added at such a rate that the temperature of the reaction mixture did not rise above −5°. The reaction mixture was refluxed for 30 min and cooled to −10°, a solution of 4.13 g of concentrated sulfuric acid in 50 ml of water was added dropwise, and again the mixture was refluxed. The layers of the reaction mixture were separated and the ether layer was extracted with two 25-ml portions of water which were combined with the aqueous layer. The aqueous solution was shaken for a short time under vacuum to remove ether and the solution was distilled to give four 15-g portions of distillate. This distillate was gas chromatographed on a 0.25 in. × 10 ft 10% Ethofat on Fluoropak column. In the aqueous distillates from the various reductions the following alcohols were found: oligomer from 2-butene, ethanol; oligomer from 2-pentene, ethanol and 1-propanol; oligomer from 3-hexene, 1-propanol.

The aqueous residue remaining after the distillation and the ether layer were placed in a continuous ether extractor. After 4 days of operation the ether was removed through a helix-packed column. The small amount of ether remaining in the flask was removed with a stream of nitrogen. The minute amount of water-insoluble residue was worked with 0.5 ml of water and this water extract was tested with periodic acid. In every instance the test for α-diol was weakly positive or negative. A firm positive test was never obtained.

Oligomer A Reduction, Quantitative Study.—The apparatus was the same as that described for the other reductions. The apparatus was flushed with nitrogen and connected to a gas collection system which was filled with saturated, aqueous salt. The oligomer (2.04 g) was dissolved in 75 ml of dry ether and the solution was placed in the reaction flask and cooled to −15°. In the dropping funnel was placed 50 ml (pipet) of a water white, ethereal solution of lithium aluminum hydride which by standardization[26] was found to contain 37.8 mmoles of hydride. The addition of the hydride was at such a rate that the temperature of the reaction mixture did not rise above −10° and required 55 min. The reaction was very exothermic and the hydride had to be added cautiously. That an excess of hydride was used was indicated by a rapid drop in the temperature of the reaction mixture before all of the hydride had been added. The reaction mixture was refluxed for 30 min. The gas evolved during the reaction was bubbled through concentrated sulfuric acid and had a volume of 709 ml (STP), 31.6 mmoles. This gas burned with a pale blue flame and it was assumed to be hydrogen.

For hydrolysis the reaction mixture was cooled to −15°, a solution of 7.8 g of concentrated sulfuric acid in 100 ml of water was added dropwise, and the mixture was refluxed for 15 min. The gas evolved was bubbled through concentrated sulfuric acid and had a volume of 1984 ml (STP), 88.6 mmoles. This gas was assumed to be hydrogen and it indicated that hydride equivalent to 15.6 mmoles of lithium aluminum hydride had reacted with the oligomer.

The layers of the reaction mixture were separated and the ether layer was extracted with four 25-ml portions of water which were combined with the aqueous layer. This aqueous solution was distilled to give four fractions (total wt, 75.8 g) which were found by gas chromatography (0.25 in × 5 ft Porapak Q column) to contain 1.46 g of 1-propanol. By gas chromatography (0.25 × 78 in. 20% Carbowax 20 M column) the ether layer was found to contain 0.36 g of 1-propanol. The total 1-propanol obtained was 1.82 g which contained 1.09 g of carbon. The oligomer used contained 1.10 g of carbon.

The aqueous residue from the distillation and the ether layer were placed in a continuous ether extractor. After 1 week of operation the ether was removed through a helix-packed column to leave a minute amount of water-insoluble oil. This was worked with a small amount of water and this aqueous extract gave a negative test for α-diol with periodic acid.

3-Hexene Ozonide Reduction.—The reaction was carried out as described immediately above for the oligomer A reduction. Lithium aluminum hydride (37.6 mmoles) and ozonide (2.04 g, 15.5 mmoles) were used. This reaction was not nearly so exothermic as the oligomer reduction; the hydride–ether solution could be added quite rapidly with the reaction flask being cooled with an ice–water bath. During the ozonide–hydride reaction, 931 ml (STP), 28.7 mmoles, of gas was evolved. By mass spectrometry[27] hydrogen was found to be the only gas evolved during the reaction. Hydrolysis of the reaction mixture gave 2127 ml (STP), 94.9 mmoles of gas. Thus, hydride equivalent to 13.9 mmoles of lithium aluminum hydride reacted with the ozonide. The aqueous distillate was found to contain 1.46 g of 1-propanol and the ether layer contained 0.42 g, making a total yield of 1.88 g. The theoretical yield of 1-propanol was 1.86 g.

Registry No.—*cis*-2-Butene, 590-18-1; *trans*-2-butene, 624-64-6; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-520-8; 2-butene ozonide, 13943-08-3; 3-hexene ozonide, 13943-09-4.

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[26] H. Felkin, *Bull. Soc. Chim. France*, 347 (1951); E. Wiberg and R. U. Lacal, *Rev. Acad. Cienc. Exact. Fis. Quim. Nat. Zaragoza*, **10**, 97 (1955); *Chem. Abstr.*, **51**, 15319*d* (1957).

[27] We are indebted to Stanford Research Institute for this analysis.

