 3.30, 3.40, 3.50, 5.50, 6.24, 6.73, 6.95, 9.32, 9.74, 9.95, 10.05, 10.91, 12.77, 13.30, 13.55, 14.65 μm; NMR ($CDCl_3$, 100 MHz) δ 1.03 (d, 3 H, J = 7.0 Hz), 3.62 (qd, 1 H, J = 7.0 and 7.0 Hz), 4.88 (d, 1 H, J = 8.0 Hz), 5.00 (d, 1 H, J = 15.0 Hz), 5.90 (ddd, 1 H, J = 15.0 and 8.0 Hz), 7.0–7.8 (*m*, 15 H); UV (95% ethanol) 335, 318, 228 nm (ϵ 16 400, 20 100, 20 800); *m/e* 322 (M^+), 320, 268, 267 (base), 265, 231, 215.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.98; H, 6.83.

A solution containing 100 mg of 3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-butene (**36**) and 100 mg of thioxanthen-9-one in 150 mL of benzene was irradiated under an argon atmosphere for 45 min by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. The solution was concentrated to about 20 mL, and the thioxanthen-9-one was removed by chromatography on a 2 × 3 cm column of neutral alumina (80–200 mesh) eluting with 200 mL of a 20% benzene–hexane mixture. Removal of the solvent under reduced pressure gave 89 mg (89%) of a crystalline solid, mp 91–92 °C, whose structure was assigned as *exo*-3-methyl-1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (**37**) on the basis of its spectral properties: IR (KBr) 3.32, 3.50, 6.25, 6.70, 6.95, 7.25, 9.28, 9.70, 11.02, 13.00, 13.12, 13.37, 13.69, 14.4 μm; NMR ($CDCl_3$, 100 MHz) δ 1.35 (d, 3 H, J = 6.0 Hz), 2.48 (d, 1 H, J = 8.0 Hz), 2.50 (d, 1 H, J = 4.0 Hz), 2.79 (q, 1 H, J = 6.0 Hz), 3.04 (dd, J = 8.0 and 4.0 Hz), 6.8–7.4 (m, 15 H); *m/e* 322 (M^+), 321 (base), 319, 266, 230.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.82; H, 6.91.

Preparation of (*E*)-34 and (*Z*)-1-(1,2,3-Triphenyl-2-cyclopropen-1-yl)-2-butene (35). A solution containing 187 mg of 3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-butene (**36**) in benzene was heated at 175 °C for 14 h in a sealed tube. Removal of the solvent left a yellow oil which was chromatographed on a thick layer plate by using a 10% ether–hexane mixture as the eluant. The fastest moving band consisted of (*E*)-1-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-butene (**34**) (55%) as a crystalline solid: mp 61–62 °C; IR (KBr) 3.33, 3.45, 3.52, 5.51, 6.24, 6.73, 6.94, 7.28, 9.31, 10.33, 13.25, 14.50 μm; NMR ($CDCl_3$, 100 MHz) δ 1.52 (d, 3 H, J = 6.2 Hz), 3.03 (d, 2 H, J = 5.2 Hz), 5.36–5.59 (m, 2 H), 7.05–7.75 (m, 15 H); UV (95% ethanol) 333, 317, 228 nm (ϵ 21 890, 26 260, 28 000); *m/e* 322 (M^+), 268, 267 (base), 265.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.93; H, 7.00.

The slower moving band contained 42 mg (22%) of (*Z*)-1-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-butene (**35**) as a white crystalline solid: mp 65–66 °C; IR (KBr) 3.27, 3.40, 5.48, 6.24, 6.70, 6.92, 9.32, 10.95, 13.20, 14.50 µm; NMR ($CDCl_3$, 100 MHz) δ 1.50 (d, 3 H, *J* = 6.0 Hz), 3.09 (d, 3 H, *J* = 5.5 Hz), 5.30–5.55 (m, 2 H), 7.05–7.80 (m, 15 H); UV (95% ethanol) 333, 317, 228 nm (ε 22 100, 26 400, 28 000); *m/e* 322 (M^+), 268, 267 (base), 265.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.76; H, 6.88.

