Preparation and Crystal Structure Analysis of 2. LDA (20 mmol) was generated in 30 mL of hexane at 0 °C in a 100-mL three-necked flask connected to a three-way stopcock, to a cool trap, and to an argon frit with a 50-mL two-necked flask with three-way stopcock as receiver. On cooling to −78 °C 2.765 g (19.2 mmol) of *tert*-butyl 2-methylpropanoate was added during 10 min. After 1 h of stirring at −78 °C, the hexane and the diisopropylamine were distilled off at a bath temperature of −25 °C. To the resultant white powder, 20 mL of hexane and 5 mL of TMEDA were added at −30 °C. After being stirred for 5 min, the suspension was quickly filtered through the argon frit by turning the apparatus. The cooled receiver with the clear filtrate was removed in an argon stream and quickly stoppered. The solution was cooled from −40 to −60 °C during 12 h. After removal of the mother liquor at −60 °C, the crystals were washed with 4 × 7 mL of hexane, dried in high vacuum at −40 °C, and mounted at 0 °C in capillary tubes with dodecane as adhesive.

Preparation and Crystal Structure Analysis of (*Z*)-3. Methyl 3,3-dimethylbutanoate (650 mg, 5 mmol) was added at −78 °C to a solution of 5 mmol of LDA (generated at −20 °C) in 5 mL of THF. After the mixture was stirred for 30 min, the solvent was removed in high vacuum. The resultant white powder was redissolved in 3.2 mL of hexane and 0.8 mL of THF. On slow cooling from −20 to −80 °C, beautiful crystals were obtained. After removal of the mother liquor, these were mounted at room temperature in capillary tubes with hexadecane as adhesive.

Trapping Experiment. A solution of **6** (5.799 g, 20.0 mmol) in 35 mL of THF was added slowly to a solution of 41 mmol of BuLi (hexane solution, c = 1.60 mol/L) in ca. 200 mL of THF at −78 °C. The clear solution was allowed to warm to room temperature overnight. The mixture was cooled again to −78 °C, then a solution of TMSCl (4.6 g, 42 mmol) in 15 mL of THF was added. After the mixture was slowly warmed to room temperature (3 h), the solvent was evaporated and the residue quickly worked up with ice-cold $NaHCO_3$ solution/pentane. The organic phase was dried over Na_2SO_4, the solvent was evaporated, and the residue was distilled in a micro-distillation apparatus. After a small forerun, 2.6 g of **7** was obtained as a colorless oil (yield: 65%). The crystalline residue is the silylated phenol.

^{1}H NMR (300 MHz, $CDCl_3$) of **7**: 0.162 (s, 9 H, $Si(CH_3)_3$), 0.902 (t, J = 7.2, 3 H, CH_2CH_3), 1.25–1.40 (m, 2 H, CH_2), 1.40–1.50 (m, 2 H, CH_2), 1.579 (s, 3 H, C=C—CH_3), 1.595 (s, 3 H, C=C—CH_3), 2.090 (t, J = 7.5, 2 H, C=C—CH_2–).

Acknowledgment. It is a pleasure to thank Paul Seiler for his help and advice with the X-ray measurements.

Registry No. [2(*Z*)-**1**·2TMEDA], 97210-50-9; [2(*Z*)·2TMEDA], 97210-51-0; [4(*Z*)-**3**·4THF], 97210-52-1; **6**, 97190-47-1; **7**, 97190-48-2; TMSCl, 75-77-4; *tert*-butyl propionate, 20487-40-5; *tert*-butyl 2-methylpropanoate, 16889-72-8; methyl 3,3-dimethylbutanoate, 10250-48-3; (2,6-di-*tert*-butyl-4-methylphenoxy)trimethylsilane, 18510-49-1.

Supplementary Material Available: Tables of atomic coordinates and displacement parameters for (*Z*)-**1**·TMEDA, **2**·TMEDA, and [4(*Z*)-**3**·4THF] (10 pages). Ordering information is given on any current masthead page.

m-Quinodimethane, Parent Hydrocarbon of the *m*-Quinonoid Non-Kekulé Series. Low-Temperature Isolation and Solution-Phase Chemical Reactivity

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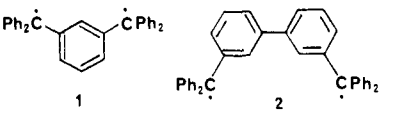
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. *Received December 26, 1984*

Abstract: The syntheses of several precursors to 2,6-dimethylenebicyclo[3.1.0]hex-3-ene (**11**) are described. Photochemical decomposition of 2,6-dimethylene-4-(2-oxopropyl)bicyclo[3.1.0]hexane (**17a**), 4-(2-oxo-2-phenylethyl)-2,6-dimethylenebicyclo[3.1.0]hexane, 4-(benzoyloxy)-2,6-dimethylenebicyclo[3.1.0]hexane, or base-induced elimination from 4-[(methanesulfonyl)oxy]-2,6-dimethylenebicyclo[3.1.0]hexane all gave [2.2]metacyclophane. In the presence of conjugated dienes (butadiene, 2,3-dimethylbutadiene, 2,4-hexadiene, and isoprene), photochemical decomposition of **17a** leads to cycloadducts (40–60%) empirically derived from 1 mol each of a C_8H_8 hydrocarbon and olefin. From butadiene, the major products are the (4*Z*)-bicyclo[6.3.1]dodeca-1(12),4,8,10-tetraene and a 13:1 mixture of 7- and 5-methyl-1-ethenylindans, respectively. The product distribution of cycloadducts is unaffected by dilution or oxygen, which is consistent with only one reactive intermediate. Mechanistic parsimony suggests that the decomposition of the above substrates initially gives the bicyclic hydrocarbon **11** which undergoes cyclopropyl ring cleavage to form the reactive diradical *m*-quinodimethane (*m*-xylylene, **3**) which then dimerizes or reacts with the included trapping reagent. Evidence for the initial formation of hydrocarbon **11** in the photochemical approaches is outlined. The intermediacy of the diradical **3** is suggested by (i) the observation of the previously identified electron paramagnetic resonance spectrum of the triplet state of **3** from the photolysis of **17a** at 77 K and (ii) the deuterium distribution in the cycloadduct from butadiene and 4-(2-oxopropyl)-2-(dideuteriomethylene)-6-methylenebicyclo[3.1.0]hexane which requires the reactive intermediate to have static or time-averaged bilateral symmetry. Stereochemical studies on the reaction of biradical **1** with 2,4-hexadienes indicate a two-step cycloaddition mechanism involving a long-lived adduct biradical.

Although *m*-quinonoid "non-Kekulé" compounds[1a] have been known and recognized for 70 years,[1b-e,2,3] the early examples, such as the Schlenk hydrocarbon **1**[1b] and the Schlenk–Brauns hydrocarbon **2**,[1c] are so heavily substituted by phenyl groups that their



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uniquely *m*-quinonoidal properties are veiled.[4]

m-Quinodimethane (*m*-xylylene, **3**) is the parent hydrocarbon of the *m*-quinonoid non-Kekulé series. The present paper[5] reports

(1) (a) For a discussion in which this term was first used, see: Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969, p 233. (b) Schlenk, W.; Brauns, M. *Ber.* **1915**, *48*, 661. (c) Schlenk, W.; Brauns, M. *Ibid.* **1915**, *48*, 725. (d) Hückel, E. *Z. Phys. Chem. Abt. B* **1936**, *34*, 339. (e) Müller, E.; Müller-Rudloff, I. *Justus Liebig's Ann. Chem.* **1936**, *517*, 134.

(2) For a review, see: Platz, M. S. In "Diradicals"; Borden, W. T., Ed.; Academic Press: New York, 1982; p 195.

(3) Clar, E. "Aromatische Kohlenwasserstoffe"; Springer: Berlin, 1941; p 311.

(4) Nevertheless, the small electron dipolar interactions can be detected by electron paramagnetic resonance spectroscopy: (a) Kothe, G.; Denkel, K.-H.; Summermann, W. *Angew. Chem., Intl. Ed. Engl.* **1970**, *9*, 906. (b) Luckhurst, G. R.; Pedulli, G. F.; Tiecco, M. *J. Chem. Soc. B* **1971**, 329. (c) Schmidt, R.; Brauer, H.-D. *Angew. Chem., Intl. Ed. Engl.* **1971**, *10*, 506.

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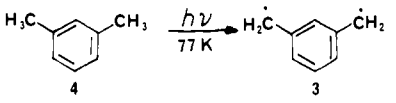
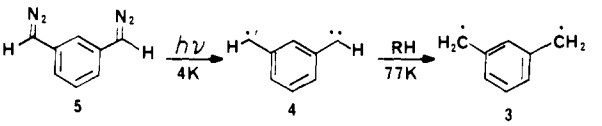
its synthesis and properties, both in isolation media at low temperature and in the solution phase. A later paper[6] will describe related experiments with the oxygen analogue *m*-quinomethane (3-methylenephenoxyl).

Synthesis of *m*-Quinodimethane. In 1975, Migirdicyan and Baudet assigned peaks in the fluorescence spectrum of a frozen irradiated sample of *m*-xylene (**4**) to *m*-quinodimethane (**3**).[7]

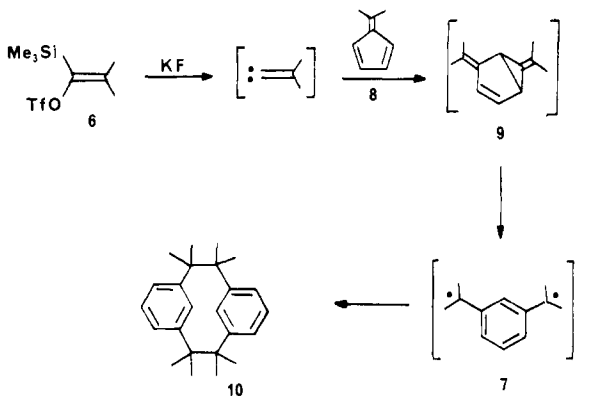


Subsequently, Wright and Platz[8] generated **3** by warming cryogenically cooled samples of the bis-carbene **4**[9] in hydrogenic matrices to 77 K. The electron paramagnetic resonance (EPR)



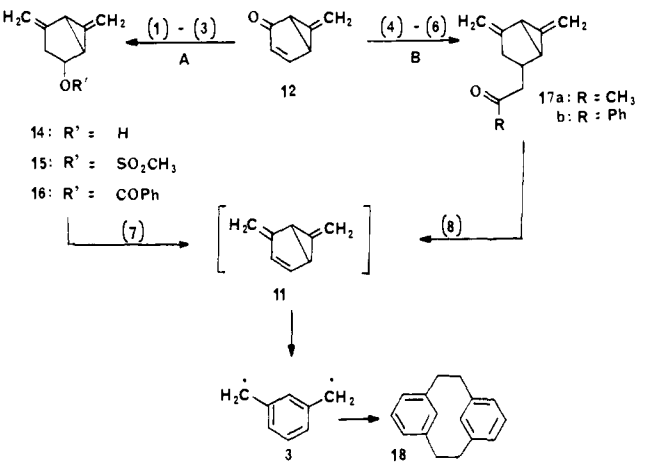
spectroscopic properties of **3** were consistent with a triplet ground state, in accord with theoretical expectation.[1a,10-12]

The first evidence that a biradical related to **3** might be generated in fluid medium was provided by the observation that dimethylvinylidene, generated from the precursor **6**, reacted with 6,6-dimethylfulvene (**8**) to give a mixture from which the *m*-cyclophane dimer **10** could be isolated.[13] The plausible interpretation given[13] for these results was that the initial cycloadduct **9** is unstable under the reaction conditions and undergoes thermal ring opening to biradical **7**, which then dimerizes. Alternative dimerization mechanisms which are not excluded by the evidence given include **9** + **7** and **9** + **9**, so that **7** has not been shown to be an obligatory intermediate.



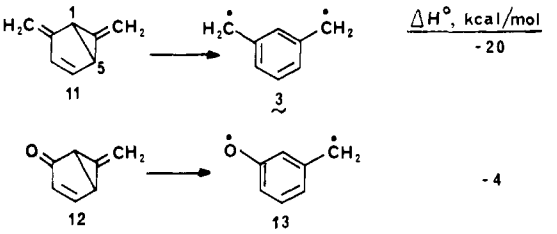
Obviously, neither of these synthetic approaches is suitable for studies of the intermolecular trapping reactions of *m*-quinodimethanes, since the carbenic precursors would be incompatible with most trapping agents. Our objective, therefore, was to develop an alternative synthesis of *m*-quinodimethane that would obviate this difficulty while still permitting direct EPR identification of the biradical **3**.

Scheme I[a]



[a] Methods: (1) NaOH, aqueous THF; (2) Ph_3PCH_2, THF; (3) esterify; (4) NaOMe, MeOH, $RCOCH_2CO_2R'$ (R = CH_3 or Ph, R' = CH_3 or Et, respectively); (5) Ph_3PCH_2, THF; (6) NaOH, aqueous THF; (7) from **15**, KO-*t*-Bu/Me_2SO; from **16**, hν; (8) hν.

The synthesis is aimed at the unknown hydrocarbon **11**, which by analogy to the corresponding ketone **12**[6,14] would be expected to suffer thermal or photochemical C_1–C_5 bond rupture. This



reaction has a much larger exothermicity in the hydrocarbon system (**11** → **3**) than in the ketone (**12** → **13**)[14c] and, moreover, might well occur at a much faster rate. The ketone **12** is kinetically stable at room temperature, but hydrocarbon **11** should be extremely labile. Rough guesses[15] at the activation parameters for thermolysis of **11**, based on literature analogies,[16] suggest half-lives of about 10^{-5} s at 25 °C and about 10^{-2} s at −78 °C.

Synthetic Approach to 2,6-Dimethylenebicyclo[3.1.0]hex-3-ene (11). After numerous unsuccessful efforts[17] to effect the apparently straightforward conversion of the carbonyl group in **12** to a methylene group in **11**, we concluded that the endocyclic double bond of **12** was a major stumbling block because it favored Michael addition, polymerization, and other side reactions. Accordingly, we developed two syntheses in which this double bond was protected, the carbonyl group was methylenated, and the ring double bond was regenerated. In both methods, provision was made to effect the last step as a photochemical reaction potentially adaptable to the low-temperature conditions needed for EPR spectroscopy. Scheme I shows the two variants of the approach, methods A and B, which differ structurally in the use of an oxygen

(5) (a) Preliminary communication: Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 1867. (b) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.*, following paper in this issue.

(6) Inglin, T. A.; Matlin, A. R.; Berson, J. A., unpublished results.

(7) (a) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400. (b) Cf. also: Lejeune, E.; Despres, A.; Migirdicyan, E. *J. Phys. Chem.* **1984**, *88*, 2719.

(8) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628.

(9) Trozzolo, A. M.; Murray, R. W.; Smolinsky, G.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526.

(10) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265, 275, 283.

(11) (a) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791. (b) Said, M.; Maynau, D.; Malrieu, J.-P.; Garcia-Bach, M.-A. *Ibid.* **1984**, *106*, 571.

(12) Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273–2280 and references cited therein.

(13) Gajewski, J. J.; Chang, M. J.; Stang, P. J.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 2096.

(14) (a) Rule, M.; Matlin, A. R.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098. (b) Seeger, D. E.; Hilinski, E. F.; Berson, J. A. *Ibid.* **1981**, *103*, 720; (c) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hillinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787. (d) Matlin, A. R.; Inglin, T. A.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4954.

(15) Goodman, J. L. Ph.D. Thesis, Yale University, New Haven, CT, 1984, p 149.

(16) For reviews, see: (a) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981. (b) Berson, J. A. In "Rearrangement in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; p 311.

(17) Matlin, A. R. Ph.D. Thesis, Yale University, New Haven, CT, 1982.

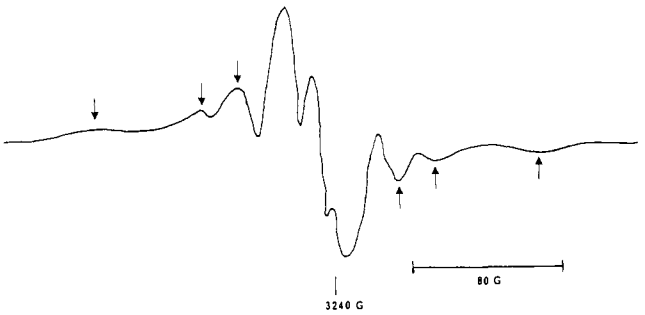


Figure 1. EPR spectrum generated by irradiation of **16** in *i*-PrOH at 77 K. The microwave frequency is 9.12 GHz. The six lines marked with arrows are assigned to the triplet state of *m*-quinodimethane **3**; the other lines arise from doublet impurities.

and a carbon functional blocking group, respectively.

Method A. Addition of water to the enone **12**, methylenation of the protected ketone **17** under standard Wittig conditions, and esterification gave the methanesulfonate **15** or benzoate **16**. The nonphotochemical version of method A involved treatment of the methyl sulfonate **15** with strong base (KO-*t*-Bu/Me_2SO). This effected elimination and gave a mixture containing the known *m*-cyclophane **18**, which was formed in 8–16% yield.

