(100), 95 (21), 94 (15), 91 (43), 79 (16); $[\alpha]_D$ +189.7°.

(+)-Car-2-en-4-one (11). A solution of the alcohol **9** (88 mg, 0.58 mmol) in methylene chloride (2 mL) was added to a stirred suspension of PCC (230 mg, 1.07 mmol) and sodium acetate (17.5 mg, 0.21 mmol) in methylene chloride. After 3 h, workup in the usual manner[16] gave the desired ketone (74 mg, 85%). This compound gave a ^{1}H NMR spectrum identical with that previously reported;[5] ^{13}C NMR, see Table I; EI GC-MS 150 (M^+, 36), 135 (15), 122 (4), 109 (13), 107 (100), 108 (89), 91 (52), 79 (37), 67 (9).

(-)-*cis*-Car-2-en-4-ol (15a). Sodium borohydride (69 mg, 1.84 mmol) was added to a stirred solution of (-)-car-2-en-4-one (184 mg, 1.22 mmol; prepared via the sequence described above for the (+)-enantiomer) and $CeCl_3 \cdot 7H_2O$ (684 mg, 1.84 mmol) in 10 mL of MeOH. After 30 min, 10 mL of water was added, and the resulting solution was extracted with ether (3 × 10 mL). The combined ether extracts were dried ($MgSO_4$) and then concentrated in vacuo to afford essentially pure (-)-*cis*-car-2-en-4-ol (145 mg, 78%): $[\alpha]_D$ -169°; ^{1}H NMR δ 5.39 (1, br s, H-2), 3.86 (1, br t, J = 6 Hz, H-4), 1.76 (3, s, H-10), 1.06, 0.95 (3, 3, s, s, H-8, H-9); ^{13}C NMR, see Table I; EI GC-MS, 152 (M^+, 1), 137 (7), 134 (7), 119 (43), 110 (8), 109 (88), 95 (32), 94 (100), 91 (52), 79 (43). An analytical sample was obtained by column chromatography.

Anal. Calcd for $C_{12}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.63; H, 10.58.

(-)-*cis*-Car-2-en-4-yl Acetate (15b). 4-(Dimethylamino)-pyridine (59 mg, 0.48 mmol) and acetic anhydride (39.5 mg, 0.37 mmol) were added to a stirred solution of the alcohol **15a** (56 mg, 0.37 mmol) in 5 mL of methylene chloride, and the resulting solution was stirred overnight at room temperature. After addition of ether (5 mL), the solution was washed first with 2 N HCl and then with 0.5 M sodium bicarbonate and dried ($MgSO_4$). Evaporation of the solvent gave 66 mg (92%) of the desired acetate: $[\alpha]_D$ -69°; ^{1}H NMR δ 5.49 (1, s, H-2), 5.46 (1, br t, J = 8 Hz, H-4), 2.06 (3, s, CH_3CO), 1.64 (3, s, H-10), 1.07, 0.96 (3, 3, s, s, H-8 and H-9); ^{13}C NMR, see Table I; EI GC-MS 134 (18), 120 (10), 119 (100), 117 (5), 109 (8), 93 (12), 91 (23), 77 (7). An analytical sample was obtained by preparative layer chromatography.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.01; H, 9.51.

Preparation of Keto Aldehyde 12. A solution of methylene chloride (3.6 mL) saturated with ozone at -78 °C was added to a solution of (-)-*cis*-car-2-en-4-yl acetate (12.3 mg, 0.6 mmol) in methylene chloride. After 20 min, dimethyl sulfide (10 μL, 0.13 mmol) was added, and the resulting solution was stirred overnight at room temperature. Evaporation of the volatile materials in vacuo gave compound **12** (12.5 mg, 88%). This material was identical (^{1}H NMR and TLC) with a sample prepared by degradation of bertyadionol;[17] EI GC-MS, 184 ($M^+ - C_2H_2O$, 4), 166 ($M^+ - CH_3CO_2H$, 5), 151 (15), 137 (24), 123 (28), 116 (25), 110 (89), 95 (81), 43 (100); CI GC-MS 227 ($M^+ + 1$, 2), 167 ($M^+ + 1 - CH_3CO_2H$, 100).

(+)-*cis*-Caran-2-one (17). A stirred solution of (-)-Car-3-en-2-one (10.8 g, 72 mmol) in ether (100 mL) was hydrogenated 0 °C and atmospheric pressure over 5% Pd/C. After 1600 mL of hydrogen was consumed, the mixture was filtered and the filtrate concentrated in vacuo to afford essentially pure ketone **17** (10.9 g, 98%). This compound gave a ^{1}H NMR spectrum identical with that reported for the (-)-enantiomer;[20] ^{13}C NMR, see Table I; EI GC-MS, 152 (M^+, 23), 137 (6), 124 (18), 110 (31), 109 (17), 95 (51), 82 (100), 81 (20), 67 (73); $[\alpha]_D$ +83.6.

Acknowledgment. We thank Prof. P. R. Jefferies for his generous gift of an authentic sample of bertyadionol. We gratefully acknowledge the financial support of the National Institutes of Health (CA-33743) and the Frasch Foundation for this project and a National Science Foundation instrumentation award (CHE 82-01836) for the 360-MHz NMR spectrometer.

Registry No. 1, 6485-40-1; **2b**, 85710-71-0; **2c**, 88390-14-1; **3**, 22327-33-9; **5**, 88390-11-8; **8**, 22327-36-2; **9**, 4017-82-7; **11**, 6617-33-0; **12**, 41437-12-1; **15a**, 88390-12-9; **15b**, 88390-13-0; **16**, 53585-45-8; **17**, 16838-48-5; HF, 7664-39-3.

Synthesis and Ring-Opening Reactions in the 1,3′-Bicyclopropenyl Series

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Several 1,3′-bicyclopropenyl compounds were prepared by treating 1,3,3-trisubstituted cyclopropenes with methyllithium followed by reaction of the lithiate with cyclopropenylium perchlorate derivatives. Thermolysis of a sample of 3-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene at 120 °C produced a mixture of diphenylacetylene and (*E*)- and (*Z*)-2,3-diphenyl-2-hexen-4-yne. A reasonable mechanism to account for the formation of these products involves opening of the diphenyl-substituted cyclopropene ring followed by a subsequent fragmentation of the adjacent three-ring system and elimination of the acetylene moiety. In marked contrast to the thermal results, photolysis produced 4-methyl-1,3-diphenyl-2-(1-methyl-2-phenylethenyl)naphthalene. Further irradiation of this material gave a benzo[*c*]phenanthrene derivative by a nonoxidative photocyclization reaction. Formation of the styrylnaphthalene derivative involves addition of the initially generated vinyl carbene across the adjacent cyclopropenyl double bond to produce a spiro diradical. This transient species is converted to the final product via a cyclopropyl ring opening followed by a 1,7-sigmatropic hydrogen shift. Photolysis of bis(2,3-diphenylcycloprop-2-enyl)methane resulted in a novel intramolecular [2 + 2] cycloaddition followed by a facile cycloreversion of the initially produced quadricyclane to give tetraphenylbicyclo[2.2.1]heptadiene.

