Intramolecular Ring Closure Reactions of Cyclopropene Derivatives as a Method for Synthesizing Novel Tricyclic Ring Compounds

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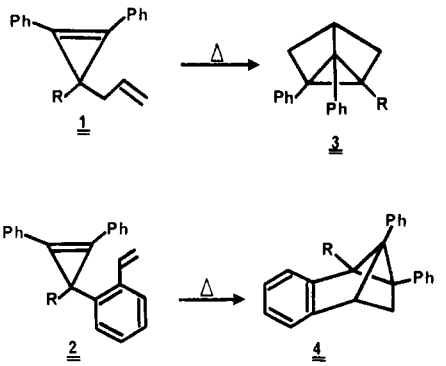
The thermal and photosensitized reactions of several 4-(methyldiphenylcyclopropenyl)-1-butenes have been studied. The thermolysis of these systems gave substituted tricyclo[3.2.0.0^{2,7}]heptanes in good yield. The formation of this ring system involves bond formation between the π-bond and the cyclopropene ring to produce a diradical intermediate which collapses to the observed cycloadduct. In addition to the [2 + 2] cycloadduct, another compound was also isolated which corresponds to an internal Diels–Alder cycloaddition followed by a subsequent 1,3-sigmatropic hydrogen shift. The sensitized photolysis afforded identical cycloadducts but in a different ratio from that encountered thermally. The intramolecular cycloaddition reactions of several 3-(*o*-allylphenyl) substituted cyclopropenes were also studied. Thermolysis of the symmetrically substituted isomer produced a single product which is formed by an intramolecular ene reaction. In contrast to the thermal results, the photosensizited irradiation afforded a mixture of products which are derived by abstraction of the benzylic hydrogen by the triplet state of the cyclopropene π-bond. The thermal and sensitized behavior of the unsymmetrically substituted isomer were also studied, and the results obtained were compared to the reactions which occur from the symmetrically substituted isomer.

Thermal [2 + 2] cycloadditions leading to four membered rings are less frequently encountered than Diels–Alder reactions or 1,3-dipolar cycloadditions. The [2 + 2] cycloaddition reaction is orbital symmetry allowed when it proceeds via a single inversion pathway at one of the reacting centers.[1] In practice, the single inversion path is difficult to realize. No example of a thermal [π_2s + π_2a] cycloaddition of two ethylenic-like bond systems has been established so far. There is good evidence, however, that cyclobutanone formation from ketenes and alkenes follows this rare mechanistic pathway.[2-7] The [2 + 2] cycloadditions of polyhaloethylenes, conjugated dienes, and strained hydrocarbons are believed to proceed via diradical or dipolar intermediates.[8,9] Polyhaloolefins are able to dimerize by the biradical route because fluorine destabilizes the π-bond and chlorine stabilizes the terminal centers of the diradical intermediate.[10,11] Conjugated dienes dimerize via a tetramethylene derivative in which the terminal radicals are allylic.[12-16] Cycloaddition across the double bond of a highly strained alkene such as cyclopropene proceeds quite readily since it reduces ring strain by 26 kcal/mol.[17,18] Our research group has been involved over the past few years in a program of synthesizing unusual polycyclic ring systems which uses the intramolecular [2 + 2] cycloaddition of cyclopropene derivatives as the primary strategy.[19-22] The primary spatial requirement for intramolecular cycloaddition is that the distance between the two reacting centers should be sufficiently short so that effective orbital overlap of the π-systems can occur. Since chemical reactivity in the intramolecular [2 + 2]-cycloaddition process can be significantly modified by the appropriate choice of substituents and geometry,[23-26] we have undertaken an investigation of the chemistry of several cyclopropenes containing π-unsaturation. We report here the results of our studies which show that the internal cycloaddition of cyclopropenes offers a high yield synthesis of some unusual tricyclic ring compounds.

Results

We had previously reported that the thermolysis of 3-allyl (1) and 3-(*o*-vinylphenyl) substituted cyclopropenes (2) results in a novel intramolecular [2 + 2] cycloaddition.[21,22] As an extension of our studies in this area



we have examined the thermal and photochemical behavior of the next higher homologous series. The several new

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cyclopropenes employed in these studies were synthesized by treating diphenylmethylcyclopropenyl cation with Grignard reagents according to the general procedure of Breslow and co-workers.[27] The mixture of symmetrical and unsymmetrical cyclopropenes formed could readily be separated by silica gel chromatography.

Thermolysis of a sample of 4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**5**) at 175 °C afforded a mixture of four compounds. The two major fractions were assigned the structures of 2-methyl-1,7-diphenyltricyclo[3.2.0.0^{2,7}]heptane (**6**, 32%) and 9-methyl-1-phenyl-3,4-benzotricyclo[4.3.0.0^{2,4}]nonane (**7**, 38%) on the basis of their spectral properties (see Experimental Section). The NMR spectrum of **6** was quite complicated since a number of overlapping peaks were present. In order to simplify the spectrum, thermolysis of the dideuterated tricycloheptane **5b** was carried out. The deuterium labeled cycloadduct **6b** showed signals at δ 1.19 (s, 3 H), 1.72 (d, 1 H, J = 12.1 Hz), 1.76 (dd, 1 H, J = 9.4 and 1.0 Hz), 2.08 (d, 1 H, J = 12.1 Hz), 2.50 (ddd, 1 H, J = 9.4, 8.4, and 1.0 Hz), 2.90 (ddt, 1 H, J = 8.4, 3.2, and 1.0 Hz), and 7.08–7.48 (m, 10 H). During our studies with tricycloheptane **6**, we found that this substrate rapidly rearranged to norbornene **10** when chromatographed on a 10% silver nitrate silica gel column. The rearrangement of **6** to **10** probably involves the addition of silver ion across the strained 6,7-σ bond. This will generate a stable carbonium ion which undergoes a subsequent 1,2-sigmatropic shift followed by elimination of the silver metal to give the observed product. The structure of the two minor products were identified as 1-methyl-6,7-diphenylbicyclo[4.1.0]hept-3-ene (**8**, 18%) and 1,2-diphenyl-3-methylbicyclo[4.1.0]hept-2-ene (**9**, 8%). In contrast to the thermolysis, the triplet sensitized photolysis (thioxanthone) of **5** afforded a 2:1 mixture of **6** and **7**. No detectable quantities of **8** and **9** were present in the crude reaction mixture.

We have also studied the thermal and triplet sensitized behavior of the closely related unsymmetrical cyclopropene **11**. Thermolysis of **11** at 175 °C produced a mixture of five compounds which could be separated by silica gel chromatography. The products were assigned as tricycloheptane **12** (22%), tricyclononane **13** (46%), bicycloheptene **14** (4%), and indenes **15** (5%) and **16** (6%). The structures of **12–14** were in accord with the NMR, UV, IR, and mass spectral data (see Experimental Section). The identity of indene **15** was confirmed by comparison with an authentic sample prepared by treating 2-methyl-3-phenylindanone (**17**) with the Grignard reagent derived from 4-bromo-1-butene followed by dehydration of the resulting alcohol. Treatment of **15** with base resulted in a 1,3-sigmatropic hydrogen shift to give indene **16**. The triplet sensitized photolysis of **11** afforded a 9:1 mixture of **12** and **13** with no detectable signs of compounds **14–16**.