The photochemical counterpart of this elimination, a Norrish type II fragmentation of the benzoate **16**, has numerous analogies in the literature.[19] A particularly relevant observation[20] is the formation of *cis*- and *trans*-2-butenes in the photolysis of *sec*-butyl acetate and *sec*-butyl formate in the solid phase at 77 K. In the event, 254-nm photolysis of **16** in cyclohexane at 25 °C was complete after 8 h and led to benzoic acid and *m*-cyclophane **18** as the only products identifiable by gas chromatography (GC) and mass spectroscopy (MS). However, a substantial amount of apparently polymeric material was formed, only part of which was soluble in acetone-d_6. The ^1H NMR of this solution showed broad featureless resonances in the aromatic and aliphatic regions.

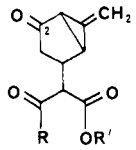
Identification of the *m*-Quinomethane Triplet State by EPR. Despite the side reactions observed in the solution-phase experiments, photolysis of benzoate **16** in glassy and polycrystalline preparations led to useful results. After about 1-h exposure at 77 K to light from an unfiltered Hg arc lamp, ethanol or 2-propanol matrices of **16** generated the EPR spectrum shown in Figure 1. Although indefinitely stable at 77 K in the dark, the signal disappeared irreversibly at higher temperatures.

The spectrum consists of a strong doublet impurity pattern flanked by a six-line array. The latter feature (marked with arrows) is assigned to the $\Delta m_s = \pm 1$ region of a randomly oriented triplet species.[21] The triplet zero-field splitting parameters deduced[22] from the spectrum are $|D|/hc \sim 0.011$ cm^{-1} and $|E|/hc > 0.001$ cm^{-1}. We assign the carrier of this spectrum as the triplet state of *m*-quinodimethane (**3**). The non-zero *E* value is consistent with a species of lower than 3-fold symmetry. The *D* value, which measures the average proximity of the two unpaired electrons, is in reasonably good agreement with the value ~0.016 cm^{-1} which we had predicted[14a,c,23] for *m*-quinodimethane by a semiempirical method. Moreover, although the spectrum recorded by Wright and Platz[8] differs from ours in the doublet impurity region, the field positions and relative intensities of the resonances in their six-line triplet pattern are essentially identical with those of ours. The present method therefore constitutes an independent synthesis of *m*-quinomethane and serves to strengthen its assignment as the EPR triplet signal carrier.

Nevertheless, method A suffers from several disadvantages, including the low quantum efficiency associated with benzoate photoeliminations[19b,c] and the need for short-wavelength light to effect the reaction. This combination of circumstances is inimical to attempts to observe the bicyclic hydrocarbon **11**, which by analogy to the model compound 2-methylenebicyclo[3.1.0]hex-3-ene, λ_{max} 245 nm (ϵ 10900), would absorb strongly at 254 nm and might well be photolabile. Consequently, we sought a precursor that could generate **11** in an efficient, low-temperature, photochemical reaction using longer wavelength light.

Method B. The Norrish type II photofragmentation of ketones to give an olefin and an enol is often highly efficient ($\phi = 0.1$–1.0) and has been shown to proceed, albeit slowly, at low temperature.[24] Appropriate substrates to generate the hydrocarbon **11** by this reaction include the ketones **17a** and **17b** (Scheme I).

The synthesis of the methyl ketone **17a** was achieved in a straightforward fashion via NaOMe-catalyzed Michael addition of methyl acetoacetate to the enone **12**, followed by selective Wittig methylenation of the C-2 position of the diketo ester **19a**, saponification, and decarboxylation. The methylenation step requires

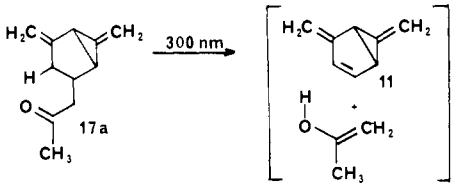


19a: R = R' = CH_3
b: R = Ph, R' = Et

2 equiv of methylenetriphenylphosphorane, one to neutralize the acidic proton of the β-keto ester system and the second to methylenate the C-2 keto function. Presumably, the side-chain keto group is inert to methylenation because it is part of the β-keto ester enolate system. Similar steps led to the analogous phenyl diketo ester **19b** and ultimately to the methylenated phenyl ketone **17b**.

The ultraviolet spectrum (nanometers, ϵ) of the methyl ketone showed $\lambda\lambda_{max}$ 270 (60), 230 (1200), and 210 (6900). Irradiation of a solution (in pentane, tetrahydrofuran, methanol, or benzene) at room temperature for 5 h at 300 nm produced acetone and metacyclophane **18** as the only products identifiable by GC, GC/MS, and ^1H NMR. As in the photolysis of the benzoate **16**, substantial quantities of insoluble higher molecular weight material were formed. The yield of metacyclophane **18** varied from 5 to 13% and that of acetone was ~15%.

In attempts to observe the anticipated primary products of the photofragmentation, 2-hydroxypropene (acetone enol)[25] and hydrocarbon **11**, photolysis of **17a** was carried out in tetrahydrofuran-d_8 or methanol-d_4 at −78 °C, and the cold reaction mixture was examined in a precooled NMR probe. Neither the known[25a] proton resonances of acetone enol nor those anticipated for hydrocarbon **11** were observed. Nevertheless, evidence obtained



in subsequent experiments points strongly toward the Norrish type II photofragmentation as the dominant reaction.

(18) (a) Vögtle, F.; Neumann, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 73 and references cited therein. (b) Flammang, R.; Figeys, H. P.; Martin, R. H. *Tetrahedron* **1968**, *24*, 1171.

(19) Cf. inter alia: (a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. (b) Barltrop, J. A.; Coyle, J. D. *J. Chem. Soc. B* **1971**, 251; (c) Pacifici, J. G.; Hyatt, J. A. *Mol. Photochem.* **1971**, *3*, 267; (d) Gano, J. E.; Eizenberg, L. *J. Am. Chem. Soc.* **1973**, *95*, 974.

(20) Borkowski, R.; Ausloos, P. *J. Am. Chem. Soc.* **1961**, *83*, 1053.

(21) We have been unable to detect the "forbidden" $\Delta m_s = \pm 2$ transitions at approximately half the magnetic field, but this is not surprising. The small *D* value implies that the magnetic sublevels are fully field-quantized, even at the lower field, and that the transition therefore is strongly forbidden.

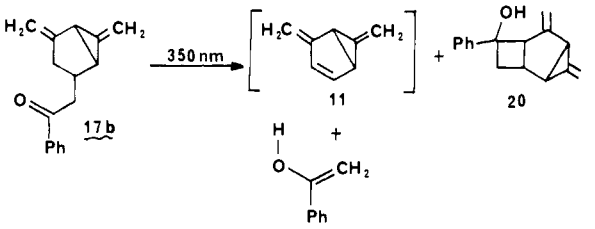
(22) Cf.: (a) Wasserman, E.; Hutton, R. S. *Acc. Chem. Res.* **1977**, *10*, 27. (b) Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance"; McGraw-Hill: New York, 1972; Chapter 10.

(23) Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. unpublished results.

(24) (a) Borkowski, R.; Ausloos, P. *J. Phys. Chem.* **1961**, *65*, 2257. (b) Ausloos, P. *Ibid.* **1961**, *65*, 1616.

(25) (a) For a report of acetone enol directly observed at <−40 °C from Norrish type II photofragmentation of 5-methyl-2-hexanone, see: Henne, A.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 435. (b) For ketonization of acetone enol at −80 to −100 °C, see: Ripoli, J. L. *Nouv. J. Chim.* **1979**, *3*, 195.

Whether the failure to observe **11** was due to secondary photolysis or to thermal instability could not be established experimentally, although, as has been indicated, the thermal lifetime might be as short as 10^{-2} s. However, this estimate was at best a crude guess, so that it seemed worthwhile to generate **11** from the phenyl ketone **17b**, whose red-shifted n–π^* transition would allow the use of longer wavelength radiation for the photofragmentation and thereby diminish the probability of secondary photolysis of hydrocarbon **11**. Photolysis of **17b** (MeOH at 25 °C) at 350 nm gave metacyclophane **18**, acetophenone, and an isomer of the ketone **17b**, characterized only by its mass spectroscopic fragmentation pattern. It seems likely that the latter substance is the cyclobutanol **20**, belonging to a structural type frequently observed as a Norrish type II side product. At −78



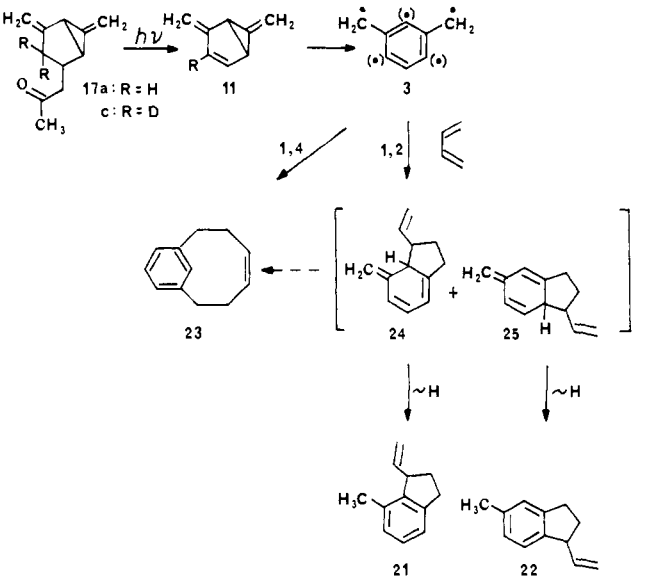
°C in acetone-d_6 or $CDCl_3$ solution, photolysis gave a reaction mixture which contained acetophenone enol, identified by its characteristic[26] methylene doublet resonances at δ 4.64 and 4.36 (J = 1.5 Hz). No evidence for hydrocarbon **11** was found in the spectrum. Warming the reaction mixture to 25 °C caused the δ 4.64 and 4.36 doublets to disappear and produced a new singlet resonance at δ 2.6, characteristic of acetophenone. In addition, products **18**, **20**, and acetophenone again were identified by GC/MS.

Phenyl ketone **17b** mimicked the behavior of methyl ketone **17a** when irradiated at 77 K in a 2-propanol matrix by giving rise to an EPR signal comprised of doublet impurity lines superimposed upon the six-line pattern of a randomly oriented triplet species. Although somewhat weaker relative to the impurity peaks, the latter pattern was essentially the same as that shown in Figure 1.

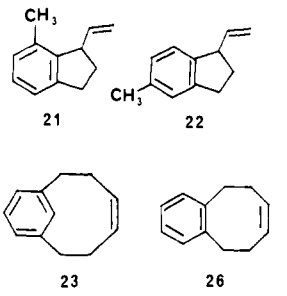
The weak EPR signals observed for the photofragmentations of the ketones **17a** and **17b** and the recovery of 95% of the ketone even after several hours of photolysis at 77 K are not surprising, since the Norrish type II reaction in aliphatic ketones is known[27] to have an excited-state thermal activation energy in the range 3.5–7 kcal/mol. This would retard the Norrish type II reaction and at low temperature might permit other excited-state deactivation processes to predominate. The poor yields of metacyclophane dimer **18** observed in the reactions in fluid media also may give a misleadingly pessimistic estimate of the efficiency of the photoelimination, since the nature of the side reactions that consume the bulk of the material is not known. Accordingly, we proposed to study the photoelimination in fluid medium in the presence of large excesses of trapping agents in hope of intercepting the reactive intermediates (hydrocarbon **11** and/or biradical **3**) more efficiently. Although a number of electronegatively substituted olefins (methyl acrylate, methyl methacrylate, and methyl crotonate) gave such adducts, most of the studies were carried out by using conjugated diene trapping agents to permit comparisons with related studies in the *m*-quinomethane series.[6]

Intermolecular Capture of *m*-Quinodimethane (3) by Olefins. Photolysis (300 nm) of the methyl ketone **17a** in degassed methanol or pentane containing a large excess of 1,3-butadiene at 25 °C gave none of the *m*-cyclophane dimer of **3**. Instead, a 40–60% yield was obtained of four major products whose molecular weights indicated them to be formal 1:1 adducts of butadiene and biradical **3**. Two of them were shown to be the methylated vinylindans **21** and **22** by hydrogenation to methylated

Scheme II

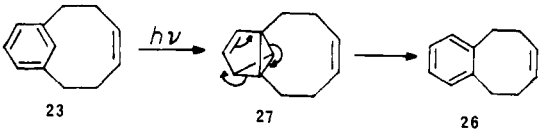


ethylindans and independent syntheses of the latter (see Appendix B). The other two[5b] were characterized spectroscopically and



identified as the symmetrical [6]metacyclophene **23** and the symmetrical benzocyclooctene **26** by diimide reduction and hydrogenation, respectively, to the known compounds [6]metacyclophane[28] and benzocyclooctane.[29]

As was shown by isolation and independent irradiation of **23**, the benzocyclooctene **26** is a secondary product resulting from the skeletal photorearrangement of **23**, presumably by way of the benzvalene intermediate **27**. Rearrangements of this type are

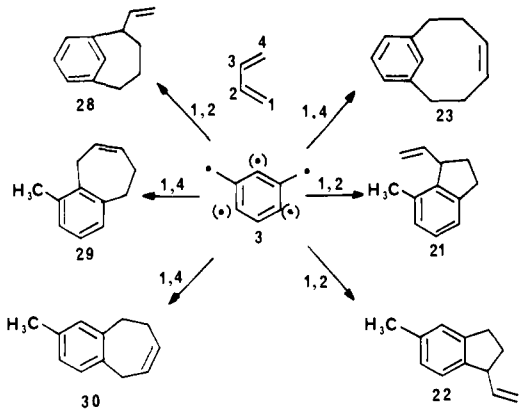


well precedented under both thermal[30] and photochemical[31,32] conditions. The possibility that the double bond in **23** and/or **24** might have the trans rather than the cis configuration is discussed elsewhere.[5b]

Regiospecificity. A working hypothesis for the mechanism of adduct formation is shown in Scheme II. The key reactive intermediate is the *m*-quinodimethane biradical **3**, which has unsatisfied valences at both exocyclic methylene groups as well as at the indicated ring positions. Formally, there are six regioisomeric ultimately aromatic adducts that could be generated by additions at the C_1–C_2 and C_1–C_4 pairs of diene sites (Scheme

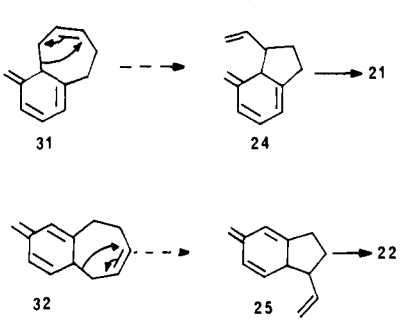
(26) (a) Rosenfeld, S. M.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* **1973**, *95*, 947. (b) Rosenfeld, S. M. *Tetrahedron Lett.* **1978**, 2655.
(27) Cf.: Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings; London, 1978; p 237.
(28) Hirano, S.; Hara, H.; Hiyama, T.; Fujita, S.; Nozaki, H. *Tetrahedron* **1975**, *31*, 2219.
(29) Bergman, R. G.; Lockhart, T. P.; Comita, P. B. *J. Am. Chem. Soc.* **1981**, *103*, 4082.
(30) van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1977**, 4667.
(31) Wilzbach, K. E.; Ritscher, J. S.; Kaplan, L. *J. Am. Chem. Soc.* **1967**, *89*, 1031.
(32) Kaplan, L.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 3291.

Scheme III. Potential Products of Cycloaddition of *m*-Quinomethane 3 to 1,3-Butadiene at Indicated Pairs of Diene Sites



III). (Nonaromatic adducts, although formally possible, are not observed.) In competition with the other pathways, the addition of the CH_2 groups of **3** to the C_1–C_2 sites of a diene is highly improbable. The resulting hypothetical adduct, **28**, would be a [4]metacyclophane, which incorporates a severe double violation of Bredt's rule (Scheme III).

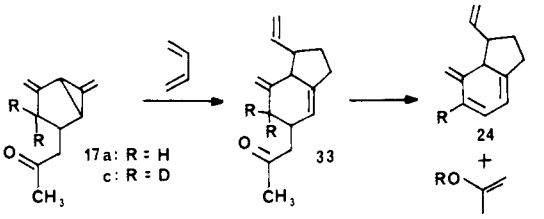
Of the five other potential adducts, three result from addition at C_1–C_4 and two from addition at C_1–C_2. The reaction shows little overall 1,2- vs. 1,4-regioselectivity, the indans **21** and **22** being preferred over the *m*-cyclophane-derived products **23** and **26** by a ratio of only about 1.2. Within each series, however, a substantial regioselectivity prevails. In the 1,2-series, the ortho para ratio **21**:**22** is about 13. The 1,4-adducts **29** and **30** (Scheme III) were not identified, and although they might have escaped detection at concentrations below about 5–10% of the *m*-cyclophene, the implication seems strong that in the 1,4-series, addition again is rather regiospecific. Although we have much evidence to present on other aspects of the mechanism, at present we can only speculate on the underlying cause of the apparent regiospecificity. One possible complicating factor whose importance is difficult to evaluate on the basis of the evidence presented so far is the multistep nature of the mechanism itself. Thus, the initial adducts when biradical **3** reacts at one CH_2 site and a ring position are not the final aromatic compounds actually isolated, **21** and **22**, but rather are the "prearomatic" species **24** and **25** (Scheme II), which require a final hydrogen shift to produce the indans. In the similar "prearomatic" adducts **31** and **32** on the pathway to the missing benzocycloheptenes **29** and **30**, it is conceivable that the corresponding aromatizing hydrogen shift might be slow relative to some other reaction, such as a formal 1,3-sigmatropic rearrangement (**31** → **24**, **32** → **25**). If this were the case, the



observed overall regiospecificity might not properly reflect the regiospecificity in the actual cycloaddition step. This difficulty arises again in the study of the stereochemistry of the cycloaddition. Anticipating a later discussion,[5b] we merely assert here that sigmatropic rearrangements **31** → **24** → **21** and **32** → **25** → **22** probably do not play a significant role in determining the observed product distribution.

