hexanone was slowly added and the resulting mixture was stirred for 24 hr at 0°. Then water was added (10–15 ml) slowly to decompose the excess hydride and to hydrolyze the reaction mixture. The boronic acid formed was oxidized by adding 66 ml of 3 *N* sodium hydroxide followed by *dropwise* addition of 66 ml of 30% hydrogen peroxide (vigorous reaction). The resulting mixture was stirred at 30–50° for 1 hr. Then the reaction mixture was extracted five times with 60-ml portions of ether and the ether extract was washed five times with equal amounts of ice water to remove diglyme. The ether extract was dried over magnesium sulfate. After the solvent was removed, the mixture was distilled at 20 mm to remove cyclohexanol (from the oxidation). The pressure was then reduced to obtain 27 g (99%) of 2-cyclohexylcyclohexanol (cis 96% by glpc analysis on a TCEP column), bp 117–118° (6 mm), mp 59–61°, *p*-nitrobenzoate mp 112–114° (lit.[21] mp 61°, *p*-nitrobenzoate mp 113°).

B. Preparation of *cis*-2-Phenylcyclopentanol. To a solution of 150 ml (150 mmol) of a 1.0 *M* solution of disiamylborane in THF in a 500-ml flask maintained at 0° under nitrogen was added 14.4 g (90 mmol) of 2-phenylcyclopentanone over a period of 15 min. The resulting mixture was stirred at 0° for 24 hr and then worked up as usual. The volatile solvents and siamyl alcohol were removed at 40–45° (10 mm). Distillation of the residue yielded 11 g (75%) of 2-phenylcyclopentanol (cis 97% by glpc), bp 118° (8 mm), n^{20}D 1.5433, *p*-toluenesulfonate mp 96–97° [lit.[22] pure cis isomer, bp 111–113° (5 mm), n^{20}D 1.5460, *p*-toluenesulfonate mp 97–98°].

Registry No.—Cholestan-6-one, 570-46-7; cholestan-6*β*-ol, 35490-51-8; 3,5-cyclocholestan-6-one, 3839-06-6; 3,5-cyclocholestan-6*α*-ol, 508-41-8; 3,5-cyclocholestan-6*α*-ol acetate, 17132-05-7; *cis*-2-cyclohexylcyclohexanol, 51175-62-3; *cis*-2-phenylcyclopentanol, 2362-73-4; 2-phenylcyclopentane, 1198-34-1; dithexylborane, 20622-63-3.

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(2) Graduate Research Assistant on Grant No. DA-ARO(D)-31-124-117 supported by the U. S. Army Research Office (Durham).
(3) (a) For a comprehensive review, see J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, pp 84–132; (b) A. V. Kamernitzky and A. A. Akhrem, *Tetrahedron*, **18**, 705 (1962); (c) O. H. Wheeler and J. L. Mateos, *Can. J. Chem.*, **36**, 1431 (1958); (d) S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956); (e) H. C. Brown and H. R. Deck, *J. Amer. Chem. Soc.*, **87**, 5620 (1965); (f) W. G. Dauben, G. J. Fonken, and D. S. Noyce, *ibid.*, **78**, 2579 (1956); (g) J. C. Richer, *J. Org. Chem.*, **30**, 324 (1965); (h) H. Haubenstock and E. L. Eliel, *J. Amer. Chem. Soc.*, **84**, 2363 (1962); (i) J. Klein, E. Dunkelblum, E. L. Eliel, and Y. Senda, *Tetrahedron Lett.*, 6127 (1968); (j) E. L. Eliel and Y. Senda, *Tetrahedron*, **26**, 2411 (1970); (k) M. Chêrest and H. Felkin, *Tetrahedron Lett.*, 2205 (1968); (l) J. A. Marshall and R. D. Carroll, *J. Org. Chem.*, **30**, 2748 (1965); (m) E. C. Ashby, J. R. Boone, and J. P. Oliver, *J. Amer. Chem. Soc.*, **95**, 5427 (1973); (n) J. Klein, *Tetrahedron Lett.*, 4307 (1973).
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Oxymercuration–Demercuration and Hydroboration–Oxidation of *endo*-Dicyclopentadiene (*endo*-Tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene)[1a]

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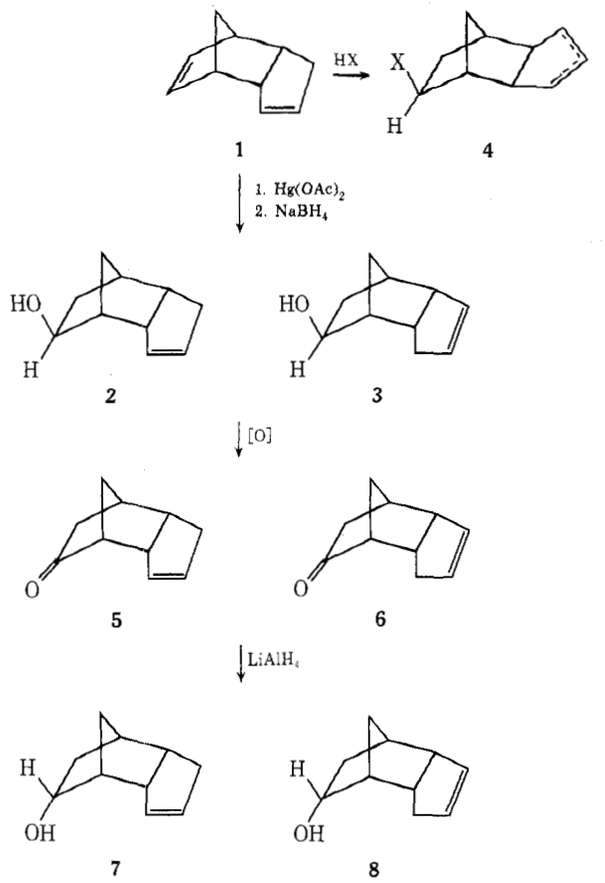
The course of monohydration of *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (1) (*endo*-dicyclopentadiene) with hydroboration–oxidation and oxymercuration–demercuration is compared and the stereochemistry of the alcohols is elucidated both by spectral studies and by acid-catalyzed and photochemical cyclizations to ethers of novel structures. The addition of nitrosyl chloride to 1 is also described.

