

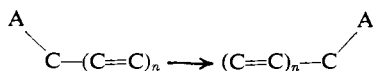
Photoisomerizations of *cis*- and *trans*-3-Methylenecyclodecene^{1a}

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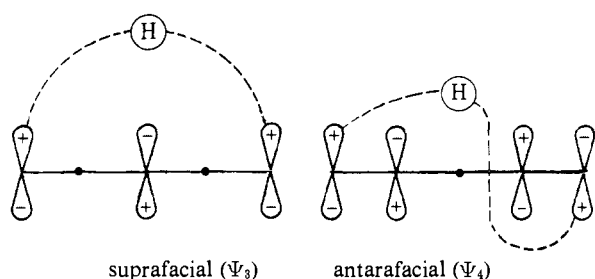
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Abstract: *cis*- and *trans*-3-methylenecyclodecene (*cis*- and *trans*-7) were prepared by acetate pyrolysis. Direct irradiation (254 nm) of *trans*-7 rapidly gave *cis*-7. Under the same conditions *cis*-7 isomerized to a 1-methylcyclodeca-1,3-diene (9). After prolonged irradiation 9 isomerized to a 2-methylcyclodeca-1,3-diene (10). The isomerizations of *cis*-7 to 9 and 9 to 10 are discussed in terms of antarafacial [1,5] sigmatropic transformations. Sensitized irradiation of *cis*- and *trans*-7 only resulted in isomerization about the endocyclic double bond.

The predictive powers of orbital symmetry rules² have been verified in numerous cases. The subcategory of sigmatropic rearrangements has received considerable attention.³ One kind of sigmatropic transformation involves the migration of an atom from one end to the other of an olefinic chain ($n = 1, 2, 3$, etc.) If the rearrangement proceeds with continuous



orbital overlap between A and the π system, the properties of the highest occupied molecular orbital of the radical derived from the olefinic system control the stereochemistry of migration. For example, the course of a [1,5] sigmatropic transformation ($n = 2$) would be controlled by the highest occupied molecular orbital of the pentadienyl radical. The nature of the orbital which binds A to the pentadienyl system must also be specified.³ When A is hydrogen, a spherical 1s orbital is involved. Concerted thermal [1,5] hydrogen migrations are restricted to suprafacial transfer of hydrogen, while concerted photochemical migrations require antarafacial hydrogen transfer. Molecular geometry also plays a critical role in concerted sigmatropic



migrations. The termini of the pentadienyl system must be sufficiently close to permit continuous overlap with the 1s hydrogen orbital during the reaction. Overlap requirements thus restrict [1,5] hydrogen migrations to cisoid conformations. Steric hindrance to hydrogen

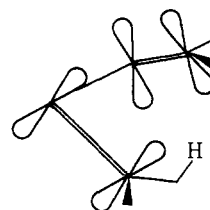
(1) (a) This work was supported in part by Public Health Service Grant No. 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, and the Hoffmann-La Roche Foundation. (b) To whom correspondence should be addressed. (c) National Institutes of Health Predoctoral Fellow, 1965-1967. (d) Postdoctoral Fellow, Stiftung für Stipendien auf dem Gebiete der Chemie.

(2) (a) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (b) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

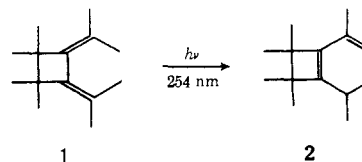
(3) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

migration through the center of a ring prevents antarafacial transfer in many cyclic compounds.⁴

Several reports of facile thermally induced [1,5] hydrogen shifts appear in the literature.² Concerted thermal migrations are electronically restricted to suprafacial hydrogen transfer, and this prediction has been verified for both cyclic and acyclic 1,3-dienes.² Examples of photochemical [1,5] hydrogen shifts are known in acyclic systems^{2,5} which can adopt a helical conformation necessary for concerted antarafacial hydro-



gen transfer. Recently, Kiefer and Fukunaga⁶ described the photoisomerization of 1 to 2 and proposed a



[1,5] antarafacial hydrogen shift to account for the results. Their observation prompts us to report an example of [1,5] hydrogen migration, which, if concerted, could only proceed by antarafacial transfer of hydrogen.

