

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

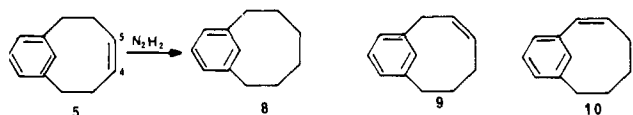
Joshua L. Goodman and Jerome A. Berson*

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

Abstract: The *m*-cyclophane (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 ¹H 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 Δ*G*[‡] 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*-cyclophane derived from *m*-quinodimethane and 2,3-dimethylbutadiene. Arguments are presented to show that the indan products which accompany the *m*-cyclophanes 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*-cyclophanes **5** or **6** (Scheme I). The present paper concerns the stereochemistry and mechanism of formation of the *m*-cyclophanes 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*-cyclophane **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*-Cyclophane Adduct (5 or 6). The ring structure of the *m*-cyclophane from 1,3-butadiene was established¹ by diimide reduction² to the known³ *m*-cyclophane **8**, which was identified by mass spectroscopic (MS) and ¹H NMR spectroscopic comparisons. The only mechanis-



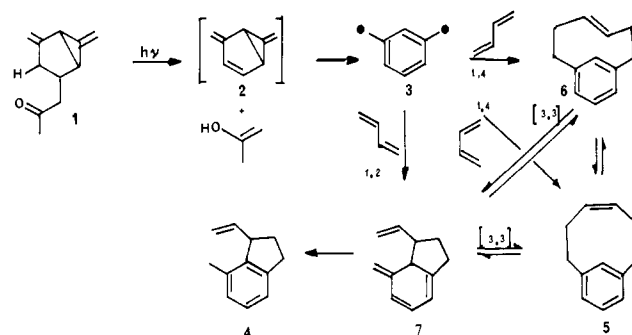
tically plausible location for the double bond is at the symmetrical C₄-C₅ position.

(1) (a) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 1867. (b) *Ibid.*, preceding 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.

Scheme I



Moreover, the ¹H and ¹³C NMR spectra are compatible only with that location, although the existence of molecular symmetry is not immediately apparent from the spectra. The ¹³C 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 ¹³C 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*-cyclophane 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 experiments⁴

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

on the 500-MHz proton spectrum. The effect was clearly seen by imposition of a second rf at the shift position associated with either of the sets of vinyl protons, which resonate as pseudotriplets centered around δ 5.40 and 4.75. The double irradiation caused not only a disappearance of the vinyl resonance being saturated and a simplification of the upfield allylic resonances but also a disappearance of the other vinyl resonance. Careful tests with diminished power levels in the second rf field showed that this was not the result of power leakage away from the nominal saturating frequency. Hence, the saturation at one frequency was being transferred by a site exchange to another frequency, presumably by interconversion of the two isomers. Similar results were obtained by irradiation at resonant fields corresponding to other sites undergoing exchange. Thus, the effect was also seen at the pair of aromatic proton resonances at δ 7.72 and 7.37.

The observed saturation transfer implied that room temperature must be close to the coalescence temperature at which interconversion between the isomers would be rapid on the NMR time scale. A variable-temperature ^1H NMR study of a solution of the *m*-cyclophane in toluene- d_8 showed a reversible coalescence of the vinyl proton resonances at a temperature of 363 K. The ΔG^\ddagger values calculated at 363 and 343 K were 16.6 and 16.5 (± 0.5) kcal/mol, determined from the vinyl and aromatic proton resonances, respectively. These values are only slightly different from that reported³ for the conformational isomerization of the dihydro analogue **8**.

The most plausible interpretation of the NMR site exchange in the *m*-cyclophane **5** is a conformational isomerization. A detailed analysis of the respective NMR spectroscopic consequences of a *cis* or *trans* configuration now permits a *cis* assignment.⁵