Some 9,10-Disubstituted Derivatives of *cis*-Decalin, *cis*-Δ^2-Octalin, and *cis*-$\Delta^{2,6}$-Hexalin

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Received April 14, 1967

The synthesis of several *cis*-decalin, *cis*-Δ^2-octalin, and *cis*-$\Delta^{2,6}$-hexalin derivatives with substituents in the 9,10-bridgehead positions is reported. Beginning with 9,10-bis(hydroxymethyl)-$\Delta^{2,6}$-hexalin (I, X = OH), displacement on its dimesyloxy derivative by cyanide ion gave the dinitrile I (X = CN) and a cyclic aminonitrile (IV). Hydrolysis of the dinitrile followed by $LiAlH_4$ reduction produced the extended diol, 9,10-bis(2-hydroxyethyl)-$\Delta^{2,6}$-hexalin (V, X = OH). This was converted in turn to the dimesylate, dibromide, and diiodide compounds. The diiodide, *cis*-9,10-bis(2-iodoethyl)-$\Delta^{2,6}$-hexalin, by several attempted cyclization reactions, gave predominately *cis*-9-ethyl-10-vinyl-$\Delta^{2,6}$-hexalin through an intramolecular hydrogen transfer. The *cis*-9,10-dimethyl decalin, octalin, and hexalin compounds were also prepared. The nmr spectra of several of the 9,10-bis-($-CH_2X$)-Δ^2-octalins (for X = OAc, O_3SCH_3, I, and the cyclic ether X = -O-) showed AB quartets for the 9,10-methylene protons. The magnetic nonequivalence of these two protons arises from the asymmetry produced by the presence of a double bond in one ring of this otherwise symmetrical bicyclic system.

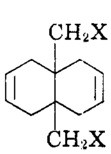
In order to dampen the rates of conformational changes (such as the chair–chair inversion of cyclohexanes), a simple intuitive approach is to build up the number and size of groups which must be eclipsed at some time during the transformation. Although the rates of bond rotations of some ethane derivatives, and correspondingly of cyclohexyl derivatives, do not seem to depend primarily on the size of substituents,[1] it is still true that *massive* substitution can slow rates of rotation. For example, the activation energy for bond rotation in ethane, 2.8 kcal,[2] is increased to 10.8 kcal in

[1] E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959).

[2] K. S. Pitzer, *Discussions Faraday Soc.*, **10**, 66 (1951).

hexachloroethane.[3] Cyclohexane itself may be considered to be an ethane derivative in which ring formation by introducing four methylene units has greatly increased the rotational barrier (*i.e.*, from 2.8 to *ca.*11 kcal). The best reported[4] activation energies for *cis*-decalin inversion tend to be only a little larger than for cyclohexane and the "second ring" of *cis*-decalin has only a small effect in further slowing the rotation–inversion process.[5] On the other hand, 9-substituted *cis*-decalins have lower activation energies for inversion than does *cis*-decalin itself, probably due to destabilization of the ground-state ring system.[4c]

It is of interest to explore further the possibility of modifying the barrier to inversion of a cyclohexane derivative by more complete substitution of large groups or rings on two adjacent positions. Related to this possibility, we report here the synthesis of some 9,10-substituted hexalin (I), octalin (II), and decalin (III) compounds.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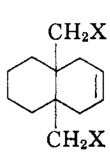
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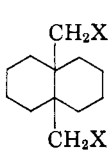
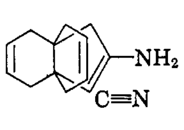

III

Results and Discussion

A compound with potentially unusual properties is tricyclo[4.4.4.0]tetradecane (III, X = $-(CH_2)_2-$), where the fusion of three cyclohexane rings at the same bridgehead carbon atoms maximizes the number of relatively inflexible six-membered carbocyclic groups on the central "ethane" carbon atoms. Directed toward this compound, a variety of attempts to affect substitution by cyanide ion on the 9,10 highly hindered positions of the dimesylate III (X = O_3SCH_3) were unsuccessful; for example, only the cyclic ether III (X = –O–) and unreacted mesylate were obtained after 6 days with CuCN in pyridine at 198°.

To moderate such steric hindrance by removal of adjacent hydrogens on the rings, the hexalin dimesylate (I, X = O_3SCH_3) was prepared and subjected to sodium cyanide or cuprous cyanide in DMSO, DMF, pyridine, and N-methyl-2-pyrrolidinone. The latter solvent prompted the best yields (20% after 4 hr at 175°) of dinitrile I (X = CN[6]), although accompanied by the cyclic aminonitrile IV, and the cyclic ether I (X = –O–). Hydrolysis of the dinitrile gave diacid I (X = CO_2H) which was best transformed to its dimethyl ester (with diazomethane) before reduction with $LiAlH_4$ led to the hexalin dialcohol V (X = OH).

This hexalin dialcohol was converted to the corresponding dibromide with PBr_3 or to the diiodide V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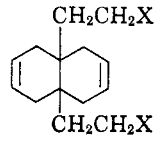
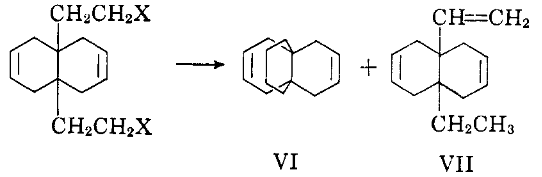

V

(X = I) by action of NaI in acetone on the dimesylate derivative V (X = O_3SCH_3).[7]

The coupling of the two ethyl groups in the diiodide to form a third six-membered ring, and hence obtain tricyclo[4.4.4.0]-3,8-tetadecadiene (VI), was attempted with *n*-butyllithium in ether and in heptane,[8] with zinc, and with magnesium in glyme and THF.[9] The major product, isolated by vpc, was in each case *cis*-9-ethyl-10-vinyl-$\Delta^{2,6}$ hexalin (VII) formed by a β elimination rather than ring formation of VI by direct substitution of bromide (eq 1). There were present small quantities


(1)

(4–9%) of a compound with the spectral characteristics consistent with structure VI (typical olefinic hydrogens at τ 4.5; prominent parent peak at *m/e* 188 with relatively little loss of simple fragments indicative of absence of terminal alkyl groups as in VII), but further characterization and preparation of usable amounts of this compound were not undertaken.[10]

Utilizing the hexalin and octalin dimesylates (I and II, where X = O_3SCH_3), the syntheses of *cis*-9,10-dimethyl-Δ^2 -hexalin and *cis*-9,10-dimethyl-$\Delta^{2,6}$-octalin were carried out by analogous two-step sequences. First each mesylate was treated with NaI in refluxing DMF, giving yields of 59 and 9% of the hexalin and octalin diiodides, respectively. The difference in yields apparently reflected the difference in steric environments of the methylene groups on the hexalin and octalin rings.[11,12] The diiodides were then treated with $LiAlH_4$ in glyme to produce the 9,10-dimethylhexalin and octalin compounds (I and II, X = H). 9,10-Dimethyldecalin was easily prepared through catalytic hydrogenation of the dimethylhexalin.