Hydroboration–oxidation[2] and oxymercuration–demercuration[3,4] have proved to be efficient methods for the hydration of carbon–carbon double bonds without appreciable rearrangement. The hydroboration of unsymmetrical olefins normally leads to the anti-Markovnikov hydration product, while oxymercuration–demercuration is equally convenient for the preparation of Markovnikov alcohols. Synthesis of hydroxy olefins by monohydration of dienes has been accomplished using these procedures.[5,6] Previous studies of electrophilic addition to *endo*-dicyclopentadiene (1) have been concerned with the determination of the stereochemistry of addition (exo *vs.* endo, cis *vs.* trans) and the effect of the reagent upon the ring system, namely the tendency toward rearrangement to a derivative of *exo*-dicyclopentadiene (4).[7-11] Although the possibility of isomers differing only in the position of a double bond is often acknowledged, amounts have seldom been reported and specific structures have rarely, if ever, been proposed. In the present work the monohydration of 1 by these two methods is compared and the stereochemistry of the alco-

Scheme I



holic products is elucidated, in part, by acid-catalyzed and photochemical cyclizations to provide ethers of novel structure.

Results

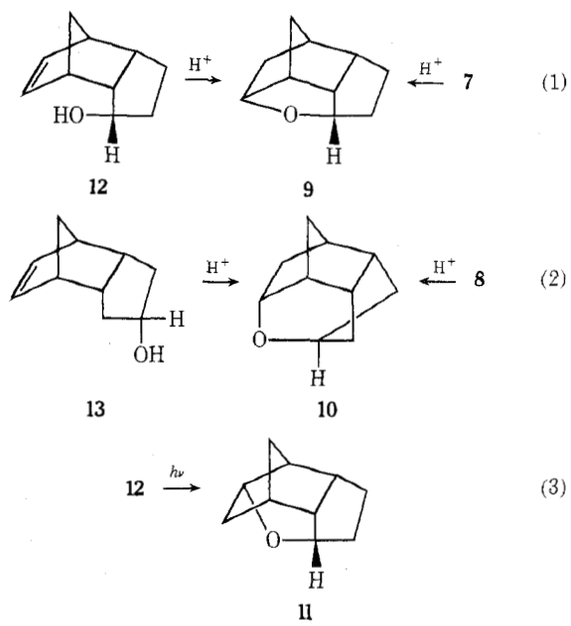
Oxymercuration–Demercuration. The reaction of **1** with mercuric acetate has been reported[10,12] to give exo,-cis addition exclusively to the norbornyl double bond without rearrangement. Reduction of the organomercurial[13] was assumed[10] to yield a mixture of alcohols **2** and **3**. The existence of a mixture could not be confirmed because of an unfortunate similarity of glpc retention times and nmr spectral absorbances.

The presence of a mixture was indicated when oxidation of this hydration product yielded isomeric ketones, **5** and **6**, with one isomer predominant (70%). Conversion of the alcohols to the corresponding acetates gave another mixture of similar composition. These should also reflect relative amounts of exo alcohols derived from oxymercuration–demercuration of **1** assuming complete conversion of both exo-hydroxy isomers in the oxidation and esterification reactions. Hydride reduction of the ketones afforded a mixture of the endo alcohols **7** and **8**, with one isomer again predominant by about 2:1. This series of reactions is summarized in Scheme I.

Addition of dry hydrogen bromide to an ether solution of the major endo-hydroxy isomer resulted in almost immediate reaction (*ca.* 20 min). The lone product is a volatile solid containing no bromine and exhibiting neither vinyl proton resonances in the nmr spectrum nor hydroxyl stretching absorbance in the infrared. Indeed, the product of the reaction would appear to be one of three cyclic ethers, **9**, **10**, or **11**. Cyclizations such as this during electrophilic addition are well known in structurally related norbornenyl compounds[14,15] as well as in acyclic systems.[11,13]

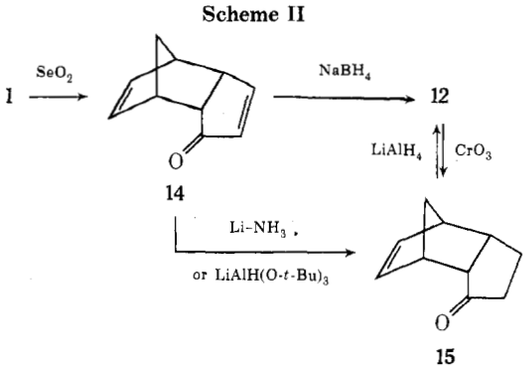
Only after prolonged reaction (*ca.* 24 hr) with dry hydrogen bromide did the minor endo-hydroxy alcohol yield a similar solid, which was, however, clearly different from that obtained with the major isomer. Again, one of the three cyclic ethers is possible depending upon the structure of the starting alcohol and the site of protonation in the cyclopentenyl ring.