Although details are given elsewhere,[5b] cycloadditions of biradical **3** to 2,3-dimethylbutadiene gave a set of products similar

Scheme IV



to those obtained with 1,3-butadiene: two indans, a [6]metacyclophene, and a benzocyclooctene.

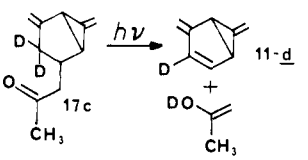
Mechanism of the Cycloaddition. The formation of cycloaddition products formally composed of 1 mol each of diene and biradical **3** of course constitutes only permissive evidence for the mechanism of Scheme II. A more compelling argument would be based on experimental indications that hydrocarbon **11** is on the photolysis pathway and on a demonstration of a structural relationship between the trappable reactive intermediate in the solution-phase reaction and the symmetrical biradical **3** detected by EPR spectroscopy. Two further crucial mechanistic questions arise concerning the reactions of **3**: Are both new C–C bonds in the cycloadditions formed simultaneously? Do reactions of **3** occur through a triplet or a singlet species?

Evidence That Norrish Type II Elimination Generates Hydrocarbon 11. Primary Deuterium Isotope Effect on the Quantum Yield. That Norrish type II elimination occurs in the photolysis of the phenyl ketone **17b** already has been substantiated by the observed formation of the fragmentation product acetophenone enol. A reasonable assumption by analogy would be that a similar mechanism prevails in the cycloadditions of the methyl ketone **17a**, even though acetone enol has not been observed. However, it does not necessarily follow that hydrocarbon **11** is an intermediate. In fact, a subtle logical trap awaits the unwary at this point. Note that Scheme II incorporates a sequence in which Norrish photoelimination is followed by cycloaddition of the diene to the intermediate. Strictly, no evidence has yet been brought forth to exclude the possibility that a different sequence obtains, namely, cycloaddition of the diene to the ketone *first*, followed by Norrish photoelimination (e.g., **17a** → **33** → **24**, Scheme IV).

Scheme IV also produces acetone enol, so that a distinction between it and Scheme II could not be made even if the enol could be observed. The main significance of the alternative pathway is that it bypasses hydrocarbon **11** and biradical **3** entirely. Therefore, until Scheme IV can be excluded, the central thrust of our experimental design is called into question.

To distinguish between the mechanisms of Schemes II and IV, we have focused on the step that actually consumes the ketone **17a**. In Scheme II, this is a true Norrish type II hydrogen transfer, whereas in Scheme IV it is a cycloaddition involving the formation of new C–C bonds but no bond breaking at C_3–H. Therefore, in the mechanism of Scheme II, the quantum yield for consumption of ketone **17** should be influenced by a primary deuterium isotope effect, but in that of Scheme IV, it should not.

A synthesis of the deuterated ketone **17c** (≡**17a**-*3,3*-d_2) is described in the Experimental Section. The photochemical reaction was restricted to the singlet manifold by the presence of a high concentration of 2,3-dimethylbuta-1,3-diene, which efficiently



quenches the n, π^* triplet state of the ketone.[33] The isotope effect was determined by a competition method (supplementary material) which gave $\phi_H/\phi_D \sim 2.2$, a value very similar in magnitude to

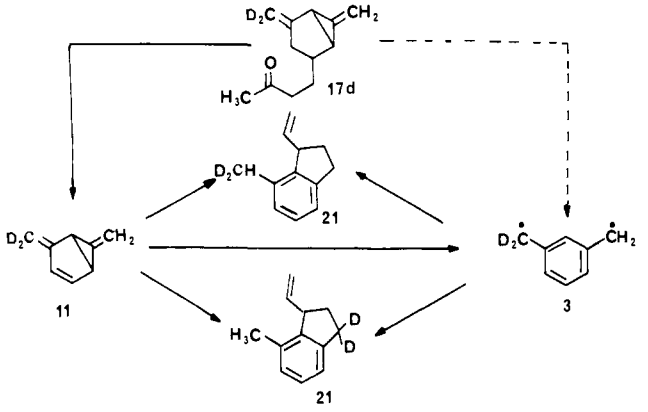
(33) Cf.: (a) Wagner, P. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 4009. (b) Dougherty, T. J. *Ibid.* **1965**, *87*, 4011. Casey, C. P.; Boggs, R. A. *Ibid.* **1972**, *94*, 6457.

Table 1. Quantum Yields for the Photolysis of Ketone **17a**[a]

substrate	ϕ_A[d]	ϕ_R[e]
17a[a]	0.12 ± 0.01	0.43 ± 0.05
17a + 2,3-DMB[b]	0.13 ± 0.02	0.13 ± 0.02
17a + CDE[c]	0.10 ± 0.01	0.30 ± 0.04

[a] In solvent pentane. [b] 2 M DMB in pentane. [c] 2 M CDE in pentane. [d] Quantum yield for acetone formation. [e] Quantum yield for total disappearance of ketone **17a**.

Scheme V



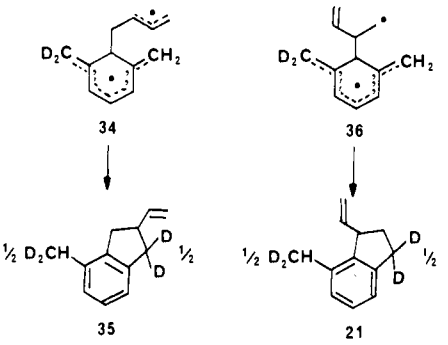
isotope effects in Norrish type II singlet processes reported in other systems.[34] The result argues against the mechanism of Scheme IV and is consistent with the mechanism of Scheme II.

Absolute Quantum Yields. Some further insights into the mechanism of the photoelimination are available from absolute quantum yields. We have studied the quantum yield for the overall reaction of ketone **17a** (ϕ_R) and for the acetone-forming portion of the reaction (ϕ_A) by 2-hexanone actinometry.[34-36] The effects of two addenda, 2,3-dimethylbuta-1,3-diene (2,3-DMB) and *cis*-1,2-dichlorethylene (CDE), on the quantum yields also have been determined. These species were chosen because both are good triplet ketone quenchers,[33,34] but only one, 2,3-DMB, is a good trapping agent for the biradical **3**. The results are given in Table I.

The observation that ϕ_A is virtually insensitive to the presence of triplet ketone quenchers suggests that most of the Norrish type II elimination occurs in the singlet manifold. In contrast, ϕ_R, which measures the efficiency of overall disappearance of ketone, is much higher than ϕ_A when a good biradical trap is not present (no addendum or added CDE), but ϕ_R and ϕ_A become equal in the presence of the efficient trap 2,3-DMB. The simplest explanation for this behavior is that the ketone **17a** is itself a good trapping agent for biradical **3**. The nature of the product from such a reaction has not been determined, but the nonvolatile higher molecular weight materials observed in the runs with **17a** alone and with **17a** + CDE may be oligomeric or polymeric materials of this provenance.

Until **11** can be isolated, we cannot exclude the possibility that biradical **3** is formed directly from the photoelimination excited state rather than by a further reaction of hydrocarbon **11**, but this minor detail does not interfere with the major conclusion from the isotope effect and quantum yield studies, which support the postulate that the photoreaction of ketone **17a** is a Norrish type II photoelimination.

Symmetry Properties of the Cycloadditive Reactive Intermediate. Scheme V shows that rationale of an experiment designed to elucidate the nature of the species that forms indan cycloadducts with 1,3-dienes. When one of the two exocyclic methylene groups of starting ketone **17a** is CD_2 and the other CH_2, their positions will become equivalent if the true intermediate is indeed the bilaterally symmetrical biradical **3** postulated in Scheme II. Disregarding a small secondary isotope effect, this symmetry predicts equal deuterium incorporations in the methyl group and the indicated ring methylene position of the adduct **21**. Generally, any intermediate lacking bilateral symmetry, and specifically the hydrocarbon **11**, can give this result only by fortuitous equivalence of cycloaddition rates or by passing through *another* symmetrical intermediate. Attempts to formulate the latter species quickly founder. For example, one can image adduct species **34** resulting from addition of butadiene to the bridge bond of hydrocarbon **11**.



This biradical can become symmetrical by a simple rotation of the side chain into a plane perpendicular to the ring, but it has the undeniable disadvantage of being the precursor of a molecule **35** that has its vinyl group at C_2 instead of at C_1 and is not among the observed adducts. The correct product **21**, with the C_1 vinyl group, can be obtained by this type of hypothetical pathway only through the symmetrical but energetically unlikely biradical **36**.

Synthesis of **17d** was accomplished in the same manner as that of **17a** (Scheme I) with the exception that Ph_3PCD_2 was used instead of Ph_3PCH_2 in the Wittig methylenation step. The ketone **17d** was obtained with >92% deuterium incorporation in the indicated position.

Photolysis of **17d** in pentane-containing butadiene gave the four previously described adducts, from which **21** was separated by GC. The location of the deuterium label was determined by both ^1H and ^2H NMR integration: the ratio of methyl to C_3 deuterium was 1.04. If the slight departure from the value 1.00 predicted by a symmetrical intermediate is real, the direction and magnitude of the discrepancy are about what would be expected for a secondary isotope effect. The result strengthens the designation of symmetrical biradical **3** as the cycloadditive intermediate.

Sequential or Concerted Bond Formation? Stereochemistry of the Cycloadditions. In proposing to use the stereochemistry of the cycloaddition as a basis for distinguishing a stepwise from a concerted mechanism, we employ arguments whose basic premises are precedented[37] but whose applicability in the present context nevertheless may be clarified by an explicit reexamination. For purposes of logical categorization, the possible experimental outcome may be divided into two extremes: stereospecific or nonstereospecific. The number of interpretations of these results, however, exceeds the number of results, since by common consent, a stereospecific cycloaddition may be caused by either a concerted reaction or a stepwise one with a fast second step, and a nonstereospecific cycloaddition may be caused by either a stepwise mechanism or by two competing concerted mechanisms, one cis and one trans in the stereochemical mode. That the experimental system *in this form* is underdetermined need not cause the test to be abandoned, however. The apparent difficulty is a consequence of oversimplification in the presentation of the logical outline. Specifically, in the present case, the *details* of the nonspecificity furnish information which is not explicitly included in the above stylized categorization. This provides the basis for a choice between the two mechanisms with nonstereospecific outcomes.

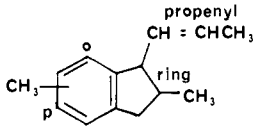
(34) Coulson, D. R.; Yang, N. C. *J. Am. Chem. Soc.* **1966**, *88*, 4511.
(35) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 126.
(36) Wagner, P. J. *Tetrahedron Lett.* **1968**, 5795.
(37) Cf.: inter alia (a) Montgomery, L. K.; Schueller, K.; Bartlett, P. D. *J. Am. Chem. Soc.* **1964**, *86*, 622. (b) Berson, J. A.; Dervan, P. B.; Malherbe, R.; Jenkins, J. A. *Ibid.* **1976**, *98*, 5937.

Table II. Products[c,d] from Reactions of *m*-Quinodimethane (**3**) with Hexa-2,4-dienes

products				
ring	propenyl			
		o-Methylindan (*o*-**37**)		
cis	cis	6.0	*a*	3.1
trans	cis	20.5	*a*	13.9
cis	trans	*a*	9.2	7.5
trans	trans	*a*	49.9	25.9
		p-Methylindan (*p*-**37**)		
cis	cis	*a*	*a*	*a*
trans	cis	12.0	*a*	7.9
cis	trans	*a*	*a*	*a*
trans	trans	*a*	13.8	5.0
		m-Cyclophane (**38**)		
cis		42.2	3.5	37.3[b]
trans		19.3	23.6	

[a] Could not be detected. [b] Total of cis + trans. [c] Relative percent. [d] Absolute yields (%) corrected for recovered starting material (**17a**): from cis,cis, 25.8; from trans,trans, 21,2; from cis,trans, 27.9.

We have studied the cycloadditions of the biradical **3**, generated by photolysis of ketone **17a**, with *cis*, *cis*-, *trans*, *trans*-, and *cis*,*trans*-hexa-2,4-diene. In each case, the products have structures analogous to those already described as resulting from the reactions of **3** with buta-1,3-diene and 2,3-dimethylbuta-1,3-diene, namely alkenyl methylated indans and [6]metacyclophenes. The structures and configurations were assigned by techniques described in Appendix B. Table II collects the data. To aid in reading



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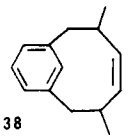

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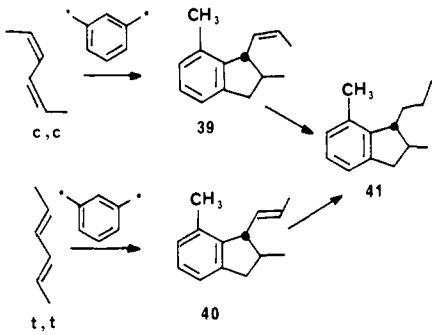
the table, structures **37** and **38** show generalized formulas for the regiochemical and stereochemical features of the products.

Regiospecificity. Although the cycloadditions to 2,4-hexadienes do not show as marked a preference for ortho vs. para orientation in the indan product as those to butadiene (where the ortho/para ratio was about 13), some ortho regiospecificity does survive, ratios of 2.2, 4.3, and 3.9 being observed from *cis*, *cis*-, *trans*, *trans*- and *cis*,*trans*-2,4-hexadienes, respectively.

Stereospecificity. A consistent feature of the cycloadditions is the persistence of the geometry of the nonreacting olefinic unit of the diene in the propenyl group of the indan product. This is clearly the case for *cis*, *cis*- and *trans*, *trans*-dienes, which give only *cis*- and *trans*-propenyl products, respectively. For *cis*,-*trans*-diene, both propenyl configurations are observed in the product, and it is a reasonable assumption that these are simply carried through from the reactant. If this is true, the regioselectivity for the *cis*- vs. the *trans*-diene double bond of *cis*,-*trans*-2,4-hexadiene may be calculated from the data as about 2.0 in the ortho product and about 1.6 in the para. The fact of this feeble regioselectivity will become useful soon.

The decisive indicator of mechanism is the indan (**37**) ring configuration. Table II shows that the *dominant stereochemistry at this site is trans, regardless of the initial diene configuration* and regardless of whether the aromatic methyl group of the product is ortho or para. This point was established not only by NMR spectroscopy but also by a direct chemical correlation of the major products, **39** and **40**, respectively, from *cis*,*cis*- and *trans*,*trans*-hexa-2,4-diene, which both give the same derivative **41** upon diimide reduction of the propenyl side chain.

These observations may be restated to emphasize the fact that in cycloaddition, a *trans*-olefin gives an adduct with dominant retention of configuration, whereas a cis olefin gives an adduct with dominant inversion. To interpret this behavior in terms of two competing concerted cycloadditions requires the extra hypothesis that, for some reason, a change in olefin geometry induces a switch in the order of preference of the two pathways. The stepwise mechanism, on the other hand, implies the possibility of crossover as an inherent property and therefore is preferred on grounds of mechanistic economy.



Although stereoisomerization of the reactant hexadienes does occur slowly under the (photochemical) conditions of the cycloadditions, this cannot contribute more than a minor amount to the observed loss of stereospecificity in adduct formation. To account on this basis for the inversion observed in the reaction cis,cis → **39**, one would have to postulate cis,cis → cis,trans isomerization followed by highly regiospecific reaction at the trans double bond of the latter. This requirement conflicts with the already reported weakly regiospecific reaction at the cis double bond of cis,trans and permits the conclusion that the loss of stereospecificity in the products is inherent in the cycloaddition mechanism and is not an artifact caused by diene stereoisomerization.

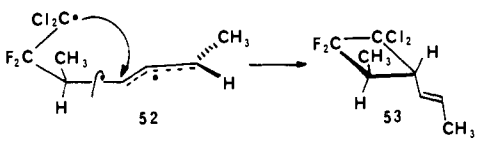
Although a fuller discussion of the effect of dilution on the product composition is deferred, we note here that the results shown in Table II all refer to solutions 2 M in diene. The relative amounts of the indicated products are essentially invariant between 1 and 8.8 M.

A stepwise mechanism is the simplest way to account for the stereochemistry of the cycloaddition (Scheme VI). We imagine that the first bond is formed between a terminal diene position and an exocyclic carbon of the biradical. This gives an adduct biradical (e.g., **42**) which is both allylically and benzylically stabilized. In Scheme VI, the second bond is shown as having formed at the ring position ortho to the methyl group, but the para product presumably also can be formed from the same adduct biradical. Internal rotations in the intermediate can cause loss of stereospecificity, provided that they are competitive with ring closure.

