Synthesis and Reactivity of an Exo,endo-4,6-Disubstituted Bicyclo[3.1.0]hex-2-ene[1]

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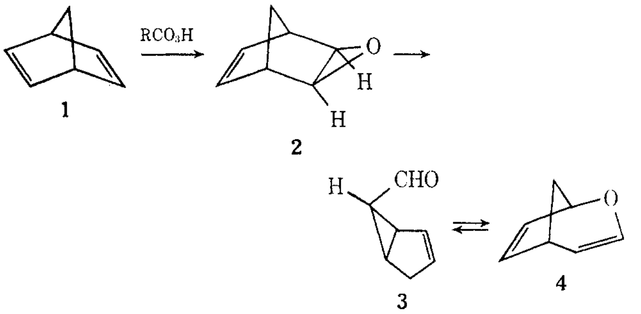
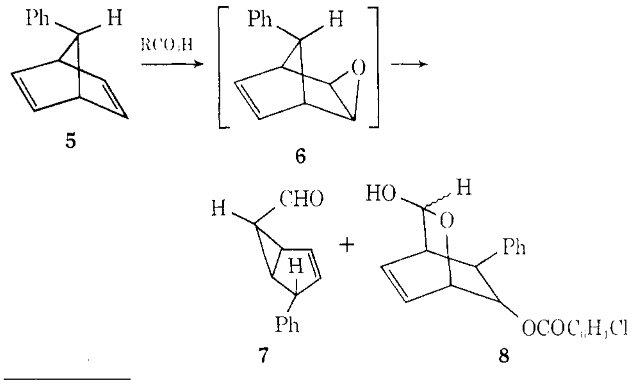
The peracid oxidation of 7-substituted norbornadienes has been found to afford exo-4,endo-6-disubstituted bicyclo[3.1.0]hex-2-enes. The photo- and thermal chemistry of *exo*-4-methylbicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde (**10**) has been studied. The photolysis of **10** results in photoepimerization by external cyclopropyl bond cleavage whereas the thermolysis proceeds predominantly by a suprafacial homo [1,7] hydrogen shift.

As an extension of our studies on the photochemical Diels–Alder reaction,[3] we became interested in determining the stereochemical consequences attending the thermal and photochemical cycloreversion of the bicyclo[3.1.0]hex-2-ene system. Some recent work in the literature suggests that the thermal rearrangements of bicyclo[3.1.0]hex-2-enes with electron-withdrawing substituents at the 6 position may be proceeding through a [2 + 4] cycloreversion.[4–6] The influence of the electron-withdrawing group at the 6 position of the bicyclohexene ring in the cycloreversion process can be understood in terms of recent discussions of substitutent effects of the cyclopropane ring.[7–9] If there is a π-electron acceptor, such as a carbonyl group, attached to the cyclopropane ring, then the lowest unoccupied orbital of the π-electron acceptor can interact with the antisymmetric component of the occupied degenerate Walsh orbital pair in cyclopropane. This interaction removes electron density from the cyclopropane ring and therefore it weakens the bonding between C_1 and C_6 and C_5 and C_6 but strengthens the bond between positions 1 and 5. Weakening of the C_1–C_6 bond would be expected to promote the cycloreversion reaction.

Synthesis of a bicyclo[3.1.0]hex-2-ene with an electron-withdrawing group at the 6 position and a stereochemical marking group at the 4 position, which would thermally decompose at a convenient rate and would also be photochemically reactive, was desired. Of the several possible methods to gain synthetic entry into such a system, the route involving the peracid epoxidation of a 7-substituted norbornadiene was considered most feasible. Meinwald and coworkers[10] have reported the formation of exo epoxide **2** and its rapid rearrangement to bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde[11] (**3**). The latter compound was found to exist in mobile equilibrium with 2-oxabicyclo[3.2.1]octa-3,6-diene[13,14] (**4**). The above sequence holds unquestionable promise for the synthesis of an exo,endo-4,6-disubstituted bicyclohexene, since it provides substantial opportunity of controlling the nature of the substituents and their stereochemical relationship. Brown has recently demonstrated that the epoxidation of norbornene proceeds almost exclusively from the exo direction.[15] He has also shown that the presence of a syn-7-methyl group on the norbornene skeleton will retard the rate of epoxidation by a factor of *ca.* 100.[15] Consequently, treatment of a 7-substituted norbornadiene with *m*-chloroperbenzoic acid will be expected to proceed by exo epoxidation of the least hindered double bond. Thermal rearrangement of the initially formed epoxide should be facilitated by back-side participation of the neighboring transannular double bond and give a exo-4,endo-6-disubstituted bicyclo[3.1.0]hex-2-ene.