Triplet-Sensitized Irradition of (*E*)-1-(1,2,3-Triphenyl-2-cyclopropen-1-yl)-2-butene (34) in Benzene. A solution containing 100 mg of (*E*)-1-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-butene (**34**) and 100 mg of thioxanthen-9-one in 150 mL of anhydrous benzene was irradiated for 45 min under an argon atmosphere by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. The reaction mixture was concentrated to a volume of approximately 10 mL and chromatographed through a 2.5 × 5 cm column of silica gel eluting with 200 mL of hexane. Removal of the solvent under reduced pressure afforded 90 mg (90%) of a crystalline solid which was identified as *exo*-3-methyl-1,2,6-triphenyltricyclo$[2.2.0.0^{2,6}]$hexane (**37**) by comparison with an authentic sample.[34]

The sensitized irradiation of the corresponding *Z* isomer **35** failed to afford any characterizable materials.

Triplet-Sensitized Irradiation of *E*-38 and (*Z*)-1-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (39) in Benzene. A solution containing 100 mg of (*E*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**38**)[34] and 80 mg of thioxanthen-9-one in 150 mL of anhydrous benzene was irradiated under an argon atmosphere for 1 h by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. The reaction mixture was concentrated under reduced pressure to a volume of approximately 5 mL and chromatographed through a 2.5 × 5 cm column of silica gel eluting with 200 mL of hexane. Removal of the solvent under reduced pressure left 75 mg (75%) of a colorless oil which was identified as *exo*-3,6-dimethyl-1,2-diphenyltricyclo$[2.2.0.0^{2,6}]$hexane (**40**) on the basis of its characteristic spectral data.[34]

The sensitized irradiation of the corresponding *Z* isomer **39**[34] was carried out under identical conditions and was found to give *endo*-3,6-dimethyl-1,2-diphenyltricyclo$[2.2.0.0^{2,6}]$hexane (**41**) as the exclusive photoproduct.[34]

Triplet-Sensitized Irradiation of (*E*)-42 and (*Z*)-1-(2-Methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (43) in Benzene. A solution containing 117 mg of (*E*)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**42**)[34] and 70 mg of thioxanthen-9-one in 150 mL of anhydrous benzene was irradiated under an argon atmosphere for 17 min by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. The reaction mixture was concentrated under reduced pressure to a volume of approximately 5 mL and chromatographed through a 2.5 × 5 cm column of silica gel eluting with 200 mL of hexane. Removal of the solvent under reduced pressure left 89 mg (76%) of a colorless oil which was identified as *exo*-5,6-dimethyl-1,2-diphenyltricyclo$[2.2.0.0^{2,6}]$hexane (**44**) on the basis of its characteristic spectral data.[34]

The sensitized irradiation of the corresponding *Z* isomer **43**[34] was also carried out under identical experimental conditions and was found to give *endo*-5,6-dimethyl-1,2-diphenyltricyclo$[2.2.0.0^{2,6}]$hexane (**45**) as the exclusive photoproduct.[34]

Preparation of 3-Methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-4-penten-1-yne (59). To a stirred suspension containing 3.9 g of diphenylmethylcyclopropenium perchlorate in 150 mL of ether at −78 °C was added the Grignard reagent derived by treating 8.5 g of magnesium turnings with 7.0 g of 5-chloro-3-methyl-3-penten-1-yne in 150 mL of ether. The reaction mixture was stirred at 25 °C for 12 h and was then quenched by the addition of an ice-cold saturated solution of ammonium chloride. The aqueous layer was extracted with ether, and the combined ether layer was dried over sodium sulfate. Removal of the solvent left a yellow oil which was chromatographed on a silica gel column by using hexane as the eluant. The major component isolated from the column was a clear oil whose structure was assigned as 3-methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-4-penten-1-yne (**59**) on the basis of its spectral properties: IR (neat) 3.0, 3.30, 5.50, 6.00, 6.20, 6.60, 6.90, 7.30, 9.00, 9.70, 10.05, 10.80, 13.10, 14.50 µm; NMR ($CDCl_3$, 100 MHz) δ 1.10 (s, 3 H), 1.60 (s, 3 H), 2.50 (s, 1 H), 5.20 (d, 1 H, *J* = 10.0 Hz), 5.50 (d, 1 H, *J* = 19.0 Hz), 5.90 (dd, 1 H, *J* = 19.0 and 10.0 Hz), 7.0–7.9 (m, 10 H); UV (95% ethanol) 229, 320, 338 nm (ε 21 900, 26 000, 18 900); *m/e* 284 (M^+), 283, 269, 252, 239, 207, 206 (base), 204, 203, 202.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.68; H, 7.18.