During the last decade there has been an increasing interest in small ring containing compounds. Some of these strained rings are of theoretical interest, and others are important in synthetic routes or as intermediates in reactions. Small-membered rings are also known to have a tremendous effect on reaction rates and reaction pathways when compared to larger ring containing compounds. Among the multitude of small-ring polycycles, cyclopropene represents one of the more intriguing systems. This molecule was first prepared some 60 years ago[1] but,

* Alexander von Humboldt senior visiting scientist, 1983-1984, University of Wurzburg.

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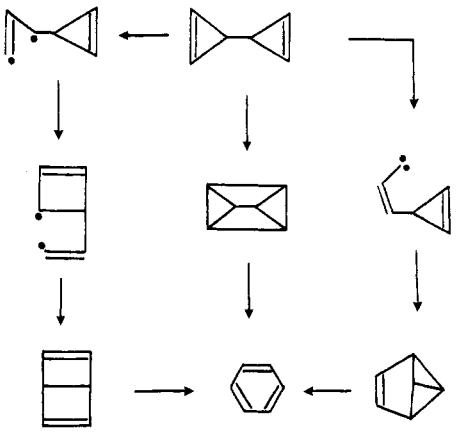
0022-3263/84/1949-0856$01.50/0

despite its unusual structure exhibiting high Baeyer strain, cyclopropene received minimum attention until the late 1950s. Since that time chemical and theoretical interest has been considerable, and a number of reviews have appeared describing the thermal[2-8] and photochemical behavior[9] of this highly strained class of hydrocarbons. The relief of ring strain combined with resonance stabilization of the corresponding ring-opened species accounts for the relatively facile ring-opening reaction of this molecule. Suitably substituted cyclopropenes suffer the ene reaction[10,11] and also readily undergo dimerization,[12] cycloaddition,[13] and complexation with transition metals[8] as a means of releasing strain.

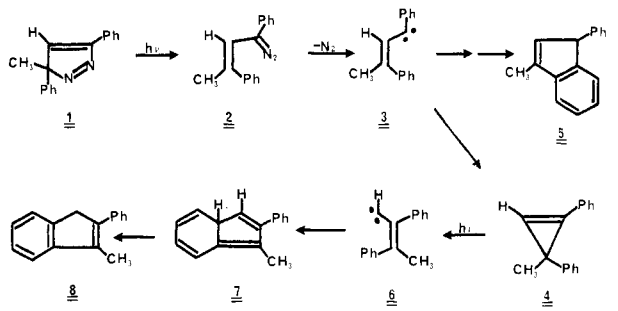
The rearrangement of 3,3′-bicyclopropenyls to benzene derivatives represents one of the more fascinating unimolecular isomerizations known in the cyclopropene field.[14-22] Its mechanism has been a source of controversy over the years. At various times the rearrangement has been postulated to proceed through Dewar benzene,[16] benzvalene,[22] prismane,[14] or diradical[19] and ionic pathways.[16] So far as we know, there were no reports in the literature describing the chemistry of the closely related 1,3′-bicyclopropenyl system when we started our work in this area.[23] This paper describes some novel reactions that occur when a representative 1,3′-bicyclopropenyl derivative is subjected to thermal and photochemical excitation.



Results and Discussion

Part of the ring strain in cyclopropene can be minimized by hybridization of the carbon atomic orbitals. This results in an enhanced acidity of the vinyl C–H bond.[8] Thus, 1,3,3-trisubstituted cyclopropenes react rapidly with alkyllithium reagents to produce relatively stable cyclopropenyllithium derivatives.[24] The lithium compounds can be of considerable synthetic value because they make possible the introduction of a number of functional groups at the vinyl position. The use of 3*H*-pyrazoles for the preparation of cyclopropene derivatives has been previously reported in the literature.[25,26] The reaction is thought to involve the cyclization of a vinyl carbene derived by extrusion of nitrogen from the pyrazole ring. Vinyl diazo species have been implicated as intermediates in this process.[26] Our intention was to generate a representative 1,3′-bicyclopropenyl derivative by first irradiating a 3*H*-pyrazole and then treating the resulting cyclopropene with methyl lithium followed by reaction of the lithiate with an appropriate cyclopropenyl perchlorate.

With this in mind, we photolyzed a sample of 3-methyl-3,5-diphenyl-3*H*-pyrazole (1). When a 5×10^{-2} M solution of 1 is irradiated for 10 min, the deep red coloration associated with diazo compound 2 was detected. On



further irradiation (15 min), the coloration disappears and a mixture of 1,3-diphenyl-3-methylcyclopropene (4) (60%) and 3-methyl-1-phenylindene (5) (20%) was formed. With longer irradiation times, 3-methyl-2-phenylindene (8) was also isolated. The product distribution was found to vary as a function of irradiation time. At longer exposures, owing to a secondary photoreaction of 4, the amount of 8 increased. This was independently demonstrated by the conversion of a pure sample of 4 to 8 under comparable photolytic conditions.

The formation of 4 and 5 can be accounted for by cyclization of vinyl carbene 3 onto either the vinyl or phenyl group.[27] Yet another reaction resulting from a vinyl carbene intermediate (i.e., 6) is the formation of indene 8 from cyclopropene 4. The photolysis proceeds via an isoindene intermediate (7), which subsequently undergoes a thermally allowed 1,5-sigmatropic hydrogen shift to give 8. Earlier work by Padwa[27] and Zimmerman[28] has shown that an unusual substitutent effect operates in the photorearrangement of a series of unsymmetrically substituted cyclopropenes. The major product obtained from a 1-phenyl-substituted cyclopropene was always found to correspond to preferential cleavage of the cyclopropene bond, which is hydrogen rather than phenyl substituted. This unusual regioselectivity was attributed to a funneling