When 7-phenylnorbornadiene (**5**) was allowed to react with *m*-chloroperbenzoic acid, the expected exo epoxide **6** was not obtained, but rather two new compounds were isolated. The minor component of the mixture was established as *exo*-4-phenylbicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde (**7**) through a combination of infrared, ultraviolet, and nmr spectroscopy (see Ex-



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(1) Photochemical Transformations of Small Ring Carbonyl Compounds. LI. For part L see A. Padwa and G. Lee, *J. Amer. Chem. Soc.*, **95**, 6147 (1973).

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(11) The corresponding endo epoxide has been found to be thermally stable and not prone to isomerization.[12]

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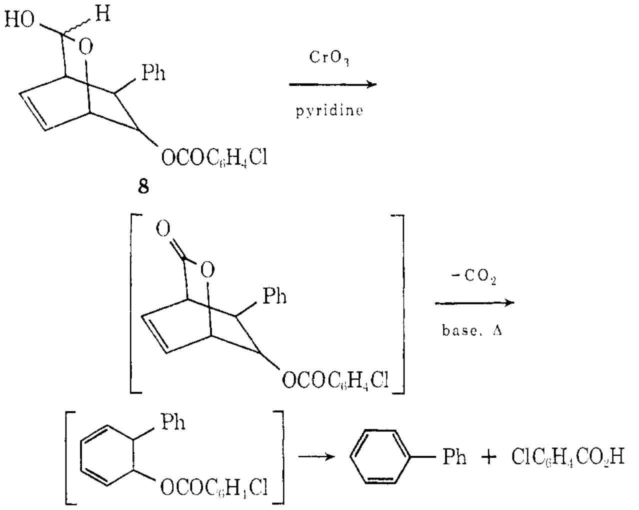
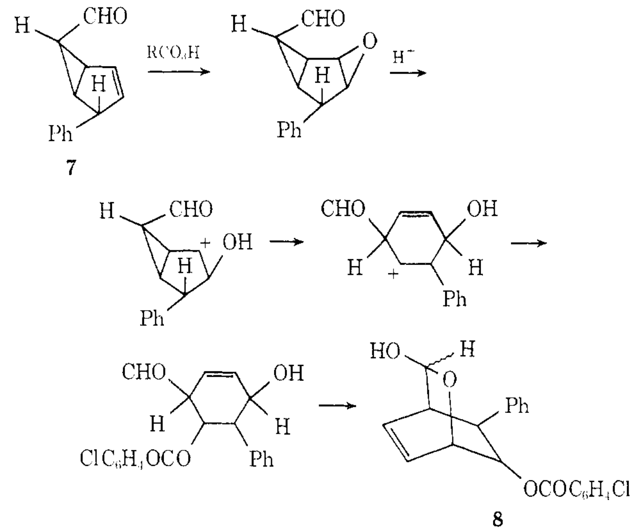
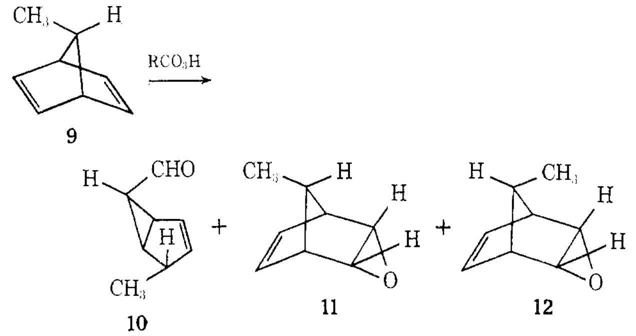
perimental Section). The formation of **7** can best be rationalized as proceeding through the intermediacy of exo epoxide **6** followed by its acid-catalyzed rearrangement to **7**. The major component of the reaction mixture was a white, crystalline solid, mp 153–154°, whose structure is assigned as 2-oxa-3-hydroxy-7-phenyl-8-(*m*-chloro)benzoxybicyclo[2.2.2]oct-5,6-ene (**8**) on the basis of its spectroscopic (see Experimental Section) and chemical data. The elemental analysis of this compound ($C_{20}H_{17}ClO_4$) suggests that it is a further oxidation product of the initially formed bicyclo[3.1.0]hex-2-ene aldehyde (**7**). This suggestion was confirmed by the finding that **7** was smoothly converted to **8** on treatment with *m*-chloroperbenzoic acid. Evidently, the initially formed bicyclohexene **7** undergoes further oxidation at a faster rate than starting material. This explanation accounts for the large amount of starting material that can be recovered when equivalent amounts of peracid were used. Chemical confirmation of the structure of **8** was obtained by its conversion with chromium trioxide in pyridine to biphenyl. This reaction presumably proceeds by loss of carbon dioxide from the initially formed lactone followed by elimination of *m*-chlorobenzoic acid. A reasonable mechanism for the formation of **8** is presented below.