For the hypothetical *trans* isomer **6**, molecular models show that only one conformation would avoid severe interpenetration of the van der Waals' envelopes of the C_{12} hydrogen and the olefinic carbons (Figure 1). If this conformation were static on the NMR scale, all the carbons would have different chemical shifts, and the ^{13}C spectrum would show 12 lines. A bridge flip, which could be achieved by rotations about bonds $\text{C}_1\text{-C}_2$ plus $\text{C}_7\text{-C}_8$, would have the effect of reproducing the same conformation, preserving the chemical shifts of C_{10} and C_{12} , and interchanging the chemical shifts of the other ten carbons pairwise. Thus, if bridge flip were rapid on the NMR time scale, **6** should show seven lines in the ^{13}C spectrum. Another conceivable conformational isomerization could occur by rotations about bonds $\text{C}_3\text{-C}_4$ plus $\text{C}_6\text{-C}_5$. This would lead to an enantiomeric configuration, but again seven ^{13}C resonances would be expected. No obvious conformation, static or dynamically averaged, of **6** alone seems capable of accounting for the observed 14-line spectrum. Moreover, the hypothesis of an equimolar mixture of **6** with a *cis* isomer would not offer a reasonable way to explain the observation that interconversion of the isomers is fast on the time scale (of the order of 1 s) of the spin saturation experiment. This would require implausibly fast *trans* \rightleftharpoons *cis* olefin isomerization at ambient temperature.

A more satisfactory interpretation can be developed from the hypothesis of an equimolar mixture of two *cis* conformers, *endo*-**5** and *exo*-**5** (Figure 1), which interconvert too slowly at ambient temperature to average the chemical shifts of the site-exchanging nuclei. In contrast to the *trans* isomer **6**, each of the *cis* isomers is bilaterally symmetrical and hence each should give rise to seven ^{13}C lines. The spectrum in the slow-exchange limit thus would show 14 lines. The proton spectrum would correspond well to that observed under both slow- and fast-exchange conditions.

Figure 1 shows the total steric energies (in kcal/mol) of **6** and the two conformations of **5** as calculated by molecular mechanics.⁶

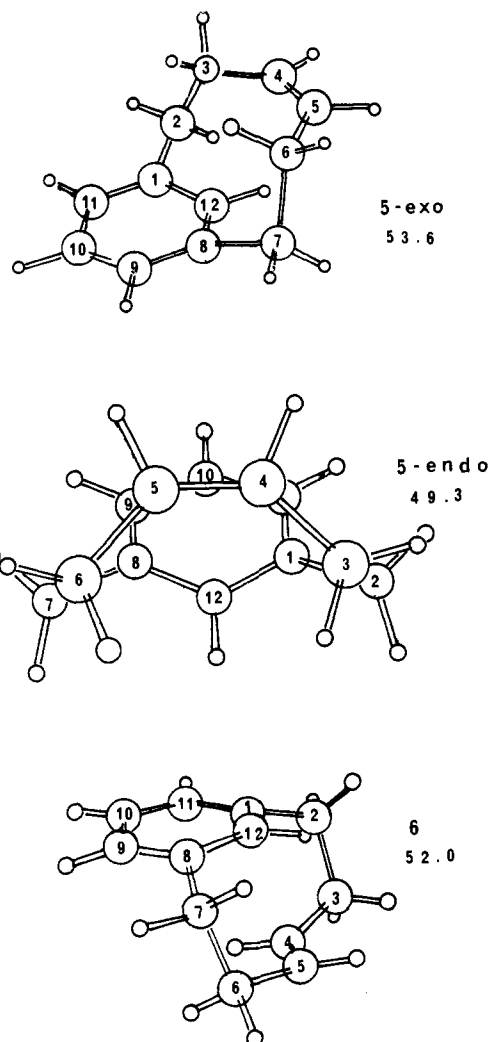


Figure 1. Optimized geometries and energies (in kcal/mol) calculated by MMII for the isomers for the *cis*- (**5**) and *trans*-*m*-cyclophanes (**6**).

Although the absolute values probably should be treated with some reserve, the results do suggest that large endothermicity barriers to the conformational interconversion *endo*-**5** \rightleftharpoons *exo*-**5** are not to be expected. The actual pathway for this process is not known but presumably involves rotations at bonds $\text{C}_1\text{-C}_2$ plus $\text{C}_8\text{-C}_7$ and/or $\text{C}_3\text{-C}_4$ plus $\text{C}_6\text{-C}_5$.