The nmr spectra of the octalin derivatives contain interesting examples of magnetic nonequivalence due to molecular asymmetry. Thus, for each of the octalin

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(3) Y. Marino and E. Hirota, *J. Chem. Phys.*, **28**, 185 (1958).

(4) (a) F. R. Jensen and B. H. Beck, *Tetrahedron Letters*, 4523 (1966); (b) J. T. Gerig and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 2791 (1966); (c) J. D. Roberts, *Chem, Brit.*, **2**, 529 (1966).

(5) Studies of rates of conversion between two equally populated conformations of more highly substituted cyclohexane derivatives have been carried out by, *e.g.* (a) R. K. Harris and N. Sheppard, *Proc. Chem. Soc.*, 419 (1961); (b) S. Brownstein, *Can. J. Chem.*, **40**, 871 (1962); (c) H. Friebolin, W. Faisst, and H. G. Schmid, *Tetrahedron Letters*, 1317 (1966); (d) F. G. Riddell and M. J. T. Robinson, *Chem. Commun.*, 227 (1965). See also ref 4.

(6) The preparation of this dinitrile and the Thorpe condensation product (IV) was recently reported by J. J. Bloomfield and A. Mitra., *Chem. Ind.* (London), 2012 (1966). See also ref 10b.

(7) The relatively mild conditions required for preparation of the diiodide V (X = I) by displacement on the corresponding dimesylate contrasts sharply with the extreme conditions which had to be employed to prepare dinitrile or the diiodide (I, X = CN or I) by displacement on the hindered dimesylate of structure I.

(8) *Cf.*, K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *J. Am. Chem. Soc.*, **86**, 1733 (1964); K. Mislow and H. B. Hopps, *ibid.*, **84**, 3018 (1962).

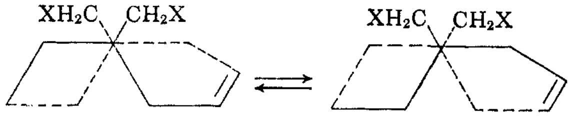
(9) D. McGreer, *Can. J. Chem.*, **38**, 1638 (1960); W. B. Smith, *J. Org. Chem.*, **26**, 509 (1958).

(10) (a) A synthesis of tricyclo[4.4.4.0]tetradecane ([4.4.4.]-propellane), has recently been reported: J. Altman, D. Becker, D. Ginsburg, and H. J. E. Loewenthal, *Tetrahedron Letters*, 757 (1967). A number of related propellanes have been reported in (b) J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron Suppl.*, **8**, Part 1, 279 (1966).

(11) The highly hindered environment of these 9,10-methylene groups is further shown by the fact that attempted preparation of 9,10-dimethyldecalin by direct displacement of the mesylate groups in III (X = O_3SCH_3) with hydride ion ($LiAlH_4$) gave the tricyclic ether III (X = O) rather than the dimethyldecalin.[12]

(12) G. Snatzke and G. Zanati, *Ann.*, **684**, 62 (1965).

compounds (II, X = OAc, O_3SCH_3, I, and for the ether X = –O–), the 9,10-methylene protons exhibited simple AB quartets with a chemical-shift difference of 0.12–0.25 ppm and J_{AB} = 7.8–11.2 cps. The first three compounds may be expected to exist as a pair of interconverting enantiomers whose geometry are as follows (looking down the C_9–C_{10} bond). In each case, the



conformation of the cyclohexane ring is a chair and the cyclohexene ring is a half-chair.[13a] Although the two bridgehead methylene groups in each enantiomer are not in identical environments, in the nmr spectra they do become magnetically equivalent when the rate of interconversion is rapid. The appearance of a *single* AB quartet for the methylene groups in the room-temperature spectra shows that the rate of interconversion of the Δ^2-octalin ring system is fast, thus averaging out the two positions of the $-CH_2X$ groups. The observed simple AB pattern arises from magnetic nonequivalence of the methylene protons due either to preferred conformation(s) with respect to the $C-CH_2X$ bond, or to a temperature-independent intrinsic diastereomerism of these two geminal hydrogens.[13b] In either case, the fundamental asymmetry giving rise to the AB quartet is produced by the relative magnetic anisotropy of the two cyclohexyl rings, one differing only by the presence of a double bond some distance away from the observed methylene hydrogens.[14]

Just as cyclohexene is more conformationally mobile than cyclohexane,[13a] the presence of double bonds in the 9,10-disubstituted hexalins and -octalins is expected to make ring conformational changes more facile than with decalins. For this reason, preliminary variable-temperature nmr spectra were obtained for the saturated compound, *cis*-9,10-dimethyldecalin. As with *cis*-decalin, no significant broadening of the resonance peak for the methylene hydrogens occurred down to −50°, although below 0° a number of small peaks appeared on the low-field side of the methylene peak and at −50° the methylene peak itself showed partly resolved fine structure.[15] The fact that changes in the *cis*-dimethyldecalin spectrum occur at a higher temperature than those in *cis*-decalin (used for comparison) suggests that the barrier to interconversion is higher in the former case. However, even such a qualitative comparison of the two compounds assumes that the difference in chemical shifts for axial and equatorial protons is the same for 9,10-dimethyldecalin as for decalin. As well illustrated for *cis*-decalin itself,[4,16a] a proper estimate of the effect of 9,10-alkyl groups on the rate of inversion of this ring system will probably require the preparation of deuterio- or fluoro-substituted derivatives.[16b]