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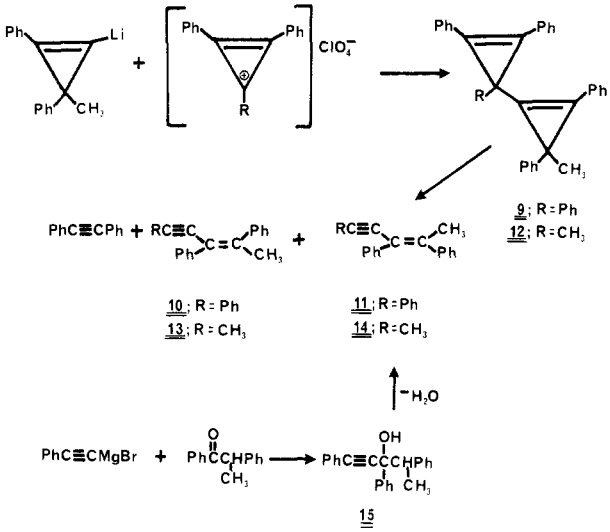
of the excited state of the cyclopropene to the energy surface of the higher lying carbene state.[27] The formation of indene 8 from the irradiation of 4 is perfectly compatible with the earlier observations.

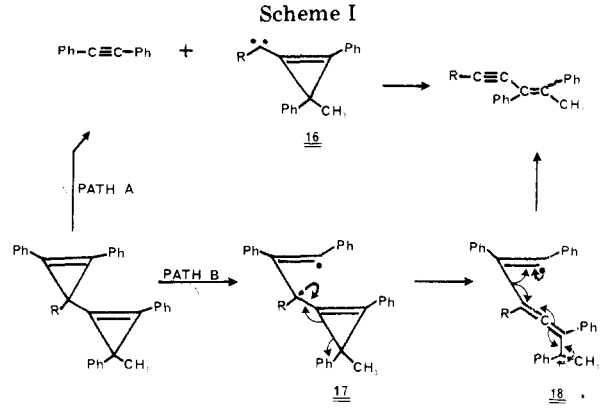
3-Methyl-1-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (9) was prepared in 89% yield by treating 1,3-diphenyl-3-methylcyclopropene (4) with methyllithium followed by addition of the resulting organolithiate to triphenylcyclopropenyl perchlorate. Thermo-



lysis of a benzene solution of 9 at 120 °C produced a mixture of diphenylacetylene and (*E*)- (10) (50%) and (*Z*)-2,3,5-triphenyl-2-penten-4-yne (11) (30%). The two isomeric ene–ynes could be readily interconverted on photolysis or on heating in benzene with a trace of iodine. The assignment of structure 11 was verified by an independent synthesis. The Grignard reagent derived from phenylacetylene was allowed to react with 1,2-diphenylpropan-1-one, and the resulting alcohol was dehydrated to give 11 in high yield. Heating a sample of the closely related 3-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (12), resulted in a similar reaction and gave rise to diphenylacetylene as well as a mixture of (*E*)- (13) and (*Z*)-2,3-diphenyl-2-hexen-4-yne (14).

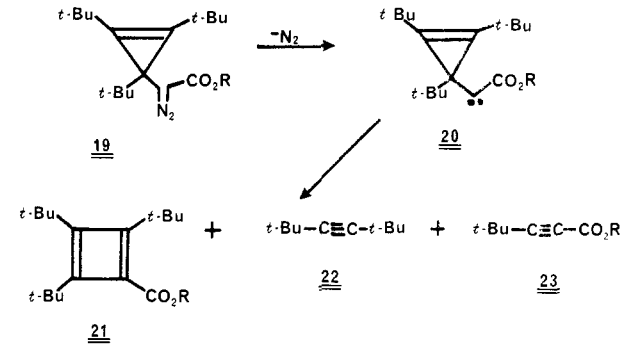
A reasonable explanation to account for the formation of these products involves opening of the diphenyl-substituted cyclopropene ring followed by elimination of the acetylene moiety. Two possibilities are available. One path (path A, Scheme I) involves a concerted cycloreversion to give a 2-cyclopropen-1-ylcarbene (16), which undergoes a subsequent fragmentation. This route corresponds to the reverse of the well-known addition of singlet carbenes to alkynes. The alternate possibility (path

Scheme I



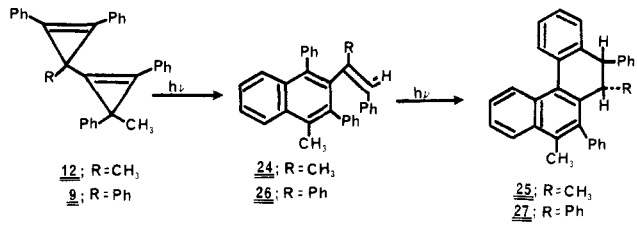
B) involves a series of stepwise fragmentations of the cyclopropene ring via diradical (or ionic) intermediates 17 and 18.

Very recently, Regitz and Eisenbarth generated a representative 2-cyclopropen-1-ylcarbene (i.e., 20) from the



thermolysis of diazomethylcyclopropene 19.[29] The carbene was shown to be responsible for the formation of both cyclobutadiene 21 (70%) and acetylenes 22 and 23 (30%). The different product distribution obtained in this experiment with that encountered from the thermolysis of the 1,3′-bicyclopropenyl system provides reasonable but not absolute evidence for pathway B.

In marked contrast to the thermal results, the photolysis of 1,3′-bicyclopropenyl 12 under an argon atmosphere gave rise to an isomer (24, 70%), mp 220–221 °C, whose structure was assigned as 4-methyl-1,3-diphenyl-2-(1-methyl-2-phenylethenyl)naphthalene (24) on the basis of



its spectra data: NMR ($CDCl_3$, 90 MHz) δ 1.37 (3 H, d, J = 1.4 Hz), 2.52 (s, 3 H), 6.11 (q, 1 H, J = 1.4 Hz), 6.65 (m, 2 H), 7.0–7.6 (m, 16 H), 8.15 (m, 1 H). The UV spectrum of this material was very characteristic of a substituted naphthalene with maxima at 308 nm (ϵ 5600), 286 (13 000), 267 (18 400), 235 (60 100). Unequivocal proof of this assignment derives from a single-crystal X-ray structure analysis. The compound crystallizes in the triclinic space group P_1 with a = 10.5252 (16) Å, b = 11.1005 (19) Å, o = 11.2777 (20) Å, α = 63.436 (14)°, β = 86.535 (13)°, γ = 80.907(13)°, and two molecules per unit cell. Intensity data were collected with copper radiation using the ω scan method for $3 < 2\theta < 100°$. The structure was solved by direct methods using the random starting point tangent refinement routines of the SHELXTL software package[30] and was refined to R_1 = 5.0% and R_2 = 6.4% for 2195 independent observed reflections.