Results

cis- and *trans*-3-methylenecyclodecene (*cis*- and *trans*-7) were prepared by a sequence similar to that employed by Bailey and Goossens⁷ for 3-methylenecyclohexene (see Scheme I). Treatment of cyclodecanone (3)⁸ with diethyl carbonate and sodium hydride cleanly gave keto ester 4. 2-Carbethoxycyclodecanone (4) was reduced with lithium aluminum hydride to a mixture of 2-methylenecyclodecanol (5-OH) and 2-hy-

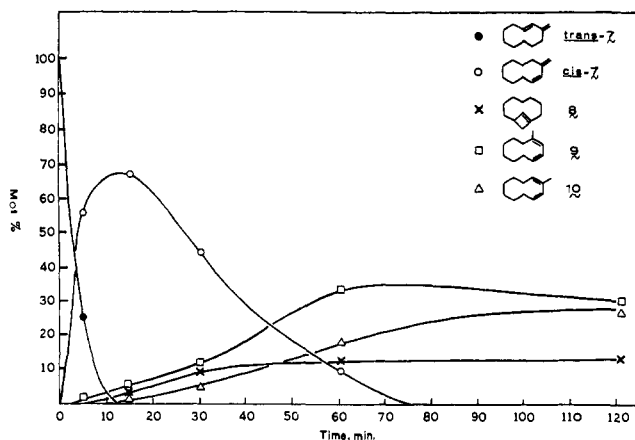
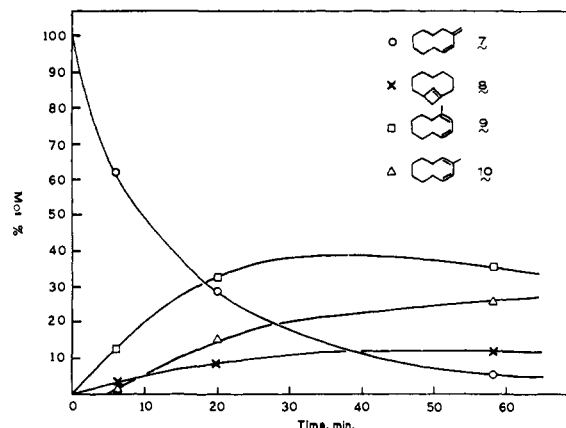
(4) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

(5) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(6) E. F. Kiefer and J. Y. Fukunaga, *Tetrahedron Lett.*, 993 (1969).

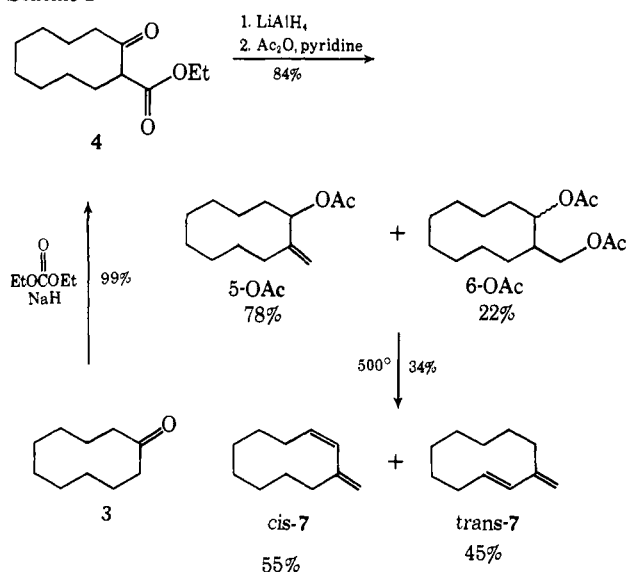
(7) W. J. Bailey and J. C. Goossens, *J. Amer. Chem. Soc.*, **78**, 2804 (1956).

(8) A. C. Cope, J. W. Barthel, and R. D. Smith, "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 218.

Figure 1. Rate of product production upon irradiation of *trans*-7.Figure 2. Rate of product production upon irradiation of *cis*-7.

droxymethylcyclodecanol (**6-OH**). Column chromatography of a portion of the mixture served to separate the products. Acetylation of the mixture followed by pyrolysis of acetates **5-OAc** and **6-OAc** at 500° gave *cis*- and *trans*-3-methylenecyclodecene (*cis*- and *trans*-7).

Scheme I



The diene mixture was easily separated by glpc, and each isomer was identified from spectral data. The exocyclic methylene group of *cis*-3-methylenecyclodecene (*cis*-7) gave a strong ir band at 898 cm^{-1} , and two one-proton nmr absorptions at 4.70 and 4.89 ppm. The proton at C_1 appeared as a doublet of triplets ($J_{1,2} = 12.0$ Hz, $J_{1,10} = 7.8$ Hz) at 5.38 ppm. The *cis* stereochemistry of the disubstituted double bond was established by comparing the relative magnitudes of $J_{1,2}$ coupling for *cis*-7 and *trans*-7 (*vide infra*). The uv spectrum of *cis*-7, $\lambda_{\text{max}}^{\text{cyclohexane}}$ 218 nm (ϵ 5100), requires that the dihedral angle between the double bonds be near 60°. Models clearly indicate that a planar *s-trans* conformation results in severe transannular steric interactions. The exocyclic methylene group of *trans*-7 gave a strong ir band at 896

(9) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Elmsford, N. Y., 1959, p 85.