The high strain energy of **5** implied by the molecular mechanics calculations is probably related to the unusual electronic spectrum, λ_{max} 287 nm, $\log \epsilon = 2.52$ (compare *m*-xylene λ_{max} 264.5, $\log \epsilon = 2.47$), suggestive^{3,6,8,9} of a distorted aromatic chromophore. Similarly, the ^1H NMR spectrum showed low-field signals at δ 7.7 and 7.4, typical of aromatic protons in strained meta-cyclophanes.³

Attempts to prepare the *trans* isomer **6** by photochemical isomerization of the *cis* compound **5** with or without sensitizers were unsuccessful. When **5** was heated with I_2 in toluene at 100 $^\circ\text{C}$, the only isomerization product observed was the known³ tetrahydroacenaphthene **11**.



(6) (a) Allinger, N. L.; Miller, M. A.; Van Catledge, F. A.; Hirsch, J. J. *Am. Chem. Soc.* **1967**, *89*, 4345. (b) Allinger, N. L.; Hirsch, J. A.; Miller, M. A.; Tyminski, T.; Van Catledge, F. A. *Ibid.* **1968**, *90*, 1199.

(7) Doub, L.; Vandenberg, J. M. *J. Am. Chem. Soc.* **1949**, *71*, 2414.

(8) van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1977**, 4667.

(9) Tsuji, T.; Shibata, T.; Hienuki, Y.; Nishida, S. *J. Am. Chem. Soc.* **1978**, *100*, 1806.

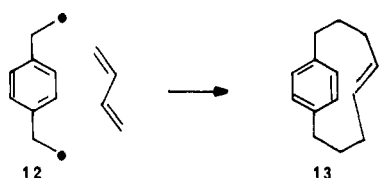
(5) Note that there is no immediately obvious way to obtain this information independently. A frequently used criterion, the vinyl proton-proton NMR coupling, is not readily applicable in this case because of the chemical shift equivalence of these two protons in each conformational isomer. Moreover, because of interference by aromatic ring-hydrogen absorptions in the diagnostic olefinic region, the infrared spectrum does not offer a clear choice either.

Table I. Yields^a of Products as a Function of Time of Irradiation in the Photolysis of Ketone 1-2,3-Dimethylbutadiene Mixtures

| time, min | % conv. | product, % yield ^d | | | | |
|-----------|---------|--------------------------------|--------------------------------|-------------------------------------|------------------------|---------------------------|
| | | indans 14 + 15 ^c | <i>cis-m</i> -cyclophene 16 | <i>trans-m</i> -cyclophene 17(?) | benzocyclooctene 18 | tot 14-18 ^a |
| 15 | 14 | 4 | 3 | 3 | <i>b</i> | 70 |
| 30 | 26 | 9 | 8 | 3 | <i>b</i> | 78 |
| 60 | 41 | 15 | 12 | 3 | 1 | 75 |
| 120 | 63 | 27 | 13 | 2 | 4 | 69 |
| 210 | 76 | 28 | 10 | 1 | 9 | 67 |
| 420 | 93 | 33 | 5 | <i>b</i> | 14 | 55 |

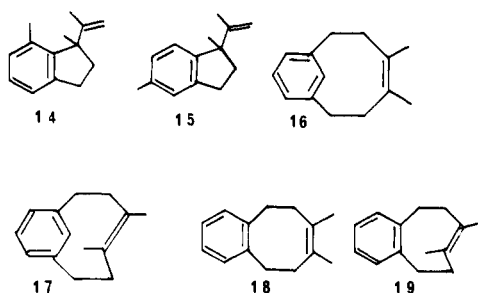
^aAbsolute yield corrected for unreacted ketone 1. ^bWas not detected (<0.5%). ^cRatio 14:15 about 2.7. ^dAbsolute yield unless otherwise indicated.