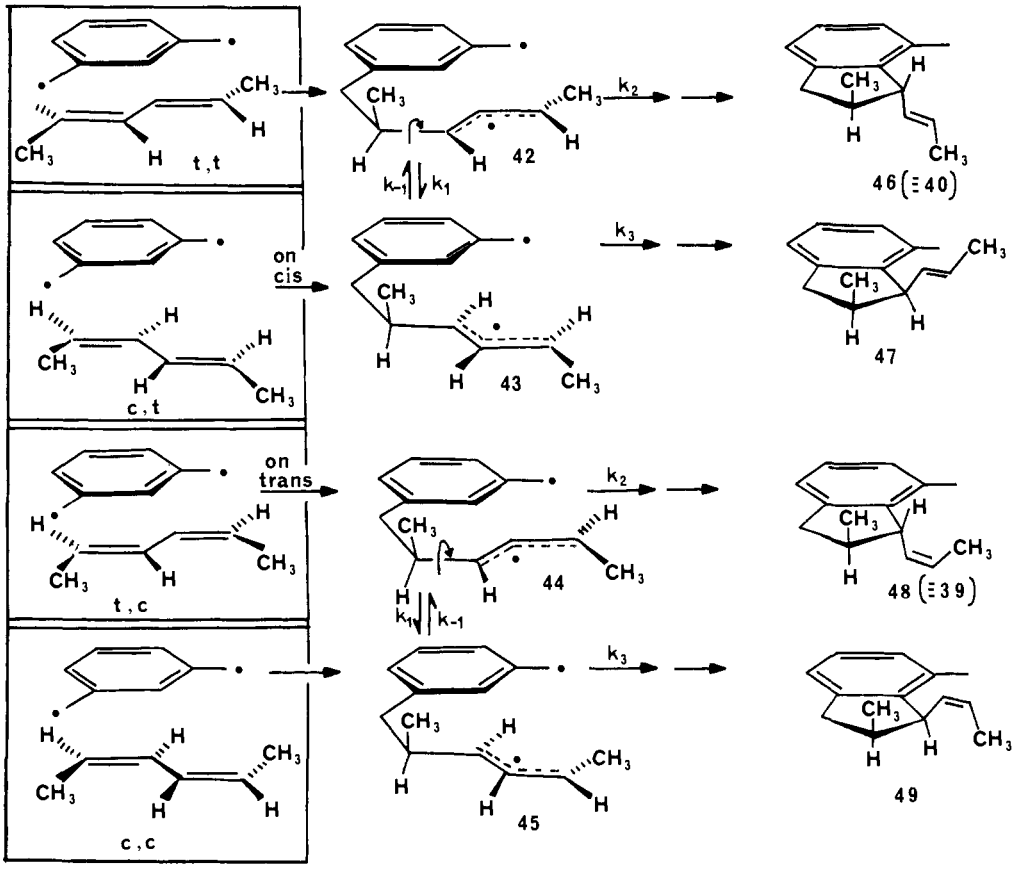
One might question whether cyclization to give the nonaromatic precursor **50** of the ortho product should compete with mere collapse at the exocyclic position to give a *m*-cyclophene (**51**, Scheme VII) in which the aromatic ring is not disrupted. We defer a discussion of the mechanism of cyclophene formation[5b] but note here that the energetic benefit of preservation of aromaticity is largely offset by the strain energy of the *m*-cyclophene product.

One also might raise the possibility that the cyclophene could undergo secondary sigmatropic rearrangements to give the indan adducts. This would be an unwelcome perturbation in the mechanistic study, but the evidence[5b] against such indirect mechanisms for indan formation seems decisive.

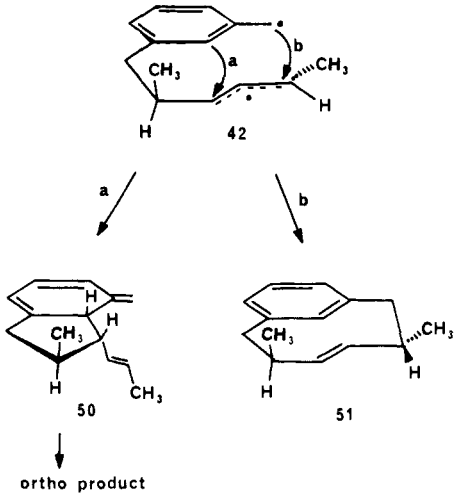
The competition between cyclization and internal rotation (Scheme VI, k_2 vs. k_1) may be analyzed quantitatively by using the procedure that Montgomery, Schueller, and Bartlett[37a] developed in their study of the additions of 1,1-dichloro-2,2-difluoroethene (1,1,2,2) to the 2,4-hexadienes. Their mechanism also involved a biradical adduct intermediate (e.g., **52**) in which



Scheme VI



Scheme VII



a similar competition controlled the stereochemistry of the ring carbons in the cyclobutane product (e.g., **53**).

Following the previous notation[37a], we define the quantities p and q as the experimental retention/inversion ratio in the products' ring positions from, respectively, *cis,cis*- and *trans,trans*-hexa-2,4-diene. For example (see Scheme VI), p = [**49**]/[**48**] from cis,cis and q = [**46**]/[**47**] from trans,trans. From the steady-state assumption, it can be shown[37a] that the experimental ratios may be expressed in terms of mechanistic rate constants as $p = (a/c) + b$, and $q = (c/a)(1 + b)$, where $a/c = (k_1/k_3)(k_2/k_1)$ and $b = k_2/k_1$. By solving the simultaneous equations defining p and q for a/c and b, it is possible to extract the competition ratios for rotation vs. cyclization in the biradical intermediates **42**–**45**. Thus, $a/c = (p + 1)/(q + 1)$, and $b = (pq - 1)/(q + 1)$. Independent checks on both the p and the q values can be obtained (see Scheme VI) from the cycloadditions of *cis,trans*-hexa-2,4-diene.

Table III. Comparison of Experimental Values and Derived Mechanistic Rate Constants in the Cycloadditions of the 2,4-Hexadienes to Dichlorodifluoroethene (1,1,2,2) and *m*-Quinodimethane (**3**)

	p	q	a/c	b
		1,1,2,2[a,b] with		
cis,cis	0.29			
cis,trans	0.32	5.03		
trans,trans		5.07		
av	0.31	5.05	0.217	0.099
		3[c] with		
cis,cis	0.29			
cis,trans	0.29	4.5		
trans,trans		5.4		
av	0.29	5.0	0.21	0.075

[a] Data from ref 37a. [b] At 80 °C. Values obtained at 100.6 °C did not differ appreciably. [c] Present work, at 25 °C.

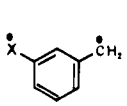
In the corresponding case of the dichlorodifluoroethene (1,1,2,2) additions, Bartlett and co-workers[37a] deduced the values of p, q, a/c, and b shown in Table III. Appropriate arrangement of our data from Table II gives the values for the *m*-quinodimethane cycloadditions also shown in Table III. Although technical difficulties prevent a comparison of results from experiments carried out at a common temperature, the temperature effect has been studied in the 1,1,2,2 system and found to be small.[37a] It is clear that a remarkable correspondence exists between the 1,1,2,2 data and the results obtained with biradical **3**. In both systems, the ratios of competing rate constants for internal rotation vs. cyclization may be expressed as $k_1/k_2 = 11.5 \pm 1.5$, and $k_{-1}/k_3 = 2.5 \pm 0.3$.

Interpretations of this correspondence can vary in detail but generally conform to one of two extreme categories or to a blend of the two: (1) the absolute rate constants for corresponding processes differ greatly between the two systems, but the rotation/cyclization rate ratio fortuitously remains constant because of compensating nonequivalences, or (2) the ratio remains constant

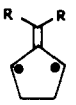
because the individual rate constants in the two systems are nearly the same. Although the first interpretation cannot yet be ruled out, the second and its corollaries seem to offer a more fruitful hypothesis for designing further tests.

An inspection of the actual processes involved in the internal rotations in the adduct biradical from the *m*-quinomethane system (e.g., **42**, Scheme VI) and in that from the 1,1,2,2 system (**52**) shows that in both instances, a 3-methylallyl radical fragment must rotate about the bond joining it to a group $RCX_2CH(CH_3)$. In both cases, R is remote, and structural variations in it are not expected to change the rotational rate greatly. The X groups are H in the **3** system and F in the 1,1,2,2 system. Because of the small steric requirements of F,[38] and because rotational barriers in any case are not sensitive to substitution until the point of real steric hindrance is reached,[39] the internal rotational rates in the biradical intermediates **42** and **52** might well be very similar. If this is correct, then in order to preserve equivalence in the competition ratios, the cyclization rate constants also must be similar. One conceivable reason for this might be that there is little or no potential energy barrier to cyclization[40,41] and that therefore the rate is controlled by entropy losses as loose internal rotations of the biradical are converted to tighter vibrational modes in the transition state.[42] To a rough approximation, the entropy cost will be related to the *number* of bonds whose modes must be so tightened. This number is three in both **42** and **52**, so that it is quite reasonable that the cyclization rates should be similar. Whether these anticipated similarities should be exact enough to result in the observed near-identities in the competition ratios or whether compensatory nonequivalences help to bring the ratios close together cannot yet be answered.

Mechanistic Comparisons with Additions of Other Non-Kekulé Molecules. The limitations associated with the method of generating *m*-quinodimethane biradical **3** cause some difficulty in comparisons of its intermolecular reactivity with those of other known biradical species such as 2-alkylidenecyclopentane-1,3-diyls (**54**)[43] and *m*-quinomethane (**13**).[6,14] For example, although for



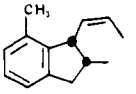
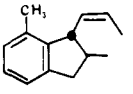
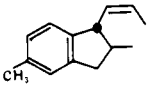
3: X = CH_2
13: X = O



54a: R = H
b: R = Me

54b a body of information is available on the concentration-dependent stereospecificities of cycloadditions to electron-deficient olefins,[43] comparable studies on cycloadditions to dienes are lacking. This temporary mismatch of information leads to an ambiguity in interpretation of the observations that at high concentration of trapping agent, cycloadditions of **54b** are highly stereospecific, but those of **3** are almost stereorandom. The difference in behavior might persist when the stereochemistry of additions of **54b** to dienes eventually is studied, but for the present, the possibility remains open that the **54b** + diene reaction may be nonstereospecific also. Dienes are expected to be less efficient traps for singlet **54b** than the other olefins studied[43] and, hence, even at high concentrations may permit a heavy incursion of product originating from nonstereospecific[43] reaction of triplet **54b**.

Table IV. Effect of Dilution on the Percentage Yields of Products from the Photolysis of the Methyl Ketone **17a** and *cis,cis*-Hexa-2,4-diene

product	diene concn, M 8.8	0.88	0.176
	8.6	6.7	4.9
	21.6	20.2	22.2
	15.4	14.7	9.3
	54.4	58.4	63.6
ketone consumed	36.0	50.4	66.6
tot yield[a]	11.0	22.8	13.5

[a] Corrected for recovered starting material.

However, a study of the *regiospecificity* of the addition of **54a** to a diene, 1,3-cyclopentadiene, is available.[44] The strong concentration dependence observed clearly shows the participation of two intermediates, presumably a singlet and a triplet, formed sequentially, a typical pattern in the chemistry of trimethylenemethane derivatives.[43] Accordingly, we have studied the concentration dependence of the products from *m*-quinodimethane (**3**) and *cis,cis*-hexa-2,4-diene. The results are collected in Table IV.

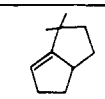
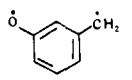
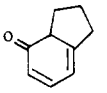
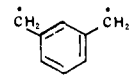
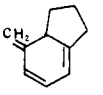
The data are probably reliable enough to suggest the reality of a small dilution effect which is just discernible at the lowest diene concentration studied (0.176 M). What is remarkable, however, is the insensitivity of the overall distribution to even a 50-fold dilution of the diene. Both the stereospecificity and the regiospecificity respond sluggishly at best, which is especially surprising because it seems likely that at the lowest diene concentration, a substantial fraction of the Norrish type II cleavage of ketone **17a** may occur in the triplet manifold. This is also suggested by the increased consumption of ketone at the lower diene concentrations (see Table IV). The triplet photoelimination would open the possibility of populating the triplet state of bicyclic hydrocarbon **11**, which might be a source of the triplet state of biradical **3**.

If one were to argue the position that two intermediates are formed sequentially in the region of high concentration of diene, the observed sluggish dilution effect would have to mean either that only one of them reacts, or that both react but that the product distribution from each is essentially the same, or that the two intermediates interconvert rapidly. Moreover, it would follow that either the triplet form of biradical **3** reacts in preference to the singlet or that the singlet reacts nonstereospecifically. The latter would contrast sharply with the observed[43] highly stereospecific cycloadditions of the trimethylenemethane (TMM) singlet biradical **54b** to olefins.

Another point of contrast with the TMM chemistry is noted in the absence of any substantial effect of O_2 on the product ratios in the photoreactions of **17a** with dienes (see Experimental Section). The triplet reactions of the TMM **54b** are selectively quenched by O_2, which sharply increases the proportion of the singlet-derived product and hence the overall regio- and stereospecificity.[43] The insensitivity of the product composition to dilution and oxygen in the reactions of the *m*-quinodimethane biradical seems to signal the participation of only one kind of intermediate in the cycloaddition chemistry. Although the motivation would be even stronger were data available on the ste-

(38) Jensen, F. R.; Bushweller, C. H.; Beck, B. H. *J. Am. Chem. Soc.* **1969**, *91*, 5937.
(39) Wilson, E. B. *Proc. Natl. Acad. Sci. U.S.A.* **1957**, *43*, 816.
(40) Doubleday, C., Jr.; Camp, R. N.; King, H. F.; McIver, J. W., Jr.; Mullaly, D.; Page, M. *J. Am. Chem. Soc.* **1984**, *106*, 447.
(41) Doering, W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *78*, 5279.
(42) (a) For calculational evidence of this effect in a simple model, tetramethylene, see ref 40. (b) Cf.: Bartlett, P. D.; Dempster, C. J.; Montgomery, L. K.; Schueller, K. E.; Wallbillich, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 405. (c) For discussion of competition between cyclization and internal rotation in substituted tetramethylenes, see: Dervan, P. B.; Dougherty, D. A. In "Diradicals"; Borden, W. T., Ed.; Academic Press: New York, 1982; p 122*ff* and references cited therein.
(43) For reviews, see: (a) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446; (b) Berson, J. A. In "Diradicals"; Borden, W. T. Ed.; Wiley: New York, 1982; p 151.
(44) Siemionko, R. K.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3870.

Table V. Estimated[a] Reaction Enthalpies of Biradical–Olefin Cycloadditions

biradical	product	$\Delta H°$, kcal/mol
 54		−77
 13		−52
 3		−31

[a] By the method of group equivalents (see ref 47).

reospecificity of the **54b** + diene reaction, one already is stimulated to ask whether nonstereospecific cycloadditions of singlet biradicals may occur under some circumstances. It may be instructive to pursue briefly the consequences of the hypothesis that concerted and stepwise cycloadditions of *singlet* biradicals are *in competition*. What factors may be expected to favor one or the other of these pathways?

The stepwise reaction consists of a radical–olefin addition followed by a biradical cyclization, symbolically **55** → **56** → **57**.

55 56 57

In most cases, step a will be rate-determining, and its kinetics probably can be approximated by those of alkyl monoradical additions to olefins, which typically have Arrhenius activation parameters near $E_a \cong 7$–8 kcal/mol and $A \cong 10^{7.5-8.5}$ M^{-1} s^{-1}, corresponding to $\Delta G^{\ddagger} \cong 15$–13 kcal/mol and rate constants $k_a \cong 50$–3000 M^{-1} s^{-1} at room temperature.[45] Note that the activation entropies are in the range $\Delta S^{\ddagger} \cong -22$ to −27 eu. This is less negative than would be expected if the total translational entropy cost of making one particle out of two had to be paid, since this would lead to a $\Delta S^{\ddagger} \cong -35$ eu.[46] Presumably, it is the additional low-frequency torsional and vibrational modes created in the transition state that partially offset the translational effect.

The model monoradical addition, methyl plus ethylene → propyl, is modestly exothermic ($\Delta H° \cong -17$ kcal/mol),[47] largely because of the exchange of a σ for a π bond. The corresponding biradical addition, step a of the stepwise mechanism, when the biradical is conjugated as in **54**, **3**, and **13**, is even less exothermic, with $\Delta H°$ values, respectively, of about 8, 2, and 2 kcal/mol. To a good approximation, therefore, one does not expect the rate of step a to vary greatly as a function of biradical structure in this series.

The situation is quite different, however, in the hypothetically competing concerted additions, where both new bonds are forming in a single step. The exothermicities for the cycloadditions are large and depend sharply on structure (Table V). It is reasonable to expect the activation energies to be sensitive to structure in such a way that the more exothermic the reaction, the lower the $\Delta H^{\ddagger}$. Each of the concerted transition states, like a Diels–Alder transition state,[48] should be highly organized and have $\Delta S^{\ddagger} \cong -35$ eu. The $\Delta H^{\ddagger}$ term therefore should dominate the response of the rate to structural variation.

The competition hypothesis thus would predict that the relative importance of the concerted pathway would decrease along the series of singlet biradicals TMM (**55**) > *m*-quinomethane (**13**) > *m*-quinodimethane (**3**). If the concerted and stepwise mechanisms are respectively, identified with stereospecific and nonstereospecific singlet processes, it is clear that the relevant experimental facts in the present and related[6,43] cases conform exactly to the predicted pattern.

In the case of *m*-quinodimethane, the analysis is, of course, over-simplified because the extent to which triplet **3** may be involved is not known. Moreover, even if singlet **3** is the reactive intermediate, it is not yet possible to predict what fraction of the exothermicity changes of Table V will be incorporated into $\Delta H^{\ddagger}$ changes, and therefore one cannot predict the structural alteration that will cause a switchover from the concerted to the stepwise mechanism. Nevertheless, at least for the present, the correspondence of speculation and experiment forms the basis for a self-consistent hypothesis of singlet biradical cycloadditions and for further tests.

