(7.2 mmol) of paraformaldehyde. The solution was refluxed, and the H_2O formed was removed via a Dean-Stark trap. After 4 h, the benzene was removed under reduced pressure. The residue was separated on a silica gel column with diethyl ether as the mobile phase. The 3-[(1-adamantyl)methyl]-1,3-oxazolidine (R_f 0.8) was obtained as a liquid: 2.84 g (89%); ^1H NMR ($CDCl_3$) δ 4.10 (s, 2, OCH_2N), 3.60 (m, 2, CH_2O), 2.85 (m, 2, CH_2N), 2.1 (s, 2, CH_2N), 1.9 (m, 3, CH of adamantyl), 1.6 (d, 6, CH_2 of adamantyl), 1.46 (d, 6, CH_2 of adamantyl); IR ($HCCl_3$) 2905 (m), 2850 (m), 1450 (m), 1005 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 75.68; H, 10.58; N, 6.16.

6-Tosyl-β-cyclodextrin.[15] To 2.5 g (2.2 mmol) of freshly dried β-cyclodextrin (heated at 100 °C under vacuum) was added approximately 600 mL of freshly distilled pyridine (from BaO). This mixture was stirred until the β-cyclodextrin was completely dissolved, and 10 g of toluenesulfonyl chloride was added. The reaction mixture was stirred at room temperature for 40 min, and 20 mL of H_2O was added. The pyridine was then removed under reduced pressure. The resulting syrup was shaken with 100 mL of acetone, and the acetone was decanted off. This procedure was repeated in order to remove all the toluenesulfonic acid. The solid remaining in the flask was recrystallized from an ethyl acetate/2-propanol/water (10/13/7) solvent system to give a white powder: 0.83 g (27%); mp 157.5-158.5 °C; ^1H NMR (Me_2SO-d_6) δ 7.8 (d, CH=CSO_3), 7.3 (d, CH=CCH_3), 4.4-3.5 (br m, cyclodextrin), 2.40 (s, CH_3). Anal. Calcd for $C_{49}H_{76}SO_{37}$: C, 45.54; H, 5.16. Found: C, 44.55; H, 5.12.

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6-Morpholino-β-cyclodextrin. To 100 mg of 6-tosyl-β-cyclodextrin was added 2 g of morpholine. This mixture was heated for 48 h at 75 °C. The solution was then diluted to 10 mL with acetone and placed on a silica gel column with acetone as the mobile phase (R_f 0.9). The fraction containing the substituted β-cyclodextrin was separated, and the solvent was removed under reduced pressure. To the resulting syrup was added 1 mL of H_2O, and the mixture was then freeze-dried to give a white powder: 0.026 g (25%); mp 254-256 °C dec; ^1H NMR (Me_2SO-d_6) δ 4.88 (br m, HC(O)O), 3.83-3.08 (br m, cyclodextrin), 3.52 (m, ring CH_2O), 2.69 (m, ring CH_2N).

6-(4,4-Dimethylpiperidino)-β-cyclodextrin. To 100 mg of 6-tosyl-β-cyclodextrin was added 2 g of 4,4-dimethylpiperidine. This mixture was heated for 48 h at 75 °C. The solution was cooled, diluted to 10 mL with acetone, and eluted on a column of silica gel with acetone as the mobile phase (R_f 0.9). The fraction containing the substituted β-cyclodextrin was collected, and the acetone was removed under reduced pressure. The resulting syrup was dissolved in H_2O, and the solution was freeze-dried to give a white powder: 65 mg; mp 151 °C dec; ^1H NMR δ 4.88 (br m, HC(O)O), 3.83-3.08 (br m, cyclodextrin), 2.88 (m, ring CH_2N), 2.44 (t, CH_2N), 1.38 (m, $CH_2C(CH_3)_2$), 0.97 (s, $(CH_3)_2C$).

Registry No. 1 (R = CH_3), 1003-84-5; 1 (R = $AdCH_2$), 82679-29-6; 1 (R = β-CD), 82679-30-9; 1 (R = CH_3CO), 82679-31-0; 1 (R = AdCO), 82679-32-1; 2 (R = CH_3), 109-02-4; 2 (R = $AdCH_2$), 22508-54-9; 2 (R = β-CD), 82679-33-2; 2 (R = CH_3CO), 1696-20-4; 2 (R = AdCO), 22508-50-5; 3 (R = CH_3), 27970-32-7; 3 (R = $AdCH_2$), 82679-34-3; 3 (R = CH_3CO), 3672-60-4; 3 (R = AdCO), 82679-35-4; 6-tosyl-β-cyclodextrin, 67217-55-4; 2-aminoethanol, 141-43-5; 1-adamantylcarbonyl chloride, 2094-72-6; 2-[[(1-adamantyl)-carbonyl]amino]ethanol, 78743-65-4; 2-[[(1-adamantyl)methyl]-amino]ethanol, 65738-69-4.

Synthesis of the Benzotricyclooctane Ring System. Intramolecular [2 + 2] Cycloaddition of Indene Derivatives

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The photosensitized triplet reactions of several 1-allyl-substituted indenes have been studied. The triplet-sensitized irradiations gave benzotricyclo[3.3.0.$0^{2,7}$]octanes in good yield by means of a novel intramolecular [2 + 2] cycloaddition. The effect of substituents on the regioselectivity of the sensitized rearrangement was studied in some detail. With the simple 1-allyl-substituted isomer, 1,5-cyclization of the excited state is the preferred path. This mode of cyclization is favored on the basis of strain, radical stability, and entropy factors. We have found, however, that the normal closure predicted by the rule of five does not occur in the photosensitized irradiation of the 1-prenyl-substituted isomer. With this system, intramolecular [2 + 2] cycloaddition gives rise to the benzotricyclo[3.2.1.$0^{3,8}$]octane system. The diradical produced from the sensitized 1,4-cyclization path is long lived enough to allow internal disproportionation to compete with radical coupling. The facility with which the intramolecular [2 + 2] indene photocycloadditions occur makes this type of approach particularly attractive for the synthesis of some unusual polycyclic ring compounds.

In recent years organic chemists have become increasingly aware of the power of photochemical [2 + 2] cycloadditions for the construction of complex polycyclic molecules.[1-4] In particular, the photocycloaddition reactions of α,β-unsaturated carbonyl compounds has been the subject of intensive study.[5] More recently, a number of approaches to the synthesis of a variety of tricyclic ring systems have used an intramolecular variant of this reaction.[6-16] Strained polycyclics containing bicyclo[2.1.0]pentane and bicyclo[2.2.0]hexane units have also been prepared by this method.[17-20] These compounds play an important role in the understanding of many aspects of organic chemistry.[20-25] For this reason, synthetic efforts using the photochemical [2 + 2] cycloaddition reaction

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have been extensive. Our research group has been involved over the past few years in a program of synthesizing strained polycyclic rings that uses the intramolecular [2 + 2] cycloaddition of alkenes as the primary strategy.[26-30] Within the context of this work, we felt that it was important to know more about the details affecting the regiochemistry of the intramolecular [2 + 2] cycloaddition. We have used allyl-substituted indenes as model systems to probe the effects of substitution on the regiochemistry of the internal cycloaddition reaction.[31] In this paper we describe the results of our study that shows that the sensitized photolysis of allyl-substituted indenes can lead to the elaboration of the benzotricyclo[3.3.0.0^{2,7}]octane and benzotricyclo[3.2.1.0^{3,8}]octane ring systems.

Results

Previous studies of the photochemistry of indene and alkyl-substituted indenes have only dealt with the sensitized rearrangement[32-35] and bimolecular cycloadditions of these systems.[36] While intramolecular [2 + 2] photocycloadditions of olefins to carbon–carbon double bonds are well-documented reactions,[37-39] similar internal photoreactions of indene derivatives are unknown. We began our search for an intramolecular [2 + 2] cycloaddition by studying the photosensitized behavior of 1-allylindene (1). The thioxanthone-sensitized photolysis of 1 produced a major photoisomer in 66% yield. This material was assigned as 2,2a,7,7a-tetrahydro-2,7-methano-1*H*-cyclobut[*a*]indene (**2**): NMR ($CDCl_3$, 270 MHz) δ 0.80 (ddd, 1 H,

Table I. NMR Spectral Data of Benzotricyclo[3.2.0.0^{2,7}]octanes

H	2	7	8	9	14
H_1	1.88 (ddd, $J_{1,2}$ = 7.3, $J_{1,9}$ = 2.9, $J_{1,10}$ = 2.0, $J_{1,3}$ = 2.0 Hz)	2.16 (m)	2.22 (m)	1.97 (br dd, $J_{1,2}$ = 7.3, $J_{1,3}$ = 2.2, $J_{1,9}$ = 1.5, $J_{1,10}$ = 1.0)	2.20–2.26 (m)
H_2	1.11 (d)	1.10 (d, $J_{1,2}$ = 7.5 Hz)	1.19 (d, $J_{1,2}$ = 7.5 Hz)	1.24 (d)	1.19 (d, $J_{1,2}$ = 8.1)
H_3	2.89 (ddd, $J_{3,10}$ = 7.0, $J_{3,4}$ = $J_{3,7}$ = 2.0 Hz)	2.16 (m)	2.22 (m)	2.85–2.94 (m)	3.02 (dd, $J_{3,10}$ = 6.6, $J_{1,3}$ = 2.9)
H_4	3.21 (m)				
H_7	3.21 (m)	3.20 (dd, $J_{7,8}$ = 7.0 Hz)			
H_8	1.92 (dd, $J_{8,9}$ = 10.2, $J_{7,8}$ = 7.0 Hz)	1.90 (dd)	2.22 (m)	1.74 (d, $J_{8,9}$ = 10.3)	2.20–2.26 (m)
H_9	0.78 (ddd)	0.83 (ddd, $J_{8,9}$ = 10.5, $J_{7,9}$ = 3.0, $J_{1,9}$ = 2.3 Hz)	0.92 (ddd, $J_{8,9}$ = 9.5, $J_{7,9}$ = 3.0, $J_{1,9}$ = 2.0 Hz)	1.17 (br dd, $J_{9,10}$ = 2.0, $J_{3,9}$ = 1.5)	1.40 (ddd, $J_{8,9}$ = 10.3, $J_{9,10}$ = 2.2, $J_{1,9}$ = 2.0)
H_{10}	2.55 (ddd)	2.59 (m)	2.22 (m)	2.85–2.94	2.37–2.43 (m)

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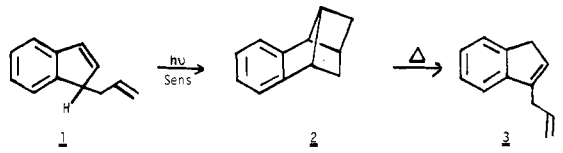
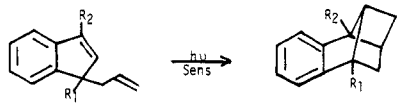
J = 10.2, 2.9, 2.0 Hz), 1.13 (d, 1 H, J = 7.3 Hz), 1.78 (ddd, 1 H, J = 7.3, 2.9, 2.0 Hz), 1.91 (dd, 1 H, J = 10.2, 7.0 Hz), 2.55 (dt, 1 H, J = 7.0, 2.0 Hz), 2.89 (dq, 1 H, J = 7.0, 2.0 Hz), 3.20–3.22 (m, 2 H), 7.10–7.23 (m, 4 H). The identity of structure **2** was based on its spectroscopic and analytical properties and was further supported by its chemical behavior. Photoproduct **2** undergoes a thermal cycloreversion reaction to 3-allylindene (**3**) in toluene at 160 °C with a half-life of 38 h.