In order to determine the structures of these ethers and thereby the structures of the hydroxy precursors, unequivocal syntheses of **9**, **10**, and **11** were undertaken. For this purpose, compounds **12** and **13** were prepared, since they contained the hydroxyl group of appropriate stereochemistry in the cyclopentyl ring and the olefinic function in the norbornenyl portion of the molecule. Thus cyclization to **9** and **10**, if effected, would be in the direction opposite to that for **7** and **8**.

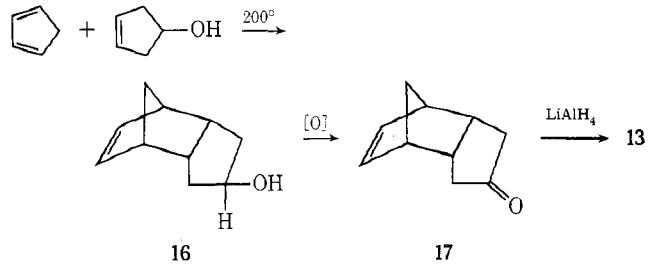


Anti 3-hydroxy olefin **12** was prepared by oxidation of **1** to ketone **14** with selenium dioxide[16] followed by hydride reduction to the alcohol.[17] Other routes to **12** included reductions of **14** with lithium in liquid ammonia[18] or with lithium tri-*tert*-butoxyaluminum hydride[19] to ketone **15**, which was reduced with hydride to the desired compound (Scheme II). Cyclization of **12** with dry hydrogen bromide gave an ether to which structure **9** has been assigned and which was identical with the ether obtained from the acid-catalyzed cyclization of the major endo-hydroxy isomer (eq 1). Alcohol **7** can afford **9** directly, whereas **8** could yield **9** only after the isomerization of the double bond. Thus structure **7** is assigned to the major endo-hydroxy isomer and **2** is the corresponding exo-hydroxy olefin (70%) formed initially in the oxymercuration–demercuration of **1**.

Scheme II



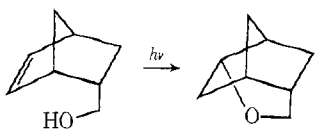
Scheme III



16 17

Synthesis of anti-4 alcohol **13** was accomplished beginning with the Diels–Alder addition of cyclopentadiene to 4-hydroxycyclopentene. The endo-addition product **16** is the predominant isomer of the reaction and the configuration of the 4-hydroxyl group is syn.[20] Oxidation of **16** to the 4-keto derivative **17** followed by hydride reduction gave anti-4 alcohol **13** (Scheme III). Cyclization of **13** afforded ether of structure **10**, identical with that obtained from the minor endo-hydroxy isomer (eq 2). This confirms structure **8** as that of the minor endo alcohol and **3** is assigned as the minor alcohol (30%) obtained from the oxymercuration–demercuration of **1**.

Under photochemical conditions, 5-norbornene-2-*endo*-methanol (**18**) has been shown to cyclize to the six-membered ring ether **19**[21] (eq 4). Similarly, in order to com-



(4)

18 19

plete the series of ether derivatives of **1**, a photochemically induced cyclization was attempted with anti-3 alcohol **12**. Irradiation of **12** afforded a single volatile product. In addition to distinctive chromatographic and spectral characteristics indicative of cyclization, this ether is also distinguishable from **9** and **10** by being a liquid. Structure **11** is assigned to this photoether (eq 3).

Hydrogen bonding between hydroxyl groups and π bonds has been observed in alcohols **7** and **8** as well as in other compounds where orientation of the hydroxyl group toward a π system permits similar interactions.[22] Specifically, the infrared spectrum at low concentration (0.005 *M* in CCl_4) has been reported[23] to exhibit two different hydroxyl absorptions for each alcohol. One isomer had absorptions at 3575 and 3624 cm^{-1} or a difference of 49 cm^{-1}. This shift to lower frequency, attributed to the OH–π interaction, was present to a lesser extent in the other isomer, which exhibited an absorption at 3591 cm^{-1}, a difference of only 31 cm^{-1} from the free hydroxyl absorption at 3622 cm^{-1}. Structure **7** was thus assigned to the isomer having the larger difference between "free" and "bonded" hydroxyl absorptions on the basis that the double bond is closer to the hydroxyl group in **7** than in **8**, permitting a stronger OH–π bond.[23]

This technique was applied in the present study to the separated endo alcohols **7** and **8**. The results in Table I are consistent with the assignment of structure **7** to the major endo alcohol and **8** to the minor isomer.