In view of the stringent spatial requirements associated with the intramolecular [2 + 2] cycloaddition reaction of cyclopropenes, we thought it worthwhile to consider what effect a variation in the spatial proximity between the cyclopropene and the internal double bond would have on the course of the intramolecular cycloaddition. This led us to examine the thermal and photosensitized behavior of several 3-(*o*-allylphenyl) substituted cyclopropenes so as to compare their behavior with the homologous *o*-vinylphenyl systems (i.e., **2**). Heating a sample of 3-methyl-1,2-diphenyl-3-(*o*-allylphenyl)cyclopropene (**18**) at 175 °C for 5 h gave a quantitative yield of benzocyclopropa[*c*]cycloheptene **19**. In dramatic contrast with the thermal results, the sensitized irradiation of **18** produced a mixture of three compounds whose structures were assigned as **20–22** on the basis of their characteristic spectral data (see Experimental Section). Dihydronaphthalene **22** was readily oxidized with DDQ to the corresponding napthalene derivative.

Attention was next turned to the thermal and photosensitized behavior of the closely related unsymmetrical isomer **23**. Thermolysis of a sample of **23** at 175 °C afforded a single product in high yield whose structure was assigned as spiroindene **24** on the basis of its spectral properties. The sensitized irradiation, on the other hand, produced a mixture of cyclopropa[*a*]indene **25** (75%) and cyclopropa[*de*]naphthacene **26** (16%).

With these results in hand, we decided to investigate the chemistry of the homologous 3-(*o*-allylbenzyl)phenylcyclopropene in order to probe the effect of chain length on the reactivity of the system. The major product formed on thermolysis or direct irradiation of **27** corresponds to

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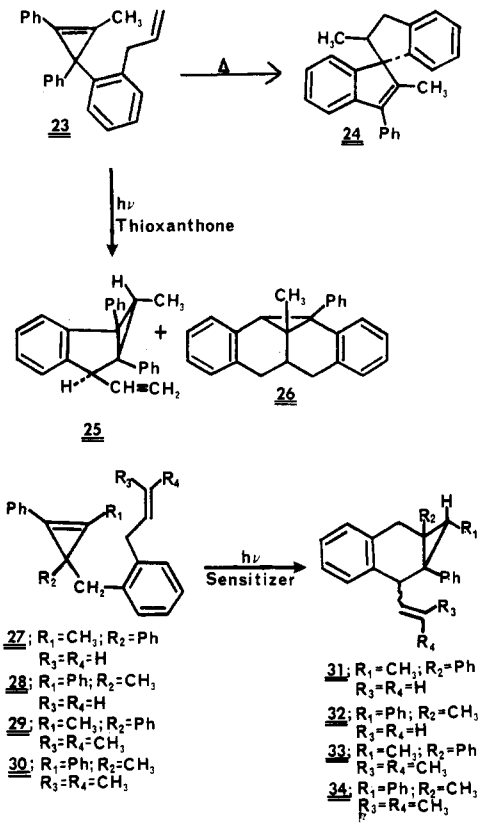
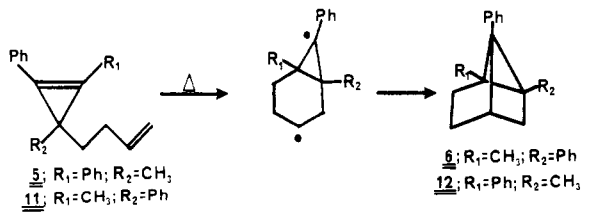


indene formation, a well-precedented reaction.[28,29] The sensitized irradiation of **27** (or **28**) in benzene, however, afforded a mixture of exo and endo benzobicycloheptenes. No signs of a [2 + 2] or [4 + 2] cycloadduct could be detected in the crude reaction mixture. Similar results were obtained with the related prenyl systems (i.e., **29** and **30**).

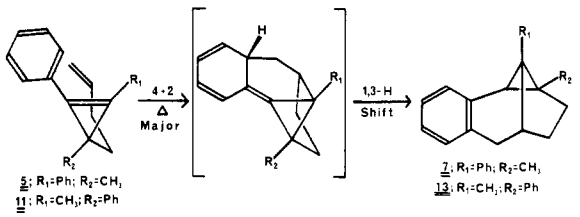
Discussion

Cyclopropenes readily undergo Diels–Alder reactions and dipolar cycloadditions with a variety of 1,3-dipoles.[18] The strained double bond present in the cyclopropene ring is higher in energy and considerably more reactive than a simple unstrained cycloalkene. Thus, the facility of the cycloaddition is related to the considerable relief of bond angle strain of the cyclopropene ring. The torsional angle present in the three-membered ring is close to zero and p–p overlap should not be significantly different from that of a normal olefin. The ease of the cycloaddition is primarily due to relief of angle bending rather than torsional strain. The intramolecular [2 + 2] cycloaddition encountered on thermolysis of cyclopropene **5** or **11** is unique in



that the other reported examples of thermal olefin cycloadditions either occur in compounds in which the double bond is subjected to severe torsional strain[30–35] or else involve reactants that bear substituents capable of stabilizing diradical or dipolar intermediates.[9] The formation of tricycloheptane **6** (or **12**) from the thermolysis of **5** (or **11**) may be most simply interpreted on the basis of an unusually easy bond formation between the double bond and the cyclopropene ring to produce a diradical intermediate which collapses to the observed cycloadduct. In the case of the unsymmetrically substituted cyclopropene system (i.e., **11**), there is a distinct preference for that product arising from bonding between the terminal olefinic carbon and the cyclopropene carbon bearing the methyl group. This is undoubtedly related to the fact that π–π bridging will give the most stable biradical and thus lead to the exclusive formation of regioisomer **12**.

While the formation of the tricycloheptane ring is straightforward, the production of the benzotricyclo[4.3.0.0^{2,4}]nonane system (i.e., **7** and **13**) represents a more



complicated process. This reaction may be pictured as proceeding by way of an intramolecular Diels–Alder cycloaddition followed by a subsequent 1,3-sigmatropic hydrogen shift. Examination of molecular models indicates that the geometry for such a process is quite good. The highly favorable entropic assistance that is inherent in intramolecular processes seems to augur well for the facile [4 + 2] cycloaddition across the π-bond of the aromatic ring. Thus, the transition state for the formation of the thermally allowed [4 + 2] cycloadduct (i.e., **7** or **13**) is of lower energy relative to the alternative [2 + 2] cycloaddition reaction.