1 2 3

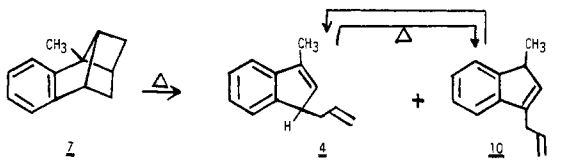
The sensitized conversion of 1-allyl-substituted indenes to benzotricyclo[3.3.0.0^{2,7}]octanes was found to be a general reaction. Thus, irradiation of indenes **4–6** in the presence of thioxanthone afforded the internal photoadducts **7–9** in high yield.



4; R_1=H; R_2=CH_3
5; R_1=R_2=CH_3
6; R_1=CH_3; R_2=Ph

7; R_1=H; R_2=CH_3
8; R_1=R_2=CH_3
9; R_1=CH_3; R_2=Ph

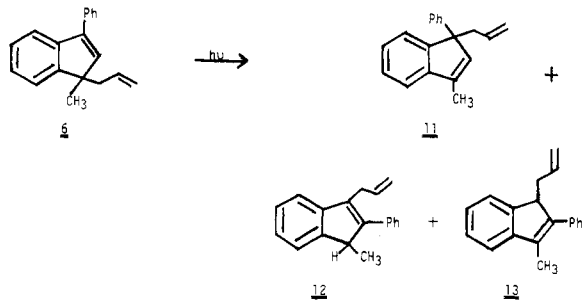
In Table I are presented the interpretable portions of the spectra of the benzotricyclo[3.3.0.0^{2,7}]octane derivatives **7–9**. The recorded assignments are internally consistent and also agree well with earlier data for the related tricyclo[3.3.0.0^{2,7}]octanone ring system.[40] Photoproduct **7** was found to isomerize thermally to indenes **4** and **10** at 150 °C. Subsequent studies showed that this reaction



7 4 10

proceeds via conversion first to indene **4** followed by a thermal or perhaps acid-catalyzed 1,3 hydrogen shift. Photoproducts **8** and **9** were also found to undergo a smooth thermal [2 + 2] retrogression reaction to indenes **5** and **6** in toluene at 150 °C.

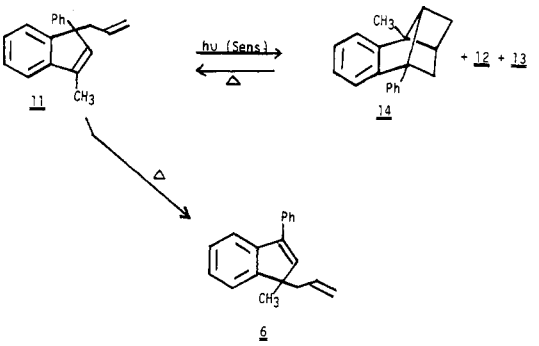
In contrast to the sensitized photolysis, the direct irradiation of indene **6** was found to proceed differently in that the major product (35%) corresponded to indene **11**. The



6 11 12 13

structure of this material was unambiguously established by comparison with an independently synthesized sample. The structures of the two minor photoproducts [**12** (5%) and **13** (5%)] produced were assigned on the basis of their spectral properties and were further confirmed by comparison with independently synthesized samples. No signs of the isomeric methanocyclobut[*a*]indene ring system **9** could be detected in the crude photolysate.

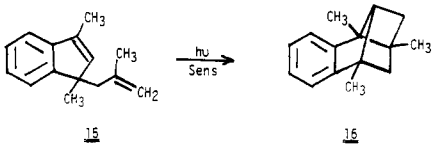
The photosensitized behavior of 1-allyl-1-phenyl-3-methylindene (**11**) was also studied and was found to give rise to a mixture of three compounds. The major product



11 14 6

formed was assigned as 2,2a,7,7a-tetrahydro-2a-methyl-7-phenyl-2,7-methano-1*H*-cyclobut[*a*]indene (**14**; 32%) on the basis of its spectral properties and thermal behavior; NMR ($CDCl_3$, 270 MHz) δ 1.19 (d, 1 H, J = 8.1 Hz), 1.40 (br d, 1 H, J = 10.3 Hz), 1.69 (s, 3 H), 2.21–2.25 (m, 2 H), 2.39–2.43 (m, 1 H), 3.02 (dd, 1 H, J = 6.6, 2.9 Hz), 6.80–7.41 (m, 9 H). Photoproduct **14** was found to isomerize thermally to indene **6** at 160 °C. Subsequent studies showed that this reaction proceeds via conversion first to indene **11** followed by a thermal Cope rearrangement to **6**. This was confirmed by carrying out the thermolysis of **14** at 150 °C for short periods of time and isolating indene **11** in quantitative yield. Heating a pure sample of **11** at 160 °C resulted in the exclusive formation of the thermodynamically more stable indene **6**. The structures of the two minor photoproducts were established as indenes **12** (30%) and **13** (24%). It should be mentioned here that the direct irradiation of **11** produced a mixture of indenes **12** and **13** in the same distribution as that obtained from the sensitized photolysis. No signs of benzotricyclooctane **14** could be detected in the crude photolysate derived from the direct photolysis of indene **11**.

Attention was next turned to the triplet-induced photobehavior of the 3-substituted 2-methylallyl-substituted indene system. The sensitized irradiation of indene **15** produced a single photoproduct whose structure was assigned as benzotricyclooctane **16** on the basis of its spectral and thermal properties (see the Experimental Section).



15 16

We have also examined the sensitized behavior of the 1-substituted 2-methyl-2-butenyl-substituted indene system in order to probe the regiochemical aspects of this novel intramolecular photocycloaddition reaction. The thioxanthone-sensitized reaction of indene **17** gave rise to a [2 + 2] cycloadduct, **18** (26%), as well as two rearranged indenes [**19** (34%) and **20** (33%)]. The structures of the latter two compounds were established by comparison with independently synthesized samples. The structure of the [2 + 2] cycloadduct **18** was assigned as 2,2a,7,7-tetrahydro-2,2,2a-trimethyl-7-phenyl-1,7-methano-1*H*-cyclobut[*a*]indene, mp 75–76 °C, on the basis of its characteristic NMR spectrum, which showed methyl singlets at δ 0.59, 1.20, and 1.42, a doublet of doublets at 2.34 (J = 12.0,

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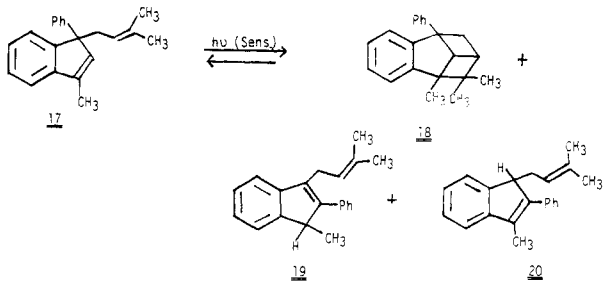
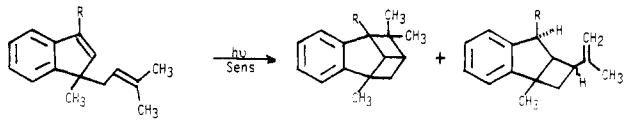
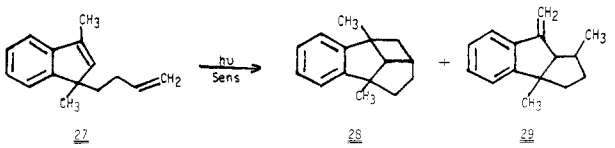


2.0 Hz) and 2.98 (J = 12.0, 9.0 Hz), a doublet at 3.30 (J = 5.0 Hz), a doublet of double doublets at 2.24 (J = 9.0, 5.0, 2.0 Hz), and a multiplet at 6.4–7.3 (9 H). The alternative mode of photocyclization of **17** would lead to a structure having an NMR spectrum quite different from that observed (see Table I). Thermolysis of cycloadduct **18** at 170 °C led to the rupture of the cyclobutane ring and regeneration of indene **17**.

Subjection of the isomeric phenyl-substituted indene **21** to similar sensitized conditions resulted in the formation of three products that could be separated and purified by silica gel chromatography. The major photoproduct (55%) isolated was a crystalline solid, mp 91–92 °C, whose structure was assigned as benzotricyclo[3.2.1.$0^{3,8}$]octane **22** on the basis of its spectroscopic and thermal properties; NMR ($CDCl_3$, 270 MHz) δ 0.84 (s, 3 H), 1.00 (s, 3 H), 1.60 (s, 3 H), 2.12 (d, 1 H, J = 11.7 Hz), 2.27 (dd, 1 H, J = 8.8, 5.1 Hz), 2.35 (dd, 1 H, J = 11.7, 8.8 Hz), 3.63 (d, 1 H, J = 5.1 Hz), 7.03–7.36 (m, 9 H). In addition to **22**, a mixture of isomeric 2,2a,7,7a-tetrahydro-1-isopropenyl-2a-methyl-7-phenyl-1*H*-cyclobut[*a*]indenes (**23**; 37%) were also formed. Subjection of the closely related indene **24** to similar photolysis conditions resulted in the formation of a set of analogous photoproducts (see Experimental Section).