Experimental Section[17]

$\Delta^{2,6}$-Hexalin-9,10-dicarboxylic anhydride was prepared from acetylenedicarboxylic acid and 1,3-butadiene in glyme at 190° for 8 hr.[18,19]

***cis*-9,10-Bis(hydroxymethyl)-$\Delta^{2,6}$-hexalin** (I, X = OH) was prepared by $LiAlH_4$ reduction of the anhydride in refluxing glyme. After crystallization from ethanol–water, this hexalin dialcohol had mp 174.5–176° (sealed tube) (lit. mp 130–134°,[20] 125–127°,[12] 165–168°[10b]). The nmr spectrum (23% in DMSO) showed a triplet at τ 4.48 (olefinic H), a triplet at 5.43 (–OH, J = 5.0 cps), a doublet at 6.60 ($-CH_2O-$, J = 5.0 cps), and a singlet at 8.07 (allylic H) in the ratio of 2:1:2:4.

***cis*-9,10-Bis(acetoxymethyl)-$\Delta^{2,6}$-hexalin (I, X = OAc)** was prepared by reaction of the alcohol with acetic anhydride. The diacetate was purified by sublimation at 80° (1 mm), mp 65.5–67.0°.

Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.08; H, 8.02.

***cis*-9,10-Bis(mesyloxymethyl)-$\Delta^{2,6}$-hexalin (I, X = O_3SCH_3)**, mp 115°, was prepared from the diol and methansulfonyl chloride in dry pyridine at −5 to −10°.[12,19]

***cis*-9,10-Bis(iodomethyl)-$\Delta^{2,6}$-hexalin** (I, X = I).—A mixture of 10 g (26.5 mmoles) of dry hexalin dimesylate, 13 g (87 mmoles) of dry sodium iodide, and 150 ml of dry purified N,N-dimethylformamide was stirred and refluxed for 10 hr. After extraction into benzene and washing with 10% HCl solution, the crude product was boiled in 150 ml of petroleum ether (bp 30–60°), treated with charcoal, and filtered. On cooling the hexalin, diiodide crystallized out as fine needles, yield 6.5 g (59%), mp 98–99°. The infrared spectrum (Nujol mull) showed strong bands at ν_{max} (cm^{-1}) 2920, 1180, and 673. The nmr spectrum (15% in $CDCl_3$) showed a triplet at τ 4.42 (olefinic H), singlets at 6.34 ($-CH_2I$), and 7.87 (allylic H) in the ratio of 1:1:2.

Anal. Calcd for $C_{12}H_{16}I_2$: C, 34.81; H, 3.90; I, 61.30. Found: C, 34.76; H, 4.00; I, 61.37.

***cis*-9,10-Dimethyl-$\Delta^{2,6}$-hexalin** (I, X = H).—For this reaction the hexalin diiodide must be free of any hexalin dimesylate impurity (accomplished by several crystallizations from petroleum ether. A solution of 4.0 g (9.6 mmoles) of the dry pure hexalin diiodide in 50 ml of dry glyme was added dropwise to a stirred suspension of 1.1 g (29 mmoles) of powdered lithium aluminum hydride in 50 ml of dry glyme. The mixture was stirred and refluxed for 16 hr, then cooled to 0°. After acidification with 10% sulfuric acid, the mixture was extracted with dichloromethane. The crude product was isolated as an oil by carefully evaporating off the dichloromethane and glyme on a rotary

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[13] (a) F. A. L. Anet and M. Z. Haq, *J. Am. Chem. Soc.*, **87**, 3147 (1965); F. R. Jensen and C. H. Bushweller, *ibid.*, **87**, 3286 (1965). (b) *Cf.* G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964); N. S. Bowman, D. E. Rice, and B. R. Switzer, *ibid.*, **87**, 4477 (1965); M. Rabin, *Tetrahedron Letters*, **27**, 3105 (1966), and references therein. The methylene hydrogens of the ethyl group in 10-carboethoxy-1,1-dimethyldecalin show a nonequivalence; see W. L. Meyer, D. L. Davis, L. Foster, A. S. Levinson, V. L. Sawin, D. C. Shew, and R. F. Weddleton, *J. Am. Chem. Soc.*, **87**, 1573 (1965); see also ref 16b.

[14] The allylic protons in each of Δ^2-octalin-9,10-dicarboxylic anhydride and dicarboximide, together with the $\Delta^{2,6}$-hexalin analogs, exhibited a group of resonance peaks having the general shape of an AB system (J_{AB} = *ca.* 16 cps). The spectra of these protons were complicated however by spin-spin coupling with the neighboring olefinic protons, which caused additional splitting to appear in the four main peaks.

[15] It should be mentioned that the methyl resonance peak in 9,10-dimethyldecalin remained constant as a sharp singlet down to −50°; the conformational interconversion only oscillates the methyl groups between two identical positions with respect to the rings.

[16] (a) W. B. Moniz and J. A. Dixon, *ibid.*, **83**, 1671 (1961). (b) J. Altman, H. Gilboa, D. Ginsburg, and A. Loewenstein (*Tetrahedron Letters*, 1329 (1967)) have recently obtained activation energies for ring inversion of 9,10-disubstituted *cis*-decalins by nmr measurements of lower temperature AB patterns for 9,10-methylene hydrogens.