An additional point worth noting concerns the distribution of cycloadducts (i.e., **6** and **7**) upon sensitized irradiation of cyclopropene **5**. The formation of **7** from the sensitized reaction may be pictured as proceeding by attack at the ortho position of the triplet state of the cyclopropene on the terminal vinyl carbon followed by diradical coupling and a subsequent aromatization. The preference for the [2 + 2] cycloadduct (i.e., **6**:**7** = 2:1) can be rationalized if one assumes that the system stays most of the time on the triplet surface until the cycloaddition is complete. The triplet product then collapses to its ground-state singlet. The pathway to **6** will be a [π_2s + π_2s] "allowed" excited-state reaction. Even if collapse to the ground state occurs along the cycloaddition pathway, the [π_2s + π_2s] path will still be substantially favored over the other possible mode of cycloaddition (i.e., [4 + 2]).[36,37]

The most reasonable explanation to account for the formation of bicycloheptene **9** from the thermolysis of **5** involves a sequence consisting of ring opening of the cyclopropene ring to a vinylcarbene intermediate. The thermolysis of cyclopropenes is known to produce a ring-

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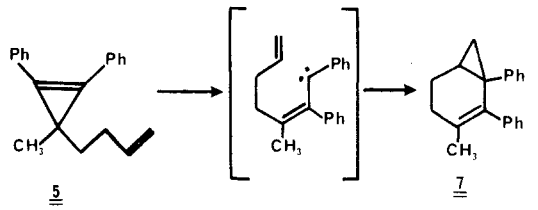

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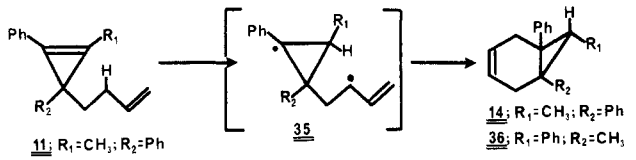
opened species which can cyclize back to the cyclopropene[38] or undergo reactions characteristic of singlet methylene.[39,40] These include intramolecular hydrogen transfer,[41] insertion in a C–H bond,[42] alkyl group migration,[43] electrocyclization,[28,29] and cycloaddition to π bonds.[44] Thus, the formation of **7** from the thermolysis of **5** can be rationalized in terms of intramolecular addition of the carbene carbon onto the neighboring double bond. The formation of indenes **15** and **16** from the thermolysis of **11** is also consistent with a vinylcarbene intermediate which attacks the π-electrons of the adjacent aromatic ring to give an isoindene intermediate. A subsequent, 1,5-sigmatropic hydrogen shift produces indene **15** and **16**.

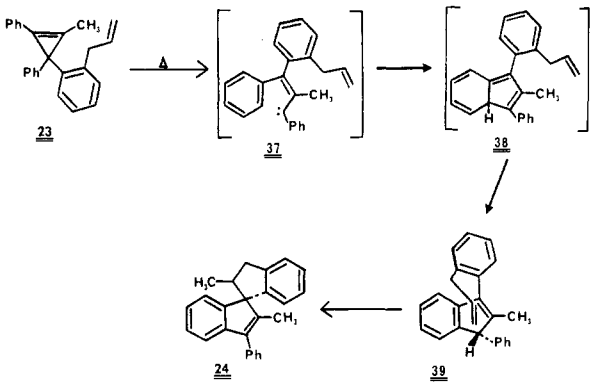
The formation of bicycloheptenes **8** and **14** from the thermolysis of **5** and **11** can be interpreted in terms of an



11; R_1=CH_3; R_2=Ph 35 14; R_1=CH_3; R_2=Ph 36; R_1=Ph; R_2=CH_3

intramolecular ene reaction.[45,46] The ene reaction is usually considered to proceed in a symmetry allowed concerted process[47-51] involving a six-membered cyclic transition state, unless prohibited by steric factors.[52] Olefins with strained double bonds seem particularly prone to enter into ene reactions.[45] Although bimolecular ene reactions of cyclopropenes are known,[53,54] the above reactions represent rare examples of an intramolecular version of the ene process.[55] It should be noted that in the case of the unsymmetrical substituted cyclopropene system (i.e., **11**), only bicycloheptene **14** is formed. No signs of the other regioisomeric bicycloheptene (i.e., **36**) could be detected in the crude reaction mixture. This can best be explained by a stepwise mechanism in which formation of the C–H bond precedes C–C bond formation. The most stable diradical intermediate (i.e., **35**) formed will undergo a subsequent diradical coupling to give the observed product. While most ene reactions are considered to be concerted, stepwise processes may occur[56,57] provided the optimum geometry of the transition state is inaccessible and the intermediate diradical can be stabilized by the substituent groups. With the above systems, the geometry necessary for the concerted ene reaction is not possible.

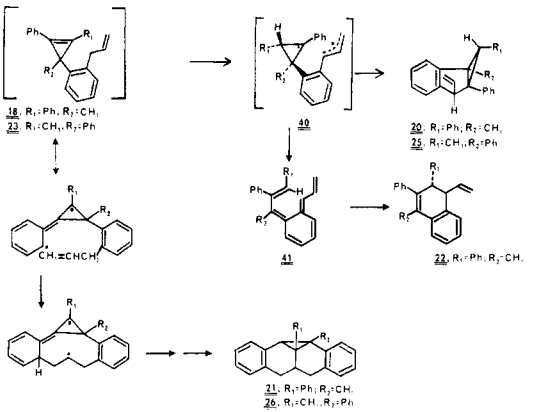
In contrast to the plethora of products produced from the thermolysis of cyclopropene **5** (or **11**), heating a sample of **18** gave rise to the ene product **19** in quantitative yield. In this case molecular models indicate that the geometry of the transition state is suitable for the reaction to proceed in a symmetry allowed concerted sense. While the formation of **19** from the thermolysis of **18** is uneventful, the isolation of **24** from the thermolysis of **23** represents a more



23 37 38 24 39

complicated process. This reaction may be pictured as proceeding via vinylcarbene **37** which cyclizes onto the adjacent aromatic ring to give isoindene **38**. A 1,5-sigmatropic hydrogen shift followed by a subsequent intramolecular ene reaction nicely accounts for the spiro ring compound. The last step of this sequence is not unreasonable since there are several reports in the literature which proceed in an analogous fashion.[46]

Triplet states of tetrasubstituted cyclopropenes which possess γ-hydrogens are known to undergo an intramolecular hydrogen-transfer reaction[58] by a mechanism analogous to the well-known Norrish type II photoreaction of carbonyl compounds.[59] Thus, the triplet state of cyclopropene **18** can readily abstract a hydrogen from the



18; R_1=Ph, R_2=CH_3 23; R_1=CH_3, R_2=Ph 40 20; R_1=Ph, R_2=CH_3 25; R_1=CH_3, R_2=Ph 41 22; R_1=Ph, R_2=CH_3 21; R_1=Ph, R_2=CH_3 26; R_1=CH_3, R_2=Ph

neighboring benzylic carbon to produce a biradical intermediate (**40**) which either collapses to give **20** or undergoes cyclopropyl ring opening in competition with coupling.[60]

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The ring-opened species **41** would be expected to cyclize in a disrotatory fashion to give dihydronaphthalene **22**. It should be noted that the sensitized irradiation of the unsymmetrically substituted cyclopropene **23** proceeds via hydrogen transfer to the carbon bearing the methyl group. The complete regiospecificity of the reaction is undoubtedly related to the fact that the diradical produced on hydrogen transfer to the methyl-bearing carbon allows maximum delocalization of the radical centers in the resulting diradical intermediate. Finally, the formation of the dibenzotricyclodecane ring system (i.e., **21** and **26**) in the sensitized irradiation may be pictured as proceeding by attack of the ortho position of the triplet state of **18** (or **23**) on the terminal olefinic carbon followed by diradical coupling and subsequent aromatization.