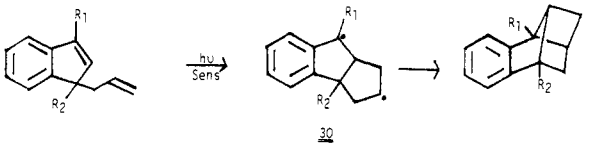
With these results in hand it was of interest to investigate the photochemistry of 4-(1,3-dimethylindenyl)-1-butene (**27**), a higher homologue of **5**. This indene was prepared by hydroboration of **5** followed by pyridinium chlorochromate oxidation and treatment of the resulting aldehyde with methylenetriphenylphosphorane. Irradiation of **27** in the presence of thioxanthone yielded a mixture of two products, **28** (61%) and **29** (28%). These structural assignments are based on their characteristic spectral properties (see the Experimental Section).



Discussion

The photocycloaddition reactions of simple indene derivatives has been shown to be dependent on the multiplicity of the excited state involved.[34] Triplet-sensitized irradiation of indene itself afforded the *cis-anti-cis*-cyclobutane dimer in high yield.[41-43] However, on direct irradiation, in which the light is absorbed by indene, extensive polymerization occurs. Cycloadducts can also be obtained by sensitized cross-addition reactions of indene with coumarin[41,43] or acrylonitrile.[36] Photolysis of indene and acrylonitrile with no sensitizer results in the formation of 2-(1-indenyl)propionitrile as the major product.[36] The triplet energy of these 3-alkyl- and phenyl-substituted indenes is not known; however, it should be close to the value reported for styrene (E_T = 61.5 kcal/mol).[44] Since thioxanthone has a much higher triplet energy (E_T = 65.5 kcal),[44] efficient energy transfer between the sensitizer and the indene occurs. All of the intramolecular cycloaddition reactions that we have encountered proceed via the triplet state with moderate quantum efficiency ($\Phi \sim 0.05$–0.2). Singlet states of these 1-allyl-substituted indenes do not undergo internal cycloaddition. Instead, the photoreaction observed corresponds to a 1,3 substituent shift.

Formation of the benzotricyclo[3.3.0.$0^{2,7}$]octane ring system (i.e., **2**, **7–9**) can be considered to be the result of an intramolecular cross-cycloaddition of the double bonds present in the 1-allyl-substituted indenes. The preference for forming cross-addition products over parallel-addition products in the photocycloaddition reaction of 1,5-hexadienes is a well-known phenomenon.[45] Thus, the photochemistry of 1,5-hexadienes is known to be largely controlled by an initial C_1–C_5 bonding, giving a five-membered-ring biradical intermediate that ultimately affords the observed products through disproportionation and closure.[46,47] This selectivity was originally attributed to a kinetic preference for the formation of five-membered rings. This mode of cyclization was suggested to be closely related to the proclivity of 5-hexenyl radicals to cyclize to cyclopentenylmethyl radicals rather than cyclohexyl radicals.[48-50] More recently, it has been proposed that the selectivity observed in the photocyclizations may arise from orbital-symmetry factors[51] or specifically oriented complexes.[52] With the simple 1-allyl-substituted indene systems, the formation of the five-membered intermediate **30** is preferred to the other possible ring intermediate in terms of strain, entropy factors, and radical stability.



Regiospecificity in intramolecular photocycloaddition of 1,5-hexadienes to yield bicyclo[2.1.1]hexanes (and not bicyclo[2.2.0]hexanes) is quite common and has been generally thought to be insensitive to the nature and position of substituents on the reacting double bonds.[45] The double bonds can be incorporated into dienes, trienes, tetraenes, enones, and other related systems.[53,54] with little

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(42) Krauch, C. H.; Metzner, W.; Schenck, G. O. *Naturwissenschaften* **1963**, *50*, 710.
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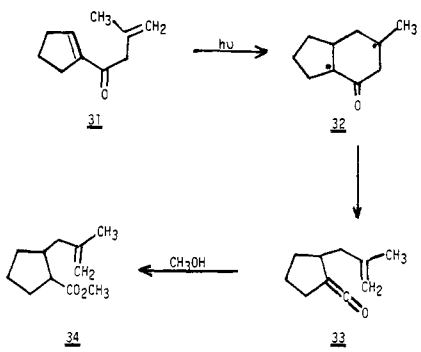
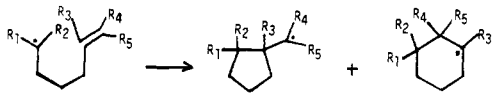
(47) Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 4936.
(48) Beckwith, A. L. J.; Ingold, K. U. "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, p 161.
(49) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.
(50) Surzur, J. M. In "Reactive Intermediates"; Abramovitch, R. A., Ed., Plenum Press: New York, 1981; Vol. 2, Chapter 3.
(51) Scheffer, J. R.; Wostradowski, R. A. *J. Org. Chem.* **1972**, *37*, 4317.
(52) White, J. D.; Gupta, D. N. *Tetrahedron* **1969**, *25*, 3331.

or no effect on the reaction. There are, however, a number of exceptions to this behavior.[15,16,55] For example, Agosta and Wolff[15] have observed that exclusive 1,6-cyclization occurs when cyclopentenone **31** was irradiated. These

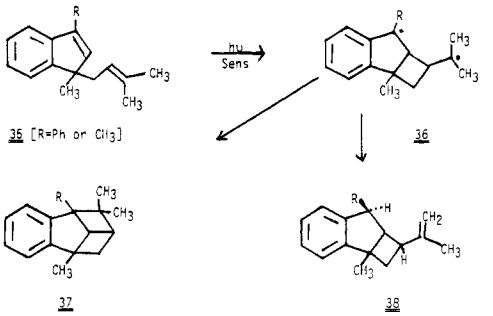


workers also found that the effect of substituents on the photochemistry of a series of dienones is virtually identical with that observed for the cyclization of 5-hexenyl radicals.[15] Substituent effects of the regiochemistry of cyclization of 5-hexenyl radicals has been studied in some detail by Beckwith[57] who has summarized his findings as follows.[58] (1) Substituents at the new radical center (R_4, R_5)

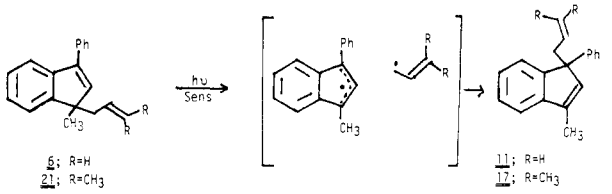


show little effect. (2) Substituents on the attacking radical center (R_1, R_2) also show small effects. (3) Substituents on the 2-position of the alkene (R_3) greatly retard the rate of reaction. When a large substituent group is present at C_5 (R_3 = large group), the rate of 1,5-cyclization is lowered to the point where 1,6-cyclization becomes the preferred pathway. Agosta and Wolff have encountered identical effects in the photochemistry of variously substituted 1,5-hexadien-3-ones.[15]

Inspection of the data obtained from our studies indicates that the normal closure predicted by the "rule of five"[46,47] does not occur in the photosensitized irradiation of the 1-prenyl-substituted indene system. Cyclization of the triplet state of the prenyl-substituted indene proceeds to give intermediate **36**. Inspection of molecular models indicates that the normal 1,6-cyclization mode is highly improbable as a result of the geometric restrictions imposed on the system. Instead, the triplet excited state undergoes four-membered-ring formation, presumably because the rate of 1,5-cyclization is sterically retarded by the presence of the methyl groups on the π bond. Another factor that would also tend to promote four-ring closure is the added stabilization imparted to the radical center by the two methyl groups. In simple cases, the activation energies for combination and disproportionation of radicals have been found to be equal.[59] This would explain the formation of both **37** and **38** in the above reaction. It should also be noted that the diradical (i.e., **36**) produced from the sensitized cyclization of **35** is long-lived enough to allow internal disproportionation to compete with radical coupling.



In marked contrast to the sensitized results, we have found that the direct irradiation of the 1-allyl-substituted indene system produces an entirely different set of photoproducts. The main photoreaction observed corresponds to a 1,3 substituent shift. Reasonable mechanistic options include a photoinduced (concerted) Cope rearrangement,[60] a concerted 1,3 sigmatropic allyl shift or a stepwise process involving a dissociation–reassociation path. The formation of **17** from the irradiation of **21**, however, rules out the concerted 3,3 sigmatropic path. We believe that the data obtained is most consistent with the dissociation–reassociation path. For example, the quantum efficiency for the rearrangement was found to increase with alkyl substitution on the side chain ($\Phi(R = H) = 0.05$ vs. $\Phi(R = CH_3) = 0.25$). This result is perfectly consistent with the proposition that the rearrangement occurs through a transition state that resembles a diradical intermediate. Introduction of methyl groups on the γ position of the allyl side chain will stabilize the radical-pair intermediate and enhance the quantum yield for rearrangement.



The 1,3 allyl shift occurs with quantum efficiencies significantly less than unity. One possibility to account for the low values involves cage (or noncage) recombination of the initially formed radical pair. No effect on the quantum yield of rearrangement of indenes **6** and **21** was noted when the irradiations were carried out in the presence of 0.03 M 1-dodecanethiol. This would tend to suggest that noncage recombination of indenyl–allyl radical pairs is not very important. The preferential formation of the 1-phenyl-1-allyl-substituted isomer (i.e., **11** or **17**) is quite understandable in terms of the dissociation–reassociation mechanism since the transition state of these systems prefers to localize the odd electron on the phenylated carbon. The product distribution on the allyl end reflects the greater steric hindrance to recombination of a tertiary site compared with a primary site.[61]

The 1-allyl-1-phenyl-substituted indene system (i.e., **11** or **17**) was found to undergo a novel rearrangement on further irradiation. Thus, photolysis of a benzene solution of **11** (or **17**) gave rise to a mixture of rearranged indenes (i.e., (**12** + **13**) or (**19** + **20**)). This reaction occurs under both direct and sensitized photolysis conditions, thereby

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(54) Gibson, T. W.; Erman, W. F. *J. Org. Chem.* **1972**, *37*, 1148.
(55) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 522.
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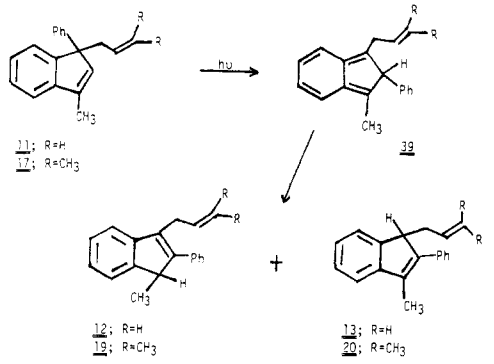
(59) Kraus, J.; Calvert, J. *J. Am. Chem. Soc.* **1957**, *79*, 5921.
(60) Shaikk, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 3184.
(61) Engel, P. S.; Bishop, D. J. *J. Am. Chem. Soc.* **94**, 2148 (1972).

implying that the rearrangement can occur from both the singlet and triplet state. The reaction proceeds exclusively in one direction since the irradiation of indene **12** or **13** resulted in recovered starting material, even under lengthy photolytic conditions. The formation of the rearranged indenes most likely proceeds via a 1,2 phenyl shift to give isoindene **39** followed by a 1,5 sigmatropic hydrogen migration. This process is analogous to that previously described by Miller[62] and McCullough[63] for the thermolysis of 1,1-diaryl-substituted indenes. The structurally related 3-phenyl-substituted indenes **6** and **21** cannot undergo this type of di-π-methane rearrangement.