Triplet Sensitized Irradiation of 3-Methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-4-penten-1-yne (59) in Benzene. A solution containing 600 mg of **59** and 63 mg of thioanthen-9-one in 500 mL of benzene was irradiated under an Argon atmosphere for 30 min by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. Removal of the solvent under reduced pressured left a yellow oil which was subjected to silica gel column chromatography using hexane as the eluant. The major component isolated from the column contained 300 mg of a colorless oil whose structure was assigned as 1,6-diphenyl-2,3-dimethyl-3-ethynyltricyclo$[2.2.0.0^{2,6}]$hexane (**61**) on the basis of its spectral properties: IR (neat) 3.0, 3.41, 6.20, 6.70, 6.90, 7.30, 8.20, 9.30, 9.70, 10.00, 11.03, 13.15, 13.50, 14.32 µm; NMR (benzene-d_6, 100 MHz) δ 1.25 (s, 3 H), 1.50 (s, 3 H), 2.17 (s, 1 H), 2.48 (d, 1 H, *J* = 5.0 Hz), 2.75 (dd, 1 H, *J* = 9.0 and 5.0 Hz), 2.98 (d, 1 H, *J* = 9.0 Hz), 6.78–7.28 (m, 10 H); *m/e* 284 (M^+), 283, 271, 269 (base), 255, 254, 253, 252.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.64; H, 7.12.

Triplet-Sensitized Irradiation of 1,6-Diphenyl-2,3-dimethyl-3-ethynyltricyclo$[2.2.0.0^{2,6}]$hexane (61). A mixture containing 290 mg of **61** and 55 mg of thioxanthone in 300 mL of anhydrous benzene was irradiated under an argon atmosphere for 6.5 h by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. The solvent was removed under reduced pressure, and the resulting oil was chromatographed on a silica gel column by using hexane as the eluant. The major fraction contained 145 mg (50%) of a crystalline solid, mp 95–96 °C, whose structure was assigned as 6-*endo*-ethynyl-6-*exo*-methyl-2-methyl-1,3-diphenylbicyclo[3.1.0]hex-2-ene (**64**) on the basis of its spectral properties: IR (KBr) 3.04, 3.29, 3.41, 4.78, 6.25, 6.71, 6.92, 7.22, 9.33, 9.71, 10.20, 10.90, 12.80, 13.20, 13.40, 14.30, 14.90 µm; NMR ($CDCl_3$, 90 MHz) δ 1.19 (s, 3 H), 1.58 (t, 3 H, *J* − 1.5 Hz), 1.89 (s, 1 H), 2.11 (d, 1 H, *J* = 7.0 Hz), 2.64 (br d, 1 H, *J* = 18.0 Hz), 3.22 (ddq, 1 H, *J* = 18.0, 7.0, and 1.5 Hz), 7.18–7.54 (m, 1 H); UV (95% ethanol) 260 nm (ε 14 200); *m/e* 284 (M^+), 283, 271, 269 (base), 250.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.69; H, 7.14.