(10) N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **86**, 2811 (1964).

cm^{-1} and a two-proton nmr peak at 4.75 ppm. The proton at C_1 appeared as a doublet of triplets ($J_{1,2} = 16.4$ Hz, $J_{1,10} = 7.0$ Hz) at 5.73 ppm, and the proton at C_2 gave a doublet at 6.12 ppm. The *trans* stereochemistry of the disubstituted double bond was established by the magnitude of $J_{1,2}$ and a strong ir band at 978 cm^{-1} .¹¹ *trans*-3-Methylenecyclodecene (*trans*-7) has an intense uv absorption at 233 nm (ϵ 16,000) characteristic of *s-trans*-dienes.¹²

The direct irradiation of *trans*-7 through Vycor with a low-pressure mercury arc (254 nm) was followed by glpc, and the results are summarized in Figure 1. Preparative scale reactions were carried out with a 450-W Hanovia lamp using a Vycor filter, and in separate runs the various products were isolated when their concentrations reached a maximum. Bicyclo[7.1.1]-undec-1(10)-ene (**8**) gave an ir band at 1610 cm^{-1} . Its nmr spectrum had absorptions at 1.8–3.0 ppm for the five allylic protons and 5.78 ppm (broad s) for the proton at C_{10} . The uv spectrum of **8** was typical of an isolated double bond with a maximum at 195 nm (ϵ 6700). 1-Methylcyclodeca-1,3-diene (**9**) and 2-methylcyclodeca-1,3-diene (**10**) gave similar ir, uv, and nmr spectra. The ir spectra of both endocyclic dienes lack strong bands near 970 cm^{-1} characteristic of *trans*-disubstituted double bonds. In addition, both **9** and **10** gave nmr spectra with low-field doublets ($J = 11$ –12 Hz) at 5.9 ppm which integrated to one proton. Unfortunately, attempts to assign the stereochemistry of the trisubstituted double bonds have been unsuccessful.¹⁴ The positions of the double bonds in **9** and **10** were confirmed by ozonolysis followed by oxidative work-up to give keto acid **11** and suberic acid **12**, respectively.

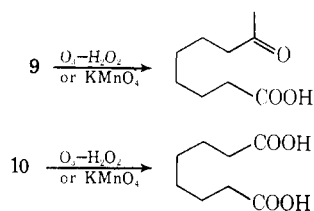
The irradiation conditions employed for *trans*-7 were repeated in sequence for *cis*-7, **8**, **9**, and **10**. The results for *cis*-7 are summarized in Figure 2. Both cyclobutene **8** and diene **9** are initial products with diene **10** showing a slight induction period. Cyclobutene **8** was inert upon exposure to ultraviolet radiation at 254 nm, while 1-methylcyclodeca-1,3-diene (**9**)

(11) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 24.

(12) Woodward's rules¹³ predict a maximum at 230 nm.

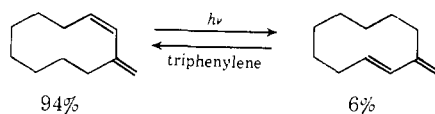
(13) R. B. Woodward, *J. Amer. Chem. Soc.*, **64**, 72 (1942).

(14) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 508; (b) W. J. Nebe and G. J. Fonken, *J. Amer. Chem. Soc.*, **91**, 1249 (1969); (c) W. G. Dauben, C. D. Poulter, and J. S. Ritscher, unpublished results.



isomerized to 2-methylcycloclodeca-1,3-diene (**10**). Prolonged exposure of **10** resulted in eventual polymerization. Both rates and product compositions of all of the photochemical reactions were insensitive to solvent changes from diethyl ether to methanol.

A solution containing *cis*-**7** (55%), *trans*-**7** (45%), tridecane (internal standard), and triphenylene was irradiated through a Pyrex probe. Under these conditions, in which only triphenylene ($E_T = 67$ kcal/mol) absorbed light, the only observed reaction was *cis*-*trans* isomerization about the endocyclic double bond of *cis*- and *trans*-**7**. The progress of the photosensitization was monitored by glpc and photoequilibrium at

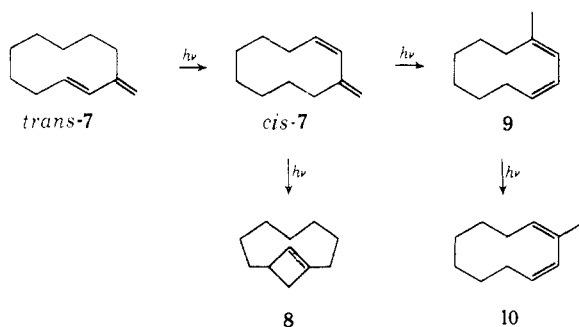


94% *cis*-**7** and 6% *trans*-**7** was reached after 12 hr. No other products were observed by glpc and the material balance was 100%.