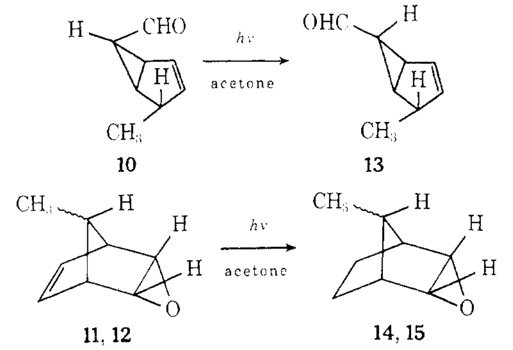




Since the overall yield of *exo*-4-phenylbicyclo[3.1.0]-hex-2-ene-*endo*-6-carboxaldehyde (**7**) was so low, we decided to investigate the peracid oxidation of another 7-substituted norbornadiene. When 7-methylnorbornadiene (**9**) was treated with *m*-chloroperbenzoic acid in methylene chloride at 0°, there was produced a mixture of three isomeric compounds. Preparative-scale vpc separation of the crude mixture led to the isolation of pure **10**. This product was identified as bicyclohexene **10** (37%) on the basis of its nmr spectrum ($CDCl_3$), which displays a methyl doublet at τ 8.92 (3 H, $J = 7$ Hz), cyclopropyl hydrogens at 8.28 (1 H, t, $J = 7$ Hz), 8.02 (1 H, t, $J = 7$ Hz), and 7.4 (m) in addition to absorptions due to the olefinic [τ 4.2 (m, 2 H)] and aldehydic [τ 0.84 (1 H, d, $J = 6$ Hz)] hydrogens. The first peak in the vpc chromatogram proved to be a mixture of *endo*-norbornene epoxides (16%). Although the epoxides, **11** and **12**, appeared as a single peak on most vpc columns, we eventually accomplished separation on a 20 ft × 0.25 in. 18% FS-1265 on 60-80 Chromosorb P column at 90°. The endo stereochemical assignment was made by the observation that both epoxides were stable when heated at reflux in benzene which contained a trace of *p*-toluenesulfonic acid.[11]

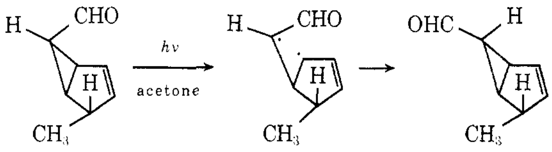


Since the separation of endo epoxides **11** and **12** from bicyclo[3.1.0]hexene **10** was only attained with great difficulty, the initial irradiation experiments were carried out on the initial epoxidized mixture. Photolysis of the epoxidation mixture in acetone with a Pyrex filter gave a mixture of products which were separated by preparative vapor phase chromatography. In addition to unreacted starting material, three new compounds were obtained and subsequently identified as *exo*-4-methylbicyclo[3.1.0]hex-2-ene-*exo*-6-carboxaldehyde (**13**, 35%) and an inseparable 1:1 mixture of the syn and anti isomers of *endo*-2,3-epoxy-7-methylbicyclo[2.2.1]heptane (**14**, **15**). Control experiments on a pure sample of **10** indicated that it afforded only *exo*-bicyclohexene **13** on irradiation. Similarly, irradiation of the mixture of norbornene epoxides (**11** and **12**) afforded only compounds **14** and **15**. The structure of bicyclohexene **13** was elucidated on the basis of its



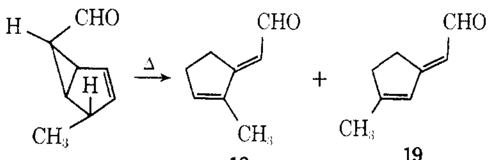
spectral properties (see Experimental Section). Structure **13** was further confirmed by the base-catalyzed epimerization of **10** to the thermodynamically more stable exo isomer (**13**). Structures **14** and **15** were established on the basis of both chemical and spectroscopic evidence (see Experimental Section). Reduction of the original epoxidation mixture over 5% palladium on carbon gave a mixture of **14** and **15**. This mixture was spectroscopically identical with the mixture of epoxides obtained from the irradiation.

