even of carbon atoms[20] and there may therefore be several, though perhaps less obvious, paths leading to species of the observed *m/e* values. Another oddity is the relatively large contributions of species of *m/e* 116 (indene or isoindene cation) in the case of 7-substituted benzonorbornenes. These exceed the C^{13} and H^2 isotopic contributions of the indenyl cation and the excess may be rationalized as the result of a random rearrangement in the course of fragmentation.

The spectra of the bromine-containing compounds bear out the greater probability of loss of bromine over that of chlorine.[21] In the 5,7 dibromide, **4**, the molecular ion intensity is much diminished and there is a relatively large abundance of fragments resulting from the loss of bromine (18.8%Σ_{74}). The increased competition of bromine loss with retro Diels–Alder fragmentation has considerably diminished the contribution of **23** (with X = Br), compared with the chlorine compounds, but the contribution still appears sufficiently significant to confirm a 7-bromo substituent. Both in **4** and **21** the base peak corresponds to the benzotropylium ion, in line with the greater probability of initial loss of bromine and/or elimination of hydrogen bromide.

The spectra of all of the benzonorbornadiene derivatives show the by far most intense peak at *m/e* 141 (benzotropylium ion). The peak next in importance occurs at *m/e* 115 (indenyl cation), but peaks at *m/e* 129 and 128 are much diminished relative to the spectra of benzonorbornene derivatives. All these relative changes can again be rationalized on the basis of the corresponding part of Scheme I (starting with the *m/e* 178/176 ion for the chlorides). Now merely the loss of a single substituent is required to arrive at a fragment of *m/e* 141. The retro Diels–Alder process, requiring here the elimination of acetylene from the molecular ion, does not appear to be of any importance. The relative ease of eliminating ethylene (from benzonorbornene) over acetylene (from benzonorbornadiene) has been pointed out.[17] The formation of the *m/e* 115 fragment in the latter case has been ascribed to expulsion of acetylene from the benzotropylium ion[17] which, in view of the reluctance of the molecular ion to undergo the retro Diels–Alder process, may be a more probable process than the retro Diels–Alder process, on the 7-benzonorbornadienyl cation also included in Scheme I.

Exceptional behavior is shown by the vinyl chloride **17**. Its molecular ion peak is considerably stronger than that of the other benzonorbornadienes; yet the remainder of the spectrum is quite similar to that of the others. One might expect a relatively larger contribution of a fragment of *m/e* 177/175, corresponding to loss of a hydrogen atom and rearrangement to a chlorine-substituted benzotropylium ion. Peaks at these *m/e* values (not inclued in Table III) amount to 5.1 %Σ_{74} for the vinyl chloride, compared with 3.0%Σ_{74} and 2.7%Σ_{74} for the *anti*- and *syn*-7-chlorobenzonorbornadienes, respectively, and 0.8%Σ_{74} at *m/e* 221/219 in the case of the *anti*-bromo compound. The fact that the vinyl chloride still has the strongest peak at *m/e* 141 indicates the importance of chlorine loss and hydrogen migration because in the benzotropylium ion (which is likely to be the major, if not the exclusive, contributor to the *m/e* 141 peak) the carbon formerly bearing the chlorine substituent must now be linked to a hydrogen.

(20) See ref 18, p 138.

(21) J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, p 417.

Registry No.—**1a**, 6991-42-0; **1d**, 14362-53-9; **1e**, 7605-10-9; **2d**, 14518-75-3; **3**, 4453-90-1; **4**, 14362-55-1; **5**, 14296-33-4; **6**, 14296-34-5; **7**, 14296-35-6; **8**, 14362-56-2; **9**, 7605-06-3; **10**, 14296-37-8; **11**, 14518-76-4; **17**, 7605-08-5; **18**, 14362-57-3; **19**, 14444-29-2; **21**, 14296-39-0; **22**, 14296-40-3.