Discussion

The data summarized in Figures 1 and 2 coupled with the separate irradiations of **8** and **9** are best explained by the series of reactions outlined in Scheme II. The scheme proposes a set of isomerizations, each

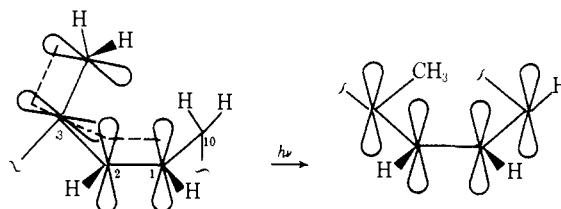
Scheme II



of which requires photoactivation. Double bond isomerization of *trans*-**7** to its *cis* isomer illustrates a common reaction of 1,3-dienes upon direct irradiation.¹⁴ Irradiation of *cis*-**7** did not give a detectable amount (<1%) of *trans*-**7**. The position of the photoequilibrium is determined by the relative molar absorptivities of the isomers at 254 nm and the decay ratio of the excited intermediate(s) to *cis* and *trans* products. At 254 nm the molar absorptivity of *trans*-**7** is 38 times greater than that of *cis*-**7**. A decay ratio favoring *cis*-**7** by only a factor of 2 or 3 would account for our results and such a ratio is not unreasonable since the sensitized *cis*-*trans* equilibrium was strongly displaced toward the *cis* isomer.¹⁵

(15) Presumably both *cis*-**7** and *trans*-**7** are efficiently sensitized by triphenylene. Liu found that triphenylene behaved as a high-energy sensitizer toward *cis,cis*- and *cis,trans*-cycloocta-1,3-diene, giving a *cis,cis*/*cis,trans* ratio of ca. 4 (R. S. H. Liu, *J. Amer. Chem. Soc.*, **89**, 112 (1967)).

The rapid photoinitiated rearrangement of *cis*-**7** to 1-methylcycloclodeca-1,3-diene (**9**) is not found in the corresponding six-, seven-, and eight-membered ring homologs.¹⁶ It is obvious that the [1,5] hydrogen shift is not a facile thermal rearrangement since *cis*-**7** was prepared by acetate pyrolysis at 500°. Molecular models indicate that *cis*-3-methylenecycloclodecene is uniquely suited for an antarafacial [1,5] hydrogen migration. A conformation which relieves transannular interactions places the diene chromophore in an *s*-



cis conformation with a dihedral angle between the double bonds of ca. 75°. The uv spectrum of *cis*-**7** is in agreement with the proposed conformation. More important, an *s*-*cis* relation of the chromophore is necessary for the observed valence isomerization of *cis*-**7** to cyclobutene **8**.⁴ A concerted photochemical sigmatropic isomerization of *cis*-**7** to **9** requires that the disubstituted double bond of **9** be *cis* and the trisubstituted bond be *trans*. Ir and nmr spectral data indicate that the disubstituted bond is indeed *cis* but the absence of a uv maximum above 220 m μ suggests a *cis* configuration for the trisubstituted double bond.¹⁷

In agreement with this suggested *cis,cis* configuration of **9** is the finding of its photochemical induced rearrangement to **10**. Molecular models show that a concerted [1,5] hydrogen shift is not sterically possible for the *cis,trans* isomer, whereas, the *cis,cis* isomer has the requisite helical geometry of the chromophore to permit a [1,5] antarafacial hydrogen transfer from C-10 to C-4. As above, such a rearrangement would lead to the *cis,trans* isomer of **10** but spectral data indicate a *cis,cis* configuration.

In this series of photochemical hydrogen rearrangements, steric restrictions induced by the ten-membered ring permit only antarafacial transfers. Such transfers require the intervention of *cis,trans* isomers and as is seen from Figures 1 and 2, no indication of their presence was found when the reaction was followed by glpc. In view of the facile *trans* to *cis* photoisomerization of **7**, and the similarity of the uv spectra of all the *cis* isomers found in this study, it is reasonable that the photoequilibrium of *cis,trans* and *cis,cis* isomers was rapidly established and strongly displaced in the *cis,cis* direction.¹⁹ If such be the case, the *cis,trans* isomer could have escaped detection. The preparation of these transient isomers is now being studied.