One additional point worth mentioning deals with the sensitized irradiation of the *o*-allylbenzyl substituted cyclopropene system (i.e., **27–30**). In all of the cases studies, the reaction proceeds by an initial hydrogen abstraction followed by diradical coupling. The fact that the triplet state prefers to abstract a hydrogen rather than add to the neighboring π-system is undoubtedly related to the ease with which the doubly activated (i.e., benzylic–allylic) hydrogen is transferred.

In conclusion, the results of our work dealing with the intramolecular cycloadditions of cyclopropene derivatives provide an attractive approach for the synthesis of some novel strained ring carbocycles. The facility of the reaction is undoubtedly associated with the considerable relief of bond angle strain of the cyclopropene ring. Further studies on the scope of the intramolecular reactions of cyclopropene derivatives are in progess and will be reported in due course.

Experimental Section

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 467 infrared 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 90 MHz by using a Varian EM-390 spectrometer. Mass spectra were determined with a Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV. All thermolyses were carried out in a 20% pyridine–benzene mixture at 175 °C in a sealed Carius tube. The crude reaction mixtures were chromatographed on silica gel using hexane as the eluent.

Preparation of 4-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (5) and 4-(2-Methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (11). To a stirred suspension containing 0.90 g of magnesium in 10 mL of anhydrous ether under a nitrogen atmosphere was slowly added 3.55 g of 4-bromo-1-butene in 40 mL of anhydrous ether so as to maintain a gentle reflux. The mixture was allowed to stir at reflux for an additional 30 min before cooling to room temperature. To a stirred suspension of 2.00 g of 1-methyl-2,3-diphenylcyclopropenylium perchlorate[27] in 125 mL of anhydrous ether at −78 °C under a nitrogen atmosphere was added the above Grignard solution. The mixture was allowed to warm to 5 °C overnight. After quenching with a saturated ammonium chloride solution, the ether layer was washed three times with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a light yellow oil which was chromatographed on a 100 × 1.5 cm silica gel column using hexane as the eluent. The first component isolated from the column contained 1.2 g (71%) of 4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**5**) as a colorless oil: IR (neat) 3030, 2880, 2825, 1810, 1640, 1595, 1490, 1445, 1440, 1370, 1075, 1030, 1000, 915, 910, 765, 760, 755, 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.46 (s, 3 H), 1.88–2.03 (m, 4 H), 4.78–5.10 (m, 2 H), 5.58–6.01 (m, 1 H), 7.17–7.73 (m, 10 H); UV (95% ethanol) 338, 320, 238, 230 nm (ϵ 22 300, 29 300, 13 200, 16 600); *m/e* 260 (M^+, base), 245, 232, 219, 218, 217, 205, 204, 203, 202, 141, 129, 128, 115, 105, 91, 77.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.24; H, 7.76.

The second component isolated from the column containing 400 mg (24%) of 4-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**11**) as a colorless oil: IR (neat) 3050, 2880, 2835, 1850, 1645, 1600, 1490, 1445, 1435, 1075, 995, 915, 910, 760, 700, 695, 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.83–2.38 (m, 4 H), 2.28 (s, 3 H), 4.81–5.12 (m, 2 H), 5.84 (ddt, 1 H, J = 16.9, 9.8, 6.0 Hz), 7.02–7.53 (m, 10 H); UV (95% ethanol) 264 nm (ϵ 15 900); *m/e* 260 (M^+), 219 (base), 218, 206, 205, 204, 203, 129, 116, 106, 90, 77.

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

Thermolysis of 4-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (5). A sample containing 641 mg of **5** was heated at 175 °C for 136 h. Chromatography of the mixture on silica gel produced four components. The first fraction isolated from the column contained 207 mg of a crystalline solid (32%), mp 77–78 °C, whose structure was assigned as 2-methyl-1,7-diphenyltricyclo[3.2.0.0^{2,7}]heptane (**6**) on the basis of its spectroscopic properties: IR (KBr) 2915, 2835, 1605, 1495, 1440, 1385, 1095, 1035, 780, 770, 720, 705, 700 cm^{-1}; NMR ($CDCl_3$, 270 MHz) δ 1.09 (s, 3 H), 1.63–1.70 (m, 2 H), 1.95–2.07 (m, 2 H), 2.35–2.46 (m, 2 H), 2.78–2.84 (m, 1 H), 7.03–7.25 (m, 10 H); ^{13}C NMR (20 MHz, $CDCl_3$) 15.7 (q, J = 126 Hz), 31.4 (t, J = 131 Hz), 32.8 (t, J = 136 Hz), 33.3 (t, J = 131 Hz), 40.0 (s), 40.3 (s), 42.7 (d, J = 146 Hz), 49.6 (s), 125.2–129.4 (m), 138.6 (s), 140.1 (s); UV (95% ethanol) 235 nm (ϵ 14 200); *m/e* 260 (M^+), 245, 232 (base), 91.

Anal. Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.74. Found: C, 92.18; H, 7.78.

The second component isolated from the column was a colorless oil (38%) whose structure was assigned as 9-methyl-1-phenyl-3,4-benzotricyclo[4.3.0.0^{2,4}]nonane (**7**) on the basis of its spectral properties: IR (neat) 3060, 3030, 2940, 2860, 2840, 1610, 1560, 1490, 1460, 1445, 1380, 1330, 1110, 1075, 1040, 1020, 780, 755, 740, 730, 700 cm^{-1}; ^{13}C NMR (20 MHz, $CDCl_3$) 20.8 (q, J = 125 Hz), 32.4 (d, J = 159 Hz), 33.7 (t, J = 128 Hz), 34.0 (t, J = 127 Hz), 34.2 (t, J = 127 Hz), 43.8 (s), 44.6 (s), 46.4 (d, J = 135 Hz), 125.4–130.1 (m), 136.1 (s), 137.3 (s), 143.2 (s); UV (95% ethanol) 228 nm (ϵ 16 900); *m/e* 260 (M^+), 245 (base), 142, 141, 115, 91, 77; NMR ($CDCl_3$, 400 MHz) δ 1.03 (s, 3 H), 1.01–1.08 (m, 1 H), 1.51 (ddd, 1 H, J = 13.2, 9.4, and 7.4 Hz), 1.82 (ddd, 1 H, J = 13.2, 12.1, and 4.5 Hz), 2.17 (s, 1 H), 2.19–2.43 (m, 1 H), 2.32 (dd, 1 H, J = 15.1 and 2.9 Hz), 2.92–3.00 (m, 2 H), 7.07–7.46 (m, 9 H).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.03; H, 7.77.