[17] Infrared spectra were recorded on a Perkin-Elmer Model 137B Infracord spectrophotometer. Relative absorption band intensities are given as w = weak, m = medium, and s = strong. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian Model A-60 60-Mc spectrometer. Resonance peak positions are given in τ units, relative to tetramethylsilane at τ 10. The nmr samples were 15% (w/v) solutions unless otherwise specified. Integrated peak areas are given as a ratio. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 502 spectrophotometer. Mass spectra were recorded by Mr. F. G. Bloss with an Atlas Model CH4 spectrometer. Microanalyses were performed by Dr. A. Bernhardt and his staff at the Max Planck Institute, Mülheim, Ruhr, West Germany. Melting points (uncorrected) were obtained using an electrically heated, circulating oil bath. Gas-liquid partition chromatography (glpc) tracings were recorded on Wilkens Model A-90 Aerograph and A-700 Autoprep chromatographs.

[18] K. Alder and K. H. Backendorf, *Ber.*, **71**, 2199 (1938).

[19] See W. B. Scott, Ph.D. Thesis, University of British Columbia, 1965. Available through the Catalog Division, National Library of Canada, Ottawa (Canadian Thesis on Microfilm No. 483).

[20] J. J. Bloomfield and W. T. Quinlin, *J. Am. Chem. Soc.*, **86**, 2738 (1964).

evaporator at 10° (20 mm). The dimethylhexalin was obtained pure by gas–liquid partition chromatography using a 10-ft Carbowax 20 M on firebrick column at 150°. The yield of the dimethylhexalin (waxy solid, quite volatile in the open air) was 0.63 g (40%), mp 69–71° (sealed tube).

The mass spectrum showed a parent peak M at *m/e* 162. The principal fragmentation peaks were M − 15 (loss of methyl radical), M − 54 (loss of butadiene), M − 71 (formation of the cycloheptatrienyl cation). The infrared spectrum (film) showed ν_{max} (cm)$^{-1}$) at 2900 (s, br), 1650 (m), 1430 (s, br), 1365 (s), 1320 (m, doublet), 1235 (s), 1220 (m), 1180 (w), 1150 (m), 1130 (m), 1085 (m), 1010 (s), 980 (m), 960 (m), 920 (m), 910 (m), 875 (m), 852 (m), 830 (s), 718 (m), and 660 (s). The nmr spectrum (15% in CCl_4) showed a triplet at τ 4.53 (olefinic H), a broad singlet at 8.15 (allylic H), and a singlet at 9.10 (CH_3–) in the ratio of 2:4:3.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18; mol wt, 162.3. Found: C, 88.72; H, 11.45; mol wt, 162 (mass spectrum).

cis-**9,10-Dimethyldecalin (III, X = H)**.—A stirred mixture of 250 mg (1.54 mmoles) of the dimethylhexalin and 22 mg of platinum oxide in 11 ml of 95% ethanol was hydrogenated at atmospheric pressure. After filtering, the solution was slowly concentrated to a thick oil by evaporating off the ethanol at 25° (20 mm) on a rotary evaporator. The pure dimethyldecalin was obtained by gas–liquid chromatography using a 10-ft Carbowax 20 M on firebrick column at 145°. The yield of the dimethyldecalin (waxy solid, quite volatile in the open air) was 200 mg (78%), m 89–91° (sealed tube). The compound could be sublimed at 25° (1 mm).

The mass spectrum showed a parent peak M at m/*e* 166. The principal fragmentation peaks were M − 15 (loss of methyl radical), M − 57, M − 71, M − 83, and M − 84. The infrared spectrum (film) showed ν_{max} (cm^{-1}) at 2940 (s, br), 2680 (m), 1460 (s, br), 1375 (m), 1350 (m), 1335 (m), 1280 (m), 1200 (m), 1180 (m), 1145 (m), 1090 (w), 1038 (m), 1005 (m), 940 (m), 930 (m), 885 (m), 858 (w), 840 (m), 815 (w), 782 (w), and 755 (w). The nmr spectrum (15% in $CHCl_3$) showed a broad singlet at τ 8.50 (–CH_2–) and a sharp singlet at 9.12 (CH_3–) in the ratio of 8:3.

Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33; mol wt, 166.3. Found: C, 86.84; H, 13.07; mol wt, 166 (mass spectrum).

cis-**9,10-Bis(cyanomethyl)-$\Delta^{2,6}$-hexalin (I, X = CN)** was prepared (20% yield) from *cis*-9,10-bis(mesyloxymethyl)-$\Delta^{2,6}$-hexalin and purified sodium cyanide in dry N-methyl-2-pyrrolidinone (NMP) at 175° for 4 hr (see ref 19 for details). This compound has also been obtained by similar reactions in DMF[6,19] and by reaction of *cis*-9,10-bis(bromo-[10b] or iodomethyl[19])-$\Delta^{2,6}$-hexalin in DMSO or DMF. After crystallization from benzene–petroleum ether (bp 65–110°), the dinitrile melted at 152–153° (lit. 152–153,[6] 154° [10b]). Little cyclic aminonitrile (IV) was found by reactions in NMP; the major side product was (13%) of 12-oxatricyclo[4.4.3.0]-3,8-tridecadiene (I, X = –O–).[20]

cis-**9,10-Bis(carboxymethyl)-$\Delta^{2,6}$-hexalin (I, X = CO_2H)**.—A mixture of 2.95 g (14 mmoles) of the hexalin dinitrile, 300 ml of aqueous 10% sodium hydroxide solution, and 60 ml of ethanol was stirred and refluxed for 34 hr. After acidification, the white precipitated was filtered off, washed with water, and crystallized from ethanol–water: yield, 2.82 g (81%) of the diacid; mp 230–233° dec (lit.[10b] 235° dec). *cis*-**9,10-Bis(Carbomethoxymethyl)-$\Delta^{2,6}$-hexalin** (I, X = CO_2CH_3) was prepared from the diacid and diazomethane in ether–glyme, bp 152° (1.5 mm) (lit.[10b] 124° (0.5 mm)).