(16) W. G. Dauben and C. D. Poulter, *Tetrahedron Lett.*, 3021 (1967).

(17) The uv spectra of *cis,cis*- and *cis,trans*-cycloclodeca-1,3-diene have been reported.¹⁸ The *cis,cis* isomer has no maximum above 210 nm (ϵ_{220} 4000), while the *cis,trans* isomer has a maximum at 220 nm (ϵ 7300). The different spectra are presumably due to conformation differences in the chromophore with the dihedral angle between the double bonds of the *cis,cis* isomer being closer to 90° than that of the *cis,trans* diene. If one assumes that a methyl group at C-1 or at C-2 does not significantly alter the conformation of the parent diene chromophoric system dienes **9** and **10** would have a *cis,cis* stereochemistry.

(18) L. A. Paquette and R. W. Begland, *J. Amer. Chem. Soc.*, **88**, 4685 (1966).

(19) At 254 nm there may be a significant difference in the molar absorptivities of *cis,trans*- and *cis,cis*-**9** and **-10** (see ref 17).

Experimental Section

General. Ir spectra were taken on a Perkin-Elmer Model 137 spectrometer. Ultraviolet spectra of compounds with maxima below 210 nm were taken on a Beckman DK-2A ratio recording spectrometer, and those with maxima above 210 nm were recorded on a Perkin-Elmer Model 202 spectrometer. Spectral grade cyclohexane was used as solvent. Nmr spectra were obtained on a Varian A-60 or HA-100 spectrometer with chemical shifts measured downfield from tetramethylsilane (δ , parts per million) internal standard. Preparative glpc separations were carried out with a 10 ft \times $\frac{3}{8}$ in. 10% Carbowax 6000-10% potassium hydroxide column (60-80 Chromosorb W) at 100-130°, and analytical glpc analyses were accomplished with a 10 ft \times $\frac{1}{8}$ in. 10% Carbowax 6000-10% potassium hydroxide column (80-100 Chromosorb W) at 100°. Combustion analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley, Calif.

2-Carboethoxycyclodecanone (4). Following the procedure described by Krapcho and coworkers,²⁰ 25.2 g (0.56 mol) of a 53.4% sodium hydride dispersion in mineral oil and 46.0 g (0.388 mol) of diethyl carbonate in 300 ml of benzene were used to convert 29.8 g (0.194 mol) of cyclodecanone⁷ into 2-carboethoxycyclodecanone (4). Work-up and distillation gave 43.8 g (99%) of colorless liquid; bp 125-128° (2.5 mm), lit.²¹ 118-120° (1 mm).

Lithium Aluminum Hydride Reduction of 2-Carboethoxycyclodecanone. To a stirred suspension of 9.5 g (0.25 mol) of lithium aluminum hydride in 300 ml of dry diethyl ether was added a solution of 43.8 g (0.194 mol) of 2-carboethoxycyclodecanone (4) in 50 ml of ether. The mixture was allowed to stir for 30 min after the addition was complete. Excess hydride was carefully decomposed with methanol and saturated ammonium chloride was added until the suspended solids coagulated. The clear ether layer was decanted and the solid material was washed several times with ether. The combined ether layers were dried, and solvent was removed at reduced pressure to yield 33.5 g of a colorless, fragrant oil. A small portion of the product (3.06 g) was separated into two fractions by chromatography on alumina (Woelm, basic, activity II).

a. 2-Methylenecyclodecanol (5-OH). The first fraction was eluted with benzene and was a single component (>97% by glpc). The product was a fragrant, viscous oil, yield 2.11 g. Samples for spectral and combustion analysis were purified by glpc: ir (CCl₄) 1815 (first overtone of 907 cm⁻¹ band), 1639, 1466, 1443, and 907 cm⁻¹; nmr (δ , CCl₄) 1.45 (14, m, H at C₅-C₁₀), 2.21 (2, m, H at C₃), 2.89 (1, s, hydroxyl H), 4.08 (1, t, H at C₁, $J_{1,10}$ = 7 Hz), and 4.89 and 5.10 ppm (2, m, exocyclic methylene H).

Anal. Calcd for C₁₁H₂₀O: C, 78.58; H, 11.90. Found: C, 78.28; H, 11.85.

b. 2-Hydroxymethylcyclodecanol (6-OH). The second fraction was eluted with diethyl ether. The product, 0.645 g, was a white solid; mp 82-84°; nmr (δ , CCl₄) 1.53 (17, m, H at C₂-C₁₀) and 3.5-4.4 ppm (5, m, H at C₁, hydroxyl H, hydroxymethylene H).