The third fraction from the column (18%) was a crystalline solid, mp 79–80 °C, whose structure was assigned as 1-methyl-6,7-diphenylbicyclo[4.1.0]hept-3-ene (**8**) on the basis of its spectroscopic properties: IR (kBr) 3020, 2910, 2870, 2820, 1645, 1590, 1485, 1440, 1435, 1420, 1370, 1210, 1050, 1020, 1010, 755, 690, 660 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.18 (s, 3 H), 2.19–2.79 (m, 4 H), 2.52 (s, 1 H), 5.62–5.76 (m, 2 H), 6.67–7.38 (m, 10 H); UV (95% ethanol) 226 nm (ϵ 16 700); *m/e* 260 (M^+), 245, 205, 169, 167, 141, 128, 115, 91 (base), 77.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.22; H, 7.75.

The last fraction isolated from the column contained 30 mg of a colorless oil whose structure was assigned as 1,2-diphenyl-3-methylbicyclo[4.1.0]hept-2-ene (**9**) (8%) on the basis of its spectroscopic properties: IR (neat) 3080, 3050, 3020, 2950, 2875, 1600, 1490, 1445, 1375, 1070, 1025, 1005, 920, 905, 775, 740, 690 cm^{-1}; UV (95% ethanol) end absorption 290 nm; *m/e* 260 (M^+), 245, 232 (base), 217, 215, 141, 129, 128, 115, 91, 77; NMR ($CDCl_3$, 400 MHz) δ 1.07 (dd, 1 H, J = 5.9 and 4.4 Hz), 1.36 (dtd, 1 H, J = 8.8, 5.9, and 3.7 Hz), 1.60 (s, 3 H), 1.60 (dd, 1 H, J = 8.8 and 4.4 Hz), 1.83 (dtd, 1 H, J = 13.4, 6.4, and 3.7 Hz), 1.94 (ddd, 1 H, J = 16.0, 7.8, and 6.4 Hz), 2.20 (ddt, 1 H, J = 13.4, 7.8, and 5.9 Hz), 2.34 (ddd, 1 H, J = 16.0, 6.4, and 5.9 Hz), 6.95–7.11 (m, 10 H).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.07; H, 7.76.

The triplet sensitized photolysis of **5** only produced a 2:1 mixture of **6** and **7**.

Silver(I)-Induced Rearrangement of 2-Methyl-1,7-diphenyltricyclo[3.2.0.0^{2,7}]heptane (6). During an attempt to separate the various products derived from the thermolysis of **5** we noted that one of the thermal products (i.e., **6**) undergoes rearrangement when chromatographed on a silica gel column impregnated with 10% silver nitrate. The silver induced rearrangement was studied in more detail by treating a sample of **6** with silver ion. Thus, a solution containing 123 mg of 2-methyl-1,7-diphenyltricyclo[3.2.0.0^{2,7}]heptane (**6**) and 200 mg of silver perchlorate in 25 mL of anhydrous benzene was heated at 60 °C for 108 h. The resulting solution was washed several times with a sodium sulfide solution followed by a saturated sodium chloride solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a light yellow oil which was chromatographed on a 2 cm × 0.5 cm silica gel column using hexane as the eluent. The resulting white crystalline solid (111 mg, 90%) that was obtained was identified as 2-methyl-1,3-diphenylbicyclo[2.2.1]hept-2-ene (**10**) on the basis of its spectral properties: mp 67–68 °C; IR (neat) 3100, 3075, 3050, 2975, 2880, 1595, 1490, 1445, 1375, 1310, 1130, 1090, 1025, 970, 750, 690, 660 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.42 (dd, 1 H, J = 8.3, 1.6 Hz), 1.46–1.70 (m, 2 H), 1.53 (s, 3 H), 1.84–2.18 (m, 3 H), 3.21 (br p, 1 H, J = 1.6 Hz), 7.06–7.45 (m, 10 H); ^{13}C NMR (20 MHz, $CDCl_3$) 12.2 (q, J = 127 Hz), 2.4 (t, J = 133 Hz), 29.8 (t, J = 133 Hz), 46.3 (d, J = 145 Hz), 52.0 (t, J = 133 Hz), 62.3 (s), 125.9–128.1 (m), 137.6 (s), 141.0 (s), 141.2 (s), 143.4 (s); UV (95% ethanol) 260 nm (ϵ 8200); m/e 260 (M$^+$), 245, 233, 232 (base), 216, 215, 202, 115, 91.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 91.99; H, 7.77.

Thermolysis of 4-(1,2-Diphenyl-3-methyl-2-cyclopropen-1-yl)-1-butene (11). A sample containing 368 mg of **11** was heated at 175 °C for 55 h. Chromatography of the crude mixture gave four products. The first component isolated from the column was a white solid (22%), mp 74–75 °C, whose structure was assigned as 7-methyl-1,2-diphenyltricyclo[3.2.0.0^{2,7}]heptane (**12**) on the basis of its spectroscopic properties: IR (KBr) 3060, 2990, 2970, 2940, 2870, 2860, 1595, 1495, 1435, 1280, 1230, 1065, 1025, 1020, 1010, 770, 750, 690 cm^{-1}; ^{13}C NMR (20 MHz, $CDCl_3$) 16.0 (q, J = 126 Hz), 31.3 (t, J = 137 Hz), 33.5 (t, J = 132 Hz), 33.9 (t, J = 132 Hz), 34.4 (s), 43.5 (d, J = 146 Hz), 47.0 (s), 47.4 (s), 124.9–130.5 (m), 139.9 (s), 140.3 (s); UV (95% ethanol) 234 nm (ϵ 13400); m/e 260 (M$^+$), 245, 232 (base), 217, 115, 91; NMR ($CDCl_3$, 400 MHz) δ 1.35 (s, 3 H), 1.56 (d, 1 H, J = 9.5 Hz), 1.73 (ddd, 1 H, J = 10.7, 7.8, and 1.2 Hz), 2.04–2.19 (m, 2 H), 2.24 (dd, 1 H, J = 9.5 and 8.1 Hz), 2.56–2.66 (m, 1 H), 2.89 (ddd, 1 H, J = 8.1, 2.8, and 1.2 Hz), 6.8–7.3 (m, 10 H).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.23; H, 7.76.