cis-**9,10-Bis(2-hydroxyethyl)-$\Delta^{2,6}$-hexalin (V, X = OH)**.—A solution of 2.50 g (9.0 mmoles) of the hexalin dimethyl ester in 20 ml of dry glyme was added dropwise to a stirred suspension of 0.70 g (18.5 mmoles) of powdered lithium aluminum hydride in 20 ml of dry glyme. The resulting mixture was stirred and refluxed for 24 hr. After acidification and ether extraction, the combined crude products were crystallized from ethyl acetate–petroleum ether (bp 65–110°), yielding 1.22 g (62%) of the dialcohol, mp 149.5–150.5°. The infrared spectrum (Nujol mull) showed ν_{max} (cm^{-1}) at 3300 (m), 3030 (w), 2920 (s), 1660 (w), 1460 (s), 1380 (m), 1020 (s), 1005 (m), 985 (w), 930 (w), and 700 (w).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.67; H, 9.70.

cis-**9,10-Bis(2-bromoethyl)-$\Delta^{2,6}$-hexalin (V, X = Br)**.—Freshly distilled phosphorus tribromide (7.2 g, 26.5 mmoles) was added dropwise to a stirred suspension of 1.27 g (5.7 mmoles) of the dry bis(2-hydroxyethyl)hexalin in 20 ml of dry glyme maintained at 0°. The mixture was stirred and allowed to warm to room temperature, then refluxed for 5 hr. The mixture was poured into 100 ml of water, extracted with ether, and washed with 10% Na_2CO_3 solution. After evaporation the residue was crystallized from acetone–water, yielding 0.32 g (16%) of the dibromide, mp 132–133°. The nmr spectrum (10% in CCl_4) showed a triplet at τ 4.46 (olefinic H), a triplet with maxima at 6.54, 6.68, 6.82 (–CH_2Br, J = 8.5 cps, superimposed on a singlet at 8.02 for allylic H) in the ratio of 1:1:3.

Anal. Calcd for $C_{14}H_{20}Br_2$: C, 48.31; H, 5.79; Br, 45.91. Found: C, 48.40; H, 5.69; Br, 45.82.

cis-**9,10-Bis(2-mesyloxyethyl)-$\Delta^{2,6}$-hexalin (V, X = O_3SCH_3)**.—A solution of 1.35 g (6.1 mmoles) of the dry bis(2-hydroxyethyl)hexalin in 10 ml of dry pyridine was added dropwise to a stirred solution of 1.1 ml (1.65 g, 14.5 mmoles) of methanesulfonyl chloride in 10 ml of dry pyridine. The temperature of the reaction mixture during the addition was maintained at −10° in order to eliminate ether formation. The resulting mixture was stirred for 1.5 hr while the reaction mixture temperature was allowed to rise slowly to 0°. The mixture was allowed to stand at 0° for 20 hr. Water (15 ml) was then added and the resulting solution made acidic with aqueous hydrochloric acid (10% by weight). After cooling to 0°, the precipitate was filtered off, washed with water, dried, and crystallized from 95% ethanol, yielding 1.6 g (70%) of the dimesylate, mp 124–125° dec. The nmr spectrum (15% in $CHCl_3$) showed a singlet at τ 4.39 (olefinic H), a triplet with maxima at 5.55, 5.68, and 5.80 (–CH_2OSO_2–, J = 7.5 cps), a singlet at 6.96 (–OSO_2CH_3), and a triplet with maxima at 7.97, 8.09, and 8.21 (a triplet for –$CH_2CH_2OSO_2$–, J = 7.5 cps suprimposed on a singlet at 7.97 for the allylic H) in the ratio of 2:2:3:6.

Anal. Calcd for $C_{16}H_{26}O_6S_2$: C, 50.77; H, 6.93; S, 16.94. Found: C, 50.98; H, 6.86; S, 16.83.

cis-**9,10-Bis(2-iodoethyl)-$\Delta^{2,6}$-hexalin (V, X = I)**. **Method 1**.—A solution of 0.31 g (0.89 mmole) of the dry bis(2-bromoethyl)hexalin and 400 mg (2.7 mmoles) of dry sodium iodide in 10 ml of dry purified acetone was stirred and refluxed for 5 hr. After addition of H_2O, ether extraction, and crystallization from 95% ethanol, 300 mg (76%) of the diiodide was obtained, mp 147–148° dec. The nmr spectrum (10% in $CDCl_3$) showed a triplet at τ 4.46 (olefinic H) and triplets with maxima at 6.70, 6.85, and 7.00 (–CH_2I, J = 9.0 cps) and at 7.80, 7.95, and 8.07 (a triplet for –CH_2CH_2I, J = 9.0 cps, superimposed on a singlet at 8.07 for the allylic H) in the ratio of 1:1:3.

Anal. Calcd for $C_{14}H_{20}I_2$: C, 38.03; H, 4.56; I, 57.41. Found: C, 38.22; H, 4.50; I, 57.53.

Method 2.—A solution of 2.4 g (6.35 mmoles) of the dry bis(2-mesyloxyethyl)hexalin and 3.0 g (20 mmoles) of dry sodium iodide in 100 ml of dry purified acetone was stirred and refluxed for 8 hr. Water and solid sodium thiosulfate (0.5 g) were added and the white precipitate was then filtered off, washed with water, dried, and crystallized from benzene–petroleum ether (bp 65–110°), yielding 1.3 g (46%) of the diiodide, mp 147–148° dec.