Anal. Calcd for C₁₁H₂₂O₂: C, 70.93; H, 11.90. Found: C, 71.04; H, 11.70.

Acetylation of 2-Methylenecyclodecanol and 2-Hydroxymethylcyclodecanol. A solution of 30.4 g of 2-methylenecyclodecanol (5-OH) and 2-hydroxymethylcyclodecanol (6-OH) in 125 ml of anhydrous pyridine was cooled in an ice-water bath. To the cold solution was added 108 g of acetic anhydride and 5 ml of glacial acetic acid. The solution was allowed to warm to room temperature. After 24 hr, the mixture was poured onto cracked ice and 20 ml of concentrated hydrochloric acid. The resulting mixture was extracted with pentane, and the combined pentane extracts were washed with 1 N hydrochloric acid until the aqueous layer remained acidic. The pentane extracts were washed with water and dried over anhydrous magnesium sulfate. Solvent was removed at reduced pressure, and the products separated by distillation.

(a) The first component to distil gave 24.4 g (64%) of 5-OAc: bp 108-111° (2 mm); ir (CCl₄) 1730, 1637, 1235, and 900 cm⁻¹; nmr (δ , CCl₄) 1.44 (14, m, H at C₅-C₁₀), 1.93 (3, s, methyl H), 2.2 (2, m, H at C₃), 4.99 and 5.14 ppm (2, m, exocyclic methylene H), and 5.24 ppm (1, t, H at C₁, $J_{1,10}$ = 7 Hz).

Anal. Calcd for C₁₃H₂₂O₂: C, 74.25; H, 10.54. Found: C, 74.38; H, 10.44.

(b) The higher boiling component gave 9.7 g (20%) of 6-OAc: bp 145-147° (2 mm); ir (CCl₄) 1736, 1357, and 1235 cm⁻¹; nmr (CCl₄) 1.57 (17, m, H at C₂-C₁₀), 1.95 and 1.98 (6, s, methyl H), 3.94 (2, m, acetoxymethylene H), and 5.1 (1, m, H at C₁).

Anal. Calcd for C₁₅H₂₆O₄: C, 66.64; H, 9.69. Found: C, 66.39; H, 9.68.

Pyrolysis of 2-Methylenecyclodecyl Acetate and 2-Acetoxy-methylcyclodecyl Acetate. A clean reaction tube packed with glass helices was slowly heated to 500° while being swept with ca. 200 ml/min of dry nitrogen. A 10-g portion of a mixture of 2-methylenecyclodecyl acetate (5-OAc) and 2-acetoxy-methylcyclodecyl acetate (6-OAc) was dropped into the hot tube. The pyrolysate was condensed and trapped by a spiral condenser and ice-water and Dry Ice-acetone traps in sequence. The contents of both traps were poured into water, and the aqueous mixture was extracted with pentane. The combined pentane extracts were washed with saturated sodium bicarbonate solution and dried over magnesium sulfate. Solvent was removed at reduced pressure, and the products were distilled to give 2.12 g (34%) of a mixture of *cis*- and *trans*-3-methylenecyclodecene (*cis*- and *trans*-7), bp 86-90° (20 mm), and 4.1 g of recovered acetates. Dienes *cis*-7 and *trans*-7 were separated by glpc, and samples were collected for spectra and combustion analyses.

(a) ***cis*-3-Methylenecyclodecene (*cis*-7).** The diene with the shorter glpc retention time comprised 55% of the diene mixture: ir (CCl₄) 1631 and 898 cm⁻¹; uv (max) 218 nm (ϵ 5100); nmr (δ , CCl₄) 1.38 (10, m, H at C₅-C₉), 2.27 (4, m, H at C₄ and C₁₀), and 4.70 and 4.89 (2, broad s, exocyclic methylene H), 5.38 (1, d of t, H at C₁, $J_{1,2}$ = 12.0 Hz, $J_{1,10}$ = 7.8 Hz), and 5.78 ppm (1, d, H at C₂).

Anal. Calcd for C₁₁H₁₈: C, 87.92; H, 12.08. Found: C, 88.22; H, 12.11.

(b) ***trans*-3-Methylenecyclodecene (*trans*-7).** The product with the longer glpc retention time comprised 45% of the diene mixture: ir (CCl₄) 1653, 1616, 978, and 896 cm⁻¹; uv (max) 233 nm (ϵ 16,100); nmr (CCl₄) 1.38 (10, m, H at C₅-C₁₀), 2.10 (4, m, H at C₄ and C₁₀), 4.75 (2, broad s, exocyclic methylene H), 5.73 (1, d of t, H at C₁, $J_{1,2}$ = 16.4 Hz, $J_{1,10}$ = 7.0 Hz), and 6.12 ppm (1, d, H at C₂).