The second component isolated from the column was a colorless oil (46%) whose structure was assigned as 1-methyl-9-phenyl-3,4-benzotricyclo[4.3.0.0^{2,9}]nonane (**13**) on the basis of its spectroscopic properties: IR (neat) 3080, 3040, 2950, 2880, 2860, 1605, 1495, 1465, 1450, 1390, 1130, 1095, 1020, 925, 790, 770, 755, 735, 705 cm^{-1}; ^{13}C NMR (20 MHz, $CDCl_3$) 19.4 (q, J = 125 Hz), 32.8 (d, J = 159 Hz), 34.3 (t, double intensity, J = 127 Hz), 36.1 (s), 36.6 (t, J = 128 Hz), 44.9 (d, J = 132 Hz), 51.2 (s), 125.6–130.0 (m), 135.9 (s), 37.7 (s), 143.7 (s); m/e 260 (M$^+$), 245 (base), 232, 142, 141, 115, 91; NMR ($CDCl_3$, 400 MHz) δ 1.04 (dddd, 1 H, J = 13.2, 9.3, 3.2, and 2.7 Hz), 1.13 (s, 3 H), 1.61 (ddd, 1 H, J = 13.6, 9.3, and 8.1 Hz), 1.95 (ddd, 1 H, J = 13.6, 11.7, and 3.2 Hz), 2.22 (s, 1 H), 2.30 (dddd, 1 H, J = 13.2, 11.7, 10.2, and 8.1 Hz), 2.40 (dd, 1 H, J = 15.1 and 2.9 Hz), 2.75 (dddd, 1 H, J = 10.2, 3.5, 2.9, and 2.7 Hz), 2.96 (dd, 1 H, J = 15.1 and 3.5 Hz), 7.09–7.40 (m, 9 H).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.15; H, 7.81.

The third component isolated from the column was a white crystalline solid (4%), mp 111–112 °C, whose structure was assigned as 7-methyl-1,6-diphenylbicyclo[4.1.0]hept-3-ene (**14**) on the basis of its spectroscopic properties: IR (KBr) 3020, 3000, 2960, 2870, 2820, 1595, 1490, 1465, 1440, 1425, 1200, 1080, 920, 795, 765, 715, 705, 665 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.18 (d, 3 H, J = 6.6 Hz), 1.73 (br q, 1 H, J = 6.6 Hz), 2.54–2.63 (m, 4 H), 5.65 (br t, 2 H, J = 1.9 Hz), 6.94–7.46 (m, 10 H); m/e 260 (M$^+$, base, 245, 232, 169, 167, 156, 155, 154, 142, 141, 128, 115, 91.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.04; H, 7.77.

The fourth component isolated from the column was a colorless oil (5%) whose structure was assigned as 2-methyl-3-(3-butenyl)-1-phenylindene (**15**) on the basis of its spectroscopic properties and by comparison with an independently synthesized sample: IR (neat) 3070, 3030, 2930, 2860, 1740, 1600, 1490, 1470, 1450, 1070, 1030, 1020, 990, 910, 750, 740, 730, 700, 660 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.76 (s, 3 H), 2.13–2.47 (m, 2 H), 2.51–2.73 (m, 2 H), 4.22 (br s, 1 H), 4.87–5.17 (m, 2 H), 5.87 (ddt, 1 H, J = 17.2, 10.0, and 6.0 Hz), 6.87–7.28 (m, 9 H); UV (95% ethanol) 262 nm (ϵ 11000); m/e 260 (M$^+$), 221, 219, 206, 205, 191, 165, 91 (base), 77.55.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.82.

This material was further verified by comparison with an independently synthesized sample. To a stirred suspension of 0.50 g of magnesium in 5 mL of anhydrous ether was added slowly 1.22 g of 4-bromo-1-butene in 15 mL of anhydrous ether. The reaction was allowed to stir at reflux for 30 min and was then cooled to room temperature. To a stirred solution of 1.00 g of 2-methyl-3-phenylindanone[28] (**17**) in 25 mL of anhydrous ether was added the above Grignard solution via syringe. The reaction was allowed to stir for 12 h at room temperature. The excess Grignard reagent was carefully quenched by the addition of a saturated ammonium chloride solution. The reaction mixture was stirred until both phases became clear. The organic phase was separated, washed twice with water and a saturated sodium chloride solution, and then dried over magnesium sulfate. Removal of the solvent under reduced pressure left 0.88 g (70%) of 2-methyl-1-(3-butenyl)-3-phenyl-1-indanol. This material was used without further purification.

To the above indanol was added a solution containing 10 mL of acetic acid, 1 mL of sulfuric acid, and 1 mL of water. The reaction mixture was stirred for 15 min. The organic material was taken up in benzene and was washed five times with water followed by a saturated sodium bicarbonate solution. The benzene layer was then dried over magnesium sulfate and the solvent removed under reduced pressure. The resulting yellow oil was subjected to chromatography on a 5 × 1.5 cm silica gel column using hexane as the eluent. The resulting colorless oil (0.74 g, 90%) was identical with a sample of 2-methyl-3-(3-butenyl)-1-phenylindene (**15**) obtained from the thermolysis of cyclopropene **11**.

The last component isolated from the column was a colorless oil (6%) whose structure was established as 2-methyl-1-(3-butenyl)-3-phenylindene (**16**) on the basis of its spectroscopic data: IR (neat) 3070, 3010, 2970, 2920, 2850, 1630, 1590, 1485, 1455, 1435, 1350, 1150, 1065, 1015, 1000, 990, 905, 770, 745, 695 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.69–2.28 (m, 4 H), 2.00 (s, 3 H), 3.44 (br t, 1 H, J = 6.8 Hz), 4.82–5.10 (m, 2 H), 5.78 (ddt, 1 H, J = 17.0, 10.2, 5.7 Hz), 7.06–7.57 (m, 9 H); UV (95% ethanol) 259, 223 nm (ϵ 9130, 19600); m/e 260 (M$^+$), 221, 219 (base), 218, 206, 205, 204, 203, 202, 191, 189, 154, 91, 77, 55, 43, 41.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.01; H, 7.78.

The structure of this material was further verified by comparison with an independently synthesized sample. A solution containing 351 mg of indene **16** was heated in 5 mL of a 20% pyridine–benzene mixture at 162 °C in a sealed tube for 14 h. The major product isolated contained 114 mg (32%) of 2-methyl-1-(3-butenyl)-3-phenylindene (**16**) which was identical in every detail with the sample obtained from the thermolysis of cyclopropene **11**.

The sensitized photolysis of **11** produced a 9:1 mixture of **12** and **13** as the only two observable products.

Preparation of 3-Methyl-1,2-diphenyl-3-(*o*-allylphenyl)-cyclopropene (18) and 2-Methyl-1,3-diphenyl-(*o*-allylphenyl)cyclopropene (23). To a stirred suspension containing 4.76 g of magnesium metal in 75 mL of anhydrous ether under a nitrogen atmosphere was added slowly, over a 40 min period, a solution containing 25.00 g of *o*-chlorobromobenzene in 175 mL of anhydrous ether. The reaction mixture was heated at reflux for 1 h and was then cooled to room temperature. To a stirred solution containing 31.60 g of allyl bromide in 200 mL of anhydrous ether under a nitrogen atmosphere was added, over a

40 min period, the above Grignard solution. The mixture was allowed to stir at room temperature and was then quenched with a saturated ammonium chloride solution. The ethereal solution was washed twice with water followed by a saturated sodium chloride solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a light yellow liquid which was fractionally distilled through a 10-cm Vigeraux column at 0.5 mm. The fraction boiling at 32–33 °C contained 16.81 g (94%) of a colorless liquid which was identified as *o*-chloroallylbenzene: NMR ($CDCl_3$, 60 MHz) δ 3.28–3.50 (br d, 2 H, J = 6.5 Hz), 4.72–5.18 (m, 2 H), 5.53–6.23 (m, 1 H), 6.83–7.38 (m, 4 H).