The photochemical isomerization of bicyclohexene **10** to **13** may be rationalized on the assumption that the reaction proceeds *via* diradical **17**, a species derived by cleavage of the external cyclopropyl bonds. Such a process is not without analogy. Several examples of photosensitized epimerizations in related systems have recently been reported.[16-20] Garin and coworkers,[17] for example, have described the photosensitized epimerization of bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxylic acid and its methyl ester. The photoepimerization reaction was shown to occur by cleavage of the external cyclopropyl bond. The photochemical reduction of norbornene epoxides **11** and **12** to **14** and **15** is not an unprecedented reaction. Kropp[21] and Sauers[22] have shown that various derivatives of norbornene can be reduced when irradiated in the presence of a triplet sensitizer. It would appear that the triplet state of norbornene epoxide (**11** or **12**) is sufficiently long lived to participate in an intermolecular hydrogen atom abstraction.



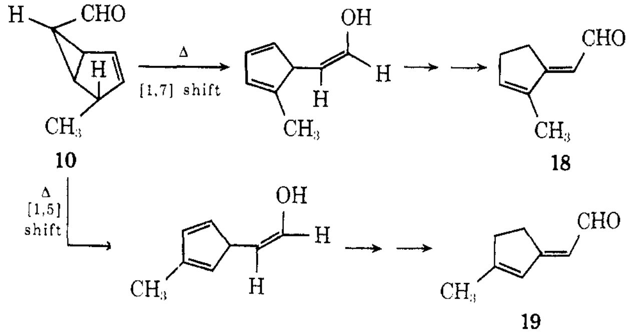
10 **17** **13**

Since bicyclo[3.1.0]hexene **10** did not undergo cycloreversion to a 1,3,5-hexatriene on electronic excitation, we decided to study the thermal chemistry of this system with the hope that we could promote the cycloreversion reaction at elevated temperatures. Heating a benzene solution of **10** at 150° afforded a mixture of two isomeric aldehydes (**18** and **19**). Control experiments showed that the products were stable under the reaction conditions. The structure of the major reaction product **18** (87%) was based on its characteristic spectral data: ir 3.42, 3.68, 6.02, 8.70, and 11.55 μ; uv (cyclohexane) λ_{max} 282 nm (s 16,600); m/e 122 (M^+); nmr (CCl_4, 100 MHz) τ 8.2 (s, 3 H), 7.4 (m, 2 H), 6.96 (m, 2 H), 4.28 (m, 1 H), 3.74 (broad s, 1 H), and 0.25 (1 H, d, $J = 6$ Hz). Saturation of the signal at τ 4.28 with an external field caused the doublet at τ 0.25 to collapse to a singlet. The minor product of the reaction mixture could not be readily separated from **18** by vapor phase chromatography. While our studies were in progress, a report by Gilbert and Klumpp appeared describing the thermal chemistry of bicyclohexene **10**.[23] These workers assigned structure **19** to the minor reaction component of the thermal mixture. They also identified structure **18** as the major thermal product.



10 **18** **19**

The formation of bicyclohexene **18** from **10** can be rationalized as proceeding *via* a homo [1,7] hydrogen migration as shown below. The minor product is derived by a related suprafacial homo [1,5] hydrogen shift. Although the geometries of the transition states for the homo [1,5] and [1,7] hydrogen shifts are similar, the available data suggests that the activation energy for the [1,7] process is somewhat lower than that for the [1,5] transfer.[23] Both the [1,5] and [1,7] hydrogen transfer processes have lower activation energies than the sought-after thermal cycloreversion process. This same conclusion was reached by Gilbert and Klumpp.[23] The above thermal transformations also shed light on the mechanism of the rearrangement of the closely related bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde (**20**).[24] The rate-determining step in the rearrangement of **20** was assumed to involve a homo [1,5] hydrogen shift on the basis of numerous precedents in the literature.[25] From our results, as well as those from Gilbert and Klumpp's group,[23] it would appear as though the thermal rearrangement of **20** actually involves both the π electrons of the carbon–carbon double bond and the σ electrons between C-5 and C-6. This is most reasonable, since it is known that systems possessing the potential for competitive thermal sigmatropic migrations of order $[i,j]$ favor rearrangement by the higher order pathway.[26-28]



Experimental Section

All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian

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Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany, The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associates high-resolution spectrometer and at 100 MHz using a Jeolco MH-100 spectrometer.