Anal. Calcd for C₁₁H₁₈: C, 87.92; H, 12.08. Found: C, 87.95; H, 12.04.

Preparative Scale Irradiations. In a typical experiment, 1.63 g (0.011 mol) of a mixture of *cis*- and *trans*-3-methylenecyclodecene (*cis*- and *trans*-7) in 750 ml of anhydrous methanol (0.015 M in diene) was irradiated with a 450-W Hanovia lamp through a Vycor filter for 6 hr. The sample was outgassed with helium for 2 hr prior to irradiation and throughout the run. The reaction mixture was poured into an equal volume of water and extracted with pentane. The combined pentane extracts were washed with brine and dried over magnesium sulfate. Solvent was carefully removed at reduced pressure to give 1.43 g of a light yellow oil. The components of the mixture were separated by glpc and their relative retention times using the conditions outlined earlier are: **10**, 1; **9**, 1.23; *cis*-7, 1.32; **8**, 1.43; *trans*-7, 1.82.

(a) **2-Methylcyclodeca-1,3-diene (10).** The product with the shortest retention time had the following properties: ir (CCl₄) 1630, 870, and 715 cm⁻¹; uv 185 nm (ϵ 13,200) no maximum above 185 nm; nmr (δ , CCl₄) 1.31 (8, m, H at C₆-C₉), 1.71 (3, broad s, methyl H), 2.08 (4, m, H at C₅ and C₁₀), 5.10 (1, t, H at C₁, $J_{1,10}$ = 8.1 Hz), 5.28 (1, d of t, H at C₄, $J_{3,4}$ = 11.0 Hz, $J_{4,5}$ = 7.7 Hz), and 5.92 ppm (1, broad d, H at C₃).

Anal. Calcd for C₁₁H₁₈: C, 87.92; H, 12.08. Found: C, 87.90; H, 12.13.

(b) **1-Methylcyclodeca-1,3-diene (9).** The second eluted product had the following properties: ir (CCl₄) 1664, 835, 717 cm⁻¹; uv 183 nm (ϵ 14,000) no maximum above 183 nm; nmr (δ , CCl₄) 1.30 (8, m, H at C₆-C₉), 1.65 (3, t, methyl H, J = 2 Hz), 2.1 (4, m, H at C₅ and C₁₀), 5.3 and 5.6 (2, m, H at C₂ and C₄), and 5.90 ppm (1, d, H at C₃, $J_{3,4}$ = 11.9 Hz).

Anal. Calcd for C₁₁H₁₈: C, 87.92; H, 12.08. Found: C, 88.23; H, 11.87.

(c) **Bicyclo[7.1.1]undec-1(10)-ene (8).** The product with the longest retention time had the following properties: ir (CCl₄) 1610 and 823 cm⁻¹; uv (max) 195 nm (ϵ 6740); nmr (CCl₄) 1.4 (12, m, H at C₃-C₈), 1.8-3.0 (5, m, H at C₂, C₉, and C₁₁), and 5.78 ppm (1, broad s, H at C₁₀).

Anal. Calcd for C₁₁H₁₈: C, 87.92; H, 12.08. Found: C, 87.78; H, 11.94.

Analytical Irradiations. In a typical experiment, a 20-mg (0.16 mmol) sample of diene and 10 μ l of *n*-decane in 80 ml of diethyl ether (0.002 M in diene) were irradiated with a Nester Faust low-

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pressure mercury lamp (NFUV-300) through a Vycor probe. The solution was outgassed with helium for 2 hr prior to and during the irradiation. The progress of the reaction was monitored by glpc.

(a) *trans*-3-Methylenecyclodecene. The diene was irradiated under the usual conditions, and the glpc results are summarized in Figure 1.

(b) *cis*-3-Methylenecyclodecene. Irradiation of *cis*-7 gave the results summarized in Figure 2.

(c) Bicyclo[7.1.1]undec-1(10)-ene. Irradiation of the cyclohexene for 2 hr produced no change.

(d) 1-Methylcyclodeca-1,3-diene. Upon irradiation, diene 9 slowly isomerized to 10. After 334 min approximately 50% of the starting material had polymerized.

(e) 2-Methylcyclodeca-1,3-diene. After 1140 min approximately 80% of the diene had disappeared. Only 10% of the products were monomeric, and none of the components corresponded to previously identified C₁₁H₁₈ hydrocarbons.