The apparent absence of the *trans m*-cyclophene 6 initially was a puzzling feature of the additions of biradical 3 to butadiene (Scheme I). As the molecular mechanics calculations suggest (Figure 1) adduct 6, although strained, actually should be about as stable as the observed *cis* adduct 5. Moreover, analogy to the addition of the biradical 12 to dienes, which gives substantial quantities of *trans-p*-cyclophene products 13,⁹ suggests that the 3 + butadiene reaction should give *trans* adduct 6. We suspect



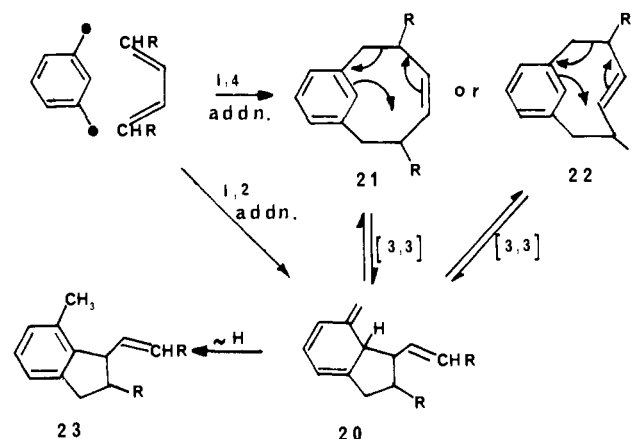
that 6 may in fact be formed but may be labile under the reaction conditions. Experiments in the analogous series of adducts derived from 2,3-dimethylbuta-1,3-diene tend to support this view.

Adducts of *m*-Quinodimethane 3 and 2,3-Dimethylbuta-1,3-diene. Photolysis of ketone 1 in the presence of a large excess of this diene gave five 1:1 biradical-diene adducts in combined absolute yield of 65-75% (corrected for recovered starting material). Two of these were indans 14 and 15, one was a *cis* metacyclophene 16, and one was a benzocyclooctene 18. The latter was not detected



at low conversion and seems to be a product of secondary photolysis of the metacyclophene 16. These products are analogous to those obtained from butadiene. However, a fifth product 17 was observed from dimethylbutadiene which suffered secondary photolysis even more rapidly than 16. After 14% conversion of ketone 1, 17 constituted about 19% of the reaction mixture, but this proportion rapidly declined as photolysis proceeded, reaching 1% after 76% of ketone 1 had been consumed (Table I). Because the amount of 17 was very small, characterization was limited to GC/MS, which was similar to that of 16, as would be expected of the *m*-cyclophene structure. The GC/MS data alone do not rule out the *trans*-benzocyclooctene 19, but this seems less likely on mechanistic grounds since, as a secondary rearrangement product, 19 would not be expected to appear early in the reaction course. If the tentative assignment as 17 to this barely observable product is correct, it would not be surprising if the corresponding *trans-m*-cyclophene 6 (Scheme I) from the butadiene reaction might have escaped detection.

Conformation of the *m*-Cyclophene 16. Like the NMR spectra of the *cis-m*-cyclophene 5 from the butadiene reaction, those of *m*-cyclophene 16 are best interpreted in terms of a mixture of two conformational isomers, *endo*-16 and *exo*-16 which may be vis-

Scheme II. Hypothetical Direct and Indirect Pathways to 1,2- and 1,4-Cycloadducts

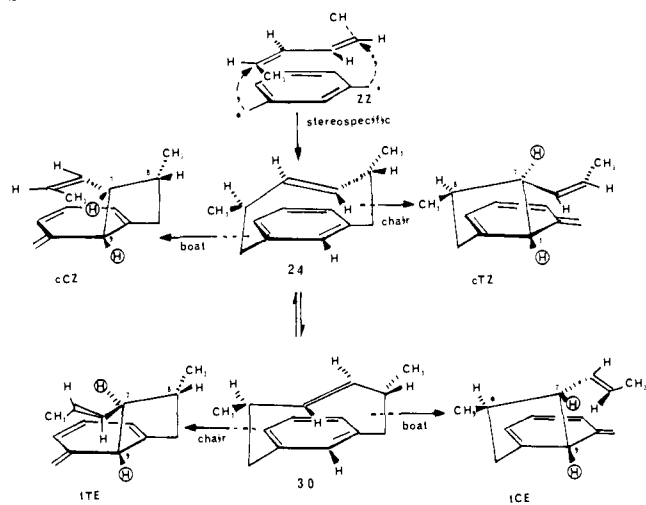
ualized by replacing the olefinic hydrogens of *endo*-5 and *exo*-5 with methyl groups. The *endo* isomer appears to be favored as judged by the relative intensities of the upfield (δ 1.1) and downfield (δ 1.8) allylic methyl resonances (\sim 3:1). This preference is to be contrasted with *endo*-5 and *exo*-5 pair, which coexist in a 1:1 ratio. Molecular mechanics calculations suggest that the energy gap favoring the *endo* form should be about 0.5 kcal/mol greater in the pair of 16 conformers than in the pair of 5 conformers, which agrees at least qualitatively with the present observations.