Peracid Oxidation of 7-Phenylnorbornadiene.—A solution of 8.4 g of 7-phenylnorbornadiene[29] and 17.2 g of *m*-chloroperbenzoic acid in 200 ml of methylene chloride was allowed to stand at room temperature for 3 hr. At the end of this time the precipitated *m*-chlorobenzoic acid was removed by filtration and the solution was washed with saturated sodium carbonate and dried over sodium sulfate. The solvent was removed *in vacuo* to give 12.6 g of an orange oil. The crude mixture was dissolved in hexane and passed through a Florisil column. Elution of the chromatographic column with 5% ethyl acetate–hexane gave 0.58 g of recovered starting material. The second peak isolated from the chromatographic column amounted to 0.25 g (3%) of a crystalline solid, mp 67–68°, whose structure is assigned as *exo*-4-phenylbicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde (**7**): ir (KBr) 5.95, 6.76, 6.92, 8.34, 9.25, 10.21, 10.65, 11.65, 12.51, 13.40, and 14.45 μ; uv (cyclohexane) λ_{max} 232, 252, and 258 nm (ε 2000, 670, and 590); nmr (CCl_4) τ 7.8–8.5 (m, 2 H), 6.4 (broad s, 1 H), 6.1 (broad s, 1 H), 4.1 (m, 2 H), 2.7 (m, 5 H), 0.6 (d, 1 H, *J* = 5 Hz); mass spectrum *m/e* 184 (M^+), 156, 155, 142, 129, 128, 115, and 77 (base).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.60; H, 6.47.

The remaining component of the reaction mixture consisted of white, crystalline solid (6.8 g), mp 153–154°, which could be separated from aldehyde **7** by fractional crystallization from pentane–ether. This same compound could be prepared in high yield by treating bicyclohexene **7** with *m*-chloroperbenzoic acid. The infrared spectrum of this compound showed bands at 2.90, 5.78, 7.01, 7.82, 7.91, 9.10, 9,80, 10.21, 10.38, 13.40, 13.60, and 14.35 μ. The ultraviolet spectrum (95% ethanol) has maxima at 282 and 290 nm (ε 590 and 510). The nmr spectrum (pyridine d_5, 60 MHz) shows broad singlets at τ 6.65 (1 H), 6.40 (1 H), 5.50 (2 H), 5.10 (1 H), and 3.20 (1 H), and multiplets at 3.70 (2 H) and 2.0–2.9 (9 H); mass spectrum *m/e* (base, parent − $C_7H_5ClO_2$), 171, 156, 142, 115, 105, and 77.

Anal. Calcd for $C_{20}H_{17}O_4Cl$: C, 67.32; H, 4.78. Found: C, 67.27; H, 4.89.

The structure of this material is assigned as 2-oxa-3-hydroxy-7-phenyl-8-(*m*-chloro)benzoxybicyclo[2.2.2]oct-5,6-ene (**8**) on the basis of its spectroscopic properties and by an oxidative elimination to biphenyl. To a solution of 0.16 g of chromium trioxide in 25 ml of pyridine at 0° was added a solution of 0.2 g of **8** in 5 ml of pyridine. The mixture was stirred at room temperature for 3 days. At the end of this time 100 ml of ether was added to the mixture and the resulting ethereal solution was washed with 5% hydrochloric acid. Evaporation of the ether gave 0.14 g of a yellow oil which was placed on a preparative thick layer plate. The plate was developed using a 1:1 pentane–ether mixture and the two major bands were extracted with acetone. The first band amounted to 39 mg and was identified as biphenyl by comparison with an authentic sample. The material in the second band (65 mg) was recovered starting material.

Peracid Oxidation of 7-Methylnorbornadiene.—To a stirred suspension of 4.5 g of sodium carbonate and 5.0 g of 7-methylnorbornadiene[29] in 350 ml of methylene chloride at 0° was added a solution of 7.65 g of *m*-chloroperbenzoic acid in 100 ml of methylene chloride. The mixture was stirred at 0° for 3 hr. At the end of this time the mixture was washed with water and dried over sodium sulfate. The solvent was removed *in vacuo* and the residual oil was distilled under reduced pressure to give 2.1 g of a colorless oil, bp 61–63° (20 mm). Analysis of this material by glpc (16% FS-1265 column at 100°) showed that it contained at least two components. The second and largest peak (37%) to be eluted from the vpc column was a colorless liquid whose structure is assigned as *exo*-4-methylbicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde (**10**) on the basis of the spectroscopic data cited: ir (neat) 3.40, 5.88, 6.85, 8.35, 9.30, 9.40, 9.60, 10.40, 11.50, 12.80, 13.20, and 13.50 μ; uv (cyclohexane) λ_{max} 230 and 235 nm (ε 580 and 600); nmr ($CDCl_3$, 100 MHz) τ 8.92 (d, 3 H, *J* = 7 Hz), 8.28 (1 H, t, *J* = 7 Hz), 8.02 (1 H, t, *J* = 7 Hz), 7.2–7.5 (m, 2 H), 4.20 (m, 2 H), 0.84 (d, 1 H, *J* = 6 Hz); mass spectrum *m/e* (M^+) 12a, 107, 93, 79, and 77.