Structure 24 was found to undergo rearrangement on further irradiation. Thus, photolysis of a benzene solution of 24 through a Pyrex filter for 90 min produced 5,6-dihydro-6,8-dimethyl-5,7-diphenylbenzo[*c*]phenanthrene (25) as the exclusive photoproduct: NMR ($CDCl_3$, 90 MHz) δ 0.77 (d, 3 H, J = 7.0 Hz), 2.34 (s, 3 H), 2.90 (qd, 1 H, J = 7.0, 4.0 Hz), 4.33 (d, 1 H, J = 4.0 Hz), 7.0–7.6 (m, 15 H),

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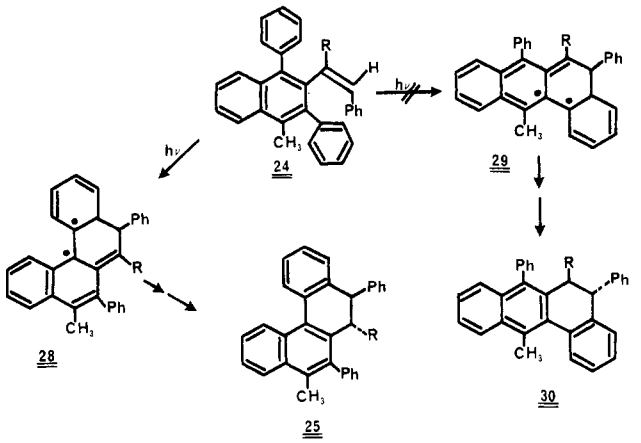
(30) We thank Dr. Charles F. Campana, Nicolet Corp., for the single X-ray structure determination of naphthalene 24. Details will be reported elsewhere.

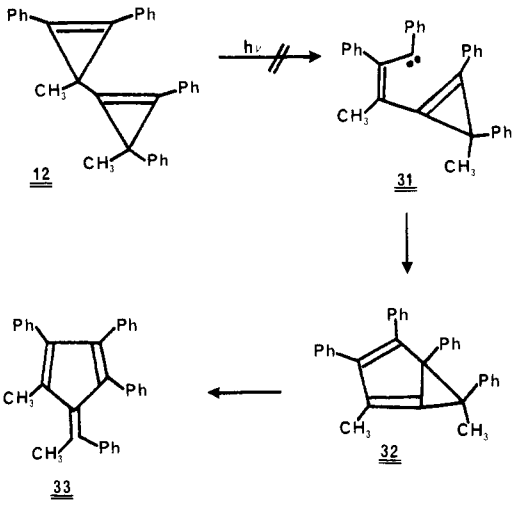
7.9–8.2 (m, 2 H), 8.5–8.7 (m, 1 H). A related set of transformations occurred on photolysis of bicyclopropene **9**. Brief irradiation of **9** resulted in the formation of a major photoproduct (**26**, 76%) whose spectral properties are very similar to those of structure **24** (see Experimental Section). Further irradiation of **26** produced 5,6-dihydro-8-methyl-5,6,7-triphenylbenzo[*c*]phenanthrene **27** in good yield.

The formation of photoproducts **25** and **27** may be conveniently viewed as proceeding by a mechanism that involves an initial stilbene–phenanthrene-type cyclization followed by a 1,5-sigmatropic hydrogen shift. Related nonoxidative photocyclizations are known in the literature and provide good analogy for the above transformation.[31-33] It should be noted that two modes of cyclization are possible, leading to either a benzo[*c*]phenanthrene (**25**) or a benz[*a*]anthracene (**30**) ring system. By analogy with



other cases,[34-39] photocyclization of naphthylstyrene **24** probably takes place by way of a diradical and exclusive reaction at the α-position is presumably due to the greater stability of intermediate **28** compared with the alternative **29**.

The formation of naphthylstyrene **24** from the irradiation of bicyclopropene **12** represents an unusually complex rearrangement, which merits some discussion. Photolysis of 1,2-diaryl-substituted cyclopropenes generally results in σ-bond cleavage to give products that are explicable in terms of the chemistry of vinyl carbenes.[40] One of the more frequently encountered reactions of butadienyl carbenes involves cyclization to cyclopentadiene derivatives.[41-43] Thus, we expected that bicyclopropene **12** would rearrange to fulvene **33** via a process involving electrocyclization of the initially formed vinyl carbene onto the

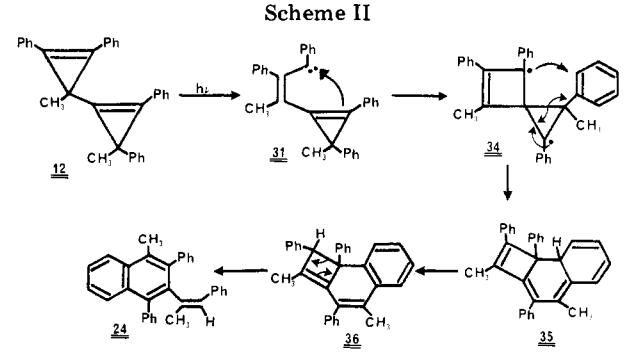


adjacent cyclopropene ring followed by a 1,5-sigmatropic shift. Examination of the crude reaction mixture, however, clearly indicated the absence of fulvene **33**.

We consider that the most economical explanation for the formation of naphthalene **24** is that illustrated in Scheme II. Electrocyclization of **31** to cyclopentadiene **32** does not occur, probably as a consequence of a too highly strained transition state. Instead, the initially generated vinyl carbene **31** adds across the neighboring cyclopropenyl double bond to produce spiro diradical **34**. This transient species is rapidly converted to **36** via a cyclopropyl ring opening followed by a 1,7-sigmatropic hydrogen shift. Retrocyclization of **36** results in the formation of **24**. It should be pointed out that the carbene mechanism outlined in Scheme II may well be a "vinyldiradical like" process. It is also possible that the actual reaction mechanism may involve diradical bridging of the excited state of the diphenyl-substituted cyclopropene to the adjacent cyclopropene π-bond prior to ring opening. This mechanism differs from the carbene pathway only in the chronology of bond breaking and formation. Intermediate gradations between these extremes is also possible.[42]

At this stage of our studies we decided to investigate the photochemical behavior of a bicyclopropene where the three-membered rings are separated by a methylene chain. We were particularly interested in determining whether bis(cyclopropen-2-yl)alkane derivatives could be used as possible models for light-energy storage systems. Photochemical syntheses of strained polycyclic molecules and their catalytic cycloreversions have attracted considerable attention in recent years.[44-49] Among the criteria im-