Can the *m*-Cyclophene Adducts be Precursors to the "Pre-Indans" or Vice Versa? We have previously¹ used a stereochemical criterion to elucidate the pathway leading to 1,2-adducts (indans) of dienes and the *m*-quinodimethane biradical 3. The reliability of this criterion now must be scrutinized because of the possibility that the indan products 23 may not result directly from a 1,2-cycloaddition to give a pre-indan 20 followed by aromatizing hydrogen shift but instead may be formed indirectly via a 1,4-cycloaddition to a *m*-cyclophene 21 or 22 followed by [3,3]-sigmatropic rearrangement to 20. An associated converse possibility is that the *m*-cyclophenes observed may arise indirectly via initial 1,2-cycloaddition, giving a pre-indan followed by [3,3]-sigmatropic rearrangement 20 \rightarrow 21 (Scheme II).

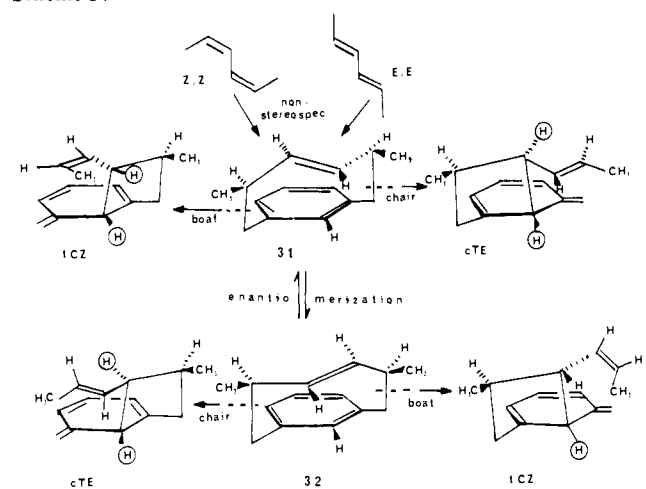
Two lines of argument may be used against the indirect alternative for indan formation. The first is based on straightforward experimental controls, which show that neither the *cis-m*-cyclophenes 21 nor the indans 23 are converted into each other under the reaction conditions. More subtle considerations must be used to exclude indirect pathways involving the presently unknown pre-indan (20) and *trans-m*-cyclophene (22) species.

The 1,4-addition of the *m*-quinodimethane biradical 3 to *cis,cis*-hexa-2,4-diene (*Z,Z*) to give a *trans-m*-cyclophene hypothetically might occur in a stereospecific or a nonstereospecific fashion. Assume for the sake of argument that the addition is stereospecific (Scheme III). The resulting *trans-m*-cyclophene 24 can give pre-indan products by either of two [3,3]-sigmatropic transition states, a boat, or a chair, depending upon which of two bonds breaks. (Note that only ortho pre-indans are formed by this pathway; para pre-indans would be formed by [3,5] processes).

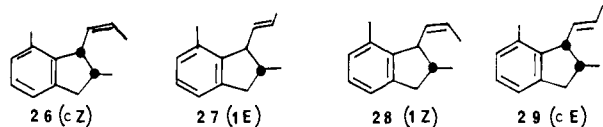
Scheme III



Scheme IV



The boat [3,3] rearrangement would lead to an ortho pre-indan whose stereochemistry is designated cCZ, where the symbols refer, respectively, to configurations at the indan chiral centers (C_7 relative to C_8), at C_1 relative to C_7 , and at the side-chain propenyl group. Chair rearrangement of **24** would give pre-indan tTZ, but the C_1/C_7 configuration is lost on aromatization to the indan product, so that *trans*-*m*-cyclophene **24** would give only the cZ indan **26**. The tE indan **27** could be generated by a



conformational isomerization of **24** to the diastereomeric *trans*-*m*-cyclophene **30** (Scheme III), which by [3,3]-sigmatropic rearrangement could give rise to the pre-indans tTE and tCE, precursors to indan **27** (tE). Significantly, Scheme III does not provide mechanisms for the formation of either of the other two indan diastereomers **28** (tZ) or **29** (cE). It therefore represents an incomplete if not wholly incorrect mechanism, since it fails to reproduce the observed¹ product tZ, in which the diene stereochemistry is lost at the newly created indan positions but is faithfully preserved in the propenyl side chain.