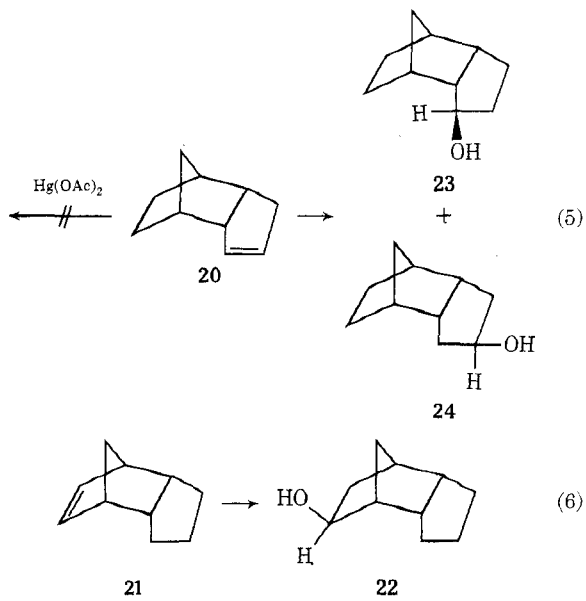
It is significant that under normal reaction conditions mercuric acetate does not attack the cyclopentenyl ring in **1** even if the norbornyl double bond is saturated as in **20**[24] (eq 5). However, alcohols **7** and **8** react rapidly with mercuric acetate and upon reduction yield ethers **9** and **10**, respectively.

Hydroboration–Oxidation. Reaction of 1,2-dihydro-*endo*-dicyclopentadiene (**21**) with diborane followed by oxidation with basic hydrogen peroxide has been reported to give the anticipated exo-hydroxy alcohol **22**[25] (eq 6). Hydroboration of **20**, unlike oxymercuration, proceeds efficiently to give a mixture of syn alcohols **23** and **24**[24] in a ratio of about 3:2[26] (eq 5). The ready hydroboration of the cyclopentenyl ring in **20** has been difficult to explain in view of the normal chemical inertness of this double bond toward electrophilic reagents.[8,12,27] It is not surprising, then, that a significant amount of the product (63%) from **1** was derived from hydroboration of the cyclopentyl double bond (**16** and/or **25**) while the remainder exhibited the hydroxy function in the norbornyl ring (**2** and/or **3**).[26]

Table I

Endo alcohol isomer	Observed ir, cm^{-1}	Reported[a] ir, cm^{-1}	Assigned structure[a]
Major (70%)	3572	3624 (free) 3575 (bonded)	**7**
Minor (30%)	3623 3589	3622 (free) 3591 (bonded)	**8**

[a] Reference 23.

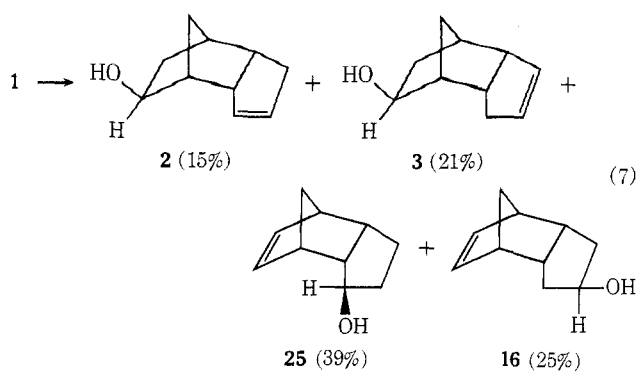


(5)

(6)

20 23 24 21 22

Oxidation of this mixture of hydroxy olefins with chromic acid gave a mixture of isomeric ketones. Chromatographic retention times of the components from this mixture were compared with those of authentic ketones **5**, **6**, **15**, and **17** synthesized by unequivocal routes during the oxymercuration study of **1**. Indeed, all four ketones were found to be present in this mixture, confirming alcohols **2**, **3**, **16**, and **25** as the original products of hydroboration–oxidation of **1**.



(7)

2 (15%) 3 (21%) 25 (39%) 16 (25%)

Recently norbornyl double bonds have been found to form strong complexes with silver ion.[28] Like alcohols **16** and **25**,[26] ketones **15** and **17** readily react with silver ion to

form water-soluble complexes, whereas ketones **5** and **6** are relatively unreactive. Thus extraction with aqueous silver nitrate of an ether solution containing the four ketones results in quantitative separation of **5** and **6** from complexed ketones **15** and **17**. Ketone **6** was found to be the major isomer (58%) derived from reaction at the norbornyl double bond during hydroboration. Saturation of the aqueous layer containing the complexed ketones with sodium chloride permitted recovery of ketones **15** and **17**. Analysis of this mixture showed ketone **15** to be the major isomer (62%) derived from hydroboration in the cyclopentenyl ring.

Also ketones **15** and **17** gave quantitative yields of insoluble bisulfite addition complexes, while **5** and **6** were relatively unreactive toward the reagent. Separation and analysis by this method gave results in complete agreement with those obtained in the silver ion complexation separation.

Extrapolation of the results obtained from analysis of the ketone mixture to the original mixture of alcohols gave the following alcohols from the hydroboration–oxidation of **1**: 39% **25**, 25% **16**, 21% **3**, and 15% **2** (eq 7). It is consistent that the major alcohol derived from hydroboration of the norbornyl double bond (**3**) is isomeric with the major product (**2**) obtained *via* oxymercuration–demercuration.