The first peak present in the glpc chromatogram could not be easily separated from bicyclohexene **10**. In order to facilitate the separation, the above mixture was treated with silver oxide. A solution of 0.31 g of the above mixture in 12 ml of 25% ethanol containing 1.4 g of silver nitrate was treated with 15 ml of an aqueous solution of sodium hydroxide (0.5 g). The above reaction mixture was allowed to stir for 3 days at room temperature and was then filtered to remove the precipitated silver oxide. The aqueous solution was extracted with ether and the ethereal extracts were dried over sodium sulfate. Evaporation of the solvent gave 0.098 g of a yellow oil which was analyzed by vpc using a 15% FS-1265 column at 100°. The vpc scan showed the complete absence of bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde **10**. The oil consisted of a 1:1 mixture of the two endo norbornene epoxides (**11** and **12**) (16%) which could be separated by glpc. Both epoxides could be recovered from a refluxing benzene solution which contained a trace of *p*-toluenesulfonic acid. This provides strong support for the endo epoxide assignment. The first epoxide to be eluted from the column was a colorless oil: ir (CCl_4) 3.40, 6.85, 7.27, 7.45, 8.42, 10.10, 11.05, 11.23, and 11.52 μ; nmr (CCl_4, 100 MHz) τ 9.18 (3 H, d, *J* = 6 Hz), 7.44 (3 H, m), 6.60 (2 H, m), and 4.32 (2 H, m); mass spectrum *m/e* 122 (M^+), 107, 93, and 44 (base). On the basis of the spectra this compound is assigned as *endo*-2,3-epoxy-*syn*-7-methylbicyclo-[2.2.1]hept-5,6-ene (**11**). The second epoxide collected from the glpc chromatogram had very similar spectral properties and is assigned the isomeric structure **12**: nmr (CCl_4) τ 9.00 (3 H, d, *J* = 6 Hz), 7.58 (3 H, m), 6.58 (2 H, m), and 4.20 (t, *J* = 2 Hz, 2 H).

The aqueous solution from the above experiment was acidified with hydrochloric acid and extracted with ether. The ether was dried over sodium sulfate and the solvent was removed under reduced pressure to give a white, crystalline solid: mp 76–78° (42%); ir (KBr) 2.9–3.7, 5.84, 6.93, 8.15, 8.62, 10.71, 11.14, 12.90, 13.40, and 14.35 μ; nmr ($CDCl_3$, 100 MHz) τ 9.0 (3 H, d, *J* = 7 Hz), 8.32 (2 H, q, *J* = 8 Hz), 7.56 (1 H, t, *J* = 7 Hz), 7.00 (1 H, q, *J* = 7 Hz), 4.30 (2 H, m), and −1.28 (1 H, s); mass spectrum *m/e* 138 (M^+), 123, 105, 93 (base), and 77. On the basis of the data this material is assigned the structure of *exo*-4-methylbicyclo[3.1.0]hex-2-ene-*endo*-6-carboxylic acid.

Irradiation of *exo*-4-Methylbicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde (10).—Since the separation of endo epoxides **11** and **12** from bicyclohexene **10** was only attained with great difficulty, the irradiation was carried out on the initial epoxidized mixtures. A 0.5-g sample of this mixture was irradiated for 4 hr in 200 ml of acetone using a 550-W Hanovia lamp equipped with a Pyrex filter. Vpc analysis of the crude mixture on a 15% FS-1265 column at 100° indicated the presence of three major components. The second component on the chromatogram was identified as recovered bicycloaldehyde **10**. The third peak was a colorless oil (35%) whose structure is assigned as *exo*-4-methylbicyclo[3.1.0]-hex-2-ene-*exo*-6-carboxaldehyde (**13**) on the basis of the chemical and physical data cited: ir (CCl_4) 3.25, 3.35, 3.46, 3.67, 5.83, 6.91, 7.45, 9.10, 10.15, 11.87, 13.10, 13.35, and 14.45 μ; nmr (CCl_4, 100 MHz) τ 8.96 (3 H, d, *J* = 7 Hz), 8.06 (1 H, m), 7.4–7.6 (3 H, m), 4.56 (1 H, m), 4.20 (1 H, m), 0.86 (1 H, d, *J* = 4 Hz); mass spectrum *m/e* (M^+) 122, 107, 93, 79, and 77.