The nonstereospecificity observed in the cycloaddition of *m*-quinodimethane **3** to conjugated dienes is expected of the biradical's triplet ground state. However, no direct evidence on the spin state of the reactive species in these cycloadditions is available at present, and it is possible that the singlet is partly or fully responsible for all the observations.

The *m*-quinodimethane biradical under static conditions is a spectroscopically well-understood triplet species. Its chemical dynamics, however, are still in an early stage of investigation, and a detailed elucidation of its behavior remains to be accomplished.

Table VI. Gas Chromatography Columns

column	description
A	5 ft × 1/8 in. 2% OV-101 on Anakrom AS 100/120
B	20 ft × 1/8 in. 5% OV-101 on Chromasorb W-DMCS 100/120
C	13 ft × 1/8 in. 5% FFAP on Chromasorb P-AW 100/120
D	15 ft × 1/8 in. 10% XF-1150 on Chromasorb P-AW DMCS 100/120
E	5 ft × 1/8 in. 15% γγ on Chromasorb P-AW 100/120
F	5 ft × 1/4 in. 5% OV-101 on Chromasorb W-DMCS 60/80
G	11 ft × 1/4 in. 17.5% FFAP on Chromasorb P 60/80
H	15 ft × 1/4 in. 10% OV-101 on Chromasorb W-DMCS 60/80
I	5 ft × 1/4 in. 10% OV-101 on Chromasorb W-DMCS 60/80

Table VII. Response Factors

C_3H_6O/C_9H_{20}	0.461	$C_{14}H_{18}/C_{16}H_{34}$	0.652
$C_6H_{12}O/C_9H_{20}$	0.707	$C_{12}H_{16}/C_{16}H_{34}$	0.559
$C_{11}H_{14}O/C_{16}H_{34}$	0.592	$C_9H_{20}/C_{16}H_{34}$	0.563
$C_{16}H_{16}/C_{16}H_{34}$	0.723		

Experimental Section

Instruments and Equipment. Proton nuclear magnetic resonance spectra were recorded on a Jeol FX 90-Q (90 MHz), a Bruker HX-270 (270 MHz), or a Bruker WM-500 (500 MHz) spectrometer. ^{13}C NMR spectra were obtained on a Jeol FX 90-Q (22.5 MHz) or a Bruker WM-500 (125.7 MHz) spectrometer. Chloroform (δ 7.24), acetone (δ 2.1), or tetramethylsilane (TMS, δ 0.0) were used as internal references for ^1H NMR. Chloroform (δ 77.7) was used as an internal standard for ^{13}C NMR. The spectra are reported as follows: chemical shift, multiplicity, number of protons, coupling constant (when measured), and assignment (if known). Variable temperature ^1H NMR were obtained on the Bruker HX-270 spectrometer by using a Bruker Model B-ST 100/700 variable-temperature controller.

Low-resolution mass spectra were recorded on a Hewlett-Packard 5985A GC/MS spectrometer. The glass column used, unless otherwise noted, was a 3 ft × 1/8 in., 2% OV-101 on Anakrom ABS 110–120 mesh. The spectra are reported as follows: initial column temperature (°C), time at initial temperature (min), temperature program rate (°C/min), final temperature, and retention time. Parent *m/e* values are shown as M^+, and fragment *m/e* values are shown as M^+ minus the indicated neutral or as the indicated cation. Isothermal runs are indicated by a single temperature. High-resolution mass spectra were done by Dr. Frank W. Crow at the Midwest Center for Mass Spectrometry at the

(45) Kerr, J. A. In "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. I, p 26.
(46) Cf.: Wiberg, K. B. "Physical Organic Chemistry"; Wiley: New York, 1964; p 221.
(47) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.
(48) Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183.
(49) Walling, C.; Mayo, F. R. *Chem. Rev.* **1950**, *46*, 191.

University of Nebraska—Lincoln. Analytical GC was performed on a Perkin-Elmer 900 gas chromatograph by using a flame ionization detector and nitrogen as the column carrier gas. Preparative GC was done on a Varian Aerograph 90-P by using helium as the carrier gas. Quantification of GC peaks was performed by using a Hewlett-Packard 3390A integrator. Relative detector response factors were determined by coinjections of known amounts of the compound of interest and an appropriate standard using the equation

$$\text{response factor} = \frac{A_1 M_2}{A_2 M_1}$$

where A is the peak area and M is the number of moles. The columns used for analysis are indicated in Table VI. The response factors used are given in Table VII. Isomers were assumed to have the same response factor.

Infrared spectra (IR) were recorded on either a Nicolet 7199 FT-IR or a Nicolet 55X FT-IR spectrometer. Ultraviolet–visible (UV–vis) spectra were obtained on a Cary 219 spectrophotometer.

Electron paramagnetic resonance spectra (EPR) were taken on a Varian E-9 EPR spectrometer. The temperature was controlled by using a Varian Model V-4540 variable-temperature accessory. A gold chromel thermocouple, affixed to the sample tube, was used to monitor the temperature. An unfiltered Oriel Model 6137 mercury arc lamp was used for sample irradiations.

All computations were performed either on a TI programmable 58C calculator or on the Digital Equipment VAX/VMS computer.

Photolyses were carried out by using either a Rayonet Photochemical Reactor Model RPR-100 equipped with 16 3000- or 3500-A bulbs, or a 450-W medium-pressure Hanovia lamp.

Reagents. Reagent grade chemicals were used in most experiments. If further purification was necessary, procedures recommended in "Purification of Laboratory Chemicals"[56] were used. Tetrahydrofuran (THF) and benzene were distilled from sodium benzophenone ketyl under nitrogen before use. Ethanol, methanol, propylene glycol, and 2-propanol used for EPR studies were spectrophotometric grade and were distilled from CaH_2 before use.

6-Methylenebicyclo[3.1.0]hex-3-en-2-one (12). This material was obtained as previously described.[14a,c] The product was purified either by distillation (bp 35 °C, 0.5 mm) or by preparative GC (column F, 70 °C, injector 110 °C, detector 90 °C).

4-Hydroxy-6-methylenebicyclo[3.1.0]hexan-2-one (Scheme I, Method A). A solution of 40 mg (0.47 mmol) of **12**, 37.7 mg (0.94 mmol) of NaOH, and 10 mL of 1:1 THF/H_2O was stirred at 0 °C for 4 h. The solution was acidified with 10% HCL solution and then saturated with NaCl. The solution was transferred to a separatory funnel with 25 mL of ether. The layers were separated and the organic phase was washed with 10% HCl (1 × 20 mL), H_2O (1 × 20 mL), and brine (1 × 20 mL) and then dried over $MgSO_4$. The organic phase was filtered, and the solvent was removed under reduced pressure to yield 42 mg of crude **48** (72%): GC–MS (80, 1, 20, 200) (4.1 min), *m/e* 124 (M^+, 5%), 123 (H, 21%), 95 (C_2H_5, or CHO, 92%), 82 (C_3H_6, or C_2H_2O, 100%).

4-Hydroxy-2,6-dimethylenebicyclo[3.1.0]hexane (14). In a dry, 50-mL, round-bottomed flask equipped with magnetic stirring were placed 600 mg (1.68 mmol) of methyltriphenylphosphonium bromide and 20 mL of dry THF. The solution was cooled to 0 °C, and 1.2 mL of 1.2 M CH_3Li (1.44 mmol) was added slowly by syringe. After the solution was stirred for 30 min at 0 °C, 42 mg (0.34 mmol) of the hydroxyketone in 5 mL of dry THF was slowly added. The solution was stirred for 2 h and then allowed to warm to room temperature. The mixture was acidified with 10% HCl and then saturated with NaCl. The solution was transferred to a separatory funnel with 20 mL of ether. The layers were separated and the organic phase was washed with H_2O (1 × 20 mL) and brine (1 × 20 mL) and then dried over $MgSO_4$. The organic phase was filtered, and the solvent was removed under reduced pressure to give crude **14**. The material was purified by preparative GC (column F, 70 °C, 9 min). The mixture contained endo and exo isomers in a ratio of 1.5:1: ^{1}H NMR (500 MHz, $CDCl_3$) (two isomers) major, 5.41 (br s, 2 H), 5.06 (d, 1 H, J = 2.6 Hz), 4.85 (d, 1 H, J = 2.1 Hz), 4.28–4.29 (d × d, 1 H, J = 4.7, 7.0 Hz), 2.5 (m, 1 H), 2.34–2.30 (m, 2 H), 2.13 (d, 1 H, J = 16.1 Hz), 1.60 (d, 1 H, J = 7.3 Hz); minor, 5.57 (s, 1 H), 5.54 (s, 1 H), 4.86 (d, 1 H), 4.7 (d, 1 H, J = 1.8 Hz), 4.6 (d × d, 1 H), 2.5 (m, 1 H), 2.42–2.41 (m, 2 H), 2.18–2.14 (d, 1 H), 1.50 (d, 1 H, J = 8.4 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) (two isomers) major, 150.2 (s), 136.5 (s), 106.6 (t), 105.0 (t), 74.0 (d), 39.7 (t), 33.3 (d), 28.8 (d); minor, 148.8 (s), 135.4 (s), 105.8 (t), 105.2 (t), 74.2 (d), 37.8 (t), 30.4 (d), 29.8 (d); FT-IR ($CDCl_3$) 3605 (m), 3577 (m), 3443 (br), 3070 (m), 2978 (m), 2908 (m), 1738 (m), 1654 (s), 1421 (m), 1372 cm^{-1} (m); GC–MS (80, 1, 20, 200) (2.7 min) *m/e* 122 (M^+, 1.1%), 93 (C_2H_5, or CHO, 100%), 91 (CH_3O, 74%), 79 (C_2H_3O, 80%), 77 (C_2H_5O, 90%); MS calcd mass for $C_8H_{10}O$ 122.0731, found 122.0728.

Methanesulfonate 15. A solution of 2 mg (0.016 mmol) of **14**, 4.56 μL of triethylamine (distilled from KOH, 0.0344 mmol), 1.92 μL (0.0249 mmol) of methanesulfonyl chloride (MsCl) (Aldrich) and 1 mL of CH_2Cl_2 was stirred at 0 °C for 1 h. The reaction was monitored by analytical GC for consumption of **14**. If necessary, equal molar amounts of MsCl and triethylamine were added. When consumption of **14** was complete, the solvent was removed under reduced pressure. The residue was extracted with ether and then the ether was removed under reduced pressure to give crude mesylate **15**. The material was used without further purification: ^{1}H NMR (90 MHz, $CDCl_3$) (two isomers) δ 5.5–5.4 (m, 2 H), 5.2–4.8 (m, 2 H), 3.4–2.4 (m, 5 H), 3.0 (s, 3 H); MS(DIP), *m/e* 200 (M^+, 1.9%), 121 (CH_3SO_2, 40%), 104 (CH_4SO_3, 100%), 91 ($C_2H_5SO_3$, 74%).

4-(2-Keto-1-carbomethoxy-1-propyl)-6-methylenebicyclo[3.1.0]hexan-2-one (19a). In a 100 mL, one-neck, round-bottomed flask equipped with a magnetic stirring bar and N_2 inlet were placed 25 mL of methanol, 10 mg 0.185 mmol) of $NaOCH_3$, and 2.6 mL (24.12 mmol) of methyl acetoacetate (Eastman). After the solution was cooled to 0 °C, 640 mg (6.04 mmol) of **12** was added. The solution was stirred for 2 h at 0 °C. The solution was then concentrated under reduced pressure. Excess methyl acetoacetate was removed by placing the flask under vacuum (<0.01 mm), and the residue was used without further purification. However, if analytically pure Michael adduct **19a** was desired, the residue was flash chromatographed on silica gel (230–400 mesh) by using 3:1 hexane/ethyl acetate (R_f = 0.3). ^{13}C NMR showed a mixture of endo and exo isomers in a 1.5:1 ratio: ^{1}H NMR (90 MHz, $CDCl_3$) (two isomers) δ 5.5–5.6 (m, 2 H), 3.73 major (s, 3 H), 3.7 minor (s, 3 H), 3.61 minor (d, 1 H, J = 2.3 Hz), 3.51 major (d, 1 H, J = 2.3 Hz), 3.09 (d × d, 1 H, J = 8 Hz), 2.25 major (s, 3 H), 2.22 minor (s, 3 H), 2.60–1.64 (m, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) 208.5 (s), 201.3 (s), 168.7 (s) major, 168.5 (s) minor, 131.7 (s), 104.9 (t), 63.0 (d) major, 62.8 (d) minor, 52.4 (q), 37.4 (t) major, 36.9 (t) minor, 35.1 (d), 31.9 (d), 29.6 (q), 28.2 (d) minor, 28.0 (d) major; GC–MS (50, 1, 20, 200) (7.9 min), *m/e* 222 (M^+, 6.5%) 127 (C_6H_7O, 64%), 95 ($C_6H_7O_3$, 100%); FT-IR ($CDCl_3$) 2957 (br), 1710 cm^{-1} (s); exact mass calcd for $C_{12}H_{14}O_4$ 222.0892, found 222.0894.

4-(2-Keto-1-carbomethoxy-1-propyl)-2,6-dimethylenebicyclo[3.1.0]-hexane. In an oven dried, one-neck, 250-mL, round-bottomed flask equipped with a magnetic stirring bar, septa, and N_2 inlet needle were placed 11.6 g (32 mmol) of methyltriphenylphosphonium bromide (Aldrich), and 100 mL of dry THF. The solution was cooled to 0 °C and then 18 mL of 1.5 M CH_3Li in hexanes (27 mmol, Alfa, low halide) was slowly added via syringe. After the addition was complete, and the solution was stirred at 0 °C for 30 min, 1.2 g (5.4 mmol) of crude **19a** in 25 mL of dry THF was added slowly via syringe. The reaction was stirred for 3 h at 0 °C and then warmed to room temperature. The reaction was then quenched with 5% HCl until acidic to litmus paper. The solution was transferred to a separatory funnel with 150 mL of ether. The layers were separated, and the organic layer was washed with H_2O (2 × 75 mL) and with brine (1 × 75 mL). The organic phase was dried over $MgSO_4$ and then filtered. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (230–400 mesh) by using 4:1 hexane/ethyl acetate (R_f = 0.4) to give 480 mg of dimethylene keto ester (36% for two steps) as a colorless oil: ^{1}H NMR (90 MHz, $CDCl_3$) (two isomers) δ 5.35 (m, 2 H), 4.84–4.63 (m, 2 H), 3.65 minor (s, 3 H), 3.63 major (s, 3 H), 3.41 minor (br s, 1 H) 3.30 major (br s, 1 H), 2.8 (d × d, 1 H), 2.18 major (s, 3 H), 2.14 minor (s, 3 H), 2.6–1.4 (m, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) (two isomers) δ 202.5 minor (s), 202.2 major (s) 169.5 major (s), 169.3 minor (s), 149.9 (s), 137.1 (s), 105.8 (t) 105.2 (t), 63.4 major (d), 63.3 minor (d), 52.7 (q), 40.5 minor (d), 40.0 major (d), 33.5 major (t), 33.3 minor (t), 29.9 (d), 28.3 (q), 27.6 minor (d), 27.5 major (d); GC–MS (150, 1, 20, 200) (1.1 min), *m/e* 220 (M^+, 1.9%), 188 (CH_3OH, 38%), 117 (C_7H_7, 56%), 43 (CH_3CO^+, 100%); FT-IR ($CDCl_3$) 2957 (br), 1740 (s), 1713 (s), 1654 cm^{-1} (m); exact mass calcd for $C_{13}H_{16}O_3$ 220.1100, found 200.1103.

2,6-Dimethylene-4-(2-oxopropyl)bicyclo[3.1.0]hexane (17a). In a 100-mL, one-neck, round-bottomed flask equipped with a magnetic stir bar were placed 480 mg (2.2 mmol) of the preceding keto ester, 15 mL of THF, 15 mL of H_2O, and 132 mg (3.3 mmol) of NaOH. The reaction was stirred at room temperature for 2 h and then acidified with 10% HCl until pH ~3. The solution was stirred for 1 h and then saturated with NaCl. The mixture was transferred to a separatory funnel by using 50 mL of ether. The layers were separated, and the organic phase was washed with 10% HCl solution (1 × 50 mL), H_2O (1 × 50 mL), and brine (1 × 50 mL). The organic phase was dried over $MgSO_4$ and filtered and then the solvent was removed under reduced pressure to give 250 mg of crude **17a** (71%). The material was purified by preparative GC (column F, 70 °C, injector 110 °C, detector 95 °C). ^{13}C NMR snowed endo and exo isomers in a 2:1 ratio: ^{1}H NMR (500 MHz,

$CDCl_3$) (two isomers) δ 5.47 minor (s, 1 H), 5.46 minor (s, 1 H), 5.42 major (s, 2 H), 4.95 minor (d, 1 H, J = 1.5 Hz), 4.86 major (d, 1 H, J = 1.3 Hz), 4.74 minor (s, 1 H), 4.69 major (d, 1 H, J = 0.9 Hz), 2.17 major (s, 3 H), 2.16 minor (s, 3 H), 2.8–1.6 (m, 7 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 208.2 (s), 151.9 minor (s), 151.1 major (s), 138.3 (s), 105.3 (t), 104.6 (t), 48.6 major (t), 48.3 minor (t), 36.1 (q), 35.1 (t), 30.7 (d), 29.8 (d), 28.3 (d); GC–MS (80, 1, 20, 200) (2.0 min), m/e 162 (M^+, 1.1%), 147 (CH_3, 11.0%), 119 (C_2H_3O, 100%); FT-IR (neat) 3010 (m), 2900 (m), 1749 (m), 1714 (s), 1657 (m), 1425 (m), 1405 (m), 1370 (s), 1355 (m), 1170 (s), 1164 (m), 1143 (m), 1121 (m), 840 cm^{-1} (s); exact mass calcd for $C_{11}H_{14}O$ 162.1036, found 162.1043; UV–vis (pentane) λ_{270} (log ϵ = 1.8), λ_{230} (log ϵ = 3.08), λ_{210} (log ϵ = 3.84).