Finally, the sensitized irradiation of 4-(1,3-dimethylindenyl)-1-butene (**27**), the higher homologue of **5**, deserves some comment. The internal cycloaddition of **27** to give a mixture of **28** and **29** can be viewed as being closely related to the proclivity of 5-hexenyl radicals to cyclize to cyclopentylmethyl radicals.[57,58] The initially formed diradical can undergo coupling to give **28** or an internal disproportionation to produce **29**.

The facility with which the intramolecular [2 + 2] indene photocycloadditions occur makes this type of approach particularly attractive for the synthesis of some unusual polycyclic ring compounds. We are continuing to explore the scope and mechanistic details of these intramolecular cycloadditions and will report additional findings at a later date.

Experimental Section[64]

Preparation of 1-Allylindene (1). To a solution containing 16 mL of a 1.6 M *n*-butyllithium solution in hexane and 4 mL of tetramethylethylenediamine in 100 mL of hexane at 0 °C was added 3.0 g of indene in 10 mL of hexane. The solution was allowed to stir at 0 °C for 1 h and then 2.6 mL of allyl bromide in 10 mL of hexane was added to the solution at 0 °C. The solution was allowed to stir for 8 h at room temperature and was then quenched with a saturated ammonium chloride solution. The hexane layer was washed with water followed by a saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure, leaving behind a yellow oil that was chromatographed on a medium-pressure silica gel column (1 × 100 cm) using hexane as the eluent. The first fraction isolated from the column contained 2.0 g (50%) of a colorless oil whose structure was identified as 1-allylindene (**1**); NMR ($CDCl_3$, 90 MHz) δ 1.97–3.00 (m, 2 H), 3.29–3.47 (m, 1 H), 4.90–5.20 (m, 2 H), 5.60–6.05 (m, 1 H), 6.47 (dd, 1 H, J = 6.0, 2.5 Hz), 7.00–7.50 (m, 4 H); IR (neat) 3076, 3020, 2900, 1640, 1520, 1440, 1415, 1360, 1020, 1000, 915, 775, 745, 725, 710 cm^{-1}; UV (95% ethanol) 252 (ϵ 8400) 213 (12 200).

Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.80.

The second fraction isolated from the column contained 0.5 g (13%) of a colorless oil whose structure was identified as 3-allylindene (**3**); NMR (CCl_4, 90 MHz) δ 3.20–3.31 (br s, 4 H), 5.0–5.23 (m, 2 H), 5.71–6.20 (m, 2 H), 6.90–7.40 (m, 4 H); IR (neat) 3080, 3020, 2980, 2890, 1640, 1610, 1460, 1430, 1400, 1260, 1020, 1000, 970, 915, 770, 725, 720 cm^{-1}; UV (95% ethanol) 270 nm (ϵ 10 200), 223 (8840), 216 (13 400).

Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.80.

Triplet-Sensitized Irradiation of 1-Allylindene (1) in Benzene. A solution containing 100 mg of 1-allylindene (**1**) and 102 mg of thioxanthen-9-one in 400 mL of anhydrous benzene was irradiated for 3 h using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a uranium filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil, which was chromatographed on a preparative thick-layer plate (six elutions) with hexane. The fastest moving band contained 66 mg (66%) of a colorless oil whose structure was assigned as 2,2a,7,7a-tetrahydro-2,7-methano-1*H*-cyclobut[*a*]indene (**2**) on the basis of its NMR spectrum ($CDCl_3$, 270 MHz): δ 0.80 (dt, 1 H, J = 10.2, 2.9, 2.0 Hz), 1.13 (d, 1 H, J = 7.3 Hz), 1.78 (ddt, 1 H, J = 7.3, 2.9, 2.0 Hz), 1.91 (dd, 1 H, J = 10.2, 7.0 Hz), 2.55 (dt, 1 H, J = 7.0, 2.0 Hz), 2.89 (dq, 1 H, J = 7.0, 2.0 Hz), 3.20–3.22 (m, 2 H), 7.10–7.23 (m, 4 H); IR (neat) 2990, 2885, 1550, 1530, 1270, 1230, 1220, 1165, 1040, 1020, 750 cm^{-1}; MS, m/e 156 (M^+), 155, 153, 152, 142, 141 (base), 129, 128, 127, 116, 89, 77 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.07; H, 7.80.

Thermolysis of a 15-mg sample of **2** at 160 °C in toluene for 76 h gave 3-allylindene (**3**) as the exclusive product.

Preparation of 1-Allyl-3-methylindene (4). To a solution containing 150 mmol of freshly prepared lithium diisopropylamine at −78 °C was added a solution containing 9.1 g of 1-indanone in 150 mL of tetrahydrofuran. The solution was stirred at −78 °C for 1 h and was then allowed to warm to room temperature over a 4-h period. At the end of this time, the solution was cooled to −78 °C and a solution containing 6.9 mL of allyl bromide in 75 mL of tetrahydrofuran was slowly added. After stirring at −78 °C for 1 h, the solution was allowed to warm to room temperature and was then quenched with a saturated ammonium chloride solution. The organic layer was washed with water followed by a saturated sodium chloride solution. The solution was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure, leaving behind a yellow oil, which was chromatographed on a medium-pressure silica gel column (1 × 100 cm) using a 5% acetone–hexane solution as the eluent. The major fraction isolated from the column contained 9.3 g (80%) of a colorless oil whose structure was identified as 3-allyl-1-indanone on the basis of its spectral properties; NMR ($CDCl_3$, 90 MHz) δ 2.15–3.00 (m, 4 H), 3.32–3.60 (m, 1 H), 4.97–5.23 (m, 2 H), 5.53–6.00 (m, 1 H), 7.26–7.86 (m, 4 H); IR (neat) 3425, 3100, 3000, 2925, 1715, 1705, 1640, 1600, 1580, 1460, 1440, 1400, 1330, 1280, 1230, 1200, 1170, 1145, 1090, 1040, 1010, 990, 980, 910, 820, 750 cm^{-1}; MS, m/e 172 (M^+), 132, 131 (base), 103.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.45; H, 7.09.

To a solution containing 750 mg of the above ketone in 50 mL of anhydrous ether at 0 °C was added 6 mL of a 1.5 M methylmagnesium bromide solution in ether. The resulting solution was allowed to stir for 3 h at 0 °C and then for an additional 3 h at room temperature. The solution was quenched with a saturated ammonium chloride solution and the organic layer was washed with water followed by a saturated sodium chloride solution. The solution was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure, leaving behind 780 mg of a pale-yellow oil whose structure was identified as 3-allyl-1-methyl-1-indanol; IR (neat) 3370, 3310, 2900, 2850, 1640, 1560, 1480, 1340, 1290, 1200, 1160, 1130, 1000, 950, 920, 765, 750 cm^{-1}; MS, m/e 188 (M^+).

(62) Miller, L. L.; Boyer, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 650.
(63) McCullough, J. J.; McClory, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 1962.
(64) All melting points and boiling points are corrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer, using 1-cm matched cells. The proton magnetic resonance spectra were determined at 90 MHz, using a Varian EM-390 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All irradiations were carried out by using a 450-W Hanovia medium pressure mercury arc lamp.

A solution containing 1.96 g of the above alcohol and 2.2 g of *p*-toluenesulfonic acid in 100 mL of benzene was allowed to stir for 15 min at 25 °C and then 100 mL of water was added followed by a saturated sodium bicarbonate solution. The benzene layer was washed with a saturated sodium chloride solution and was then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, leaving behind a yellow oil, which was chromatographed on a medium-pressure silica gel column (1 × 100 cm) using hexane as the eluent. The first fraction isolated from the column contained 1.5 g (85%) of a colorless oil whose structure was identified as 1-allyl-3-methylindene (**4**); NMR ($CDCl_3$, 90 MHz) δ 2.06 (d, 3 H, J = 2.0 Hz), 2.10–2.60 (m, 2 H), 3.23–3.50 (m, 1 H), 4.90–5.20 (m, 2 H), 5.60–6.00 (m, 1 H), 6.18 (q, 1 H, J = 2.0 Hz), 7.03–7.40 (m, 4 H); IR (neat) 3080, 3025, 2990, 2915, 2850, 1635, 1455, 1430, 1375, 1010, 980, 900, 790, 745, 735, 720 cm^{-1}; UV (95% ethanol) 255 nm (ϵ 8850), 225 (10900), 217 (16800), 212 (ϵ 20600); MS, m/e 170 (M^+, base), 155, 129, 128 127.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.45; H, 8.35.

Triplet-Sensitized Irradiation of 1-Allyl-3-methylindene (4). A solution containing 63.2 mg of 1-allyl-3-methylindene (**4**) and 10 mg of thioxanthen-9-one in 250 mL of anhydrous benzene was irradiated for 1 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a uranium filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil, which was chromatographed on a medium-pressure silica gel column (1 × 100 cm) using hexane as the eluent. The first fraction isolated from the column contained 28 mg (44%) of a colorless oil whose structure was identified as 2,2a,7,7a-tetrahydro-2a-methyl-2,7-methano-1*H*-cyclobut[*a*]indene (**7**); NMR ($CDCl_3$, 90 MHz) δ 0.83 (ddd, 1 H, J = 10.5, 3.0, 2.3 Hz), 1.10 (d, 1 H, J = 7.5 Hz), 1.59 (s, 3 H), 1.90 (dd, 1 H, J = 10.5, 6.9 Hz), 2.03–2.30 (m, 2 H), 2.50–2.68 (m, 1 H), 3.20 (dd, 1 H, J = 6.9, 3.0 Hz), 7.00–7.20 (m, 4 H); IR (neat) 2965, 2885, 1450, 1370, 1260, 1240, 1150 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.65; H, 8.20.