To a stirred suspension of activated magnesium, prepared according to the method of Rieke,[61] in refluxing tetrahydrofuran was added 1.47 g of *o*-chloroallylbenzene. The mixture was allowed to reflux for 7 h and the cooled Grignard solution was then added to a stirred slurry containing 2.20 g of 1-methyl-2,3-diphenylcyclopropenylium perchlorate in 100 mL of anhydrous ether at −78 °C under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature over a 4-h period. After quenching with a saturated ammonium chloride solution, the organic layer was taken up in ether, washed three times with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a 15 × 1.5 cm silica gel column and then on a 100 × 1.5 cm silica gel column using hexane as the eluent. The first component isolated from the column contained 894 mg (38%) of 3-methyl-1,2-diphenyl-3-(*o*-allylphenyl)cyclopropene (**18**): IR (neat) 3080, 3060, 3025, 2960, 2920, 2850, 1800, 1635, 1595, 1495, 1480, 1440, 1365, 1070, 1035, 1020, 990, 910, 750, 725, 685 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.83 (s, 3 H), 3.78 (dt, 2 H, J = 6.5, 1.5 Hz), 4.93–5.23 (m, 2 H), 5.77–6.23 (m, 1 H), 6.98–7.86 (m, 14 H); UV (95% ethanol) 317, 227 shoulder nm (ε 20 000, 22 900); m/e 322 (M^+), 307, 281 (base), 229, 215, 205, 203, 202, 115, 91, 77.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.95; H, 6.95.

The second component isolated from the column contained 251 mg (11%) of 2-methyl-1,3-diphenyl-3-(*o*-allylphenyl)cyclopropene (**23**): mp 101–102 °C; IR (KBr) 3050, 3030, 3020, 2950, 2920, 2900, 2870, 2850, 1850, 1630, 1590, 1480, 1435, 1420, 1065, 1020, 980, 900, 755, 745, 685, 655 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.45 (s, 3 H), 3.29–3.44 (m, 2 H), 4.79–5.08 (m, 2 H), 5.55–6.02 (m, 1 H), 6.92–7.61 (m, 14 H); UV (95% ethanol) 263 nm (ε 18 800); m/e 322 (M^+), 282, 281 (base), 265, 229, 215, 203, 202, 167, 165, 128, 115, 91, 77.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.97; H, 6.92.

Thermolysis of 3-Methyl-1,2-diphenyl-3-(*o*-allylphenyl)cyclopropene (18). A solution containing 108 mg of 3-methyl-1,2-diphenyl-3-(*o*-allylphenyl)cyclopropene (**18**) in 0.5 mL of a 20% pyridine–benzene mixture was heated in a sealed tube at 175 °C for 5 h. The solvent was removed under reduced pressure and the light yellow residue was chromatographed on a 3.0 × 0.5 cm silica gel column using hexane as the eluent. The white solid obtained (107 mg, 98%) was assigned as 1,1a,8,9-tetrahydro-1a-methyl-*exo*-1,9-diphenylbenzocyclopropa(*c*)cycloheptene (**19**) on the basis of its spectral properties: mp 177–178 °C; IR (KBr) 3025, 3000, 2945, 1595, 1490, 1485, 1440, 1435, 1380, 1270, 1190, 1025, 775, 770, 760, 750, 710 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.18 (s, 3 H), 2.20 (ddd, 1 H, J = 13.3, 6.1, and 2.1 Hz), 2.62 (s, 1 H), 2.64 (br dd, 1 H, J = 13.3 and 7.4 Hz), 6.10 (ddd, 1 H, J = 10.8, 7.4, and 6.1 Hz), 6.66 (br d, 1 H, J = 10.3 Hz), 6.85–7.58 (m, 14 H); UV (95% ethanol) 260 shoulder, 229 nm (ε 7960, 31 000); m/e 322 (M^+), 307 (base), 245, 229, 228, 205, 143, 115, 97, 77.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.01; H, 6.91.

Thermolysis of 2-Methyl-1,3-diphenyl-3-(*o*-allylphenyl)cyclopropene (23). A solution containing 102 mg of **23** in 0.5 mL of a 20% pyridine–benzene mixture was heated at 175 °C in a sealed tube for 17.5 h. The solvent was removed under reduced pressure and the resulting residue was chromatographed on a 100 × 1.5 cm silica gel column using hexane as the eluent. The major component isolated from the column (55 mg, 54%) was identified as 2,2′-dimethyl-3′-phenylspiro[indan-1,1′-indene] (**24**) on the basis of its spectral properties: IR (neat) 3070, 3040, 3020, 2970, 2940, 2880, 2860, 1595, 1495, 1480, 1470, 1460, 1450, 1390, 1050, 1040, 810, 800, 785, 780, 775, 770, 735, 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.80 (d, 3 H, J = 6.3 Hz), 1.58 (s, 3 H), 2.72–3.28 (m, 3 H), 6.50–6.65 (m, 1 H), 6.81–7.50 (m, 12 H); UV (95% ethanol) 273, 266, 224 nm (ε 9200, 8900, 29 500); m/e 322 (M^+), 307 (base), 229, 228, 134, 115, 91, 77.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.87; H, 6.92.

Triplet Sensitized Irradiation of 3-Methyl-1,2-diphenyl-3-(*o*-allylphenyl)cyclopropene (18) in Benzene. A solution containing 367 mg of **18** and 50 mg of thioxanthen-9-one in 250 mL of anhydrous benzene was irradiated for 1.25 h under an argon atmosphere with a 450-W Hanovia mercury arc lamp equipped with a Uranium filter sleeve. The solvent was removed under reduced pressure and the resulting yellow oil was chromatographed on a 2.5 cm × 1.5 cm silica gel column using hexane as the eluent. The solvent was removed under reduced pressure and the resulting colorless oil was subjected to chromatography on a 100 × 1.5 cm silica gel column using hexane as the eluent. The first component isolated from the column (159 mg) was identified as 1,1a,6,6a-tetrahydro-1a-methyl-*exo*-1,6a-diphenyl-*endo*-6-ethenylcyclopropa[*a*]indene (**20**) on the basis of its spectral properties: mp 125–126 °C; IR (KBr) 3010, 2950, 2795, 1590, 1490, 1470, 1435, 1375, 1065, 990, 920, 770, 760, 725, 700 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.56 (s, 3 H), 2.02 (s, 1 H), 4.07 (br d, 1 H, J = 8.0 Hz), 4.92–5.10 (m, 2 H), 6.03 (ddd, 1 H, J = 16.7, 9.6, and 8.0 Hz), 6.51–7.28 (m, 14 H); UV (95% ethanol) 241 nm (ε 18 400); m/e 322 M^+, base), 307, 251, 249, 218, 217, 215, 205, 167, 143, 91.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.06; H, 6.90.