The exo isomer **13** could also be prepared by the base-catalyzed epimerization of the endo stereoisomer **10**. A 0.1-g sample of the endo isomer **10** and 0.1 g of sodium methoxide in 10 ml of methanol was refluxed for 1 hr. After evaporation of the solvent the oily residue was taken up in ether, washed with water, and dried over sodium sulfate. Removal of the solvent under reduced pressure gave a colorless oil which showed two peaks in the vpc chromatogram. Comparison of retention times and infrared and nmr spectra with that of the exo and endo aldehydes **13** and **10** established the identity of the major components present in the residue.

***endo*-2,3-Epoxy-7-methylbicyclo[2.2.1]heptane.**—The first peak collected from the preparative vpc chromatogram of the photolysis of **10** was a colorless liquid (20%) which proved to be an inseparable mixture of the syn and anti isomers of *endo*-2,3-epoxy-7-methylbicyclo[2.2.1]heptane (**14**, **15**). This was demonstrated by the chemical and spectroscopic data cited: ir (CCl_4) 3.45, 6.12, 6.85, 7.0, 7.25, 7.57, 7.70, 8.22, 8.45, 8.62, 9.12, 9.50, 10.2, 10.5, and 11.0 μ; mass spectrum *m/e* 124 (M^+), 109, 95, 93, 80 (base), and 67; nmr (CCl_4, 100 MHz) τ 9.22 (d, *J* = 7

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[29] P. R. Story and S. F. Fahrenholdt, *J. Org. Chem.*, **28**, 1716 (1963).

Hz), 8.88 (d, J = 7 Hz) (combined integration 3 H), 8.60 (broad s, 4 H), 8.12 (broad s, 2 H), 7.76 (q, J = 7 Hz, 1 H), 6.60 (broad s), 6.50 (broad s) (combined integration 2 H). Irradiation of the quartet at τ 7.76 with an external field collapsed the methyl doublets at τ 9.22 and 8.88 to singlets and also sharpened up the broad singlets at τ 6.60 and 6.50. The structure of this mixture was further verified by comparison with a sample independently synthesized as described below.

Catalytic Hydrogenation of the Crude Epoxidation Mixture Derived from 7-Methylnorbornadiene.—The crude epoxidation mixture (0.25 g) obtained from the treatment of 7-methylnorbornadiene with *m*-chloroperbenzoic acid was hydrogenated at 15 psig in a Paar shaker over 5% palladium on charcoal for 4 hr. After filtration to remove the catalyst, the solution was concentrated and submitted to preparative vpc. The residue was shown to contain two peaks. The minor peak (35%) in the chromatogram was a colorless oil whose spectral properties were identical with those of the mixture of isomers obtained from the photolysis of **10**. The major peak present in the vpc chromatogram (49%) was a colorless liquid whose structure is assigned as *exo*-8-methyl-2-oxabicyclo[3.2.1]oct-3-ene (**16**) on the basis of the physical data cited: ir (CCl_4) 3.45, 6.14, 6.85, 7.0, 7.25, 7.57, 7.7, 8.22, 8.45, 8.62, 9.12, 9.50 (s), 10.45, and 11.0 μ (s); mass spectrum m/e 124 (M^+), 109, 96, 95, 93, 91, 81 (base), and 68; nmr (CCl_4, 100 MHz) τ 9.14 (3 H, d, J = 7 Hz), 8.10 (broad s, 5 H), 7.70 (1 H, q, J = 7 Hz), 5.86 (1 H, broad s), 5.10 (1 H, t, J = 6 Hz), and 4.04 (1 H, d, J = 6 Hz).