Heating a 20-mg sample of **7** at 160 °C in benzene for 4 h produced a 1:1 mixture of 1-allyl-3-methyl- (**4**) and 1-methyl-3-allylindene (**10**) as the exclusive products.

Preparation of 1-Allyl-1,3-dimethylindene (5). To a solution containing 1.5 mL of tetramethylethylenediamine and 6.25 mL of a 1.6 M *n*-butyllithium solution in 100 mL of hexane at 0 °C was added 1.17 g of 1,3-dimethylindene[65] in 10 mL of hexane. The solution was allowed to stir for 1 h at 0 °C and then 0.87 mL of allyl bromide in 10 mL of hexane was slowly added. After stirring at 0 °C for 3 h, the solution was allowed to warm to room temperature and was then quenched with a saturated ammonium chloride solution. The organic layer was washed with water followed by a saturated sodium chloride solution. The solution was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure, leaving behind a yellow oil. This material was chromatographed on a medium-pressure silica gel column (1 × 100 cm) using hexane as the eluent. The first fraction isolated from the column contained 1.34 g (91%) of a colorless oil whose structure was identified as 1-allyl-1,3-dimethylindene (**5**); NMR ($CDCl_3$), 90 MHz) δ 1.25 (s, 3 H), 2.12 (d, 3 H, J = 2.5 Hz), 2.24–2.48 (m, 2 H), 4.85–5.10 (m, 2 H), 5.36–5.83 (m, 1 H), 5.98 (q, 1 H, J = 2.5 Hz), 7.20 (s, 4 H); IR (neat) 3100, 3075, 3050, 3000, 2950, 2880, 1645, 1625, 1470, 1450, 1440, 1380, 1370, 1020, 990, 910, 810, 750 cm^{-1}; UV (95% methanol) 259 nm (ϵ 9560), 224 (13400), 217 (18800); MS, m/e 184 (M^+), 144, 143 (base), 128, 115.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.11; H, 8.80.

Triplet-Sensitized Irradiation of 1-Allyl-1,3-dimethylindene (5). A solution containing 120 mg of 1-allyl-1,3-dimethylindene (**5**) and 11.6 mg of thioxanthen-9-one in 400 mL of anhydrous benzene was irradiated for 1 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a uranium filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil, which was chromatographed on a preparative thick-layer plate (three elutions) using hexane as the eluent. The major band contained 100 mg (83%) of a colorless oil whose structure was assigned as 2,2a,7,7a-tetrahydro-2a,7-dimethyl-2,7-methano-1*H*-cyclobut[*a*]indene (**8**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) 0.92 (ddd, J = 9.0, 3.0, 2.0 Hz), 1.19 (d, J = 7.5 Hz), 1.42 (s, 3 H), 1.52 (s, 3 H), 2.06–2.36 (m, 4 H), 7.02–7.20 (m, 4 H); ^{13}C NMR (C_6D_6, 20 MHz) δ 13.11, 16.88, 31.96, 43.81, 44.72, 50.02, 66.49, 117.57, 121.51, 125.40, 125.99, 146.23, 157.17; IR (neat) 3020, 2940, 2850, 1490, 1445, 1355, 1330, 1260, 1230, 1190, 1130, 1110, 1035, 1015, 1005, 955, 935, 925, 895, 875, 790, 775, 745 cm^{-1}; MS, m/e 184 (M^+), 143 (base), 128. Heating a sample of **8** at 150 °C in benzene for 110 h gave 1-allyl-1,3-dimethylindene (**5**) as the exclusive product in 98% yield.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.13; H, 8.82.

Preparation of 3-(1,3-Dimethylindenyl)-2-methyl-1-propene (15). To a solution containing 0.48 mL of tetramethylethylenediamine and 2.0 mL of a 1.6 M *n*-butyllithium solution at 0 °C in 50 mL of hexane was added 420 mg of 1,3-dimethylindene in 10 mL of hexane. The solution was allowed to stir for 1 h and then 0.35 mL of 1-chloro-2-methylpropene in 10 mL of hexane was added at 0 °C. After stirring at 0 °C for 3 h, the solution was allowed to stir at room temperature for an additional 7 h. The solution was quenched with a saturated ammonium chloride solution. The organic layer was washed with water followed by a saturated sodium chloride solution. The solution was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure, leaving behind a yellow oil. This material was chromatographed on a medium-pressure silica gel column (1 × 100 cm) using hexane as the eluent. The first fraction isolated from the column contained 510 mg (88%) of a colorless oil whose structure was identified as 3-(1,3-dimethylindenyl)-2-methyl-1-propene (**15**); NMR ($CDCl_3$, 90 MHz) δ 1.26 (s, 3 H), 1.46 (d, 3 H, J = 1.5 Hz), 2.05 (d, 3 H, J = 2.0 Hz), 2.28 (d, 1 H, J = 15 Hz), 2.53 (d, 1 H, J = 15 Hz), 4.55 (dq, 1 H, J = 2.5, 1.5 Hz), 4.66 (dq, 1 H, J = 2.5, 1.5 Hz), 6.02 (q, 1 H, J = 2 Hz), 7.13–7.33 (m, 4 H). External irradiation of the doublet at δ 1.46 collapsed the doublet of quartets at δ 4.55 to a doublet and the doublet of quartets at δ 4.66 to a doublet; IR (neat) 3080, 2980, 2940, 1640, 1465, 1450, 1375, 1370, 1100, 1015, 880, 810, 740 cm^{-1}; UV (95% ethanol) 262 nm (ϵ 6800), 258 (7500) and 217 (18200).

Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.73; H, 9.19.

Triplet-Sensitized Irradiation of 3-(1,3-Dimethylindenyl)-2-methyl-1-propene (15). A solution containing 80 mg of 3-(1,3-dimethylindenyl)-2-methyl-1-propene (**15**) and 10 mg of thioxanthen-9-one in 250 mL of anhydrous benzene was irradiated for 1 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a uranium filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil, which was chromatographed on a medium-pressure chromatographic column (1 × 60 cm) using hexane as the eluent. The first fraction isolated from the column contained 50 mg (62%) of a colorless oil whose structure was identified as 2,2a,7,7a-tetrahydro-2,2a,7-trimethyl-2,7-methano-1*H*-cyclobut[*a*]indene (**16**) on the basis of its spectral properties: NMR ($CDCl_3$, 90 MHz) δ 0.73 (dd, 1 H, J = 10.0, 3.0 Hz), 1.01 (s, 3 H), 1.23 (d, 1 H, J = 7.3 Hz), 1.41 (s, 3H), 1.42 (s, 3 H), 1.52 (d, 1 H, J = 10 Hz), 1.90 (dt, 1 H, J = 7.3, 3.0 Hz), 2.28 (d, 1 H, J = 3.0 Hz), 7.03–7.30 (m, 4 H). External irradiation of the doublet of doublets at δ 0.73 collapsed the doublet at 1.52 to a singlet and the doublet of triplets at δ 1.90 to a series of two doublets; IR (neat) 3075, 3000, 2975, 2910, 2400, 2375, 1485, 1460, 1385, 1350, 1315, 1310, 1255, 1205, 1100, 1030, 1020, 940, 750 cm^{-1}; UV (95% ethanol) 275 nm (ϵ 1150), 267 (1050), 215 (5300). Heating a sample of **16** at 160 °C for 14 h in benzene gave 3-(1,3-dimethylindenyl)-2-methyl-1-propene (**15**) as the exclusive product.

Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.75; H, 9.15.

Preparation of 4-(1,3-Dimethylindenyl)-2-methyl-2-butene (24). To a solution containing 0.6 mL of tetramethylethylenediamine and 2.5 mL of a 1.6 M *n*-butyllithium solution in 100 mL of hexane at 0 °C was added 500 mg of 1,3-dimethylindene in 10 mL of hexane. The solution was allowed to stir for 1 h at

(65) Christol, H.; Plenat, F. *Bull. Soc. Chim. Fr.* **1962**, 1325.

0 °C and then 0.4 mL of 1-bromo-3-methyl-2-butene in 10 mL of hexane was slowly added at 0 °C. After stirring at 0 °C for 3 h, the solution was allowed to stir for an additional 5 h at room temperature. The mixture was quenched with a saturated ammonium chloride solution. The organic layer was washed with water followed by a saturated sodium chloride solution. The solution was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure, leaving behind a yellow oil. This material was chromatographed on a 1 × 20 cm silica gel column using hexane as the eluent. The major fraction isolated from the column contained 683 mg (92%) of a colorless oil whose structure was identified as 4-(1,3-dimethylindenyl)-2-methyl-2-butene (**24**); NMR ($CDCl_3$, 90 MHz) δ 1.23 (s, 3 H), 1.50 (br s, 3 H), 1.60 (br s, 3 H), 2.03 (d, 3 H, J = 2 Hz), 2.10–2.40 (m, 2 H), 4.86–5.13 (m, 1 H), 5.98 (q, 1 H, J = 2 Hz), 7.13–7.40 (m, 4 H); IR (neat) 3080, 3050, 3025, 2950, 2860, 1460, 1445, 1375, 1100, 1010, 805, 740 cm^{-1}; UV (95% ethanol) 258 nm (ε 8780), 223 (13 800), 217 (19 500); MS, m/e 212 (M^+), 172, 144, 143 (base), 128.

Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.23; H, 9.59.