4-(2-Keto-1-carbomethoxy-2-phenylethyl)-2-oxo-6-methylenebicyclo-[3.1.0]hexane (19b). In a 50-mL, single-neck, round-bottomed flask equipped with a magnetic stir bar were placed 217 mg (1.13 mmol) of ethyl benzoylacetate, 1 mg (0.185 mmol) of $NaOCH_3$, and 5 mL of CH_3OH. The solution was stirred for 15 min at room temperature and then 100 mg (0.94 mmol) of GC purified **12** in 4 mL of ether was slowly added via a dropping funnel. The solution was stirred for 6 h and then concentrated under reduced pressure (<0.5 mm). The residue was then used directly in the next step. In a dry, 100-mL, single-neck, round-bottomed flask equipped with a magnetic stir bar, rubber septum, and N_2 inlet needle were placed 3 g (8 mmol) of methyltriphenylphosphonium bromide (Aldrich), and 10 mL of dry THF. The solution was cooled to 0 °C and 5 mL (7.5 mmol) of 1.5 M CH_3Li (Alfa, low halide) was slowly added via syringe. After 30 min, the residue, in 5 mL of THF, was added to the solution via syringe. The solution was then allowed to warm to room temperature and stirred overnight. The reaction was acidified with 10% HCl solution until pH ~3. The solution was saturated with NaCl and then transferred to a separatory funnel by using 15 mL of ether. The layers were separated and the organic phase was washed with H_2O (2 × 50 mL) and brine (1 × 50 mL). The organic layer was dried over $MgSO_4$ and then filtered. The solvent was removed under reduced pressure, and the product was purified by flash chromatography on silica gel (230–400 mesh) by using 5:1 hexane/ethyl acetate (R_f = 0.5) to give 50 mg of **19b** (18% yield): ^1H NMR (90 MHz, $CDCl_3$) δ 7.9–7.8 (m, 2 H), 7.5–7.3 (m, 3 H), 5.4–5.3 (br s, 2 H), 4.8–4.6 (m, 2 H), 4.1–3.9 (q, 2 H), 3.2s (m, 1 H), 2.6–1.4 (m, 5 H), 1.2 (t, 3 H).

4-(2-Oxo-2-phenylethyl)-2,6-dimethylenebicyclo[3.1.0]hexane (17b). A solution of 50 mg (0.17 mmol) of **19b**, 50 mg (0.87 mmol) of KOH, 3 mL of H_2O, and 3 mL of THF was stirred at room temperature for 6 h. The solution was acidified with 10% HCl solution to pH ~3 and then allowed to stir 1 h. The solution was saturated with NaCl and transferred to a separatory funnel by using 30 mL of ether. The layers were separated and the organic phase was washed with H_2O (2 × 25 mL) and brine (1 × 20 mL) and then dried over $MgSO_4$. The solution was filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (230–400 mesh) by using 5:1 hexane/ethyl acetate to give 8 mg of **17b** (21% yield): ^1H NMR (90 MHz, $CDCl_3$) δ 8.0–7.9 (m, 2 H), 7.5–7.2 (m, 3 H), 5.4 (br s, 2 H), 5.0–4.7 (m, 2 H), 3.1–2.8 (m, 2 H), 2.6–1.4 (m, 5 H); GC–MS (80, 1, 20, 220) (6.1 min), m/e 224 (M^+, 0.8%), 209 (CH_3, 1.2%), 105 ($C_6H_5CO^+$, 100%); FT-IR ($CDCl_3$) 3063 (m), 2916 (m), 1677 (s), 1594 (m), 1577 (m), 1450 (m).

General Procedure for the Photochemical Reactions of 17a. Quantitative Runs. Freshly GC-purified **17a** (~1–2 mg) was dissolved in 200 μL of dry pentane, CH_3OH, or THF and placed in an oven-dried 5-mm Pyrex tube with a 5-cm quartz tip sealed at one end so that all the solution rested in the quartz tip. An appropriate internal standard was added via syringe. If an olefin trap was used, it (100 times) was charged into the tube. Gaseous traps were condensed into the tube at −78 °C via a needle inlet. The samples were then degassed either by three freeze–pump–thaw cycles and then sealing under vacuum (<0.1 mm) or by bubbling N_2 through the sample for 15 min at 0 or −78 °C and then capping with a rubber septum.

Photolyses were carried out in the Rayonet reactor equipped with 16 300-nm bulbs. For room-temperature photolyses, the sample was suspended in the reactor where the reactor fan provided the only cooling. Photolyses at lower temperatures were done in a large Dewar equipped with a quartz tip. The samples were photolyzed until an appreciable amount of **17a** was consumed as analyzed by GC. These times varied from 1 to 3 h depending on the olefin trap used. After photolyses, the samples were cooled to −78 °C, opened, and then allowed to warm to room temperature under a N_2 atmosphere. The samples were then analyzed on an appropriate GC column, and the chromatograms were digitally integrated with a HP 3390A integrator.

Preparative runs. Freshly distilled or GC-purified **17a** (75–100 mg) was dissolved in 20 mL of dry pentane or CH_3OH and placed in a 20-mm quartz tube sealed at one end. If required, a large excess (100 times) of olefin was added to the tube, and then N_2 was bubbled through the solution at −78 °C for 15 min. The solution was warmed to room temperature and photolyzed by using 300-nm bulbs until the desired amount of the methyl ketone **17a** had been consumed, as analyzed by GC. The solution was then transferred to a 100-mL round-bottomed flask by using 20 mL of pentane, and then the solvent was removed under reduced pressure. The residue was chromatographed on Florisil by using pentane as the eluant to remove impurities and unreacted methyl ketone **17a**. The products were separated and purified by preparative GC by using an appropriate column.

Photolysis of 17a. The samples were prepared as outlined above. In the analytical runs, hexadecane and nonane were used as the internal standards. Analytical GC (column A) showed only one product, which was isolated by preparative GC (column F, 160 °C) and assigned the following structure based on the spectral data and by comparison with independently synthesized material obtained by the procedure of Flammang.[18]

[2.2]Metacyclophane (18): ^1H NMR (90 MHz, $CDCl_3$) δ 7.2–7.0 (m, 2 H), 6.9–6.8 (m, 2 H), 4.1 (t, 1 H, J = 3.5 Hz), 2.9–2.8 (d × t, 4 H, J = 9, 8.3 Hz), 1.9–1.8 (d × t, 4 H, J = 9, 8.3 Hz); GC–MS (100, 1, 20, 200) (4.2 min), m/e 208 (M^+, 88%), 180 (C_2H_2, 100%), 165 (C_3H_7, 70%); FT-IR ($CDCl_3$) 3020 (m), 2905 (m), 1607 (m), 1470 cm^{-1} (m).

Analysis at high methyl ketone **17a** consumption (73%, column B) showed a yield of 6.7% (13.4% theoretical, column B) of cyclophane **18** while the yield of acetone was 15.2% (column E). When the reaction was run at −78 °C, the yield of cyclophane **18** was 1.9% (3.8% theoretical, column B) with 95% consumption of the methyl ketone **17a**. At 77 K, the photolysis proceeded very slowly (>95% **17a** recovered), but analysis by GC–MS and GC (column B) did show the presence of a trace amount of [2.2]metacyclophane. Qualitatively, the rate of the photochemical reaction slowed with decreasing temperature.

EPR studies were performed on samples prepared as previously described with the exception that 2-methyltetrahydrofuran, 2-propanol, ethanol, propylene glycol, and 4:1 ethanol/methanol were used as the solvents. Samples were subjected to three freeze–pump–thaw cycles and then sealed under vacuum. The samples were placed in the cavity of the EPR spectrometer, cooled to 77 K, and then photolyzed with an unfiltered Oriel lamp.

Elimination Reactions of the Methanesulfonate 15. To a dry, 10-mL, round-bottomed flask equipped with magnetic stirring and N_2 inlet were added 2 mg (0.01 mmol) of the above methanesulfonate and 1 mL of dry Me_2SO. The solution was stirred at room temperature, and 30 mg (0.267 mmol) KOtBu was added by spatula. After 30 min, the solution was transferred to a separatory funnel by using 15 mL of ether. The layers were separated and the organic phase was washed with 5% NH_4Cl (1 × 10 mL), H_2O (1 × 10 mL), and brine (1 × 10 mL) and then dried over $MgSO_4$. The organic layer was filtered, and the solvent was removed under reduced pressure. The only product observed by analytical GC (column B or C), GC–MS, and ^1H NMR was [2.2]metacyclophane (**18**). If THF was used as the solvent instead of Me_2SO, **18** again was the only product formed when the reaction was run at 0 °C. If the elimination reaction was run in THF at −78 °C, no **18** was formed as only the mesylate **15** was recovered. This failure of **15** to undergo the elimination reaction at −78 °C might only reflect solubility problems. When the reaction was run in Me_2SO with excess *cis,cis*-2,4-hexadiene, 1:1 adducts as well as [2.2]metacyclophane were formed, as analyzed by GC and GC–MS.

4-(Benzoyloxy)-2,6-dimethylenebicyclo[3.1.0]hexane (16). In a dry, 50-mL, round-bottomed flask equipped with magnetic stirring and N_2 inlet were placed 5 mg (0.04 mmol) of **14**, 6 mg (0.04 mmol) of benzoic acid, 10 mg (0.048 mmol) of dicyclohexyldicarbodiimide, and ~1 mg (0.01 mmol) of 4-(dimethylamino)pyridine in 5 mL of CH_2Cl_2. The solution was stirred overnight at room temperature. The solution was filtered to remove the urea, 10 mL of hexane and 10 mL of CH_3CO_2H were added, and the solution was stirred for 2 h at 0 °C. The solution was transferred to a separatory funnel, and the layers were separated. The organic layer was washed with water (1 × 10 mL) and brine (1 × 10 mL) and then dried over $MgSO_4$. The organic phase was filtered and concentrated in vacuo. The material was purified by flash chromatography by using 20:1 hexane/ethyl acetate: ^1H NMR (90 MHz, $CDCl_3$) (two isomers) δ 8.0–7.9 (m, 2 H), 7.4–7.2 (m, 3 H), 5.6–5.3 (m, 3 H), 5.1–4.8 (m, 2 H), 2.7–2.2 (m, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) (two isomers) δ 166.1, 149.7, 135.3, 135.1, 133.4, 130.1, 129.7, 128.8, 106.2, 105.9, 77.3, 76.5, 36.7, 34.4, 30.1, 29.9, 29.1, 26.8; GC–MS (50, 1, 20, 200) (7.6 min), m/e 226 (M^+, 0%), 105 ($C_6H_5CO^+$, 100%).

Photolysis of 17b at Low Temperature. Purified phenyl ketone (~2 mg) **17b** was dissolved in 500 μL of acetone-d_6 or $CDCl_3$ and transferred to a Pyrex NMR tube. The solution was degassed with N_2 for 15 min at 0 °C and then capped. The solution was photolyzed for 90 min in the Rayonet reactor at −78 °C by using 350-nm bulbs. The tube was then immediately placed in the Jeol FX 90Q spectrometer, and a spectrum

was taken before warming. In addition to proton resonances for unreacted phenyl ketone **17b** and some new aromatic material, the spectrum exhibited two new doublet proton resonances at δ 4.64 and 4.36 (J = 1.5 Hz). A second spectrum was taken after the sample equilibrated at room temperature for several hours, and it showed that the new resonances had disappeared and were replaced by a new singlet resonance at δ 2.6. The same spectral changes were observed if the sample was placed in a precooled (−78 °C) Bruker HX-270 probe immediately after photolysis and then allowed to equilibrate at room temperature. Analysis of the reaction mixture by GC–MS showed two products, identified as acetophenone and [2.2]metacyclophane by comparison of their GC retention times (columns B and C) and their GC–MS fragmentation patterns with those of authentic materials.

The ^{1}H NMR spectrum obtained after photolysis of the methyl ketone **17a** (300-nm bulbs) at −78 °C, under similar conditions to those employed for the phenyl ketone **17b**, did not show proton resonances for propen-2-ol at −78 °C or upon warming to room temperature.

Reaction of 17b and Butadiene. The samples were prepared as outlined above. Hexadecane was used as the internal standard for analytical runs. Analysis of GC–MS showed four M_r 158 adducts. They were isolated by preparative GC (column G, 170 °C) and assigned the following structures based on the spectral data provided. The GC yields (columns B or C) varied from 40% to 60% with (**21** + **22**)/(**23** + **26**) about 1.2:1. Compounds **21** and **22** were not separated by GC. ^{13}C NMR and ^{1}H NMR showed the ratio of **21**/**22** to be about 13:1.

1-Ethenyl-7-methylindan (21) (Retention Time, 18.0 min): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15–7.11 (m, 2 H), 7.02–7.0 (m, 1 H), 6.0–5.9 (d × d × d, 1 H, J = 17.6, 10.1, 7.8 Hz), 5.0–4.9 (m, 2 H), 3.90–3.85 (d × d, 1 H, J = 8.1 Hz), 3.08–3.00 (m, 1 H), 2.90–2.84 (m, 1 H), 2.38–2.30 (m, 1 H), 2.31 (s, 3 H), 2.32–1.97 (m, 1 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 143.9, 143.5, 140.1, 134.8, 127.6, 126.9, 121.9, 113.3, 48.3, 32.5, 31.2, 18.8; FT-IR (neat) 3074 (w), 2940 (m), 2848 (m), 1634 (m), 1473 (m), 1458 (m), 991 (m), 909 (s), 765 cm^{-1} (s); GC–MS (80, 1, 20, 200) (5.4 min), m/e 158 (M^+, 59%), 143 (CH_3, 100%), 128 (C_2H_6, 59%); exact mass calcd for $C_{12}H_{14}$ 158.1096, found 158.1103.

1-Ethenyl-5-methylindan (22) (Retention Time, 18.0 min): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.1–5.0 (m), 2.95–2.92 (m), 2.8–2.78 (m), 2.38 (s), 1.90–1.80 (m); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 49.5, 31.6. The other resonances were obscured by peaks of the major component or too small to observe.

(4*Z*)-Bicyclo[6.3.1]dodeca-1(12),4,8,10-tetraene (**27**, retention time, 35 min) and 5,6,9,10-tetrahydrobenzocyclooctene (**26**, retention time 43 min) are described in the next paper[5b] in this issue. Similar cycloadditions were observed with 2,3-dimethylbutadiene, although in higher yields (50–60%). These results were described in the next paper[5b] in this issue.

Reaction of 17a and *trans*,*trans*-2,4-Hexadiene (See Table II). The samples were prepared as outlined above. The four M_r 186 adducts were isolated by GC (column G, 175 °C) and assigned the following structures based on the spectral data provided and by comparison of the data with those of the products formed from both the reaction of **17a** and butadiene as well as the reaction of **12** and *trans*,*trans*-2,4-hexadiene.[6] Hexadecane was used as the internal standard for analytical runs, and the total yield (column C or B) of cycloadducts varied from 25% to 45%. Compounds *cis*,*trans-o*-**37** and *trans*,*trans-p*-**37** were not separated by preparative GC.

***trans*-2,7-Dimethyl-1-(*trans*-1-propenyl)indan (*trans*,*trans-o*-37) (Retention Time, 21 min)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09–7.02 (m, 2 H), 6.95 (d, 1 H, J = 7.0 Hz), 5.46–5.43 (m, 2 H), 3.3–3.28 (d × d, 1 H, J = 5.5 Hz), 3.17–3.12 (d × d, 1 H, J = 7.6, 17.6 Hz), 2.48–2.44 (d × d, 1 H J = 5.2, 15.6 Hz), 2.24–2.10 (m, 1 H), 2.25 (s, 3 H), 1.69–1.68 (d, 3 H, J = 4.8 Hz), 1.08–1.07 (d, 3 H, J = 6.9 Hz); GC–MS (100, 1, 5, 200) (2.4 min), m/e 186 (M^+, 93%), 171 (CH_3, 63%), 157 (C_2H_5, 60%), 143 (C_3H_7, 100%), 128 (C_4H_{10}, 60%); exact mass calcd for $C_{14}H_{18}$ 186.1409, found 186.1410.

***cis*-2,7-Dimethyl-1-(*trans*-1-propenyl)indan (*cis*,*trans-o*-37) (Retention Time, 25 min)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08–7.03 (m, 2 H), 6.95–6.94 (d, 1 H J = 6.8 Hz), 5.45–5.28 (m, 2 H), 3.61–3.57 (d × d, 1 H, J = 7.7 Hz), 2.89–2.85 (d × d, 1 H, J = 6.7, 14.5 Hz), 2.65–2.54 (m, 2 H), 2.22 (s, 3 H), 1.67–1.66 (d, 3 H, J = 5.6 Hz), 1.10–1.09 (d, 3 H, J = 6.7 Hz); GC–MS (100, 1, 5, 200) (3.1 min), m/e 186 (M^+, 90%) 171 (CH_3, 62%), 157 (C_2H_5, 62%), 143 (C_3H_7, 100%), 128 (C_4H_{10}, 62%). This material contains ~14% of another isomer which by ^{1}H NMR was assigned to *trans*-2,5-dimethyl-1-(*trans*-1-propenyl)indan (*trans*,*trans-p*-**37**).