Addition of Nitrosyl Chloride. The addition of nitrosyl chloride to **1** has been shown to occur exclusively at the norbornyl double bond to give a nitroso chloride dimer of unrearranged skeleton.[7a] Reaction of the dimer with zinc in acetic acid followed by hydrolysis of the resulting oximes yields ketones **5** and **6** in amounts of 51 and 49%, respectively. Thus the orientation of addition of nitrosyl chloride to **1** appears to be unaffected by the cyclopentyl double bond.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus in open capillary tubes and are uncorrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.; Atlantic Microlab, Inc., Atlanta, Ga.; and M-H-W Laboratories, Garden City, Mich. Nmr spectra were obtained with a Varian A-60, T-60, and HA-100 spectrometer using tetramethylsilane (TMS) as an internal standard. Infrared spectral data were obtained on a Perkin-Elmer Model 621 high-resolution spectrometer. Analytical glpc analyses were performed on a Varian Aerograph Model 1200 flame-ionization instrument using 5 ft × 0.125 in. columns with a helium carrier gas flow rate of 25 ml/min. Preparative glpc was performed on an Aerograph Autoprep Model A-700 thermal conductivity instrument using 10 ft × 0.375 in. and 20 ft × 0.375 in. columns with a helium carrier gas flow rate of 200 ml/min.

Oxymercuration–Demercuration of 1. Preparation of *exo*-9- and 8-Hydroxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (2 and 3). The general procedure of Brown[4] was followed using 66.0 g (0.500 mol) of **1**. Distillation of the product gave 72 g (95%) of a colorless liquid, bp 90–100° (5 mm) [lit.[7a] bp 91° (4 mm)]. Analytical glpc on a Carbowax 20M column at 140° and a SE-30 column at 100° indicated a single product.

Preparation of the Acetates of 2 and 3. The acetates of the alcohols were prepared in the usual manner using acetic anhydride in dry pyridine. The product was distilled to yield (56%) a colorless liquid, bp 92–93° (1.0 mm). Analytical glpc on 3% SE-30 at 100° gave two peaks at 28% and 72%. *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.87; H, 8.36.

Oxidation of Alcohols 2 and 3. Preparation of *endo*-Tricyclo[5.2.1.$0^{2,6}$]dec-3-en-9- and -8-ones (5 and 6). The Jones[29] oxidation procedure was employed on 40 g (0.27 mol) of the mixture of **2** and **3**. The viscous yellow oil obtained was sublimed at 50° (0.35 mm) to yield a waxy solid, mp 65–70°. Analytical glpc on a 10% Carbowax 20M column at 170° indicated the presence of two products in amounts of 72 and 28%. Preparative glpc on a 20% SE-30 column at 160° was used to separate the mixture. The 28% ismomer (**6**) had mp 85–88° and the 72% isomer (**5**) had mp 82–84° (lit.[8a] mp 83–84°). Nmr spectra showed vinyl proton resonances centered at δ 5.60 for **6** and δ 5.63 for **5**. The infrared spectrum had a strong absorption at 1740 cm^{-1}.

Lithium Aluminum Hydride Reduction of Ketones 5 and 6. Preparation of *endo*-9- and -8-Hydroxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-enes (7 and 8). To a stirred suspension of 5.0 g (0.13 mol) of lithium aluminum hydride in 250 ml of anhydrous ether was added 8.9 g (0.060 mol) of a mixture of **5** and **6** in 30 ml of dry ether. The mixture was refluxed overnight and hydrolyzed by careful addition of 9 ml of water followed by 9 ml of sodium hydroxide and then 25 ml of water. The granular precipitate was removed by filtration and the ether layer was dried. Solvent was removed to yield a light yellow oil which solidified upon standing. Sublimation at 40–50° (0.3 mm) afforded 8.0 g (89%) of isomeric alcohols **7** and **8**. Analytical glpc at a 10% Carbowax 20M column indicated two products in amounts of 67% (**7**) and 33% (**8**). Separation of the isomeric endo alcohols was accomplished on a 10% Carbowax 20M column at 140°. The minor isomer (**8**) had mp 109–110° and the major (**7**), mp 114–116°. Nmr spectra showed vinyl proton resonances centered at δ 5.73 (2 H) for **8** and at δ 5.73 (1 H) and 6.03 (1 H) for **7**.

Cyclization of 7 (Also 12 and 13) with Dry Hydrogen Bromide. Preparation of 11-Oxatetracyclo[5.2.1.$1^{5,8}$.$0^{2,6}$]undecane (9). To 50 ml of ether was added with stirring 0.8 g (5×10^{-3} mol) of **7**. Dry hydrogen bromide was generated by heating a mixture of 5.0 g of potassium bromide in 20 g of polyphosphoric acid. The evolved gas was passed through a bromine trap containing phenol, through calcium chloride drying tubes, and finally through a gas dispersion tube, into the ether solution. After 30 min chromatographic analysis showed the absence of starting alcohol. The ether mixture was then washed with saturated sodium bicarbonate and dried over $MgSO_4$. Evaporation of solvent and sublimation of the remaining solid residue at 40° (0.2 mm) gave a waxy solid, mp 97–100°. Analytical glpc on a 10% Carbowax 20M column at 140° show a single component. The nmr spectrum contained a multiplet at δ 4.35 (2 H). *Anal.* Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.84; H, 9.37.