A similar analysis applies to a variant of the *trans*-*m*-cyclophene hypothesis in which the initial cycloaddition is assumed to be nonstereospecific (Scheme IV). This would permit, for example, the formation of adduct **31** from either the (*Z,Z*)- or (*E,E*)-2,4-hexadiene as well as from the *E,Z* isomer. In the reaction with the *Z,Z* isomer, the experimental facts¹ require that the

Scheme V

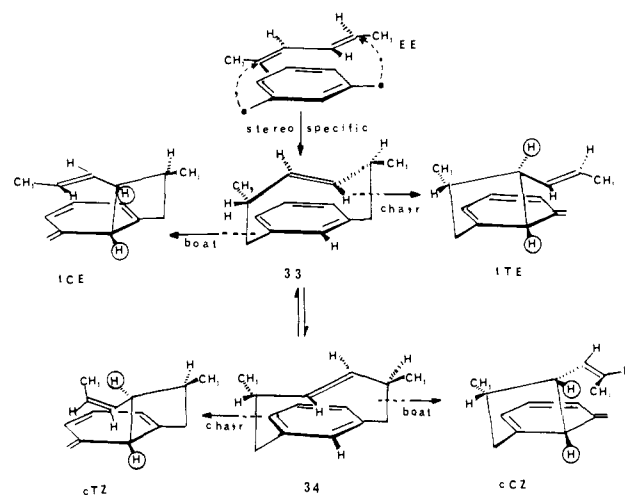


Table II. Observed and Predicted Indan Products from Cycloadditions

| prod (marked X) | reactant diene | | | | | |
|--------------------|---------------------|-------------------|---------------------|-------------------|------------|-------------------|
| | <i>Z,Z</i> | | <i>E,E</i> | | <i>E,Z</i> | |
| | pred ^{b,c} | obsd ^a | pred ^{b,d} | obsd ^a | pred | obsd ^a |
| cZ | X | X | X | | X | X |
| tZ | | X | | | X | X |
| cE | | | | X | X | X |
| tE | X | | X | X | X | X |

^a Reference 1. ^b By stereospecific formation of a *trans*-*m*-cyclophene intermediate. ^c Scheme III. ^d Scheme V.

Table III. Mechanistic Hypotheses Required to Rationalize "Unexpected" Indan Products

| react diene | "unexpected" prod | hypoth intermed | [3,3]-sigmatrop conform for prod formation |
|-------------|-------------------|------------------------------------|--|
| <i>Z,Z</i> | tZ | 31 or 32 , Scheme IV | boat |
| <i>E,E</i> | cE | 31 or 32 , Scheme IV | chair |

products be cZ and tZ. As Scheme III shows, cZ could be obtained from *m*-cyclophene **24** by either a boat or a chair Cope rearrangement, and it might be postulated that tZ would be available from *m*-cyclophenes **31** or **32**, obtained by nonstereospecific addition (Scheme IV) followed by *boat* Cope rearrangement. Even if a rationale could be found for the preferred boat pathway, this line of argument loses all validity when an attempt is made to apply it to the reaction with (*E,E*)-2,4-hexadiene, where the observed products are cE and tE. By a stereospecific addition, the (*E,E*)-diene would give a *trans*-*m*-cyclophene **33** (Scheme V) that would give only tE upon Cope rearrangement. (After diastereomerization to **34**, cZ could be formed, but this is not an observed product from (*E,E*)-diene.) In order to obtain the other observed product cE in the current hypothetical framework, one could call upon the *trans*-*m*-cyclophenes **31** and **32**, derived from *E,E*-diene by nonstereospecific addition (Scheme IV), but now one must postulate that the Cope rearrangement of **31** and/or **32** occurs only in the *chair* mode. This conflicts with the requirement, already deduced from the *Z,Z* addition, that **31** and/or **32** must react only in the *boat* mode. Thus, the hypotheses for indan formation involving *trans*-*m*-cyclophene intermediates suffer either from conflict with experimental findings (Table II) or from an internally contradictory mechanism (Table III).