Numerous attempts to cyclize the bis(2-iodoethyl)hexalin were carried out using *n*-butyllithium in hexane or ether, with zinc in glyme, and magnesium in THF, ether, and in heptane. The predominant products (among several) was an oil, separated by gas–liquid partition chromatography. The infrared spectrum (film) showed ν_{max} (cm^{-1}) at 3080 (w), 3030 (m), 2920 (s), 1660 (w), 1640 (w), 1460 (m), 1425 (m), 1380 (w), 1320 (w), 1225 (w), 1180 (w), 1038 (m), 1005 (w), 990 (w), 912 (s), 870 (w), 850 (w), 825 (w), 780 (w), and 732 (w). The nmr spectrum (dilute microsample in $CHCl_3$) showed a triplet at τ 4.40 (olefinic H), a singlet at 8.10 (allylic H), a multiplet at 8.71 (–CH_2–), and a triplet at 9.25 (–CH_3) in the approximate ratio of 1:2:1:1. The mass spectrum showed a large parent ion peak M at *m/e* 188, indicating a molecular weight of 188. The principal fragmentation peaks were M − 29 (loss of ethyl radical), M − 83 (consecutive loss of ethyl radical and butadiene), and M − 99 (formation of the cycloheptatrienyl cation). The ultraviolet spectrum (heptane solution) showed no absorption peaks in the range 210–300 mμ. On this basis this component was assigned the structure *cis*-9-ethyl-10-vinyl-$\Delta^{2,6}$-hexalin (VII).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.01; H, 10.56.

A minor component, also separated by gas–liquid partition chromatography, had the following characteristics. The infrared spectrum (film) showed ν_{max} (cm^{-1}) at 3030 (m), 2920 (s), 1660 (w), 1455 (m), 1420 (m), 1380 (w), 1320 (w), 1230 (w), 1110 (m, br), 1090 (m), 1000 (m), 944 (w), 862 (w), 848 (w), 822 (w), 795 (w), and 714 (w). The nmr spectrum (very dilute microsample in CHCl$_3$) showed a singlet at τ 4.48 (olefinic H) and a multiplet centered at 8.42 (allylic H and -CH$_2$-) in the ratio of *ca.* 1:5. The mass spectrum gave a parent ion peak M at *m/e* 188, indicating a molecular weight of 188. The principal fragmentation peaks were M − 54 (loss of butadiene), M − 96, and M − 97 (formation of the cycloheptatrienyl cation). This compound appeared to be the desired tricyclo[4.4.4.0]-3,8-tetradecadiene (VI), but variation of conditions failed to produce sufficient quantities of it.

Δ^2-Octalin-*cis*-9,10-dicarboxylic acid was prepared[21] from cyclohexene-1,2-decarboxylic anhydride and its dimethyl ester was prepared utilizing diazomethane. The nmr spectrum (15% in CCl$_4$) of the diester showed a triplet at τ 4.50 (olefinic H), a sharp singlet at 6.39 (CH$_3$O-), a broad multiplet with maxima at 7.66 and 8.30 (allylic H), and a singlet at 8.54 (-CH$_x$-) in the ratio of 1:3:6 (the multiplet and high-field singlet were not resolved in the area integral).

Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.99; H, 7.79.

Δ^2-Octalin-9,10-dicarboxylic anhydride was prepared[21] from the octalin acid by treatment with acetyl chloride at 0°. Its nmr spectrum (15% in CCl$_4$) showed a triplet at τ 4.28 (olefinic H), a complex quartet with maxima at 7.30, 7.58, 7.82, and 8.10 (allylic H), and a multiplet at 8.39 (-CH$_2$-) in the ratio of 1:2:4.

***cis*-9,10-Bis(hydroxymethyl)-Δ^2-octalin (II, X = OH).**—The procedure used was as for the preparation of the analogous hexalin dialcohol. The yield of octalin alcohol was 12.5 g (64%) from 20 g (0.10 mole) of the octalin anhydride. On crystallization ethanol-water the dialcohol melted at 147-149°. The nmr spectrum (23% in DMSO) showed a triplet at τ 4.46 (olefinic H), a triplet at 5.58 (-OH, J = 5.0 cps), a doublet at 6.57 (-CH$_2$O-, J = 5.0 cps), a singlet at 8.03 (allylic H), and a singlet at 8.57 (-CH$_2$-) in the ratio of 1:1:2:2:4.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.51; H, 10.42.

12-Oxatricyclo[4.4.3.0]-3-tridecene (II, X = -O-) was prepared from the above diol with *p*-toluenesulfonic acid in refluxing benzene. The octalin dialcohol (2.0 g, 10 mmoles) yielded 1.70 g (95%) of the cyclic ether as a clear colorless oil. The ether was obtained pure by gas-liquid partition chromatography using a 10-ft Carbowax 20 M on firebrick column at 200°, $n^{20}{}_{\mathrm{D}}$ 1.5122. The nmr spectrum (48% in CCl$_4$) showed a singlet at τ 4.47 (olefinic H), an AB quartet with maxima at 6.23, 6.34, 6.47, and 6.59 (-CH$_2$O-, J_{AB} = 7.5 cps), a singlet at 8.05 (allylic H), and a singlet at 8.53 (-CH$_2$-) in the ratio of 1:2:2:4.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.62; H, 10.37.

***cis*-9,10-Bis(acetoxymethyl)-Δ^2-octalin (II, X = OAc).**—The octalin dialcohol (1.0 g, 5 mmoles) with warm acetic anhydride yielded 1.36 g (97%) of the diacetate, mp 57.5-59.0°. The diacetate was sublimed at 75° (1 mm), melting point unchanged. The nmr spectrum (15% in CCl$_4$) showed a triplet at τ 4.44 (olefinic H), an AB quartet with maxima at 5.68, 5.87, 5.99, and 6.17 (-CH$_2$O-, J_{AB} = 11.0 cps), a singlet at 7.94 (allylic H), a singlet at 8.02 (CH$_3$CO$_2$-), and a singlet at 8.50 (-CH$_2$-) in the ratio of 1:2:2:3:4.

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.89; H, 8.70.