Preparation of 3-Methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-4-penten-1-yne (58). The Grignard reagent derived from 5-chloro-3-methyl-3-penten-1-yne was prepared according to the method of Gorê and co-workers.[54,55] This involved treating 3.1 g of magnesium turnings with 7.0 g of the above halide in 150 mL of ether at 0 °C. To a stirred suspension containing 7.12 g of triphenylcyclopropenium perchlorate in 150 mL of ether at −78 °C was added the above Grignard solution. The reaction mixture was stirred overnight and was then quenched by the addition of an ice-cold saturated ammonium chloride solution. The aqueous layer was extracted with ether, and the combined ether extracts were dried over sodium sulfate. The solvent was removed under reduced pressure to give 7.4 g of a yellow oil which was subjected to silica gel chromatography using hexane as the eluant. The first fraction contained 2.5 g (37%) of 3-methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-4-penten-1-yne (**58**) as a crystalline solid: mp 105–106 °C; IR (KBr) 3.10, 3.40, 5.50, 6.20, 6.70, 10.10, 10.80, 12.70, 13.10, 14.20, 14.50 µm; NMR ($CDCl_3$, 100 MHz) δ 1.30 (s, 3 H), 2.55 (s, 1 H), 5.10 (d, 1 H, *J* = 10.0 Hz), 5.50 (d, 1 H, *J* = 18.0 Hz), 6.10 (dd, 1 H, *J* = 18.0 and 10.0 Hz), 7.0–8.0 (m, 15 H); UV (95% ethanol) 230, 305, 320, 333 nm (ε 25 400, 18 700, 23 800, 19 200); *m/e* 346 (M^+), 331, 262, 253, 238, 217, 198.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.41. Found: C, 93.50; H, 6.41.

The second fraction contained 1.2 g (18%) of a clear oil whose structure was assigned as 3-methyl-5-(1,2,3-triphenyl-2-cyclopropen-1-yl)-3-penten-1-yne on the basis of its characteristics spectra properties: IR (neat) 3.01, 3.28, 3.40, 4.76, 5.50, 7.98, 6.25, 6.68, 6.90, 7.25, 9.31, 9.74, 10.96, 13.26, 14.56 µm; NMR ($CDCl_3$, 100 MHz) δ 1.64 (s, 3 H), 2.61 (s, 1 H), 3.11 (d, 2 H, *J* = 9.0 Hz), 6.18 (t, 1 H, *J* = 9.0 Hz), 7.01–7.80 (m, 15 H); UV (95% ethanol) 332, 316, 228 nm (ε 19 300, 23 400, 35 500); *m/e* 346 (M^+), 331, 262, 253, 238, 217, 198.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.41. Found: C, 93.48; H, 6.52.

Triplet-Sensitized Irradiation of 3-Methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-4-penten-1-yne (58). A solution containing 200 mg of **58** and 23 mg of thioxanthen-9-one in 200 mL of benzene was irradiated under an argon atmosphere for 10 min by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter

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sleeve. The solvent was removed under reduced pressure, and the resultant oil was chromatographed on a thick layer plate by using hexane as the eluant. The major band contained 100 mg of a crystalline solid, mp 87–88 °C, whose structure was assigned as 3-ethynyl-3-methyl-1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (**60**): mp 87–88 °C; IR (KBr) 3.08, 3.40, 6.30, 6.77, 7.00, 7.30, 7.76, 8.40, 13.30, 14.80, 15.05 μm; NMR (benzene-d_6, 100 MHz) δ 1.60 (s, 3 H), 2.20 (s, 1 H), 2.50 (d, 1 H, J = 5.0 Hz), 2.98 (dd, 1 H, J = 9.0 and 5.0 Hz), 3.23 (d, 1 H, J = 9.0 Hz), 6.8–7.5 (m, 15 H); *m/e* 346 (M^+), 331, 315, 293, 254, 253, 252, 239.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40. Found: C, 93.46; H, 6.47.

Triplet-Sensitive Irradiation of 3-Ethynyl-3-methyl-1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (60). A mixture containing 176 mg of **60** and 36 mg of thioxanthone in 200 mL of benzene was irradiated under an argon atmosphere for 105 min by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. The solvent was removed under reduced pressure, and the resulting oil was chromatographed on a silica gel column by using hexane as the eluant. The major fraction contained 68 mg (39%) of a crystalline solid, mp 106–107 °C, whose structure was assigned as 6-*endo*-ethynyl-6-*exo*-methyl-1,2,3-triphenylbicyclo[3.1.0]hex-2-ene (**62**) on the basis of its spectral properties: IR ($CHCl_3$) 3.03, 3.32, 3.43, 4.79, 6.28, 6.72, 6.95, 7.28, 9.35, 9.80, 10.80, 11.05, 14.05 μm; NMR ($CDCl_3$, 100 MHz) δ 1.50 (s, 3 H), 1.95 (s, 1 H), 2.20 (d, 1 H, J = 10.0 Hz), 2.75 (d, 1 H, J = 18.0 Hz), 3.50 (dd, 1 H, J = 18.0 and 10.0 Hz), 6.8–7.40 (m, 15 H); UV (95% ethanol) 280 nm (ϵ 11 000); *m/e* 346 (M^+), 345, 332, 317, 293, 291.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60, H, 6.41. Found: C, 93.83; H, 6.64.