It will be recognized that a crucial element in the refutation of the hypothetical pathway diene → *trans*-*m*-cyclophene → pre-indan → indan is the stereochemistry of the propenyl side chain in the final indan product. The rejected Schemes III–V fail ultimately because of their inability to generate the correct propenyl stereochemistry. This feature is absent in the *m*-cyclophene products and therefore cannot be used as a basis for ruling out

a hypothetical pathway diene \rightarrow pre-indan \rightarrow *m*-cyclophene for the latter product. At the moment, therefore, it cannot be determined whether the mixed stereochemistry observed¹ in the *m*-cyclophene product results from a nonstereospecific 1,4-addition or a nonstereospecific [3.3]-sigmatropic rearrangement.

The indan product, however, is formed by a nonstereospecific 1,2-cycloaddition. This excludes indirect mechanisms $3 \rightarrow 6 \rightarrow 7$ and $3 \rightarrow 5 \rightarrow 7$ (Scheme I) and provides a necessary link in our chain of mechanistic reasoning.

Experimental Section

General procedures are described in the preceding paper in this issue.^{1b}

(4Z)-Bicyclo[6.3.1]dodeca-1(12),4,8,10-tetraene (5) (Retention Time, 35 min). This substance was isolated by preparative gas chromatography (GC) from the butadiene-1 reaction mixture.^{1b} ¹H NMR (500 MHz, toluene-*d*₆) two conformational isomers, 1:1 ratio) δ 7.72 (s, 1 H), 7.37 (s, 1 H), 7.16–7.13 (t, 1 H, *J* = 7.4 Hz), 6.93–6.90 (t, 1 H, *J* = 7.4 Hz), 6.75–6.73 (d, 2 H, *J* = 7.4 Hz), 6.56, 6.54 (d, 2 H, *J* = 7.4 Hz), 5.41–5.38 (pseudo t, 2 H, *J* = 5.8 Hz), 4.76–4.74 (pseudo t, 2 H, *J* = 5.5 Hz), 3.10–3.07 (q, 2 H, *J* = 7.2 Hz), 2.50–2.34 (m, 6 H), 2.17–2.05 (m, 2 H), 1.93–1.85 (m, 4 H), 0.69–0.75 (m, 2 H); ¹³C NMR (22.5 MHz, CDCl₃) δ 144.7, 143.7, 138.6, 131.8, 131.4, 130.5, 128.9, 127.0, 124.7, 123.9, 37.3, 34.5, 33.3, 30.3; FT-IR (CS₂) 2987 (m), 2922 (m), 1602 (w), 1449 (m), 983 (m), 937 (m), 773 (m), 758 (m), 736 (s), 723 (m), 711 (m), 696 cm⁻¹ (m); GC-MS (100, 1, 20, 200) (4.9 min), *m/e* 158 (M⁺, 7%), 157 (H, 11%), 130 (C₂H₄, 100%), 104 (C₄H₆, 41%); UV-vis λ_{287} (log ϵ = 2.52), λ_{230} (log ϵ = 3.9), λ_{212} (log ϵ = 4.44); exact mass calcd for C₁₂H₁₄ 158.1096, found 158.1085

The ¹H NMR spectrum described above was observed at 303 K. When the temperature was raised to 343 K, broadening of most of the lines was observed, the interchange phenomena being most easily evident in the downfield region, where the pairs of lines at δ 7.72–7.37 and 6.74–6.55 moved together. At 378 K, complete coalescence to singlets at δ 7.55 and 6.6 was achieved.

Reaction of 1 with 2,3-Dimethylbutadiene. The samples were prepared as outlined above. The four adducts were isolated by GC (column G, 180 °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 the reaction of 1 and butadiene.^{1b} Hexadecane was used as the internal standard for analytical runs. The total yield of cycloadducts (column C or B) varied from 50% to 60%. Again 14 and 15 were not separated by GC and were analyzed as a mixture. By comparison of the aromatic region and the aromatic methyl peak position in the ¹H NMR of the mixture of 14 and 15 with that of the mixture of 4 and its para isomer,^{1b} 14 was considered to be the major isomer. By integration of

the aromatic methyl peaks in the proton NMR, the 14:15 ratio was \sim 2.7:1.