Sensitized Irradiation of *cis*- and *trans*-3-Methylenecyclodecene. Following the general procedure for analytical irradiations, a solution of 30 mg (0.20 mmol) of a mixture of *cis*- and *trans*-3-methylenecyclodecene (*cis*- and *trans*-7), 20 mg of tridecane (internal standard) and 10 mg (0.04 mmol) of triphenylene in 80 ml of diethyl ether was irradiated with a low-pressure mercury lamp through a Pyrex probe. The only observed reaction was *cis*-*trans* isomerization about the internal double bond (see Table I).

Ozonolysis of 2-Methylcyclodeca-1,3-diene. A room temperature solution of 35 mg (0.23 mmol) of 2-methylcyclodeca-1,3-diene in 8 ml of methylene chloride was ozonized until ozone was no longer consumed. The solution was then concentrated to 3

Table I. Sensitized Irradiation of *cis*- and *trans*-3-Methylenecyclodecene

	Irradiation time, min			
	0	75	280	720
% <i>cis</i> -7	60	73	93	94
% <i>trans</i> -7	40	27	7	6

ml, a mixture of 0.5 ml of hydrogen peroxide (30%), 1 ml of formic acid, and 0.5 ml of water added, and the solution refluxed for 1.5 hr and then evaporated. The resulting yellow oil (56 mg) was crystallized from ethyl acetate to give 11.5 mg (30%) of colorless crystals with mp 130–136°. After recrystallization from the same solvent the mp was 137–139° (mp of authentic suberic acid was 141–142°, mmp 138–141°; the dimethyl esters, prepared with diazomethane, showed identical retention time on SE-30 and on Carbowax columns).

Permanganate Cleavage of 1-Methylcyclodeca-1,3-diene. Following the method of Blomquist and Goldstein,²² 17 mg of 1-methylcyclodeca-1,3-diene was oxidized in aqueous potassium permanganate. After work-up, the resulting yellow oil (32 mg) was esterified with diazomethane. The main product was separated on a 20% DEGS column and showed ir and mass spectra identical with that of an authentic sample of methyl 8-oxononanoate.

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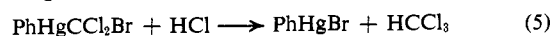
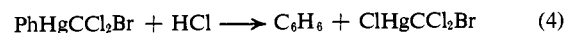
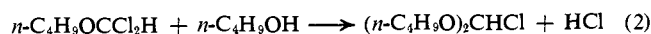
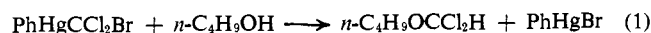
Halomethyl Metal Compounds. XXXIX. Reactions of Phenyl(trihalomethyl)mercury-Derived Dihalocarbenes with Cyclic Allylic Alcohols, Acetates, and Methyl Ethers¹

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Abstract: While dichlorocarbene (from thermolysis of PhHgCCl₂Br) appears to react exclusively at the O–H bond of allyl alcohol, it reacts with 3-cyclooctenol to give the C=C addition product, 9,9-dichlorobicyclo[6.1.0]nonanol-2, in 70% yield. Similar reactions with 3-cycloheptenol and 3-cyclononenol gave the C=C addition products in ca. 30% yield, but with 3-cyclohexenol none of the C=C addition product was detected. The successful addition of CCl₂ to the C=C bond of Me₂C=CHCH(Me)OH in 52% yield suggested that electronic factors are the most important in determining at which site in an unsaturated alcohol—the O–H bond or the C=C bond—dichlorocarbene attack will occur. Chemical and nmr studies indicated that in each case it was the *trans*-*x,x*-dichlorobicyclo[*n*.1.0]-alkanol-2 which was formed. Phenyl(bromodichloromethyl)mercury-derived CCl₂ also was added to the C₆, C₇, C₈, and C₉ cyclic allylic acetates and methyl ethers to give *trans* products, generally in good yield. The cyclopropanation of C₇, C₈, and C₉ cyclic allylic alcohols and methyl ethers with iodomethylzinc iodide also was studied.

We recently reported concerning a study of the reactions of phenyl(trihalomethyl)mercury compounds with alcohols.^{2,3} For a simple saturated alcohol such as *n*-butyl alcohol the major products were *n*-butyl formate, *n*-butyl chloride, chloroform, and benzene, in addition to phenylmercuric bromide. It was proposed that these products are formed by the scheme shown in eq 1–5. In the case of allyl alcohol,



we found that such reaction at the O–H bond (eq 1) is preferred to CCl₂ addition to the C=C bond, the isolated products being allyl formate, allyl chloride, benzene, and chloroform.³

Our interest in PhHgCX₃ reactions with unsaturated alcohols revived when a report appeared which claimed that phenyl(tribromomethyl)mercury reacts with

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