Cyclization of 8 with Dry Hydrogen Bromide. Preparation of 11-Oxatetracyclo[5.2.1.$1^{4,8}$.$0^{2,6}$]undecane (10). The procedure for the cyclization of **7** was employed using 0.8 g (5×10^{-3} mol) of **8** with the exception that the reaction mixture was stirred for 24 hr. The product was isolated from residual starting alcohol by preparatory glpc using a 20% Carbowax column at 145°. The nmr spectrum showed a broad resonance at δ 4.22 (2 H). *Anal.* Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.77; H, 9.38.

endo,syn-**Tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-ol** was prepared by the selenium dioxide oxidation procedure of Rosenblum[16] using 66 g (0.50 mol) of **1**. Distillation afforded 42 g (57%) of colorless liquid, bp 78–82° (0.8 mm) [lit.[19] bp 73–74° (0.8–0.5 mm)].

Oxidation of *endo,syn*-Tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-ol. Preparation of *endo*-Tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one (14). The procedure for the oxidation of **2** and **3** was employed with 50 g (0.33 mol) of dienol. The product was 40 g (81%) of colorless liquid which solidified upon standing. Sublimation at 90° (1.2 mm) gave colorless crystals, mp 61–62° (lit.[19] mp 65.5–67.5°).

Sodium Borohydride Reduction of Dienone 14. Preparation of *endo,anti*-Tricyclo[5.2.1.$0^{2,6}$]dec-8-en-3-ol (12). To 3.5 g (0.024 mol) of ketone **14** in 30 ml of tetrahydrofuran was added with stirring 30 ml of a basic solution (3 *M* NaOH) containing 0.60 g (0.016 mol) of $NaBH_4$. The reduction was completed within 30 min as shown by analytical glpc. After separation of the tetrahydrofuran layer and extraction of the aqueous layer with ether the organic solutions were combined and dried over $MgSO_4$. Solvent was removed under vacuum, and a clear oil which solidified upon standing was isolated. Sublimation at 100° (0.5 mm) gave 3.0 g (83%) of a colorless solid, mp 126–128° (lit.[19] mp 134.5–137.5°).

Photochemical Cyclization of 12. Preparation of 11-Oxatetracyclo[5.2.1.$1^{3,8}$$0^{2,6}$]undecane (11). The procedure of Kropp and Krauss[21] for the photochemical cyclization of **18** was used on 2.6 g (0.017 mol) of **12**. Analytical glpc using a Carbowax 20M column showed a single product (26% conversion) isolated as a liquid by preparative glpc using a 20% Carbowax 20M column at 160°. An nmr spectrum exhibited a resonance at δ 4.20 (2 H). *Anal.* Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.97; H, 9.23.

endo-**Tricyclo[5.2.1.$0^{2,6}$]dec-8-en-3-one (15). A. By Oxidation of Alcohol 12.** The oxidation procedure for the preparation of ketones **5** and **6** was used on 6.0 g (0.040 mol) of **12**. Sublimation of the resulting product at 70–75° (1.0 mm) gave 4.4 g (74%) of a waxy solid, mp 94–96° (lit.[19] mp 100–103°).

B. By Direct Lithium–Ammonia Reduction of Dienone 14. The procedure of Johns[18] was used on 10 g (0.068 mol) of **14**. The

product was purified by sublimation to give 6.2 g (61%) of ketone **15** identical with that obtained previously.

C. By Reduction of 14 with Lithium Tri-*tert*-butoxyaluminum Hydride. The procedure for the preparation of **15** employed by Dilling and Plepys[18] was employed using 35 g (0.24 mol) of **14**. The product was a brown liquid which upon sublimation at 100° (5 mm) gave 29 g (84%) of a colorless solid, 85% of which was **15** and 15%, **22** by analytical glpc.

Diels–Alder Condensation of 4-Hydroxycyclopentene with Cyclopentadiene. Preparation of *endo,syn*-Tricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-ol (16). A mixture containing 18.0 g (0.21 mol) of 4-hydroxycyclopentene and 9.5 g (0.072 mol) of **1** was sealed in a Carius tube and heated at 200° for 4 hr. After cooling, the tube was opened and ether was added to the reaction mixture. Precipitated polymers were removed by filtration and the ether layer was dried over $MgSO_4$. Solvent was removed, and the oil which remained was distilled to yield 9.1 g (42%) of the addition products. Analytical glpc analysis on a Carbowax 20M column at 150° indicated the presence of **16** (70%) and the exo-skeleton product(s) (30%). Nmr spectra showed vinyl proton resonances at δ 6.10 (endo skeleton) and 5.93 (exo skeleton) also in a ratio of about 2:1. *Anal.* Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.90; H, 9.31.

Dipyridine–Chromium(VI) Oxide Oxidation of Syn Alcohol 16. Preparation of *endo*-Tricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-one (17). To 800 ml of methylene chloride distilled from P_2O_5 was added 45 g (0.12 mol) of the dipyridine–chromium(VI) oxide complex[30] and the suspension was stirred for 1 hr to dissolve as much of the complex as possible. A solution containing 4.3 g (0.029 mol) of the alcohols from the Diels–Alder reaction in 60 ml of methylene chloride was added to the suspension over a 5-min period. Stirring was continued for about 30 min, during which time black chromium reduction products were deposited. The reaction mixture was then filtered through alumina until a clear solution was obtained. Solvent was removed under vacuum, leaving 3.3 g (78%) of a colorless liquid. Nmr analysis of the products showed vinyl proton resonance at δ 6.07 (endo skeleton, 69%) for **17** and 5.93 (exo skeleton). The infrared spectrum showed carbonyl absorption at 1740 cm^{-1}. *Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04, H, 8.16. Found: C, 81.23; H, 8.38.