Sensitized Irradiation of 4-(1,3-Dimethylindenyl)-2-methyl-2-butene (24). A solution containing 600 mg of 4-(1,3-dimethylindenyl)-2-methyl-2-butene (**24**) and 60 mg of thioxanthen-9-one in 400 mL of anhydrous benzene was irradiated for 6 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a uranium filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil, which was chromatographed on a medium-pressure chromatographic column (1 × 100 cm) using hexane as the eluent. The first fraction isolated from the column contained 186 mg (31%) of a colorless oil whose structure was assigned at 2,2a,7,7a-tetrahydro-2,2,2a,7-tetramethyl-1,7-methano-1*H*-cyclobut[*a*]indene (**25**); NMR (CCl_4, 90 MHz) δ 0.50 (s, 3 H), 1.13 (s, 3 H), 1.28 (s, 3 H), 1.45 (s, 3 H), 1.80–2.33 (m, 3 H), 2.88 (dd, 1 H, J = 4.0, 1.5 Hz), 6.97–7.28 (m, 4 H); ^{13}C NMR ($CDCl_3$, 20 MHz) 18.95 (q, J = 121 Hz), 22.54 (q, J = 124 Hz), 24.42 (q, J = 125 Hz), 27.56 (q, J = 122 Hz), 37.62 (t, J = 130 Hz), 38.17 (d, J = 148.8 Hz), 41.63 (s), 48.13 (s), 53.29 (d, J = 148 Hz), 55.71 (d, J = 148 Hz), 121.05 (d, J = 158.8 Hz), 123.30 (d, J = 158.2 Hz), 125.94 (d, J = 158.6 Hz), 126.54 (d, 161.9), 151.84 (s), 152.62 (s); IR (neat 3080, 3030, 2960, 2870, 1480 1450, 1390, 1370, 1030, 755 cm^{-1}; MS, m/e 212 (M^+), 143 (base), 128, 115.

Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.40; H, 9.44.

The second fraction isolated from the column was a clear oil containing 33 mg (6%) of a mixture of isomers of 2,2a,7,7a-tetrahydro-1-isopropenyl-7-dimethyl-1*H*-cyclobut[*a*]indene (**26**). The main characteristics of the NMR are two different methylene quartets at δ 4.20 and 4.50 as well as two methyl doublets at δ 0.93 and 0.95 with a coupling constant of 1.5 Hz.

Preparation of 4-(1,3-Dimethylindenyl)-1-butene (27). To 5.5 mL of a 1.0 M borane solution in tetrahydrofuran at 0 °C was added 5.5 mL of a 2.0 M 2-methyl-2-butene solution in tetrahydrofuran. The resulting mixture was allowed to stir for 2.5 h at 0 °C and then 670 mg (3.64 mmol) of 1-allyl-1,3-dimethylindene in 20 mL of tetrahydrofuran was slowly added at 0 °C. The mixture was allowed to warm to room temperature and was stirred for an additional 4 h and then 1.2 mL of a 2.0 N sodium hydroxide solution was added followed by 1.2 mL of a 30% hydrogen peroxide solution. The mixture was allowed to stir for 45 min at 25 °C and was then extracted with ether. The ether layer was washed with a saturated sodium sulfate solution and a saturated sodium chloride solution and was then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, leaving behind 779 mg (100%) of a pale-yellow oil whose structure was assigned as 3-(1,3-dimethylindenyl)-propan-1-ol. The NMR spectrum of the oil shows the loss of the multiplet at δ 4.85–5.10, the loss of the multiplet at δ 5.36–5.83 and the quartet at δ 5.98 now appears at 5.90 μ; IR (neat) 3350, 2950, 2860, 1460, 1450, 1380, 1320, 1105, 1050, 1020, 930, 825, 755 cm^{-1}.

To a solution containing 600 mg (2.8 mmol) of the above alcohol in 20 mL of methylene chloride was added 1.5 equiv of pyridinium chlorochromate in 20 mL of methylene chloride. After stirring for 20 min, the entire mixture was passed through a 5 × 20 cm silica gel column using methylene chloride as the eluent. The major fraction contained 516 mg (87%) of a pale-yellow oil whose structure was assigned as 3-(1,3-dimethylindenyl)-propan-1-al; NMR (CCl_4, 90 MHz) δ 1.28 (s, 3 H), 1.67–2.13 (m, 4 H), 2.04 (d, 3 H, J = 2.5 Hz), 5.83 (q, 1 H, J = 2.5 Hz), 7.15 (br s, 4 H), 9.50 (t, 1 H, J = 1 Hz); IR (neat) 2950, 2920, 2860, 2720, 1740, 1530, 1460, 1380, 1370, 1020, 870, 760 cm^{-1}.

To a mixture containing 870.6 mg (2.4 mmol) of methyltriphenylphosphonium bromide in 20 mL of anhydrous ether was added 1.6 mL of 1.5 M *n*-butyllithium solution at 0 °C. To this solution was added 420 mg (2.2 mmol) of the above aldehyde in 15 mL of anhydrous ether. The solution was kept at −78 °C for 1 h and was then allowed to warm to room temperature and allowed to stir for an additional 10 h. The entire solution was then passed through a 5 × 20 cm neutral alumina column using ether as the eluent. The major fraction contained 349 mg (80%) of a colorless oil whose structure was identified as 4-(1,3-dimethylindenyl)-1-butene (**27**); NMR (CCl_4, 90 MHz) δ 1.21 (s, 3 H), 1.48–1.80 (m, 4 H), 2.06 (d, 3 H, J = 2 Hz), 4.70–4.92 (m, 2 H), 5.28–5.85 (m, 1 H), 5.92 (q, 1 H, J = 2 Hz), (.10 (br s, 4 H); IR (neat) 3070, 2960, 2920, 2860, 1640, 1465, 1450, 1180, 1020, 990, 910, 820, 750 cm^{-1}; UV (95% ethanol) 283 nm (ε 1200), 257 (8000), 212 (19 200).

Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.73; H, 9.20.

Sensitized Irradiation of 4-(1,3-Dimethylindenyl)-1-butene (27) in Benzene. A solution containing 180 mg (0.91 mmol) of **27** and 20 mg (0.94 mmol) of thioxanthen-9-one in 250 mL of anhydrous benzene was irradiated for 1 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a uranium filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil, which was chromatographed on a medium-pressure column (1 × 100 cm) using hexane as the eluent. The first fraction contained 110 mg (61%) of a colorless oil whose structure was identified as 2,2a,7,7a-tetrahydro-2a,7-dimethyl-1,7-ethano-1*H*-cyclobut[*a*]indene (**28**); NMR (CCl_4, 90 MHz) δ 0.80–2.85 (m, 8 H), 1.33 (s, 3 H), 1.37 (s, 3 H), 6.80–7.10 (m, 4 H); ^{13}C NMR ($CDCl_3$, 20 Hz) δ 26.43 (q, J = 126 Hz), 26.83 (q, J = 126 Hz), 33.25 (t, J = 133 Hz), 33.53 (d, J = 140 Hz), 41.78 (t, 132 Hz), 44.60 (t, J = 127.5 Hz), 47.29 (s), 55.98 (s), 62.08 (d, J = 141.6 Hz), 121.92 (d, J = 158.5 Hz), 122.86 (d, 158.5 Hz), 126.86 (d, 153.1 Hz), 127.12 (d, 157.2 Hz), 151.73 (s), 151.82 Hz); IR (neat) 2940, 2915, 2850, 1470, 1440, 1375, 1310, 1020, 750 cm^{-1}.

Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.76; H, 9.17.

The second fraction contained 52 mg (28%) of a colorless oil whose structure was identified as (1*R**,3a*S**,8a*S**)-1,2-3,3a,8-8a-hexahydro-1,3a-dimethyl-8-methylenecyclopent[*a*]indene (**29**); NMR (CCl_4, 90 MHz) δ 0.70–1.10 (m, 1 H), 0.93 (d, 3 H, J = 6.5 Hz), 1.12–2.46 (m, 4 H), 1.30 (s, 3 H), 2.80 (br d, 1 H, J = 6.5 Hz), 4.9 (d, 1 H, J = 1.5 Hz), 5.52 (d, 1 H, J = 1.5 Hz), 6.90–7.30 (m, 4 H); IR (neat) 2950, 2920, 2860, 1630, 1470, 1460, 870, 790, 750 cm^{-1}.

Anal. Calcd for $C_{15}H_{16}$: C, 90.85; H, 9.15. Found: C, 90.65; H, 9.19.

Preparation of 1-Allyl-1-methyl-3-phenylindene (6) and 1-Allyl-3-methyl-1-phenylindene (11). A solution of 10.8 mL of a 1.6 M *n*-butyllithium in hexane was added to a solution containing 3.56 g of 3-methyl-1-phenylindene and 2.01 g of tetramethylethylenediamine in 75 mL of hexane at −78 °C. The resulting suspension was allowed to warm to room temperature while stirring for 3 h. The solution was cooled to −78 °C and was then allowed to react with 2.09 g of allyl bromide in 10 mL of hexane. The mixture was stirred at room temperature for 18 h and was then taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left a yellow oil, which was subjected to medium-pressure chromatography, using hexane as the eluent. The first component isolated from the column contained 1.41 g (33%) of 1-allyl-1-methyl-3-phenylindene (**6**) as a clear oil; IR (neat) 3020, 2865, 1637, 1597, 1488, 1460, 1440, 1344, 1024, 977, 919, 837, 782, 758, 697 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.30 (s, 3 H), 2.40 (m, 2 H), 4.8–5.0 (m, 2 H), 5.3–5.8 (m, 1 H), 6.27 (s, 1 H), 7.0–7.6 (m, 9 H); UV (95% ethanol) 294 nm (ε 1200), 266 (6200), 228 (22 900); MS, m/e 246 (M^+), 205 (base), 204, 203, 202.

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.50; H, 7.48.

The second component isolated from the column contained 2.42 g (57%) of 1-allyl-3-methyl-1-phenylindene (11) as a clear oil; IR (neat) 3040, 2890, 1637, 1595, 1490, 1462, 1441, 1376, 1022, 913, 814, 776, 760, 746, 695 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 2.07 (br s, 3 H), 2.74 (dd, 1 H, J = 14.0, 8.0 Hz), 2.96 (dd, 1 H, J = 14.0, 8.0 Hz), 4.7–5.0 (m, 2 H), 5.2–5.6 (m, 1 H), 6.13 (br s, 1 H), 7.0–7.3 (m, 9 H); UV (95% ethanol) 295 nm (ϵ 670), 284 (1700), 262 (6600), 259 (6800), 221 (24000); MS, m/e 246 (M^+), 205 (base), 204, 203, 202. Both allyl-substituted indenes 6 and 11 were also prepared by treating 1-methyl-3-phenylindene with n-butyllithium followed by reaction with allyl bromide. The overall yield of product isolated corresponded to 91% with a 36:64 ratio of 6 to 11.

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.56; H, 7.44.