***cis*-9,10-Bis(mesyloxymethyl)-Δ^2-octalin (II, X = O$_3$SCH$_3$).**—The procedure was that used for the preparation of the hexalin dimesylate analog. The yield of dimesylate from 3.0 g (15 mmoles) of the octalin dialcohol was 4.5 g (85%), mp 124-125°, on crystallization from methanol. On recrystallization from benzene-petroleum ether (bp 65-110°), the melting point was 125-126°. The nmr spectrum (15% in CHCl$_3$) showed a triplet at τ 4.29 (olefinic H), an AB quartet with maxima at 5.50, 5.67, 5.72, and 5.89 (-CH$_2$OSO$_2$-, J_{AB} = 10.0 cps), a singlet at 6.92 (CH$_3$SO$_3$-), a singlet at 7.80 (allylic H), and a singlet at 8.37 (-CH$_2$-) in the ratio of 1:2:3:2:4.

Anal. Calcd for $C_{14}H_{24}O_6S_2$: C, 47.41; H, 6.87; S, 18.19. Found: C, 47.85; H, 6.78; S, 18.26.

***cis*-9,10-Bis(iodomethyl)-Δ^2-octalin (II, X = I).**—A solution of 5.0 g (14.2 mmoles) of the dry octalin dimesylate and 6.0 g (40 mmoles) of dry sodium iodide in 80 ml of dry N,N-dimethylformamide (DMF) was stirred and refluxed for 5.5 hr. After extraction into benzene and washing with 10% HCl and 10% Na$_2$CO$_3$, the benzene was evaporated to dryness. The black residue was eluted through a silica gel column with petroleum ether (bp 30-60°), yielding 0.54 g (9.2%) of the octalin diiodide, mp 101-102°, from methanol. The nmr spectrum (15% in CCl$_4$) showed a triplet at τ 4.40 (olefinic H), an AB quartet with maxima at 6.28, 6.44, 6.48, and 6.75 (-CH$_2$I, J_{AB} = 10.0 cps), a singlet at 7.83 (allylic H), and a singlet at 8.45 (-CH$_2$-) in the ratio of 1:2:2:4.

Anal. Calcd for $C_{12}H_{18}I_2$: C, 34.64; H, 4.36; I, 61.00. Found: C, 34.75; H, 4.51; I, 61.00.

***cis*-9,10-Dimethyl-Δ^2-octalin (II, X = H).**—A solution of 1.0 g (2.4 mmoles) of the dry octalin diiodide in 20 ml of dry glyme was added dropwise to a stirred suspension of 0.25 g (6.6 mmoles) of powered lithium aluminum hydride in 20 ml of dry glyme. The mixture was stirred and gently refluxed for 20 hr. After normal acid work-up and ether extraction, the dry ether solution was concentrated to a thick oil on a rotary evaporator at 10° (20 mm). The crude product was purified by gas-liquid partition chromatography using a 10-ft diethylene glycol succinate column at 95°. The yield of the dimethyloctalin was 71 mg (18%), mp 51-53° (sealed tube). The compound is a waxy white solid and is quite volatile in the open air.

The infrared spectrum (film) showed $\nu_{\max}$ (cm^{-1}) at 3030 (m), 2900 (s), 1660 (m), 1450 (s), 1360 (m), 1320 (m), 1220 (m), 1180 (w), 1140 (w), 1020 (m), 1000 (m), 970 (w), 960 (m), 945 (w), 880 (w), 860 (w), 830 (m), and 795 (w). The nmr spectrum (22% in CHCl$_3$) showed a triplet at τ 4.44 (olefinic H), a multiplet at 8.10 (allylic H), a multiplet at 8.58 (-CH$_2$-), and a sharp singlet at 9.10 (-CH$_3$) in the ratio of 1:2:4:3.

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.78; H, 12.01.

***cis*-9,10-Bis(hydroxymethyl)decalin (III, X = OH)** was prepared by LiAlH$_4$ reduction of the 9,10-decalin anhydride.[12] After crystallization from ethanol-water, the alcohol melted at 183-184° (lit. 165-167°,[12] 180-182° [10b]).

***cis*-9,10-Bis(mesyloxymethyl)decalin (III, X = O$_3$SCH$_3$)** was prepared from the decalin dialcohol as outlined above for the preparation of the analogous hexalin dimesylate. After crystallization from benzene-petroleum ether, it melted at 126.5-128° (lit.[12] 116-117°). The nmr spectrum (15% in CHCl$_3$) showed singlets at τ 5.68 (-CH$_2$OSO$_2$-), 6.92 (CH$_3$SO-), and 8.40 (-CH$_2$-) in the ratio of 2:3:8.

Anal. Calcd for $C_{14}H_{26}O_6S_2$: C, 47.43; H, 7.40. Found: C, 47.85; H, 7.32.

Registry No.—I, X = OH, 3642-42-0; I, X = OAc, 13950-27-1; I, X = I, 13950-28-2; I, X = H, 13950-29-3; I, X = CN, 13553-42-9; I, X = CO$_2$H, 13553-43-0; II, X = OH, 13950-32-8; II, X = -O-, 13950-33-9; II, X = OAc, 13950-34-0; II, X = O$_3$SCH$_3$, 13950-35-1; II, X = I, 13950-36-2; II, X = H, 13950-37-3; III, X = H, 13950-38-4; III, X = O$_3$SCH$_3$, 3914-39-4; V, X = OH, 13950-40-8; V, X = Br, 13950-41-9; V, X = O$_3$SCH$_3$, 13950-47-5; V, X = I, 13950-42-0; VI, 13950-43-1; VII, 13950-44-2; Δ^2-octalin-*cis*-9,10-dicarboxylic acid dimethyl ester, 13950-45-3; Δ^2-octalin-9,10-dicarboxylic anhydride, 13950-46-4.

Acknowledgment.—This research was supported by the National Research Council of Canada and by the donors of The Petroleum Research Fund, administered by the American Chemical Society. We thank the Research Committee, University of British Columbia, for summer research stipends to W. B. S.

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(21) P. Brigl and R. Herrmann, *Ber.*, **B71**, 2280 (1938).