Lithium Aluminum Hydride Reduction of 17. Preparation of *endo,anti*-Tricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-ol (13). The procedure for the reduction of **5** and **6** was used on 3.0 g of a mixture of ketone **17** and its exo isomer. Distillation of the product gave 2.1 g (70%) of alcohol **13** and reduction products of the exo-skeleton isomer, bp 89–92° (0.5 mm). Recrystallization four times from *n*-pentane gave colorless crystals of isomerically pure **13**, mp 64–65° (lit.[20] mp 65.5–66.5°).

Hydroboration–Oxidation of 1. Preparation of *endo,syn*-Tricyclo[5.2.1.$0^{2,6}$]dec-8-en-3- and -4-ol (25 and 16) and *exo*-9- and -8-Hydroxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (2 and 3). The method of Brown[2c] for the preparation of *exo*-norborneol from norbornene was employed using 43.6 g (0.330 mol, 10% excess) of **1**. The product was distilled and 26 g (58%) of the fraction of bp 85–100° (5 mm) was obtained. Analytical glpc on an SE-30 column at 95° and a Carbowax 20M column at 140° indicated the presence of two products in amounts of 63–37%. Separation was achieved by preparative glpc using a Carbowax 20M column at 160°. The 63% fraction showed resonances centered at δ 5.55 (2 H) in the nmr spectrum.

Oxidation of the Alcohol Mixture from Hydroboration of 1. Preparation of *endo*-Tricyclo[5.2.1.$0^{2,6}$]dec-8-en-3- and -4-one (15 and 17) and *endo*-Tricyclo[5.2.1.$0^{2,6}$]dec-3-en-9- and -8-one (5 and 6). The procedure which has been employed for the oxidation of alcohols **2** and **3** was used on 9.4 g of the alcohol mixture. Sublimation at 80° (1 mm) gave 8.5 g (90%) of a colorless solid. Analytical glpc on a 10% Carbowax 20M column at 140° indicated the presence of four products. *Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.00; H, 8.24.

Separation of Ketones 5 and 6 from 15 and 17. A. By Silver Ion Complexation. A 5-ml ether solution containing 1 g of the ketone mixture was extracted six times with 3-4-ml portions of 1 *M* $AgNO_3$. The aqueous portions were extracted with ether and back extracted with the silver nitrate solution. Progress of the separation was followed by analytical glpc using a Carbowax 20M column at 140°. The combined ether solutions were washed with water and dried over $MgSO_4$. Analysis of the components of the ether extractions showed the presence of two ketones in amounts of 58% **6** and 42% **5**. The nmr spectrum show only the cyclopentenyl double bond resonance at δ 5.60 in the olefinic region.

The combined aqueous portions were extracted four times with a total of 40 ml of ether to remove small traces of ketones **5** and **6** and then were saturated with sodium chloride. Extraction with ether gave a solution of ketones **15** (62%) and **17** (38%). Nmr analysis of the olefinic region showed only the resonances of norbornenyl olefinic protons at δ 6.10 (2 H) for both isomers.

B. By Reaction with Sodium Bisulfite. To a solution of 30 g of the ketone mixture in 75 ml of ether was added 75 ml of saturated aqueous sodium bisulfite. After 48 hr the solid which had formed was removed by filtration and the ether portion was separated and dried over $MgSO_4$. Analysis of this solution indicated the presence of two ketones, **5** (42%) and **6** (58%). Separation of the ketones was accomplished by preparative glpc using a 10% Carbowax column at 160°. The nmr spectrum of each compound contained olefinic proton resonances at δ 6.10 (2 H) indicative of a cyclopentenyl double bond.

Preparation of the Oximes of 5 and 6 *via* Nitrosation. The method of Wilder and Youngblood[7a] was used on 8.4 g (0.064 mol) of **1**. After reduction with zinc and acetic acid of the nitroso chloride dimers, 4.4 g (42%) of the oximes of **5** and **6** was isolated.

Levulinic Acid Hydrolysis of the Oximes of Ketones 5 and 6. The procedure of DePuy and Ponder[31] was employed using 2.0 g (0.014 mol) of the oximes. Vacuum distillation of the product gave 1.8 g (82%) of ketones **5** (49%) and **6** (51%), as analyzed by analytical glpc on a Carbowax 20M column at 150°.

Registry No.—**1**, 1755-01-7; **2**, 36807-74-6; **2** acetate, 51175-94-1; **3**, 36807-75-7; **3** acetate, 51175-95-2; **5**, 51260-49-2; **6**, 51175-96-3; **7**, 51175-97-4; **8**, 51260-50-4; **9**, 51175-98-5; **10**, 51202-19-8; **11**, 51175-99-6; **12**, 22981-83-5; **14**, 5530-96-1; **16**, 50506-62-2; **17**, 51176-00-2; 4-hydroxycyclopentene, 14320-38-8; cyclopentadiene, 542-92-7.