(3*R,4*Z*,6*S**)-3,6-Dimethylbicyclo[6.3.1]dodeca-1(12),4,8,10-tetraene (*trans*-38) (Retention Time, 33 min)**: ^{1}H NMR (500 MHz,^{1}$CDCl_3$) (two conformational isomers in a 2:1 ratio) δ major, 7.6 (s, 1 H), 6.97–6.94 (t, 1 H, J = 7.3 Hz), 6.63–6.61 (d, 2 H, J = 7.3 Hz), 4.44, 4.39 (m, 2 H), 3.42–3.38 (d × d, 2 H, J = 7.0, 14.0 Hz), 3.05–2.99 (m, 2 H), 2.01–1.96 (d × d, 2 H, J = 13.9, 10.8 Hz), 1.02–1.00 (d, 6 H, J = 6.4 Hz), minor, incomplete 7.86 (s, 1 H), 7.19–7.17 (t, 1 H, J = 7.3 Hz), 6.84–6.83 (d, 2 H, J = 7.3 Hz), 5.20–5.18 (d, 2 H, J = 4.3 Hz), 2.61–2.57 (m, 2 H), 2.41–2.39 (d, 2 H, J = 12 Hz), 1.01–1.00 (d, 6 H, J = 5.2 Hz); GC–MS (100, 1, 10, 200) (2.8 min), m/e 186 (M^+, 14%), 144 (C_3H_6, 100%), 129 (C_4H_9, 92%), 104 (C_6H_{10}, 90%).

(3*R,4*Z*,6*R**)-3,6-Dimethylbicyclo[6.3.1]dodeca-1(12),4,8,10-tetraene (*cis*-38) (Retention Time, 40 min)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1 H), 7.12–7.09 (d × d, 1 H, J = 7.8 Hz), 6.93–6.91 (d, 1 H, J = 7.2 Hz), 6.88–6.86 (d, 1 H, J = 7.3 Hz), 5.74–5.69 (d × d, 1 H, J = 7.4, 13.0 Hz), 5.25, 5.20 (d × d, 1 H, J = 10.0, 13.0 Hz), 2.95–2.91 (d, 1 H, J = 12.6 Hz), 2.74–2.70 (m, 1 H), 2.60–2.56 (d × d, 1 H, J = 11.4 Hz), 2.47–2.44 (d, 1 H, J = 12.1 Hz), 2.40–2.37 (d × d, 1 H, J = 4.5, 12.6 Hz), 1.29–1.24 (m, 1 H), 1.02–1.01 (d, 3 H, J = 6.6 Hz), 0.18–0.10 (d, 3 H, J = 7.2 Hz); GC–MS (100, 1, 10, 200) (3.1 min), m/e 186 (M^+, 9%), 144 (C_3H_6, 95%), 129 (C_4H_9, 81%), 104 (C_6H_{10}, 100%). Analytical GC (column E, room temperature) showed the initial hexadiene composition to be 95.9% trans,trans, 4.5% cis,trans, and 1.6% cis,cis. After 300-min photolysis, the ratio was 83.8% trans,trans, 14.6% cis,trans, and 1.6% cis,cis. Analytical GC (column C, 175 °C) was used to examine the product ratios after 300 min: *trans*,*trans-o*-**37**, 1.2; *cis*,*trans-o*-**37** and *trans*,*trans-p*-**37**, 0.25; *trans*-**38**, 0.18; *cis*-**38**, 1.0.

Reaction of 17a and *cis*,*cis*-2,4-Hexadiene. The samples were prepared as outlined above. Five M_r 186 adducts were isolated by preparative GC (column G, 175 °C). Two of the products, *trans*-**38** and *cis*-**38**, were identical (NMR, GC–MS, GC retention times) with those observed from **17a** and *trans*,*trans*-2,4-hexadiene. Compound *trans*-38 contained ~15% of another isomer which was separated by preparative GC (column H, 145 °C, retention time, 30 min). The following structures were assigned to the adducts based on the spectral data provided and by comparison of that data with those of the products formed from the reaction of **17a** and butadiene and the reaction of **17a** and *trans*,*trans*-2,4-hexadiene as well as the reaction of **12** with *cis*,*cis*-2,4-hexadiene.[6] Hexadecane was used as the internal standard for the analytical runs and the yield of adducts (column C or B) varied from 28% to 40%.

***trans*-2,7-Dimethyl-1-(*cis*-1-propenyl)indan (*trans*,*cis-o*-37) (Retention Time, 27 min)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08–7.01 (m, 2 H), 6.95–6.94 (d, 1 H, J = 6.8 Hz), 5.59–5.52 (m, 1 H), 5.39–5.34 (pseudo t, 1 H, J = 10 Hz), 3.71–3.68 (d × d, 1 H, J = 10.2, 6.0 Hz), 3.17–3.12 (d × d, 1 H, J = 15.6, 7.8 Hz), 2.53–2.49 (d × d, 1 H, J = 15.6, 6.9 Hz), 2.22–2.20 (m, 1 H), 2.23 (s, 3 H), 1.8–1.77 (d × d, 3 H, J = 1.7, 6.8 Hz), 1.14–1.12 (d, 3 H, J = 6.8 Hz); GC–MS (100, 1, 20, 200) (2.8 min), m/e 186 (M^+, 94%), 171 (CH_3, 68%), 157 (C_2H_5, 74%), 143 (C_3H_7, 100%), 128 (C_4H_{10}, 56%); exact mass calcd for $C_{14}H_{18}$ 186.1409, found 186.1406.

***trans*-2,5-Dimethyl-1-(*cis*-1-propenyl)indan (*trans*,*cis-p*-37) (Retention Time, 30 min)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.0 (s, 1 H), 6.97–6.96 (d, 1 H, J = 7.5 Hz), 6.93–6.91 (d, 1 H, J = 7.5 Hz), 5.76–5.70 (m, 1 H), 5.38–5.33 (m, 1 H), 3.62–3.58 (d × d, 1 H, J = 9.5 Hz), 3.00–2.96 (d × d, 1 H, J = 7.58, 15.3 Hz), 2.58–2.52 (d × d, 1 H, J = 10.5, 15.2 Hz), 2.32 (s, 3 H), 2.22–2.14 (m, 1 H), 1.78–1.76 (d × d, 3 H, J = 1.73, 6.82 Hz), 1.19–1.18 (d, 3 H, J = 6.7 Hz); GC–MS (100, 1, 10, 200) (3.3 min), m/e 186 (M^+, 86%), 171 (CH_3, 100%), 157 (C_2H_5, 47%), 143 (C_3H_7, 96%), 128 (C_4H_{10}, 54%).

***cis*-2,7-Dimethyl-1-(*cis*-1-propenyl)indan (*cis*,*cis-o*-37) (Column G, 175 °C, 34 min; Column H, 145 °C, 37 min)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01–6.96 (m, 3 H), 5.57–5.52 (m, 1 H), 5.19–5.13 (ps tr, 1 H, J = 10.8 Hz), 4.02–3.98 (d × d, 1 H, J = 7.5, 10.2 Hz), 2.94–2.90 (d × d, 1 H, J = 8.0, 12.2 Hz), 2.67–2.55 (m, 2 H), 2.19 (s, 3 H), 1.79–1.77 (d, 3 H, J = 6.8 Hz), 1.08–1.06 (d, 3 H, J = 6.3 Hz); GC–MS (100, 1, 10, 200) (3.1 min), m/e 186 (M^+, 85%), 171 (CH_3, 66%), 157 (C_2H_5, 72%), 143 (C_3H_7, 100%), 129 (C_4H_9, 67%). Analytical GC (column E, room temperature) showed the initial hexadiene composition to be 97.8% cis,cis, 2.2% cis,trans, and 0.0% trans,trans. After 300-min photolysis, the ratio was 84.9% cis,cis, 11.4% cis,trans, and 3.7% trans,trans. Analytical GC (column C, 175 °C) was used to examine the product ratios after 300-min photolysis: *trans*,*cis-o*-**37**, 1.0; *trans*,*cis-p*-**37**, 0.45; *cis*,*cis-o*-**37** + *trans*-**38**, 2.02; *cis*-**38**, 0.59. Analytical GC (column B, 145 °C or column D, 175 °C) showed the *cis*,*cis-o*-**37**/*cis*,*trans*-**38** ratio to be 1:5.

Comparison Reaction of 17a with *cis*,*cis*- and *trans*,*trans*-2,4-Hexadiene. In a dry, 5-mL, round-bottomed flask were placed ~2 mg (0.012 mmol) of **17a**, 1 mg of hexadecane, and 200 μL of pentane. Equal amounts of the solution were transferred to two quartz tubes by syringe. To one tube, 30 μL of *cis*,*cis*-2,4-hexadiene (0.263 mmol, 2.03 M) was added, and to the other, 30 μL of *trans*,*trans*-2,4-hexadiene (0.263 mmol, 2.03 M) was added. Both tubes were purged with N_2 at −78 °C for 15 min and then warmed to room temperature. Both tubes were photolyzed for 60 min by using 300-nm bulbs in the Rayonet equipped with a merry-go-round apparatus. After photolysis, each solution was purified

Table VIII. Effect of O_2 on the Yield of Products in the Photolysis of **17a** and of *cis,cis*-2,4-Hexadiene[a,b]

	8.8 M[c] (N_2)	0.88 M (N_2)	0.88 M (O_2)
trans,cis-o-**37**	23.6[d]	22.8	23.6
trans,cis-p-**37**	18.8	13.5	16.4
cis,cis-o-**37**	12.5	7.7	9.1
trans-**38** + *cis*-**38**	45.1	56.0	50.9
17a consumed	32.0	42.7	48.0
tot prod	5.3[e] (16.5)[f]	10.6 (24.8)	3.7 (7.7)
hexadiene (final)[g]	1.0:9.0:90.0	1.4:6.1:92.5	8.5:15.9:75.6

[a] Room temperature, merry-go-round, 75-min photolysis. [b] 138:1 ratio of hexadiene **17a**. [c] [*cis,cis*-2,4-Hexadiene]. [d] Relative yields. [e] Absolute yields. [f] Absolute yields based on recovered **17a**. [g] Ratio of *trans,trans*/*cis,trans*/*cis,cis*-2,4-hexadiene (initial) 0.0:2.4:97.6.

by column chromatography on Florisil by using pentane as the eluant. The solvent was removed under reduced pressure, and the residue was then analyzed by analytical GC. The isomerization of the hexadiene was monitored by using Column E at room temperature. The consumption of **17a** was analyzed by using column B. The yield and ratio of products formed were determined by using column C at 170 °C and column D at 160 °C. The results are given in Table II.

Hydrogenation of *trans,trans-o*-37. Diimide reduction of ~1 mg of *trans,trans-o*-**37** was performed exactly as previously described in the preparation of bicyclo[6.3.1]dodeca-1(12),8,10-triene. Only one product was observed by analytical GC (column B or C) and GC–MS. The crude reaction mixture was purified by preparative GC (column G, 175 °C) to yield **41** which was assigned the following structure based on the spectral data.

***trans*-2,7-Dimethyl-1-propylindan (41) (Retention Time, 15 min):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05–7.03 (m, 2 H), 6.96–6.94 (d, 1 H, J = 7.1 Hz), 3.5–3.49 (d, 1 H, J = 5.4 Hz), 3.24–3.19 (d × d, 1 H, J = 7.5, 15.8 Hz), 2.76–2.74 (m, 1 H), 2.42–2.39 (d, 1 H, J = 15.8 Hz), 2.33–2.28 (m, 1 H), 2.23 (s, 3 H), 1.50–1.20 (m, 4 H), 0.99–0.98 (d, 3 H, J = 7.1 Hz), 0.96–0.93 (t, 3 H, J = 7.0 Hz); GC–MS (80, 1, 20, 200) (3.3 min), m/e 188 (M^+, 10%), 145 (CH_3, 100%).

Hydrogenation of *trans,cis-o*-37. Diimide reduction of ~1 mg of *trans,cis-o*-**37** was preformed exactly as described above for *trans,trans-o*-**37**. Only one product, other than starting material, was observed by analytical GC (column B or C) and GC–MS. Purification by preparative GC (column G, 175 °C) yielded **41**. ^{1}H NMR, GC–MS, and GC retention times (columns B and C) showed the product to be identical with that obtained from the reduction of *trans,trans-o*-**37**.

Reaction of 17a and *cis,trans*-2,4-Hexadiene. In a dry, 5-mL flask were placed ~1 mg (0.006 mmol) of **17a**, 1 μL of hexadecane, 30 μL (0.263 mmol, 2.03 M) of *cis,trans*-2,4-hexadiene, and 100 μL of pentane. The solution was transferred by syringe to a quartz tube and then purged with N_2 at −78 °C for 15 min. After warming to room temperature, the solution was photolyzed for 90 min at room temperature by using 300-nm bulbs in the Rayonet reactor. The reaction was analyzed by analytical GC by using the column conditions previously described for this system. The yields and ratios of products are shown in Table II.

Dilution Studies of 17a and *cis,cis*-2,4-Hexadiene. In a dry, 2-mL, round-bottomed flask were placed 3.1 mg (0.019 mmol) of **17a**, 2 mg of hexadecane, and 300 μL (2.63 mmol) of *cis,cis*-2,4-hexadiene. Equal amounts of the solution were transferred to three quartz tubes and diluted with an appropriate amount of pentane. Each tube was then purged at −78 °C with N_2 for 15 min and then warmed to room temperature. The tubes were photolyzed for 105 min at room temperature by using 300-nm bulbs, in the Rayonet reactor equipped with a merry-go-round apparatus. After photolysis, each tube was opened, concentrated if necessary, and then analyzed by analytical GC by using the column conditions previously described for this system. The yields and ratios of products with varying dilution are given in Table IV.

Effect of O_2 on the Reaction of 17a and *cis,cis*-2,4-Hexadiene. In a dry, 5-mL, round-bottomed flask were placed 3.0 mg (0.019 mmol) of **17a**, 2 μL of hexadecane, and 300 μL (2.63 mmol) of *cis,cis*-2,4-hexadiene. Equal amounts of the solution were transferred to three quartz tubes and diluted with an appropriate amount of pentane. Two tubes were purged at −78 °C with N_2 for 15 min and then warmed to room temperature. The third tube had O_2 bubbled through the solution at −78 °C for 15 min and then was warmed to room temperature. The tubes were photolyzed for 75 min under the usual conditions and then were analyzed by analytical GC. The results are given in Table VIII.

Symmetry of the Intermediate. Synthesis of 4-(2-Oxopropyl)-2-(dideuteriomethylene)-6-methylenebicyclo[3.1.0]hexane (17d). This preparation was identical with that of **17a** with the only exception being that (methyl-d_3)triphenylphosphonium bromide was used for the Wittig reaction. The deuterated ketone was purified by preparative GC (column F, 70 °C). The ^{1}H NMR of **17d** was identical with that of **17a** except for reduced intensities of the resonances at δ 4.95, 4.86, 4.74, 4.69. Careful ^{1}H NMR integration showed the deuterium incorporation to be ≥92%.

Table IX. Trapping Reagents Used in the Photochemical Reactions of **17a**[a]

1:1 adducts formed with	no. 1:1 adducts formed with
diethyl fumarate (660)	MeOH
methyl acrylate (260)	butyl vinyl ether (2)
methyl methacrylate (280)	isobutylene
maleonitrile (acrylonitrile 480)	2,3-dimethyl-2-butene
fumaronitrile	cyclohexene
2,2-dimethyl-1-vinylcyclopropane	*cis*-1,2-dichloroethylene (1)
butadiene (260)	
2,3-dimethylbutadiene	
2,4-hexadienes	
isoprene	

[a] Relative reactivities toward growing polystyrene radical are shown in parentheses (ref 45).

Table X. Rate Constants ($10^7 k_q$ M s) for Quenching the n → π* Excited States of Acetone[51]

quencher	k_q for S_1	k_q for T_1
1,3-butadiene	6.5	500
1,3-pentadiene	10	400
trans-1,2-dicyanoethene	300	600
cis-1,2-dichloroethene		20

Reaction of 17d and Butadiene. The reaction was performed as previously described for the reaction of **17a** and butadiene. The photolysis products were isolated by preparative GC (column G, 170 °C), and they were assigned structures in accordance with those previously described. The indan product **21** was examined for deuterium incorporation.

1-Ethenyl-7-methylindan-d_2 (21-d_2): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15–7.11 (m, 2 H), 7.02–7.00 (m, 1 H), 6.0–5.9 (d × d × d, 1 H, J = 17.6, 10.1, 7.8 Hz), 5.0–4.9 (m, 2 H), 3.90–3.85 (t × d, 1 H, J = 8.1, 2.5 Hz), 3.08–3.00 (m, 0.5 H), 2.90–2.84 (m, 0.5 H), 2.32–1.97 (m, 4 H); ^{2}H NMR (41.4 MHz, CCl_4) δ 3.04 (m), 2.86 (m), 2.30 (d, J = 2.1 Hz), (the integration of benzylic CH_2 vs. aromatic CH_3 resonances δ (3.04 + 2.86)/δ (2.30) was 1.04:1); GC–MS (80, 1, 20, 200) (2.8 min), m/e 160 (M^+, 84%), 145 (CH_3, 100%), 144 (60%), 129 (48%).