Triplet-Sensitized Irradiation of 1-Allyl-1-methyl-3-phenylindene (6). A solution containing 280 mg of 1-allyl-1-methyl-3-phenylindene (6) and 40 mg of thioxanthen-9-one in 450 mL of benzene was irradiated through a uranium glass filter sleeve with a 450-W Hanovia lamp for 45 min. The solvent was removed under reduced pressure and the resulting oil was recrystallized from ethanol to give 254 mg of 2,2a,7,7a-tetrahydro-7-methyl-2a-phenyl-2,7-methano-1H-cyclobut[a]indene (9) as a white crystalline solid; mp 56–57 °C; IR (KBr) 2899, 1595, 1486, 1464, 1439, 1379, 1295, 1025, 1014, 762, 753, 702 cm^{-1}; UV (95% ethanol) 275 nm (ϵ 1000), 267 (1100), 261 (890), 254 (610); MS, m/e 246 (M^+), 205 (base), 203; NMR ($CDCl_3$, 270 MHz) δ 1.17 (br d, 1 H, J = 10.3 Hz), 1.24 (d, 1 H, J = 7.3 Hz), 1.60 (s, 3 H), 1.74 (d, 1 H, J = 10.3 Hz), 1.97 (dd, 1 H, J = 7.3, 2.2 Hz), 2.85–2.94 (m, 2 H), 6.59 (d, 1 H, J = 7.3 Hz), 6.99 (dd, 1 H, J = 8.1, 6.6 Hz), 7.13 (t, 1 H, J = 7.3 Hz), 7.11–7.53 (m, 6 H). External irradiation of the doublet at δ 1.17 collapsed the doublet at δ 1.74 into a singlet. Irradiation of the signal at δ 1.24 collapsed the doublet of doublets at δ 1.97 into a doublet (J = 2.2 Hz); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 16.8 (q), 32.6 (t), 43.4 (d), 44.2 (t), 49.8 (s), 66.9 (d), 67.4 (s), 140 (s), 146 (s), 157 (s).

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.3.7. Found: C, 92.51; H, 7.45.

Further support for the structure of 9 was obtained by its conversion to 1-allyl-1-methyl-3-phenylindene (6). A 60-mg sample of 9 in 0.5 mL of a 15% pyridine-d_5–benzene-d_6 mixture was heated in a sealed tube at 130 °C for 50 h. The only product present in the reaction mixture was shown to be indene 6 by comparison with an authentic sample.

Direct irradiation of a 293-mg sample of 1-allyl-1-methyl-3-phenylindene (6) in 250 mL of benzene produced 87 mg (30%) of 1-allyl-3-methyl-1-phenylindene (11) as the major photoproduct. No detectable quantities of tricyclic structure 9 could be detected in the crude reaction mixture. In addition, small amounts of 1-methyl-2-phenyl-3-allylindene (12; 5%) and 1-allyl-2-phenyl-3-methylindene (13; 5%) were also present in the crude photolysate.

Triplet-Sensitized Irradiation of 1-Allyl-3-methyl-1-phenylindene (11). A solution containing 430 mg of 1-allyl-3-methyl-1-phenylindene (11) and 55 mg of thioxanthen-9-one in 250 mL of benzene was irradiated through a uranium glass filter sleeve with a 450-W Hanovia lamp for 9 h. Removal of the solvent under reduced pressure left a yellow oil, which was chromatographed on a silica gel column using hexane as the eluent. The first component isolated from the column contained 137 mg (32%) of a white solid, mp 47–48 °C, whose structure was assigned as 2,2a,7,7,7a-tetrahydro-2a-methyl-7-phenyl-2,7-methano-1H-cyclobut[a]indene (14) on the basis of its spectral properties; IR (KBr) 2967, 1603, 1502, 1475, 1445, 1383, 1019, 752, 699 cm^{-1}; UV (95% ethanol) 275 nm (ϵ 1050), 267 (1100), 261 (810), 254 (530); MS, m/e 246 (M^+), 205 (base), 204, 203; NMR ($CDCl_3$, 270 MHz) δ 1.19 (d, 1 H, J = 8.1 Hz), 1.40 (ddd, 1 H, J = 10.3, 2.2, 2.0 Hz), 1.69 (s, 3 H), 2.20–2.26 (m, 1 H), 2.37–2.43 (m, 1 H), 3.02 (dd, 1 H, J = 6.6, 2.9 Hz), 6.80 (d, 1 H, J = 7.3 Hz), 7.01–7.14 (m, 3 H), 7.28–7.41 (m, 5 H).

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.54; H, 7.41.

Further support for the structure of 14 was obtained by its conversion to indene 6. A 50-mg sample of 14 in 0.5 mL of a 15% pyridine-d_5–benzene-d_6 mixture was heated in a sealed tube at 160 °C for 27 h. Analysis of the crude reaction mixture showed that a mixture of 11 and 6 was present. Monitoring the thermolysis as a function of time clearly showed that 1-allyl-3-methyl-1-phenylindene (11) was initially produced and that on further heating, it was converted via a 3,3 sigmatropic rearrangement to 1-allyl-1-methyl-3-phenylindene (6).

The second material eluted from the column contained 143 mg (33%) of a clear oil whose structure was assigned as 3-allyl-1-methyl-2-phenylindene (12) by comparison with an authentic sample;[66] NMR ($CDCl_3$, 100 MHz) δ 1.20 (d, 3 H, J = 7.0 Hz), 3.38 (d, 2 H, J = 5.0 Hz), 3.86 (q, 1 H, J = 7.0 Hz), 5.05 (d, 1 H, J = 10.0 Hz), 5.10 (d, 1 H, J = 15.0 Hz), 5.86–6.28 (m, 1 H), 7.02–7.52 (m, 9 H).

The third fraction isolated from the column contained 105 mg (24%) of a clear oil, which slowly crystallized on standing. The structure of this material was assigned as 1-allyl-3-methyl-2-phenylindene (13), mp 86–87 °C, on the basis of its spectral properties; IR (KBr) 2915, 1580, 1475, 1420, 1364, 900, 740, 730, 680 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.22 (d, 3 H, J = 2.0 Hz), 2.2–2.9 (m, 2 H), 3.8–4.1 (m, 1 H), 4.6–4.8 (m, 1 H), 4.86 (br s, 1 H), 5.1–5.8 (m, 1 H), 7.2–7.6 (m, 9 H); UV (95% ethanol) 292 nm (ϵ 19800), 227 (12700); MS, m/e 246 (M^+), 205 (base), 204, 203, 202.

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.48; H, 7.48.

The structure of indene 13 was unambiguously established by comparison with an independently synthesized sample. To a solution containing 206 mg of 1-methyl-2-phenylindene[67] and 140 mg of tetramethylethylenediamine in 20 mL of hexane at −78 °C was added 0.75 mL of a 1.6 M n-butyllithium solution in hexane under a nitrogen atmosphere. The resulting solution was allowed to warm to room temperature and was then cooled to −78 °C. To this cold solution was added 150 mg of allyl bromide in 5 mL of hexane. The mixture was allowed to warm to room temperature for 15 h and was then taken up in ether. The ether layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. Removal of the solvent followed by silica gel chromatography, using a 5% ether–hexane mixture as the eluent, afforded 91 mg (37%) of 1-allyl-3-methyl-2-phenylindene (13). This material was identical in every detail with a sample of indene 13 prepared from the sensitized irradiation of 6.

Preparation of 1-(3-Methyl-2-butenyl)-1-methyl-3-phenylindene (21) and 1-(3-Methyl-2-butenyl)-3-methyl-1-phenylindene (17). A solution containing 9.4 mL of a 1.6 M solution of n-butyllithium in hexane was added to a solution containing 3.11 g of 1-methyl-3-phenylindene and 1.74 g of tetramethylethylenediamine in 50 mL of hexane at −78 °C. The resulting mixture was stirred at 25 °C for an additional 4 h. At the end of this time the mixture was cooled to −78 °C and was treated with 2.38 g of 1-bromo-3-methyl-2-butene in 10 mL of hexane. The resulting mixture was allowed to warm to 25 °C and stirred at this temperature for 20 h. The solution was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil, which was subjected to silica gel chromatography, using hexane as the eluent. The first component eluted from the column contained 1.32 g (32%) of a clear oil whose structure was assigned as 1-(3-methyl-2-butenyl)-1-methyl-3-phenylindene (21) on the basis of its spectral properties; IR (neat) 3067, 2976, 2874, 1678, 1610, 1502, 1473, 1453, 1383, 1353, 1079, 1030, 853, 849, 781, 758, 699 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.29 (s, 3 H), 1.49 (s, 3 H), 1.56 (s, 3 H), 2.21 (dd, 1 H, J = 14.0, 8.0 Hz), 2.43 (dd, 1 H, J = 14.0, 8.0 Hz), 4.94 (t, 1 H, J = 8.0 Hz), 6.21 (s, 1 H), 7.0–7.4 (m, 9 H); UV (95% ethanol) 293 nm (ϵ 1500), 266 (6700), 231 (24000); MS, m/e 274 (M^+), 205 (base), 203.

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.82; H, 8.15.

The second component isolated from the column contained 2.23 g (54%) of a clear oil whose structure is assigned as 1-(3-methyl-2-butenyl)-3-methyl-1-phenylindene (17) on the basis of its spectroscopic properties; IR (neat) 3012, 2933, 2873, 1661, 1615,

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1595, 1490, 1462, 1441, 1374, 1344, 1107, 1021, 842, 822, 816, 777, 757, 699 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.42 (s, 3 H), 1.45 (s, 3 H), 1.98 (br s, 3 H), 2.60 (dd, 1 H, J = 14.0, 7.0 Hz), 2.90 (dd, 1 H, J = 14.0, 7.0 Hz), 4.84 (t, 1 H, J = 7.0 Hz), 6.06 (br s, 1 H), 6.8–7.2 (m, 9 H); UV (95% ethanol) 295 nm (ϵ 660), 282 (1950), 260 (6700), 217 (24400); *MS*, *m/e* 274 (M^+), 205 (base), 204, 203, 202.

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.79; H, 8.16.