Scheme II



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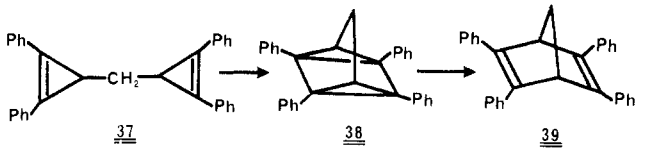
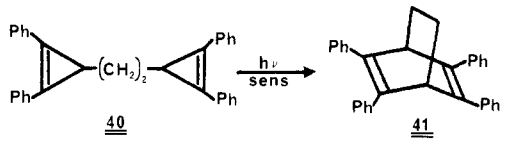
portant for an efficient energy storage system employing an interconversion of isomers A and B are (1) a large ground-state enthalpy difference, (2) high quantum efficiency, (3) good kinetic stability of the strained polycyclic ring, and (4) facile catalytic cycloreversion under mild ambient conditions. One of the most extensively studied systems for the reversible storage of light involves the interconversion of norbornadiene and quadricyclane derivatives.[50-54] During the course of our studies we found that the sensitized irradiation of a substituted bis(cyclopropen-2-yl)methane system (**37**) results in the isolation



of a norbornadiene derivative. Thus, irradiation of biscyclopropene **37** in the presence of thioxanthone as the triplet sensitizer gave rise to a single compound (96%) whose structure was identified as 2,3,5,6-tetraphenylbicyclo[2.2.1]hepta-2,5-diene (**39**) on the basis of its spectral data: mp 215–216 °C; NMR ($CDCl_3$, 100 MHz) δ 2.50 (t, 2 H, J = 1.6 Hz), 4.19 (t, 2 H, J = 1.6 Hz), 7.1–7.4 (m, 20 H); UV (cyclohexane) 289 (ϵ 27 000), 249 (18 700), 233 nm (27 000); ms, m/e 396 (M^+), 218 (base).

The sensitized irradiation of the homologous 1,2-bis(2,3-diphenyl-2-cyclopropen-1-yl)ethane (**40**) system was



also carried out. This compound was prepared by treating 1,6-diphenyl-1,5-hexadiene with chlorophenyldiazirine. The resulting dichlorobis(cyclopropane) was smoothly dehydrohalogenated with potassium *tert*-butoxide. The sensitized photolysis of **40** afforded a 92% isolated yield of bicyclo[2.2.2]octadiene **41**.

The mechanism for the formation of bicyclic compounds **39** and **41** involves an intramolecular [2 + 2] cycloaddition of the two cyclopropene units to give a transient quadricyclane derivative (i.e., **38**). Cycloreversion of this highly strained polycyclic compound readily accounts for the formation of the observed product. Of special interest is the fact that the same polycyclic ring compounds are produced on direct irradiation of the bis(cyclopropenes). Singlet states of cyclopropenes generally react by σ-bond cleavage to give products that are explicable in terms of the chemistry of vinyl carbenes, while triplet states, generated by sensitization techniques, give high yields of cyclopropane dimers.[9] The photochemical reactions of **37** and **40** are the first examples of a [2 + 2] cycloaddition reaction occurring from the singlet manifold of a cyclopropene. The close proximity of the two double bonds is presumably responsible for this unusual behavior. Attempts to detect the existence of the transient quadricyclane intermediate failed. We assume that the polycyclic ring is an extremely short-lived species as the result of severe phenyl–phenyl interactions. These steric interactions are relieved in the transition state for the cycloreversion reaction. A similar situation had been previously encountered by Kaupp and Prinzbach.[55]

Experimental Section[56]

Preparation of 3-Methyl-1-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropane (9). A solution containing 3.34 g of 3-methyl-1,3-diphenylcyclopropane (**4**)[57] and 2.0 g of tetramethylethylene diamine in 40mL of tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To this solution was added 11.4 mL of a 1.4 M solution of methyllithium–lithium bromide complex in ether. The light red solution was allowed to warm to room temperature and was stirred for an additional 40 min. The solution was then added to a mixture containing 5.87 g of 1,2,3-triphenylcyclopropenylium perchlorate[58] in 100 mL of tetrahydrofuran at −78 °C. The mixture was allowed to stir at 0 °C for 12 h. After being quenched with water, the solvent was removed under reduced pressure, leaving behind an oily residue. This material was taken up in ether, washed three times with water and once with a saturated salt solution, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting residue was chromatographed on a medium-pressure chromatographic silica gel column using hexane as the eluent. The major component isolated contained 6.38 g (89%) of 3-methyl-1-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (**9**): mp 123–124 °C; NMR ($CDCl_3$, 100 MHz) δ 1.67 (s, 3 H), 6.9–7.8 (m, 25 H); IR (KBr) 3.20, 5.50, 6.25, 6.73, 6.96, 7.15, 7.32, 9.30, 9.76, 10.93, 13.06, 13.25, 13.50, 14.55 μm; UV (cyclohexane) 328 nm (ϵ 19 700), 311 (29 000), 297 (32 800), 287 (30 600), 227 (41 900); MS, m/e 294, 279, 179, 178 (base), 176. Anal. Calcd for $C_{37}H_{28}$: C, 94.03; H, 5.97. Found: C, 94.08; H, 5.90.

Thermolysis of 3-Methyl-1-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (9). A solution containing 0.445 g of **9** in 2.0 mL of a 15% pyridine–benzene mixture was heated in a sealed tube at 120 °C for 18 h. The solvent was removed under reduced pressure, and the mixture was chromatographed on a 9% silver nitrate silica gel column using a 5% ether–hexane mixture as the eluent. The first component isolated contained 0.091 g (54%) of diphenylacetylene. The second component isolated from the column contained 132 mg (30%) of (*Z*)-2,3,5-triphenyl-2-penten-4-yne (**11**): mp 87–88 °C; NMR ($CDCl_3$, 90 MHz) δ 2.53 (s, 3 H), 7.0–7.6 (m, 15 H); IR (KBr) 3.23, 3.26, 3.29, 6.26, 6.31, 6.37, 6.72, 6.93, 7.22, 9.76, 10.96, 12.94, 13.30, 14.39, μm; 14.68 μm; UV (cyclohexane) 303 nm (ϵ 22 100), 265 (15 500), 249 (15 500), 230 (20 200); MS, m/e 294 (M^+, base), 293, 280, 279, 278, 217, 216, 215, 202. Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.62; H, 6.38.