1-(2-Methylethenyl)-1,7-dimethylindan (14) (Retention Time, 18 min): ¹H NMR (90 MHz, CDCl₃) δ 7.1–6.9 (m, 3 H), 4.8–4.6 (m, 2 H), 3.0–2.8 (m, 2 H), 2.2 (s, 3 H), 1.6 (d, 3 H, *J* = 0.6 Hz), 1.4 (s, 3 H), 2.0–1.4 (m, 2 H); GC-MS (100, 1, 10, 200) (2.5 min) *m/e* 186 (M⁺, 41%), 171 (CH₃, 60%), 145 (C₃H₅, 100%); FT-IR (CDCl₃) 2971 (br), 2922 (m), 1631 (m), 1470 (m), 1379 cm⁻¹ (m); exact mass calcd for C₁₄H₁₈ 186.1409, found 186.1412.

1-(2-Methylethenyl)-1,5-dimethylindan (15): ¹H NMR (90 MHz, CDCl₃) δ 2.3 (s), 1.4 (s). The other resonances were obscured by peaks of the major component or too small to observe.

7,8-Dimethyl-5,6,9,10-tetrahydrobenzocyclooctene (18) (Retention Time, 30 min): ¹H NMR (90 MHz, CDCl₃) δ 7.1–7.0 (m, 4 H), 3.0–2.9 (t, 4 H, *J* = 7.1 Hz), 2.5–2.4 (t, 4 H, *J* = 7.1 Hz), 1.4 (s, 6 H); ¹³C NMR (125.7 MHz, CDCl₃) δ 140.3, 129.4, 128.1, 125.8, 34.8, 33.7, 20.6; FT-IR (neat) 2943 (m), 2893 (m), 960 (m), 770 (w), 761 cm⁻¹ (w); GC-MS (100, 1, 10, 200) (3.1 min), *m/e* 186 (M⁺, 40%), 171 (CH₃, 20%), 143 (C₃H₇, 51%), 129 (C₄H₉, 63%), 104 (C₆H₁₀, 100%); Exact mass calcd for C₁₄H₁₈ 186.1409, found 186.1410.

(4Z)-4,5-Dimethylbicyclo[6.3.1]dodeca-1(12),4,8,10-tetraene (16) (Retention Time, 38 min): ¹H NMR (90 MHz, CDCl₃) two conformational isomers, 3:1 ratio) δ 7.5–6.5 (m, 8 H), 3.5–1.6 (m, 16 H), 1.8 (s, 6 H), 1.1 (s, 6 H); FT-IR (CDCl₃) 2985 (m), 2921 (m), 1639 cm⁻¹ (m); GC-MS (100, 1, 10, 200) (3.4 min), *m/e* 186 (M⁺, 13%), 171 (CH₃, 57%), 130 (C₄H₈, 98%), 104 (C₆H₁₀, 100%); exact mass calcd for C₁₄H₁₈ 186.1409, found 186.1407.

A fifth isomer 17 was observed by analytical GC and GC-MS but was not fully characterized: GC-MS (80, 1, 20, 200) (4.5 min), *m/e* 186 (M⁺, 15%), 171 (CH₃, 28%), 143 (C₃H₇, 37%), 130 (C₄H₈, 100%), 104 (C₆H₁₀, 76%).

Analytical GC (column B, 155 °C initial, 2.5%/min), using hexadecane as the internal standard, was used to monitor the formation of products with increasing time of irradiation. The results are shown in Table I.

Acknowledgment. We thank the National Science Foundation (CHE 8011399) and the National Institute of General Medical Sciences (GM-30787) for partial support of this research. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. 1, 89032-32-6; 3, 32714-83-3; 5, 97486-92-5; 8, 7125-01-1; 14, 97486-93-6; 15, 97486-94-7; 16, 97486-95-8; 17, 97486-96-9; 18, 97486-97-0; Me₂CO, 67-64-1; butadiene, 106-99-0; 2,3-dimethylbutadiene, 513-81-5.