Thermolysis of *exo*-4-Methylbicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde.—A 0.75-g sample of bicycylohexene **10** in 5 ml of benzene was heated in a sealed tube at 150° for 4 hr. The solvent was removed under reduced pressure and the residual oil was subjected to preparative thick layer chromatography. The plate was developed with a 25% ether–75% pentane solution. Extraction of the band (R_f 0.33) with methylene chloride followed by evaporation of the solvent gave 0.65 g (87%) of a colorless oil: ir (neat) 3.42, 3.52, 3.68, 6.02 (s), 6.24 (s), 6.45, 6.92, 7.45, 7.8, 7.97, 8.25, 8.70 (s), 9.7 (m), 10.8 (m), 11.55 (s), and 12.1 μ; uv (cyclohexane) λ_{max} 282 nm (ϵ 16,600); mass spectrum m/e 122 (M^+), 107, 93 (base), 91, 79, and 77; nmr (CCl_4, 100 MHz) τ 8.2 (s, 3 H), 7.4 (m, 2 H), 6.96 (m, 2 H), 4.28 (m, 1 H), 3.74 (1 H, broad s), 0.25 (1 H, d, J = 6 Hz). When the signal at τ 4.28 was saturated with an external field, the doublet at 0.25 collapsed to a singlet. On the basis of the data this compound is assigned the structure of unsaturated aldehyde **18**.

Another minor aldehyde (*ca.* 5%) was detected in the crude thermolysis residue but could not be separated from **18**. This compound has since been assigned the structure of **19** by Gilbert, Klumpp, and coworkers.[23]

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Electrochemical Preparation and Retrodiene Reaction of 1,4-Bis(methoxycarbonyl)bicyclo[2.2.2]octa-2,5-diene

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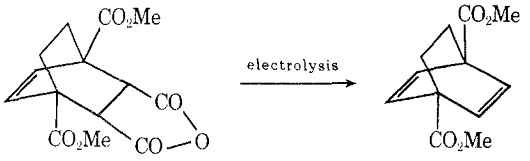
1,4-Bis(methoxycarbonyl)bicyclo[2.2.2]octa-2,5-diene (**1**) was synthesized by electrolytic decarboxylation of the adduct of maleic anhydride and dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate. Addition of a small amount of 4-*tert*-butylcatechol to the electrolysis reaction was found to increase the yield of **1** from 30 to 65%. Replacement of the usual solvent system for this reaction (pyridine, water, triethylamine) with acetonitrile, water, pyridine, triethylamine decreased the reaction time from 12 to 2 hr. Compound **1** readily undergoes a retrodiene reaction to produce ethylene and dimethyl terephthalate. Energy parameters for this reaction are $\Delta H^{\ddagger}$, 26.8 ± 0.3 kcal/mol; $\Delta S^{\ddagger}$, −0.4 ± 0.9 eu. CNDO/2 calculations performed for this reaction indicate that the lowest energy reaction pathway involves loss of an ethylene-like two-carbon fragment from a nearly planar hexadiene ring.

The retro Diels–Alder reaction, particularly when aromatic products are produced, has been extensively used to generate unstable intermediates and relatively inaccessible olefins.[1,2] We would like to report[3] the synthesis of 1,4-bis(methoxycarbonyl)bicyclo[2.2.2]-octa-2,5-diene (**1**) and the activation parameters for the retrodiene decomposition of dihydrobarrelene **1** to dimethyl terephthalate and ethylene. The key step in the synthesis of compound **1** was achieved by electrochemical oxidation of 1,4-bis(methoxycarbonyl)-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (**2**) at low temperature, a technique of considerable potential for the preparation of thermally unstable or chemically labile molecules.



2 **1**

[1] For reviews of the retrodiene reaction see (a) H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968); (b) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966); (c) A. S. Onishchenko, "Diene Synthesis," Oldbourne Press, London, 1964.

[2] For use of the retrodiene reaction to generate unstable intermediates and inaccessible olefins see (a) E. J. Corey and W. L. Mock, *J. Amer. Chem. Soc.*, **84**, 685 (1962); (b) G. D. Peddle, D. N. Roark, A. M. Good, and S. G. McGeachin, *J. Amer. Chem. Soc.*, **91**, 2807 (1969); (c) N. D. Field, *ibid.*, **83**, 3504 (1961); (d) C. M. Wynn and P. S. Klein, *J. Org. Chem.*, **31**, 4251 (1966); (e) W. S. Wilson and R. N. Warrener, *Chem. Commun.*, 211 (1972); (f) U. E. Wiersum and W. J. Myo, *ibid.*, 347 (1972); (g) R. Kreher and J. Seubert, *Z. Naturforsch. B*, **20**, 75 (1965); (h) R. N. Warrener, *J. Amer. Chem. Soc.*, **93**, 2346 (1971).

[3] This work is a continuation of a program concerned with synthesis of bicyclic molecules that are functionally substituted at the bridgehead positions. For previous papers see D. C. Owsley and J. J. Bloomfield, *J. Amer. Chem. Soc.*, **93**, 782 (1971); *J. Org. Chem.*, **36**, 4160 (1971); *Org. Prep. Proced. Int.*, **3**, 61 (1971).