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Chlorocarbonium Ions. I. Synthesis of Decachlorobicyclo[3.3.0]octa-2,6-diene and Its Chemistry

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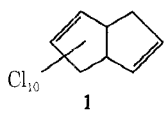
The reaction of hexachlorocyclopentadiene with 1,1,2,3,3-pentachloropropene in the presence of anhydrous aluminum chloride furnished decachlorobicyclo[3.3.0]octa-2,6-diene (**1**) in 75% yield. Evidence for the structure of **1** was obtained from its ^{13}C nmr spectrum, nuclear quadrupole resonance spectrum, elemental analysis, and hydrogenolysis. Hydrolysis of **1** with sulfuric acid afforded diketones **2** and **3** and the hydroxy diketone **4**. A part of **1** rearranged to **6** at 250–270°. The reaction of **1** with 2 equiv of potassium hydroxide in methanol afforded the monomethoxy derivative **7** in good yield, whereas a large excess of potassium hydroxide in methanol furnished small yields of **10** and **11**. Upon treatment with anhydrous aluminum chloride **7** furnished **8** and/or **9** while **10** gave **9**. Similarly, **11** furnished **12**. Treatment of **9** with sulfuric acid produced **12**.

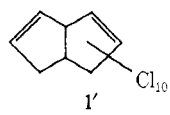
The well-known Prins reaction involves alkylation of a polyhalo olefin with a chlorocarbonium ion, derived from a halocarbon and a Lewis acid such as aluminum chloride.[1] We have extended this reaction to the synthesis of new conjugated cyclic chlorocarbons, a subject in which we have been actively interested,[2] by investigating the reaction between polyhalogenated carbocations and polyhalogenated cyclopentadienes.

Although pentachloropropenium cation[3] failed to react with hexachlorocyclopentadiene at 75–80°, 1,1,2,3-tetrachloropropenium cation[4] prepared from 1,1,2,3,3-pentachloropropene[5] and anhydrous aluminum chloride in the absence of any added solvent reacted with hexachlorocyclopentadiene at 75–80° to yield decachlorobicyclo[3.3.0]octa-2,6-diene (**1**), mp 146–147°, in 75% yield with small amounts of Prins dimer.[6] No other products could be isolated in this reaction except unreacted starting materials.

The infrared spectrum of **1** showed a single olefinic absorption at 1612 cm^{-1} and a strong absorption at 1185 cm^{-1} suggestive of a polychlorinated ring breathing mode.[7] The ultraviolet spectrum in *n*-hexane showed only end absorption with a shoulder at 230 nm, while high-pressure hydrogenation afforded *cis*-bicyclo[3.3.0]octane.[8] These observations suggested two structures, **1** or **1′**, each having two nonconjugated double bonds with cis-fused rings for this chlorocarbon.[12]



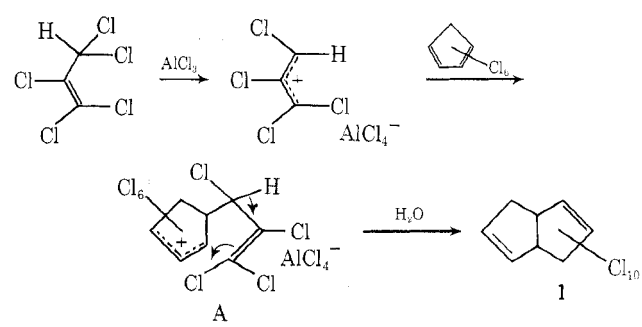
1



1′

An unambiguous choice between the two isomers was made from the ^{13}C nmr spectrum in deuteriochloroform, which showed only four different resonances in approximately equal intensities at 136.7, 132.8, 92.7, and 88.5 ppm downfield from external tetramethylsilane.[13] In addition the nqr spectrum at room temperature showed only five absorptions of equal intensities at 37.34, 38.06, 38.57, 38.94, and 39.13 MHz, indicating the presence of five different symmetry-equivalent pairs of chlorine. Structure **1** is fully consistent with these observations.[14a]

A likely mechanism for the formation of **1** involves the initial abstraction of an allylic chlorine from the propene to yield the 1,1,2,3-tetrachloropropenium cation, which is attacked by hexachlorocyclopentadiene to furnish the intermediate A. Ring closure followed by loss of a proton would furnish **1**.[14b]



A

When **1** was heated with concentrated sulfuric acid and then treated with water, a 60:40 mixture of two colorless dicarbonyl compounds was obtained. They were separated by repeated fractional crystallization or by glpc. On treatment with excess PCl_5 at 185–190°, both these compounds furnished **1**. Their infrared spectra as mulls in Nujol were also very similar. These observations suggested that the two dicarbonyl compounds had the basic bicyclo[3.3.0] ring skeleton[16] and differed only with respect to the position of the carbonyl groups.

Structure **2** was assigned to the 40% component on the basis of its ^{13}C nmr spectrum, which showed only four resonances at 181.5, 156.7, 131.5, and 72.4 ppm. The resonance at 181.5 ppm is easily assigned to the carbonyl carbon by analogy with cycloalkanones.[17,18] In a similar fashion the absorption at 156.7 ppm is assigned to the olefinic carbon β to the carbonyl group and that at 131.5 ppm to the α carbon.[19] The remaining absorption at 72.4 ppm is assigned to the bridgehead carbon. The 60% com-