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cis- and *trans*-1,4-Cyclohexadiene Dioxide[1]

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cis- and *trans*-4,8-dioxatricyclo[5.1.0.0^{3,5}]octane have been synthesized and their ring-opening reactions have been investigated. Aqueous acid, aqueous base, aqueous hydrogen bromide, sodium bromide in dimethylformamide, dimethylamine, and ethylamine lead to 1,4 attack on the *cis* isomer and 1,3 attack on the *trans* isomer. Lithium aluminum hydride leads to 1,3 attack on the *cis* isomer and 1,4 attack on the *trans* isomer. Dimethyl magnesium, magnesium iodide, and methylmagnesium iodide result in 1,3 attack on both isomers. Hydrogen and palladium-on-carbon catalyst give a mixture of diols with the *cis* isomer and no reaction with the *trans* isomer. Sodium sulfide reacts with the *cis* isomer to produce **27**. These results are correlated. The *cis*- and *trans*-N-ethylaziridines of 1,4-cyclohexadiene were also prepared.

The chemistry of *cis*- and *trans*-4,8-dioxatricyclo-[5.1.0.0^{3,5}]octane (**1** and **2**, respectively) has been investigated to determine the stereochemical course of ring-opening reactions of the bisepoxide systems as a route to polysubstituted cyclohexanes of known stereochemistry. Bisepoxide formation from 1,4-cyclohexadiene (**3**)[4] and 1,3-cyclohexadiene[5] has been re-

(1) Supported by National Institutes of Health Grant NIH-AI-05408-MCB.

(2) National Science Foundation Predoctoral Fellow, 1963–1965.

(3) Alfred P. Sloan Fellow, 1963–1967.

(4) N. D. Zelinsky and A. N. Titowa, *Chem. Ber.*, **64**, 1399 (1931).

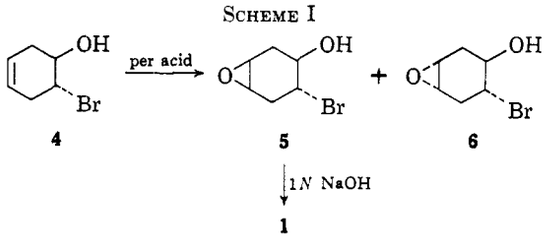
(5) P. Bedos and A. Ruyer, *Compt. Rend.*, **196**, 625 (1933); **195**, 802 (1932).

1 2

ported previously. Perbenzoic acid oxidation of **3** produced a bisepoxide which was converted to a tetrol of unknown configuration by acid hydrolysis.[4] The infrared spectrum of this product favors the bisepoxide structure rather than the bisoxetane structure.[6]

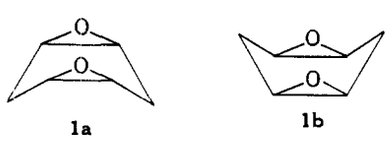
Treatment of **3** with excess perbenzoic acid or monoperphthalic acid gives rise to only the *trans*-epoxide **2**. Treatment of **3** with excess peracetic acid or treatment of the monoepoxide of **3** with excess *m*-chloroperbenzoic acid gives a 2:1 mixture of **2** and **1**, respectively. It was difficult to isolate pure **1** from the direct bisepoxidation of the diene primarily owing to the tendency of **1** and **2** to form a crystalline 1:1 complex. Consequently, **1** was prepared from **3** by an indirect procedure. Treatment of **3** with N-bromosuccinimide in water produced the monobromohydrin **4**. Epoxidation of **4** with a variety of per acids produced a mixture of **5** and **6** in a ratio varying from 62:38 to 78:22, respectively (Scheme I). The *cis*-epoxy alcohol is the major

SCHEME I



isomer owing to hydrogen bonding of the per acid with the hydroxyl group.[7] Isomer **5** is readily crystallized from **6** with ether–hexane. Treatment of **5** with aqueous sodium hydroxide produced pure **1**.

The stereochemistry of **1** and **2** was established by lithium aluminum hydride reduction to *cis*-1,3-cyclohaxanediol[8] and *trans*-1,4-cyclohexanediol,[9] respectively. The stereochemical assignment is further confirmed by the observed dipole moments of 3.38 ± 0.02 D.[10] for **1** and 0.0 D. for **2**.[11] An estimation of the dipole moment of **1** based on a value for cyclohexene oxide of 1.72[12] and 0.16 D. for the boat conformation of **3**[13] gives a value of 3.44 D. for conformer **1a** and a value of 3.42 D. for conformer **1b**. Compound **2** would be