The minor fraction contained 22 mg (13%) of a clear oil whose structure was assigned as 6-*exo*-ethynyl-6-*endo*-methyl-1,2,3-triphenylbicyclo[3.1.0]hex-2-ene (**63**) on the basis of its spectral characteristics: IR ($CHCl_3$) 3.01, 3.31, 3.40, 4.73, 6.24, 6.68, 6.90, 7.89, 8.27, 9.30, 14.30 μm; NMR ($CDCl_3$, 90 MHz) δ 1.18 (s, 3 H), 1.92 (d, 1 H, J = 6.0 Hz), 2.00 (s, 1 H), 3.04 (d, 1 H, J = 18.0 Hz), 3.49 (dd, 1 H, J = 18.0 and 6.0 Hz), 6.95–7.41 (m, 15 H); UV (95% ethanol) 275 nm (ϵ 9550); *m/e* 346 (M^+), 345, 332, 317, 313.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.41. Found: C, 93.74; H, 6.38.

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Nuclear Spin Polarization Effects in Radical Ion Pair Reactions. A Comparison between Triplet State and Radical Ion Reactivity[†]

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Abstract: A series of radical cations has been generated from appropriate hydrocarbons by photoinitiated electron transfer to chloranil and cyanosubstituted aromatic hydrocarbons. ^1H and ^{13}C CIDNP effects observed during these reactions allow an insight into the structure of the intermediates and into their rearrangements in solution. The observed reactions are quite different from those observed for triplet states. Thus the radical cations of *cis*- and *trans*-diphenylcyclopropane (**1**) were found to be conformationally stable whereas the triplet state allows ready interconversion. The radical cation, **10**, of quadricyclane was found to rearrange to **8**, the radical cation of norbornadiene, whereas the triplet state allows ready conversion in the opposite direction. The triplet state of benzonorbornadiene (**11**) rearranges to benzonortricyclene (**12**) but no interconversion is observed for the corresponding radical cations. Finally, the interconversion of three different radical cations, a monomer cation, an (open) adduct cation, and a (closed) dimer cation, is discussed in the electron transfer induced dimerization of olefins and in the cleavage of olefin cyclodimers. The observed reactivity differences between triplet states and radical ions eliminate radical ions as intermediates in typical triplet sensitized rearrangements.

The progress of solution photochemistry during the last 2 decades has been marked not only by new experimental techniques and by new mathematical approaches, but also by new ideas concerning the nature of short-lived reaction intermediates. Accordingly, the interpretation of experimental findings in terms of mechanistic details is influenced sometimes by prevailing ideas and, occasionally, published results are reinterpreted in terms of a more fashionable intermediate. Among the short-lived species, which have enjoyed "fashionable" status, are triplet states,[2] phantom triplets,[3] exciplexes,[4] and most recently, radical ions.[5]

It is not always trivial to positively identify the involvement of one of these intermediates. For example, it may be difficult to differentiate between reactions involving triplet states as key intermediates and reactions proceeding via radical ions. This potential difficulty is due to the nature of many typical triplet sensitizers. They are strong electron acceptors in the excited state and, therefore, may react with an appropriate substrate by triplet energy transfer or by electron transfer.

For several years, we have been interested in photoinitiated electron transfer reactions and have applied the CIDNP technique to gain an insight into the structure and reactivity of radical ions.[6] This technique is based on the interpretation of greatly enhanced

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[†] Dedicated to George S. Hammond, a pioneer in exploring triplet state reactivity, on the occasion of his 60th birthday.

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