The second component isolated from the column was a crystalline solid, mp 182–183 °C, whose structure was assigned as 5,5a,6,11,11a,12-hexahydro-5-methyl-5a-phenylcyclopropa[*de*]-naphthacene (**21**) on the basis of its spectroscopic properties: IR (KBr) 3080, 3040, 2930, 2880, 2850, 1480, 1450, 1440, 1380, 1110, 1070, 1030, 1000, 920, 910, 760, 730, 695 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.37 (s, 3 H), 2.22 (br d, 1 H, J = 15.5 Hz), 2.37 (br d, 1 H, J = 15.5 Hz), 2.60 (s, 1 H), 2.92 (br t, 1 H, J = 6.6 Hz), 3.20 (dd, 1 H, J = 15.5, 6.6 Hz), 3.42 (dd, 1 H, J = 15.5, 6.6 Hz), 6.73–7.49 (m, 13 H); m/e 322 (M^+), 308, 307 (base), 245, 229, 228, 216, 215, 202, 179.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.04; H, 6.92.

The third component isolated from the column was a colorless oil whose structure was assigned as *trans*-1,2-dihydro-4-methyl-2,3-diphenyl-1-ethenylnaphthalene (**22**) on the basis of its spectral properties: IR (neat) 3060, 3025, 3000, 2920, 2900, 1630, 1600, 1490, 1485, 1450, 1440, 1380, 1075, 1040, 1035, 1020, 1000, 990, 915, 760, 770 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.08 (s, 3 H), 3.55 (br d, 1 H, J = 7.1 Hz), 3.78 (br s, 1 H), 4.88–5.12 (m, 2 H), 6.20 (ddd, 1 H, J = 17.2, 9.6, and 7.1 Hz), 6.89–7.52 (m, 14 H); UV (95% ethanol) 283, 226 nm (ε 13 800, 21 700); m/e 322 (M^+), 307 (base), 231, 229, 216, 215, 179, 178, 91.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.04; H, 6.93.

The structure of this material was further supported by DDQ oxidation. A solution containing 180 mg of **22** and 500 mg of 2,3-dichloro-5,6-dicyano-1,4-bezoquinone in 50 mL of benzene was heated at reflux for 16 h. Removal of the solvent left a dark residue which was subjected to silica gel chromatography using hexane as the eluent. The major component contained 131 mg (72%) of a white solid, mp 124–125 °C, whose structure was assigned as 1-ethenyl-2,3-diphenyl-4-methyl-1,2-dihydronaphthalene (**22**) on the basis of its spectral properties: NMR ($CDCl_3$, 90 MHz) δ 2.44 (s, 3 H), 5.27 (dd, 1 H, J = 18.0, 2.1 Hz), 5.46 (dd, 1 H, J = 11.7, 2.1 Hz), 6.70 (dd, 1 H, J = 18.0, 11.7 Hz), 6.88–7.20 (*m*, 10 H), 7.42–7.68 (m, 2 H), 8.06–8.56 (m, 2 H); m/e 320 (M^+, base), 306, 289, 243.

Triplet Sensitized Irradiation of 2-Methyl-1,3-diphenyl-3-(*o*-allylphenyl)cyclopropene (23) in Benzene. A solution containing 252 mg of **23** and 17 mg of thioxanthen-9-one in 250 mL of anhydrous benzene was irradiated for 45 min under an argon atmosphere with a 450-W Hanovia mercury arc lamp

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equipped with a Uranium filter sleeve. The solvent was removed under reduced pressure and the resulting yellow oil was chromatographed on a 100 × 1.5 cm silica gel column using hexane as the eluent. The first component isolated from the column contained 188 mg (75%) of a white crystalline solid. The structure of this material was assigned as 1,1a,6,6a-tetrahydro-*exo*-1-methyl-1a,6a-diphenyl-*endo*-6-ethenylcycloprop[*a*]indene (**25**) on the basis of its spectral properties: mp 119–120 °C; IR (KBr) 3045, 3030, 3015, 3000, 2990, 2975, 2940, 2880, 1595, 1500, 1475, 1460, 1450, 1100, 1015, 950, 810, 800, 780, 740, 735, 665 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.07–1.41 (m, 4 H), 4.31 (br d, 1 H, J = 8.2 Hz), 4.99–5.30 (m, 2 H), 5.00 (ddd, 1 H, J = 16.7, 10.3, and 8.2 Hz), 6.61–6.80 (m, 1 H), 6.91–7.54 (m, 13 H); m/e 322 (M^+, base), 307, 245, 244, 229, 228, 153, 115, 91, 77.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.02; H, 6.93.

The second component isolated from the column contained 39 mg (16%) of a white crystalline solid whose structure was assigned as 5,5a,6,11,11a,12-hexahydro-5a-methyl-5-phenylcyclopropa[*de*]naphthacene (**26**) on the basis of its spectral properties: mp 113–114 °C, IR (KBr) 3070, 3020, 2940, 2890, 2845, 1595, 1495, 1465, 1450, 1385, 1285, 1040, 820, 800, 790, 780, 770, 765, 760, 735, 730, 670 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.12 (s, 3 H), 2.30 (br d, 1 H, J = 15.9 Hz), 2.35 (dd, 1 H, J = 15.2, 1.7 Hz), 2.71 (br dd, 1 H, J = 7.2, 6.1 Hz), 2.76 (s, 1 H), 3.20 (br dd, 1 H, J = 15.9, 7.2 Hz), 3.36 (br dd, 1 H, J = 15.2, 6.1 Hz), 6.52–7.49 (m, 1 H); m/e 322 (M^+), 308, 307 (base), 231, 229, 216, 215, 179, 178, 91.

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

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Supplementary Material Available: Experimental details are given for the preparation and triplet sensitized behavior of 4,4-dideuterio-4-(methyldiphenylcyclopropenyl)-1-butene, 1-(2-propenyl)-2-[(methyldiphenylcyclopropenyl)methyl]benzene and 1-methyl-2-butenyl-[(methyldiphenylcyclopropenyl)methyl]-benzene (11 pages). Ordering information is given on any current masthead page.

Practical Enzymatic Synthesis of Adenosine 5′-*O*-(3-Thiotriphosphate) (ATP-γ-S)[1]

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An enzymatic procedure for the synthesis of adenosine 5′-*O*-(3-thiotriphosphate) (ATP-γ-S) on a 50-mmol scale from dihydroxyacetone, sodium thiophosphate, ADP, and phosphoenol pyruvate is described. The synthesis uses polyacrylamide gel immobilized glycerokinase coupled to a pyruvate kinase catalyzed ATP cofactor regeneration system, and polyacrylamide gel immobilized triosephosphate isomerase, glyceraldehyde 3-phosphate dehydrogenase, and phosphoglycerate kinase coupled to a lactate dehydrogenase catalyzed NAD cofactor regeneration system. The ATP-γ-S is purified by adsorption on Dowex 1 and isolated as the sodium or barium salts in ~90% purity.

Adenosine 5′-*O*-(3-thiotriphosphate) (ATP-γ-S) is an ATP analogue useful in mechanistic enzymology.[2-19] ATP-γ-S was first synthesized by Goody and Eckstein by chemical methods.[20] It and several isotopically labeled analogues have since been prepared on 0.1–1 mmol scale

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