Triplet-Sensitized Irradiation of 1-(3-Methyl-2-butenyl)-1-methyl-3-phenylindene (21). A solution containing 408 mg of **21** and 52 mg of thioxanthen-9-one in 500 mL of benzene was irradiated through a uranium glass filter sleeve with a 450-W Hanovia lamp for 5 h. Removal of the solvent left an oily residue, which was chromatographed on a silica gel column using hexane as the eluent. The first component isolated from the column contained 250 mg (55%) of a white solid, mp 91–92 °C, whose structure was assigned as 2,2a,7,7a-tetrahydro-2,2,7-trimethyl-2a-phenyl-1,7-methano-1*H*-cyclobut[*a*]indene (**22**) on the basis of its spectral properties; IR (KBr) 2994, 2915, 1590, 1481, 1468, 1435, 1377, 1080, 1028, 760, 707 cm^{-1}; UV (95% ethanol) 277 mm (ϵ 2400), 269 (2500), and 263 nm (2100); MS, *m/e* 274 (M^+), 205 (base); NMR ($CDCl_3$, 270 MHz) δ 0.84 (s, 3 H), 1.00 (s, 3 H), 1.60 (s, 3 H), 2.12 (d, 1 H, J = 11.7 Hz), 2.27 (dd, 1 H, J = 8.8, 5.1 Hz), 2.35 (dd, 1 H, J = 11.7, 8.8 Hz), 3.63 (d, 1 H, J = 5.1 Hz), 7.03–7.36 (m, 9 H); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 23.4 (q), 30.9 (q), 36.8 (d), 38.2 (t), 44.9 (s), 48.0 (s), 52.5 (d), 63.2 (s), 144.0 (s), 149.3 (s), 152.3 (s). Further support for the structure of **22** was obtained by its thermal conversion (150 °C, 232 h) in a 15% pyridine-d_5–benzene-d_6 mixture to 1-(3-methyl-2-butenyl)-1-methyl-3-phenylindene (**21**).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.75; H, 8.19.

The second component isolated from the column contained 27 mg (6%) of a clear oil whose structure was assigned as (1*R**,2a*S**,7*R**,7a*S**)-2,2a,7,7a-tetrahydro-1-isopropenyl-2a-methyl-7-phenyl-1*H*-cyclobut[*a*]indene (**23a**) on the basis of its spectral properties; IR (neat) 3058, 3012, 2933, 2849, 1627, 1595, 1495, 1471, 1449, 1370, 1321, 885, 755, 695 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.21 (s, 3 H), 1.2–1.3 (m, 1 H), 1.52 (s, 3 H), 1.9–2.3 (m, 3 H), 3.31 (dd, 1 H, J = 10.6, 5.5 Hz), 4.15 (br s, 1 H), 4.52 (br s, 1 H, 6.9–7.4 (m, 9 H); UV (95% ethanol) 294 nm (ϵ 1300), 272 (1300), 265 (1300); MS, *m/e* 274 (M^+), 206 (base), 205, 191.

Anal. Calcd for $C_{21}H_{22}$: 274.17204 (P^+). Found: 274.17098 (P^+).

The third component isolated from the column contained 0.143 g (31%) of a white solid, mp 74–75 °C, whose structure was assigned as (1*R**,2a*R**,7*S**,7a*R**)-2,2a,7,7a-tetrahydro-1-isopropenyl-2a-methyl-7-phenyl-1*H*-cyclobut[*a*]indene (**23b**) on the basis of its spectral properties; IR (KBr) 2896, 2841, 1629, 1595, 1486, 1462, 1441, 1350, 1019, 891, 766, 745, 699 cm^{-1}; UV (95% ethanol) 272 nm (ϵ 1000), 264 (1000), 258 (820), 252 (540); MS, *m/e* 274 (M^+), 206 (base), 205, 191; NMR ($CDCl_3$, 270 MHz) δ 1.48 (s, 3 H), 1.64 (s, 3 H), 1.75 (ddd, 1 H, J = 12.5, 8.8, 2.2 Hz), 1.82 (dd, 1 H, J = 12.5, 5.9 Hz), 2.15 (dd, 1 H, J = 8.8, 2.2 Hz), 2.33 (d, 1 H, J = 8.8 Hz), 2.84 (dd, 1 H, J = 8.8, 5.9 Hz), 4.59 (br s, 1 H), 4.62 (br s, 1 H), 6.82 (*d*, 1 H, J = 7.3 Hz) and 6.99–7.4 (*m*, 8H).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.81; H, 8.14.

Triplet-Sensitized Irradiation of 1-(3-Methyl-2-butenyl)-3-methyl-1-phenylindene (17). A solution containing 160 mg of **17** and 32 mg of thioxanthen-9-one in 250 mL of benzene was irradiated through a uranium glass filter sleeve with a 450-W Hanovia mercury lamp. Removal of the solvent under reduced pressure left an oily residue, which was chromatographed through a silica gel column using hexane as the eluent. The first component contained 49 mg (26%) of a crystalline solid, mp 75–76 °C, whose structure was assigned as 2,2a,7,7a-tetrahydro-2,2,2a-trimethyl-7-phenyl-1,7-methano-1*H*-cyclobut[*a*]indene (**18**) on the basis of its spectral properties; NMR ($CDCl_3$, 100 MHz) δ 0.59 (s, 3 H), 1.20 (s, 3 H), 1.42 (s, 3 H), 2.24 (ddd, 1 H, J = 9.0, 5.0, 2.0 Hz), 2.34 (dd, 1 H, J = 12.0, 2.0 Hz), 2.98 (dd, 1 H, J = 12.0, 9.0 Hz), 3.30 (d, 1 H, J = 5.0 Hz), 6.4–6.6 (m, 1 H), 6.9–7.3 (m, 8 H); IR (KBr) 2915, 2825, 1595, 1575, 1471, 1447, 1441, 1379, 1368, 1312, 1027, 1007, 945, 912, 850, 837, 774, 765, 752, 700 cm^{-1}; UV (95% ethanol) 277 nm (ϵ 1400), 269 (1400), 263 (1100); MS, *m/e* 274 (M^+), 206, 205 (base).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.79; H, 8.19.

The second fraction eluted from the column contained 62 mg (34%) of a clear oil whose structure was assigned as 3-(3-methyl-2-butenyl)-1-methyl-2-phenylindene (**19**) on the basis of the following data; NMR ($CDCl_3$, 100 MHz) δ 1.14 (d, 3 H, J = 7.5 Hz), 1.65 (s, 6 H), 3.28 (br d, 2 H, J = 6.5 Hz), 3.75 (q, 1 H, J = 7.5 Hz), 5.18 (br t, 1 H, J = 6.5 Hz), 7.0–7.3 (m, 9 H); IR (neat) 2994, 2933, 2874, 1597, 1486, 1460, 1366, 1017, 769, 747, 699 cm^{-1}; UV (95% ethanol) 290 nm (ϵ 18500) 227 (13800); MS, *m/e* 274 (M^+), 206, 205 (base), 69.

Anal. Calcd for $C_{21}H_{22}$: 274.17204 (P^+). Found: 274.17415 (P^+).

The third component isolated from the column contained 59 mg (33%) of a clear oil whose structure was assigned as 1-(3-methyl-2-butenyl)-3-methyl-2-phenylindene (**20**) on the basis of the following data; NMR ($CDCl_3$, 100 MHz) δ 1.25 (s, 3 H), 1.50 (s, 3 H), 2.16 (d, 3 H, J = 2.0 Hz), 2.0–2.6 (m, 2 H), 3.8 (m, 1 H), 4.77 (br t, 1 H, J = 7.0 Hz), 7.0–7.4 (m, 9 H); IR (neat) 3012, 2959, 2907, 2849, 1608, 1495, 1471, 1446, 1383, 781, 763, 752, 704 cm^{-1}; UV (95% ethanol) 291 nm (ϵ 18600), 227 (12800); MS, *m/e* 274 (M^+), 206, 205 (base), 203, 105, 69.

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.82; H, 8.15.

The structures of indenes **19** and **20** were further substantiated by comparison with independently synthesized samples. To a solution containing 250 mg of 1-methyl-2-phenylindene and 160 mg of tetramethylethylenediamine in 30 mL of hexane at −78 °C was added 0.88 mL of a 1.6 M *n*-butyllithium solution in hexane under a nitrogen atmosphere. The solution was stirred at 25 °C for 1 h and was then recooled to −78 °C. To this solution was added 0.21 g of 1-bromo-3-methyl-2-butene in 10 mL of hexane. The mixture was stirred at 25 °C for 16 h and was then taken up in ether. The ethereal layer was washed with water and dried over magnesium sulfate. Removal of the solvent left a yellow oil, which chromatographed on a silica gel column using hexane as the eluent. The major fraction isolated from the column contained 152 mg (46%) of 1-(3-methyl-2-butenyl)-3-methyl-2-phenylindene (**20**), which was identical in every detail with a sample obtained from the sensitized photolysis of **17**. Heating a 180-mg sample of **20** in 0.5 mL of benzene-d_6 containing 20% pyridine-d_5 at 120 °C for 6 h resulted in the exclusive formation of 2-(3-methyl-2-butenyl)-1-methyl-2-phenylindene (**19**).

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Registry No. 1, 20258-77-9; **2**, 25459-98-7; **3**, 2294-87-3; **4**, 13860-28-1; **5**, 82614-97-9; **6**, 74534-16-0; **7**, 82614-98-0; **8**, 82614-99-1; **9**, 74534-17-1; **10**, 82615-00-7; **11**, 74534-18-2; **12**, 62907-53-3; **13**, 74534-20-6; **14**, 74534-19-3; **15**, 82615-01-8; **16**, 82615-02-9; **17**, 74534-21-7; **18**, 74534-22-8; **19**, 74534-23-9; **20**, 74534-24-0; **21**, 74534-25-1; **22**, 74534-26-2; **23a**, 82659-87-8; **23b**, 82659-88-9; **24**, 82615-03-0; **25**, 82615-04-1; **26** (isomer 1), 82615-05-2; **26** (isomer 2), 82659-89-0; **27**, 82615-06-3; **28**, 82615-07-4; **29**, 82615-08-5; indene, 95-13-6; allyl bromide, 106-95-6; 1-indanone, 83-33-0; 3-allyl-1-indanone, 79046-08-5; methyl bromide, 74-83-9; 3-allyl-1-methyl-1-indanol, 82615-09-6; 1,3-dimethylindene, 2177-48-2; 1-chloro-2-methyl-2-propene, 563-47-3; 1-bromo-3-methyl-2-butene, 870-63-3; 3-(1,3-dimethylindenyl)propan-1-ol, 82615-10-9; 3-(1,3-dimethylindenyl)propan-1-al, 82615-11-0; methyltriphenylphosphonium bromide, 1779-49-3; 3-methyl-1-phenylindene, 22360-63-0; 1-methyl-3-phenylindene, 22360-62-9.