From GC–MS analysis, the d_2 incorporation in the product was ≥85%.

Absolute Quantum Yields and Deuterium Isotope Effect on the Quantum Yield. See supplementary material.

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Appendix

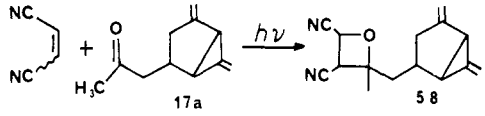
A. Scope and Limitations of the Cycloaddition Reactions of *m*-Quinodimethane Biradical 3. In attempts to extend the cycloaddition observed with dienes to other unsaturated systems, we have surveyed the photolysis of methyl ketone **17a** under the previously described conditions in the presence of a group of potential trapping agents. The reaction mixtures were analyzed by GC–MS for molecular ions corresponding to 1:1 adducts of the reagent and biradical **3**. In the cases where adducts were not observed, [2.2]metacyclophane and insoluble higher molecular weight material were obtained as products. The results are collected in Table IX.

Generation of biradical **3** in the presence of electron-deficient olefins gave cycloadducts in low yields but no [2.2]metacyclophane. With reference to the stepwise cycloaddition mechanism of Scheme VI, a reasonable model for the first step would be the addition of a benzylic radical to the olefin. Table IX shows in parentheses the relative reactivities[49] of the growing polystyrene radical with a number of monomers. Apparently, a strong reactivity correlation exists between our photochemical reaction and styrene–olefin copolymerization, since the trapping agents from which adducts with biradical **3** were obtained also are the most reactive ones

toward a benzylic monoradical.

One might have hoped therefore to observe useful yields of adducts of **3** with the reactive electron-deficient olefins. Unfortunately, this was not the case, as has been noted. With methyl methacrylate, for example, the cycloadduct yield was in the range 1–5%, even though that olefin is about as reactive toward the polystyrene radical as is butadiene, from which yields of adducts of **3** in the 40–60% range were observed.

We believe that the low yields are caused, at least in part, by a competing photochemical reaction of the starting methyl ketone **17a** with the olefin. In one case, GC–MS analysis of the reaction mixture from photolysis of **17a** with 1,2-dicyanoethene revealed not only a **3** + olefin adduct but also a **17a** + olefin adduct. Although this substance was not fully characterized, its MS fragmentation pattern was more compatible with the Paterno–Büchi-type structure **58** than with any olefin–olefin [2 + 2]-photocycloadduct structure.



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Prior studies[50] of photochemical oxetane formation from ketones and electron-deficient olefins show that these products result from quenching of the $S_1(n \rightarrow \pi^*)$ state of the ketone. Such olefins also quench the ketone's excited triplet state, causing isomerization or dimerization of the olefin.[50] Some constants[51] for quenching of the excited states of a model ketone, acetone, are presented in Table X.

If the rates of Norrish type II photoelimination of methyl ketone **17a** find good models in those of 2-hexanone,[52] $k_{II}(S_1) \sim 10^9$ and $k_{II}(T_1) \sim 10^8$ s^{-1}, Table X shows that photoelimination from T_1 of **17a** cannot compete effectively with bimolecular quenching at concentrations >1 M for typical olefins, so that T_1 of **17a** is not a useful source of bicyclic hydrocarbon **11** or the derived biradical **3**. On the other hand, the efficiency of generation of **11** and thence **3** from the S_1 state of ketone **17a** depends greatly on the trapping agent used. With 1 M dicyanoethene, the rates of quenching and photoelimination should be competitive, and the ratio of oxetane to cycloadduct should decrease as the concentration of trapping agent decreases. This predicted behavior is confirmed by experiment.[15] From the practical point of view, however, the increased proportion of cycloadduct is not very helpful, because its absolute yield decreases. Thus, with dicyanoethene, the efficient trapping of the S_1 state of the ketone is inimical to the formation of biradical **3** and its derived adducts.

The reasons for the special efficiency of conjugated dienes as trapping agents in the present context now become clear. As Table X shows, dienes quench the S_1 state of the ketone with appreciably lower efficiency than does dicyanoethene. As might therefore be expected, oxetanes are not usually observed in the photolysis of ketone–diene mixtures,[53] and no alternative bimolecular pathway competes significantly with the Norrish type II photoelimination. Moreover, while ketone T_1 is efficiently quenched by dienes, S_1 is not. The photoelimination rate from S_1 exceeds that of quenching by more than an order of magnitude at 1 M diene concentration. Thus, biradical **3** can be formed by the elimination route via its bicyclic valency tautomer **11** and, at the moment of birth, finds itself in a high concentration of trapping agent.

The phenyl ketone **17b**, however, is not a suitable precursor of **3** under these conditions. Because of the extremely efficient intersystem crossing in phenyl ketones ($\phi_{isc} \sim 1$), reactivity in these systems is effectively confined to the triplet manifold, and the rate of bimolecular quenching of T_1 at 1 M butadiene far exceeds that of the Norrish type II elimination.

To summarize this portion of the argument, we point out that the low yield of cycloadducts of biradical **3** with electron-deficient olefins does not necessarily signify an inherently low reactivity of such trapping agents, since the inclusion of these substances in the photolyses unavoidably works against the generation of **3** itself. In retrospect, we see that very few olefins could have been used to give high yields of cycloadducts. For the present at least, the methyl ketone–diene combination appears to be the only practical one.

B. Structures and Configurations of the Indan Cycloadducts. Butadiene Series 21 and 22. Hydrogenation of **21** and **22** gave, respectively, 7- and 5-methyl-1-ethylindan, which were independently prepared from the known[54] 7- and 5-methyl-1-indanones by conversion to the corresponding tertiary alcohols with EtMgBr, dehydration, and hydrogenation. The assignments were also supported by the proton NMR spectroscopic pattern in the aroomatic region. The hydrogenated para adduct showed a typical 1,2,4-trisubstituted benzene ring pattern, with two of the protons being strongly coupled to each other (J = 7.6 Hz) but not to the third ($J \sim 0$ Hz). The aromatic region of the hydrogenated ortho adduct showed a two-proton multiplet downfield (δ 7.07–7.03) and a one-proton pseudotriplet upfield (δ 6.95).

2,4-Hexadiene Series 37. The regiochemistry (ortho vs. para) of the indan adducts was assigned by inspection of the aromatic region in the proton NMR spectrum, using the hydrogenated butadiene adducts above as models. The stereochemistry of the propenyl side chain was apparent in the *cis*-propenyl isomers, derived from *cis,cis*-2,4-hexadiene, from the vinyl–vinyl proton coupling constants of ~10 Hz.

The relative stereochemistry of the propenyl and methyl groups at C_1 and C_2 of the indan was assigned by correlations of observed vicinal coupling constants with dihedral angles suggested by molecular models and by analogy to disubstituted indans of independently established configuration.[6,55] Moreover, the observation that the C_2 proton of one of the isomers resonated at a much higher field (δ 2.24–2.10) than the other (δ 2.65–2.54) suggested a cis relationship of H_2 and the propenyl group in the former and a trans in the latter.

Note Added in Proof. Very recently, the tetramethyl derivative **7** of biradical **3** has been generated by a ring-contraction in the decomposition of a salt of 2-isopropylidene-6,6-dimethylbicyclo[3.2.0]hept-3-en-7-one *p*-toluenesulfonylhydrazone.[57]

Registry No. **1**, 26298-19-1; **3**, 32714-83-3; **11**, 97521-44-3; **12**, 71946-85-5; **13**, 71946-86-6; **14** (isomer 1), 97521-47-6; **14** (isomer 2), 97521-48-7; **15** (isomer 1), 97521-49-8; **15** (isomer 2), 97521-50-1; **16** (isomer 1), 97521-57-8; **16** (isomer 2), 97521-58-9; **17a** (isomer 1), 97521-55-6; **17a** (isomer 2), 97521-56-7; **17b**, 89032-34-8; **17c**-*3,3-d*$_2$, 97521-69-2; **17c**-*3-d*, 97521-70-5; **17d**, 97521-62-5; **18**, 2319-97-3; **19a** (isomer 1), 97521-51-2; **19a** (isomer 2), 97521-52-3; **19b**, 97521-45-4; **20**, 97521-71-6; **21**, 89032-36-0; **21**-*3,3-d*$_2$, 97521-63-6; **21**-*methyl-d*$_2$, 97521-74-9; **22**, 89032-38-2; **23**, 89032-35-9; **26**, 97521-59-0; **27**, 97521-73-8; *cis*-**38**, 97521-60-3; *trans*-**38**, 97589-50-9; **46**, 89032-37-1; **47**, 89032-40-6; **48**, 89032-44-0; **49**, 89032-42-8; **54**, 97521-72-7; **54b**, 32553-01-8; O_2, 7782-44-7; $CD_3Me_3P^+Br^-$, 97521-61-4; *m*-$MeC_6H_4(CH_2)_2CO_2H$, 3751-48-2; NCCH=CHCN, 17656-09-6; $PhCO_2H$, 65-85-0; D_2, 7782-39-0; *cis,cis*-$CH_3CH{=}CHCH{=}CHCH_3$, 6108-61-8; *cis,trans*-$CH_3CH{=}CHCH{=}CHCH_3$, 5194-50-3; $MePh_3P^+Br^-$, 1779-49-3; $CH_3C(O)CH_2C(O)OMe$, 105-45-3; $CH_2{=}CH_2$, 74-85-1; *cis*-ClCH=CHCl, 156-59-2; BuOCH=CH_2, 111-34-2; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; ethyl benzoylacetate, 94-02-0; 1,3-butadiene, 106-99-0; 2,3-dimethyl-1,3-butadiene, 513-81-5; isoprene, 78-79-5; *trans,trans*-2,4-hexadiene, 5194-51-4; 4-hydroxy-6-methylenebicyclo[3.1.0]hexan-2-one, 97521-46-5; 4-(2-oxo-1-carbomethoxy-1-propyl)-2,6-dimethylenebicyclo[3.1.0]hexane (isomer 1), 97521-53-4; 4-(2-oxo-1-carbomethoxy-

(50) (a) Reference 27, p 432 and references cited therein. (b) Dalton, J.; Wriede, P.; Turro, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 1318. (c) Gale, D. *J. Org. Chem.* **1970**, *35*, 970.

(51) Reference 27, p 437 and references cited therein.

(52) Reference 27, p 388.

(53) Cf., inter alia: (a) Hautala, R.; Dawes, K.; Turro, N. *Tetrahedron Lett.* **1972**, 1129. (b) Shima, K.; Sakai, Y.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 215.

(54) (a) Elvidge, J. A.; Foster, R. G. *J. Chem. Soc.* **1963**, 590. (b) These ketones were prepared by poly(phosphoric acid) cyclization of 3-(3-methylphenyl)propionic acid.

(55) Austin, R. A.; Lillya, C. P. *J. Org. Chem.* **1969**, *34*, 1327.

(56) Perrin, D. D.; Armarego, W.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1966.

(57) Stadler, H.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1984**, *67*, 1379.

1-propyl-2,6-dimethylenebicyclo[3.1.0]hexane (isomer 2), 97521-54-5; *cis*-2,5-dimethyl-1-(*cis*-1-propenyl)indan, 89032-43-9; *trans*-2,5-dimethyl-1-(*cis*-1-propenyl)indan, 89032-45-1; *cis*-2,5-dimethyl-1-(*trans*-1-propenyl)indan, 89032-41-7; *trans*-2,5-dimethyl-1-(*trans*-1-propenyl)-indan, 89032-39-3; 5-methylindan-1-one, 4593-38-8; 7-methylindan-1-one, 39627-61-7; 1-ethyl-7-methylindan, 97521-64-7; 1-ethyl-7-methylindan-1-ol, 97521-65-8; 7-methyl-1*H*-indene, 7372-92-1; 1-ethylidene-7-methylindan, 97521-66-9; 1-ethyl-5-methyl-1*H*-indene, 97521-67-0; 1-ethyl-5-methylindan, 97521-68-1; isobutylene, 115-11-7; cyclohexene, 110-83-8; diethyl fumarate, 623-91-6; methyl acrylate, 96-33-3; methyl methacrylate, 80-62-6; maleonitrile, 928-53-0; fumaronitrile, 764-42-1; 2,2-dimethyl-1-vinylcyclopropane, 7736-30-3.

Supplementary Material Available: Experimental data for listed compounds (14 pages). Ordering information given on any current masthead page.

Stereochemistry and Mechanism of *m*-Cyclophane Formation in the 1,4-Additions of Dienes to the *m*-Quinodimethane Biradical. On the Question of Formal 1,2-Addition via Sequential 1,4-Addition and Rearrangement

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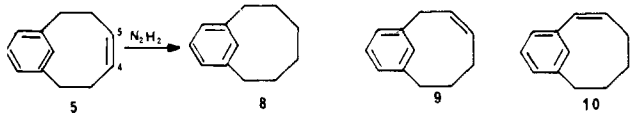
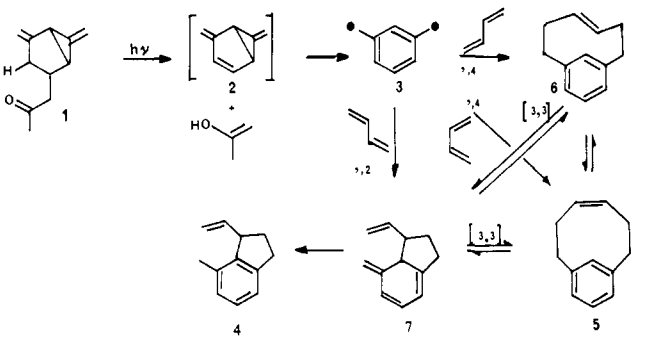
Abstract: The *m*-cyclophene (4*Z*)-bicyclo[6.3.1]dodeca-1(12),4,8,10-tetraene obtained from the *m*-quinodimethane–butadiene addition was shown to have the *Z*-olefinic configuration by analysis of its variable-temperature ^{1}H NMR spectrum and by magnetic saturation-transfer experiments. The substance exists as an approximately 1:1 mixture of interconverting conformational isomers at room temperature, with $\Delta G^{\ddagger}$ for the interconversion (bridge flip) being 16.5 kcal/mol. A similar interconversion occurs in the ~3:1 mixture of conformational isomers of the 4,5-dimethyl-substituted *m*-cyclophene derived from *m*-quinodimethane and 2,3-dimethylbutadiene. Arguments are presented to show that the indan products which accompany the *m*-cyclophenes are formed by a true 1,2-cycloaddition of the *m*-quinodimethane biradical and the diene, rather than by an indirect route involving initial 1,4-cycloaddition followed by [3,3]-sigmatropic rearrangement.

Photoelimination of acetone enol from the ketone **1** gives the *m*-quinodimethane (*m*-xylylene) biradical **3**, presumably via the bicyclic hydrocarbon **2**.[1] Conjugated dienes, e.g., 1,3-butadiene, capture the biradical to give two classes of cycloadducts, the methylated vinyl indans **4** (only the ortho isomer is shown) and the *m*-cyclophenes **5** or **6** (Scheme I). The present paper concerns the stereochemistry and mechanism of formation of the *m*-cyclophenes as well as a closely related question: Do the indan products **4** truly arise via a "pre-indan" **7** that is formed by 1,2-cycloaddition, or is the actual cycloaddition step 1,4-reaction, giving the *trans*- and/or *cis*-*m*-cyclophene **6** or **5**, which then form "pre-indan" by a [3,3]-sigmatropic rearrangement? This point is obviously of crucial importance in the interpretation of the steric course of indan formation from stereochemically labeled dienes.[1]

Stereochemistry of the Double Bond in the *m*-Cyclophene Adduct (5 or 6). The ring structure of the *m*-cyclophene from 1,3-butadiene was established[1] by diimide reduction[2] to the known[3] *m*-cyclophane **8**, which was identified by mass spectroscopic (MS) and ^{1}H NMR spectroscopic comparisons. The only mechanistically plausible location for the double bond is at the symmetrical C_4–C_5 position.



Scheme 1



Moreover, the ^{1}H and ^{13}C NMR spectra are compatible only with that location, although the existence of molecular symmetry is not immediately apparent from the spectra. The ^{13}C spectrum of the cis isomer **5** would be expected to show 7 distinct resonances, whereas that of the trans isomer should show either 7 or 12 lines (see below) and those of either of the unsymmetrical isomers **9** or **10** should show 12 or more. In fact, the ^{13}C spectrum shows *14* distinct peaks grouped into pairs of closely matched chemical shifts and intensities. The proton spectrum also contains pairs of resonances with approximately equal intensity components.

These observations suggest that the *m*-cyclophene product is made up of approximately equal amounts of two *symmetrical* isomers. That these isomers are in rapid equilibrium at room temperature and hence cannot be simply the *Z* and *E* isomers **5** and **6** was indicated by magnetic saturation-transfer experiments[4]

(1) (a) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 1867. (b) *Ibid.*, preceeding paper in this issue.

(2) Attempted catalytic hydrogenation over Pd/C gave a product (not further characterized) whose molecular ion was of the mass corresponding to the fully saturated bicyclo[6.3.1]dodecane.

(3) Hirano, S.; Hara, H.; Hiyama, T.; Fujita, S.; Nozaki, H. *Tetrahedron* **1975**, *31*, 2219.

(4) Cf.: Noggle, J. H; Schirmer, R. E. "The Nuclear Overhauser Effect"; Academic Press: New York, 1971.

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