The third component isolated from the column contained 225 mg (50%) of (*E*)-2,3,5-triphenyl-2-penten-4-yne (**10**): mp 78–79 °C; NMR ($CDCl_3$, 90 MHz) δ 2.14 (s, 3 H), 7.1–7.7 (m, 15 H); IR (KBr) 3.23, 3.26, 3.29, 3.31, 6.26, 6.32, 6.72, 6.95, 7.24, 9.31, 9.78, 10.05, 10.16, 10.97, 12.89, 13.23, 14.27 14.49 μm; UV (cyclohexane) 301 nm (ϵ 18 600), 247 (20 300), 226 (16 900); MS, m/e 294 (M^+, base), 279, 278, 178. Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.76; H, 6.24.

The structure of (*Z*)-2,3-5-triphenyl-2-penten-4-yne (**11**) was verified by an independent synthesis. To a solution containing

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(56) 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 on a Varian EM-390 spectrometer. Mass spectra were determined with a Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV.
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1.02 g of phenylacetylene in 50 mL of tetrahydrofuran was added 3.3 mL of an ethereal 3.0 M methylmagnesium bromide solution. The mixture was stirred for 2 h at room temperature and was heated for an additional hour at reflux. The mixture was cooled to 0 °C, and a solution containing 2.10 g of 1,2-diphenylpropan-1-one in 10 mL of tetrahydrofuran was added. The solution was stirred at 25 °C for 14 h. The reaction was then quenched with a saturated ammonium chloride solution, and the mixture was taken up in ether. The aqueous layer was separated, and the organic layer was washed twice with water and once with a saturated salt solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure, leaving behind a yellow oil, which consisted mostly of 1,3,4-triphenyl-1-pentyn-3-ol (**15**); NMR ($CDCl_3$, 60 MHz) δ 1.31 (d, 3 H, J = 7.5 Hz), 2.67 (br s, 1 H), 3.22 (q, 1 H, J = 7.5 Hz), 7.0–7.5 (m, 15 H). This material was used in the next step without purification. The crude alcohol was added to a solution containing 1 mL of water and 2 mL of concentrated sulfuric acid in 20 mL of acetic acid. The mixture was stirred at room temperature for 30 min and was then poured into water, extracted with ether, washed twice with water, twice with a sodium carbonate solution, and once with a saturated salt solution, and dried over magnesium sulfate. Removal of the solvent left a crude residue, which was chromatographed through a silica gel column using hexane as the eluent to give (*Z*)-2,3,5-triphenyl-2-penten-4-yne (**11**), which was identical in all respects with the substance isolated from the thermolysis of **9**. The *E* and *Z* isomers of triphenyl-2-penten-4-yne were interconverted by heating a sample of either isomer in benzene in the presence of a trace of iodine (*Z*:*E* = 2:1). The two isomers were also interconverted by irradiation in benzene (pss *Z*:*E* = 1:2).

Preparation of 3-Methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (12). A solution containing 2.66 g of 3-methyl-3,5-diphenyl-3*H*-pyrazole[57] in 200 mL of hexane was irradiated through a Pyrex filter sleeve for 1 h. The solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column using hexane as the eluent. Evaporation of the solvent under reduced pressure left a clear oil, which contained mostly 3-methyl-1,3-diphenylcyclopropene. This material was immediately taken up in 50 mL of tetrahydrofuran that contained 1.1 g of tetramethylethylene diamine, and the solution was cooled to −78 °C under a nitrogen atmosphere. To this solution was added 5.0 mL of a 1.8 M solution of methyllithium–lithium bromide complex in ether. The dark red mixture was allowed to warm to room temperature and was stirred for an additional 30 min. The mixture was added to a suspension contain 2.77 g of 1-methyl-2,3-diphenylcyclopropenylium perchlorate[58] in 200 mL of tetrahydrofuran at −78 °C. After being warmed to room temperature, the mixture was quenched with water and the solvent was removed under reduced pressure, leaving behind a dark oily residue. This material was taken up in ether, washed twice with water and once with a saturated salt solution, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was then passed through a silica gel column using hexane as the eluent. The resulting material was rechromatographed on a medium-pressure silica gel column using a 8% benzene–hexane mixture as the eluent. The major component isolated from the column contained 1.79 g (48%) of 3-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (**12**): mp 109–110 °C; NMR ($CDCl_3$, 100 MHz) δ 1.62 (s, 3 H), 1.81 (s, 3 H), 6.9–7.7 (m, 20 H); IR (KBr) 3.3, 5.51, 6.26, 6.71, 6.94, 7.16, 9.32, 9.73, 10.89, 12.99, 13.19, 13.37, 14.21, 14.40, 14.58 μm; UV (95% ethanol) 331 nm (ϵ 21 400), 313 (28 500), 296 (29 700), 226 (30 200); MS, *m*/*e* 410 (M^+), 232, 217, 216, 215, 202, 179, 178 (base), 176, 152. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.55; H, 6.37.

Thermolysis of 3-Methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (12). A solution containing 0.175 g of **12** in 0.5 mL of a 15% pyridine–benzene mixture was heated in a sealed tube at 120 °C for 10 days. Removal of the solvent left a yellow residue, which was chromatographed on a 9% silver nitrate silica gel column using a 2% ether–hexane mixture as the eluent. The first component isolated contained 0.037 g (49%) of diphenylacetylene. The second component isolated from the column contained 0.033 g (33%) of (*Z*)-2,3-diphenyl-2-hexen-4-yne (**14**): mp 66–67 °C; NMR ($CDCl_3$, 100 MHz) δ 2.07 (s, 3 H), 2.43 (s, 3 H), 7.0–7.2 (m, 10 H); IR (KBr) 3.2, 6.19, 6.65, 6.89, 7.08, 9.21, 9.64, 12.92, 13.24, 14.25 μm; UV (cyclohexane) 283 nm (ϵ 12 500), 229 (16 800); MS, *m*/*e* 232 (M^+), 218, 217 (base), 216, 215, 202. Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.86, H, 7.10.

The third component isolated from the column contained 0.046 g (46%) of (*E*)-2,3-diphenyl-2-hexen-4-yne (**13**): mp 68–69 °C; NMR ($CDCl_3$, 100 MHz) δ 1.79 (s, 3 H), 2.07 (s, 3 H), 7.1–7.7 (m, 10 H); IR (KBr) 3.2, 6.18, 6.65, 7.17, 13.29, 13.43, 14.50 μm; UV (cyclohexane) 275 nm (ϵ 12 500); MS, *m*/*e* 232 (M^+), 218, 217 (base), 216, 215, 202. Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.98; H, 6.99. The *E* and *Z*-isomers of 2,3-diphenyl-2-hexen-4-yne were interconverted by heating a sample of either isomer in benzene in the presence of a trace of iodine (*Z*:*E* = 4:1). The two isomers could also be interconverted by carrying out an irradiation in benzene (pss *Z*:*E* = 1:3).

Irradiation of 3-Methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (12). A solution containing 0.201 g of **12** in 250 mL of benzene was irradiated in a Pyrex photolysis well with a 450-W Hanovia lamp for 10 min. The solvent was removed under reduced pressure, leaving behind a solid, which was recrystallized from benzene–hexane to give 0.138 g (69%) of a white crystalline solid, which was identified as (*Z*)-4-methyl-1,3-diphenyl-2-(1-methyl-2-phenylethenyl)-naphthalene (**24**) on the basis of the following data: mp 220–221 °C; NMR ($CDCl_3$, 100 MHz) δ 1.37 (d, 3 H, J = 1.4 Hz), 2.52 (s, 3 H), 6.11 (br s, 1 H), 6.6–6.7 (m, 2 H), 7.0–7.6 (m, 16 H), 8.1–8.2 (m, 1 H); IR (KBr) 3.2, 6.23, 6.70, 6.93, 7.12, 9.31, 9.67, 9.93, 13.16, 13.29, 13.39, 13.56, 14.35 μm; UV (cyclohexane) 308 nm (ϵ 5640), 286 (13 100), 267 (18 400), 235 (60 100); MS, *m*/*e* 411, 410 (M^+, base), 395, 380, 319, 317, 304, 303, 166, 121, 105. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.49; H, 6.47.

Irradiation of **24** in benzene for 20 min produced a mixture of **24** plus another compound whose structure was assigned as the *E* isomer of 4-methyl-1,3-diphenyl-2-(1-methyl-2-phenylethenyl)naphthalene as a consequence of its NMR spectrum: ($CDCl_3$, 100 MHz) δ 1.58 (s, 3 H, J = 1.5 Hz), 2.41 (s, 3 H), 5.83 (br s, 1 H). When a solution of **24** in benzene was irradiated for longer periods of time, a third component was produced. Removal of the solvent under reduced pressure left a brown residue, which was subjected to medium-pressure silica gel chromatography using a 1% acetone–hexane mixture as the eluent. The first component eluted from the column contained 0.071 g (37%) of a white crystalline solid whose structure was identified as 5,6-dihydro-6,8-dimethyl-5,7-diphenylbenzo[*c*]phenanthrenje (**25**) on the basis of the following data: mp 214–215 °C; IR (KBr) 3.27, 3.31, 3.37, 6.27, 6.34, 6.40, 6.71, 6.79, 6.91, 7.26, 7.38, 10.01, 12.71, 13.30, 13.39, 14.06, 14.47 μm; UV (cyclohexane) 340 nm (ϵ 11 200), 323 (15 400), 242 (50 800); MS, *m*/*e* 410 (M^+), 395, 317, 207 (base). Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.33; H, 6.61. The NMR spectrum ($CDCl_3$, 90 MHz) showed the following: δ 0.77 (d, 3 H, J = 7 Hz), 2.34 (s, 3 H), 2.90 (d, 1 H, J = 7, 4 Hz), 4.33 (d, 1 H, J = 4 Hz), 7.0–7.6 (m, 16 H), 7.9–8.2 (m, 2 H). External irradiation of the doublet at δ 0.77 collapsed the doublet of quartets at δ 2.90 to a doublet (J = 4 Hz). Irradiation of the doublet of quartets at δ 2.90 collapsed the doublet at δ 0.77 to a singlet and the doublet at δ 4.33 to a singlet. Irradiation of the doublet at δ 4.33 collapsed the doublet at δ 0.77 to a singlet and the doublet of quartets at 2.90 to a quartet (J = 7 Hz).

Irradiation of 3-Methyl-1-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene (9). A solution containing 0.221 g of **9** in 250 mL of benzene under an argon atmosphere was irradiated in a Pyrex photolysis well for 20 min with a 450-W Hanovia lamp. The solvent was removed under reduced pressure to leave behind a light brown residue, which was chromatographed on a medium-pressure silica gel column using a 4% acetone–hexane mixture as the eluent. The first component eluted from the column contained 0.499 g (76%) of a white solid whose structure was identified as 4-methyl-1,3-diphenyl-2-(1,2-diphenylethenyl)naphthalene (**26**) on the basis of the following data: mp 154–155 °C; NMR ($CDCl_3$, 100 MHz) δ 2.47 (s, 3 H), 6.4–7.6 (m, 24 H), 8.0–8.2 (m, 1 H); IR (KBr) 3.28, 6.22, 6.70; 6.90, 7.21, 9.28, 9.64, 9.87, 10.78, 11.44, 12.83, 12.98, 13.09, 13.52, 13.71, 14.4 μm; UV (cyclohexane) 304 nm (ϵ 18 100), 287 (22 100), 234 (73 000); MS, *m*/*e* 473, 472 (M^+, base), 457, 394, 381, 380, 379, 378, 305, 303, 302, 289, 189, 178, 167, 165, 158, 131, 91, 78, 77. Anal. Calcd for $C_{37}H_{28}$: C, 94.03; H, 5.97. Found: C, 93.80; H, 6.26.

Upon extended irradiation a new product was formed that could also be obtained by an independent irradiation of **26**. Thus a solution containing 0.200 g of **26** in 250 mL of benzene was irradiated for 2.5 h. The solvent was removed under reduced pressure, leaving behind a red oil, which was chromatographed on a medium-pressure silica gel column using a 1% acetone–hexane mixture as the eluent. The major component eluted contained 0.144 g (72%) of a white solid whose structure was identified as 5,6-dihydro-8-methyl-5,6,7-triphenylbenzo[*c*]-phenanthrene (**27**) on the basis of the following data: mp 231–232 °C; NMR ($CDCl_3$, 90 MHz) δ 2.28 (s, 3 H), 3.88 (d, 1 H, J = 5.5 Hz), 4.62 (d, 1 H, J = 5.5 Hz), 5.99 (br d, 2 H, J = 6.5 Hz), 6.15 (br d, 1 H, J = 7.0 Hz), 6.5–7.6 (m, 17 H), 7.9–8.2 (m, 2 H), 8.6–8.8 (m, 1 H). External irradiation of the doublet at δ 3.88 collapsed the double at δ 4.63 to a singlet. Irradiation of the doublet at δ 4.63 collapsed the doublet at δ 3.88 to a singlet: IR (KBr) 3.26, 3.29, 6.26, 6.73, 6.90, 7.23, 9.38, 9.75, 13.16, 13.39, 14.49 μm; UV (cyclohexane) 339 nm (ϵ 12400), (15300), 311 (11600), 251 (47500), 241 (47500), 226 (39200); MS, m/e 472 (M^+), 379, 303, 302, 289, 158 (base), 105, 91, 78, 77. Anal. Calcd for $C_{37}H_{28}$: C, 94.03; H, 5.97. Found: C, 93.87; H, 6.06.

Preparation of Bis(2,3-diphenylcyclopropen-2-yl)methane (37). A mixture containing 2.37 g of 1,5-diphenyl-1,4-pentadiene and 3.27 g of chlorophenyldiazirine[59] in 200 mL of benzene was heated at reflux for 4 h. At the end of this time the solvent was removed under reduced pressure, and the brown residue was immediately dissolved in 250 mL of tetrahydrofuran and cooled to −78 °C. To this stirred solution was added 12.3 g of potassium *tert*-butoxide. The mixture was allowed to warm to room temperature and was stirred for an additional 16 h. The reaction mixture was then quenched with water and concentrated under reduced pressure. The residue was extracted with ether, washed four times with water and once with a saturated salt solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a red residue, which was filtered through a silica gel column using hexane as the eluent to give 2.92 g (67%) of a pale yellow solid identified as bis(2,3-diphenylcyclopropen-2-yl)methane (**37**)[60] on the basis of the following data: mp 118–119 °C; NMR ($CDCl_3$, 100 MHz) δ 1.96 (t, 2 H, J = 5.2 Hz), 2.42 (t, 2 H, J = 5.2 Hz), 7.3–7.6 (m, 12 H), 7.7–7.9 (m, 8 H); IR (KBr) 3.2, 3.46, 5.50, 6.25, 6.70, 6.94, 7.15, 9.59, 9.85, 10.98, 12.01, 13.32, 14.70 μm; UV (cyclohexane) 342 nm (ϵ 35500), 330 (41 00), 323 (46000), 313 (39000), 240 (27600), 230 (32700), 225 (31800).

Triplet-Sensitized Irradiation of Bis(2,3-diphenylcyclopropen-2-yl)methane (37). A solution containing 0.113 g of **37** and 0.015 g of thoxanthen-9-one in 250 mL of benzene was irradiated through a Uranium filter sleeve for 30 min. Removal of the solvent under reduced pressure followed by crystallization of the residue from benzene–hexane gave 0.108 g (96%) of a white solid whose structure was assigned as 2,3,5,6-tetraphenylbicyclo[2.2.1]hepta-2,5-diene (**39**) on the basis of the following data: mp 215–216 °C; NMR ($CDCl_3$, 100 MHz) δ 2.50 (t, 2 H, J = 1.6 Hz), 4.19 (t, 2 H, J = 1.6 Hz), 7.1–7.4 (m, 20 H); IR (KBr) 3.31, 3.37, 6.15, 6.26, 6.35, 6.71, 6.94, 7.12, 7.91, 9.23, 9.74, 12.70, 13.1, 13.78, 14.4 μm; UV (cyclohexane) 289 nm (ϵ 27000), 249 (18700), 233 (27000); MS, m/e 396 (M^+), 395, 219, 218 (base), 217, 178, 131, 130, 91, 85, 78, 77, 71. Anal. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10. Found: C, 94.19; H, 6.07.

Attempts to detect the presence of a transient quadricyclane were unsuccessful. The irradiation was also run at 10 °C in an attempt to trap the quadricyclane with dimethylacetylene dicarboxylate. This was also unsuccessful.

Preparation of 1,2-Bis(2,3-diphenyl-2-cyclopropen-1-yl)-ethane (40). A mixture containing 1.55 g of 1,6-diphenyl-1,5-hexadiene[61] and 2.01 g of chlorophenyldiazirine was heated at reflux for 4 h in 200 mL of benzene. At the end of this time, the solvent was removed under reduced pressure, leaving behind a yellow residue. The residue was immediately dissolved in 200 mL of tetrahydrofuran and cooled to −78 °C. To this stirred solution was added 9.0 g of potassium *tert*-butoxide. The mixture was allowed to warm to room temperature and was stirred for an additional 18 h. The reaction mixture was then quenched with water and concentrated under reduced pressure. The residue was extracted with ether, washed four times with water and once with a saturated salt solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow residue, which was filtered through a silica gel column eluting with hexane in to give 1.23 g (45%) of a white solid whose structure was assigned as 1,2-bis(2,3-diphenyl-2-cyclopropen-1-yl)ethane (**40**) on the basis of the following data: mp 119–120 °C; NMR ($CDCl_3$, 100 MHz) δ 1.8–1.9 (m, 4 H), 2.1–2.2 (m, 2 H), 7.1–7.5 (m, 12 H), 7.6–7.8 (m, 8 H); IR (KBr) 3.2, 3.44, 5.5, 6.25, 6.69, 6.91, 7.12, 9.30, 9.77, 13.25, 14.55 μm; UV (95% ethanol) 339 nm (ϵ 29500), 320 (41200), 300 (36200) 238 (24900), 229 (28800), 224 (27300); MS, m/e 410 (M^+), 382, 324, 220, 207, 206, 205, 203, 193, 180, 179, 178, 165, 129, 115, 105, 91 (base), 89, 77. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.49; H, 6.49.

Triplet-Sensitized Irradiation of 1,2-Bis(2,3-diphenyl-2-cyclopropen-1-yl)ethane (40). A solution containing 0.072 g of **40** and 0.010 g of thioxanthen-9-one in 250 mL of benzene was irradiated through a Uranium filter sleeve for 35 min. Removal of the solvent under reduced pressure left a solid, which was crystallized from benzene–hexane to give 0.066 g (92%) of 2,3,5,6-tetraphenylbicyclo[2.2.2]octa-2,5-diene (**41**): mp 182–183 °C; NMR ($CDCl_3$,100 MHZ) δ 1.84 (br s, 4 H), 4.25 (br s, 2 H), 7.09 (br s, 14 H), 7.28 (br s, 6 H); IR (KBr) 3.2, 3.36, 6.21, 6.67, 6.90, 7.11, 8.65, 12.86, 13.15, 13.25, 14.26, 14.35 μm; UV (cyclohexane) 270 nm (ϵ 23800), 224 (30400); MS, m/e 383, 382 (base), 220, 69. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.52; H, 6.46.

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