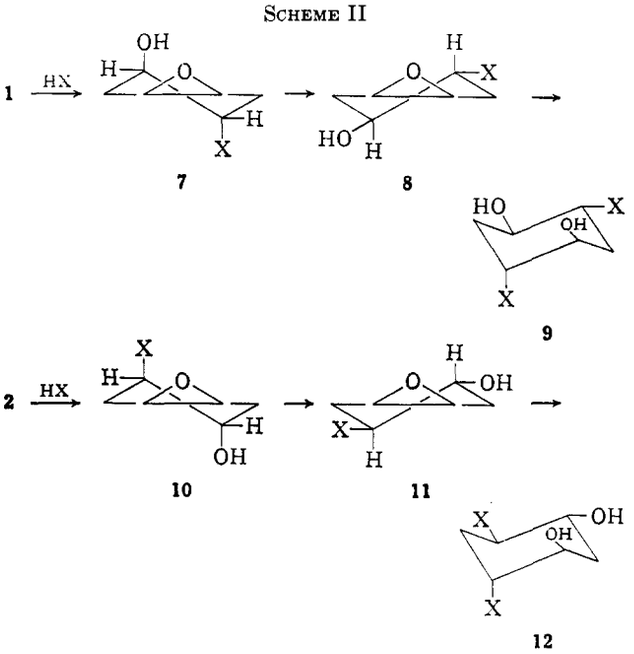
1a 1b

expected to have no dipole moment if it rapidly equilibrates between the two boat conformations of equal energy. The nmr spectrum of **2** indicates the equivalence of the four methylene protons at δ 2.33 which are finely coupled to the four epoxide hydrogens at δ 3.05. The nmr spectrum of **1** (unchanged from −40 to 140°) shows the nonequivalence of the methylene protons at δ 2.23 and 2.76 which are strongly coupled to one another (J = 17 cps) and weakly coupled to the epoxide hydrogens at δ 3.09.

The stereochemical course of ring-opening reactions of epoxides is well developed.[14–17] It was of interest to determine the extent to which these may be applied in the case of the dual epoxide functionality in **1** and **2**.

Table I lists the products formed from bisepoxide ring opening of **1** and **2** with a variety of reagents. In reactions 1–6 the products from the *cis*-bisepoxide **1** arise from axial attack to open the first epoxide ring, followed by inversion of the diaxially substituted epoxide intermediate **7** to the diequatorial isomer **8** which suffers axial attack to form product **9** resulting from 1,4 attack (Scheme II). Similarly the products from the *trans*-bisepoxide **2** in reactions 1–6 arise from axial

SCHEME II



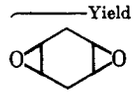
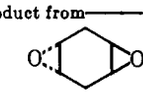
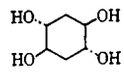
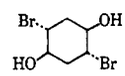
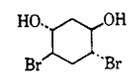
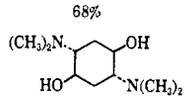
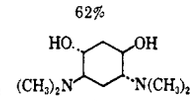
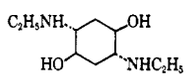
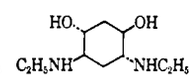
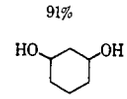
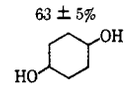
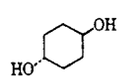
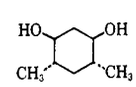
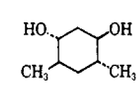
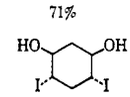
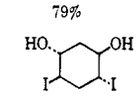
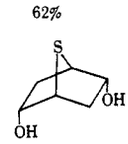
attack to open the first epoxide ring, followed by inversion of the diaxially substituted epoxide intermediate **10** to the diequatorial isomer **11** which suffers axial attack to form product **12** resulting from 1,3 attack.

Reduction of **1** with 1400 lb/sq in. of hydrogen using palladium on charcoal for 36 hr at room temperature (reaction 7) gave a colorless oil in 97% yield which was shown to be 63 ± 5% *cis*-1,3-cyclohexanediol (**20**) and 37 ± 5% *cis*-1,4-cyclohexanediol (**21**). This preponderance of 1,3 attack over 1,4 attack is not surprising in view of the known effect of oxygen atoms in directing the approach of the molecule to the catalyst surface in catalytic reductions.[18] The *trans* isomer **2** was not reduced under similar conditions or when the temperature was raised to 80°.

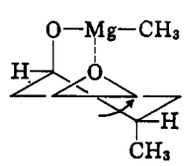
Reaction of **1** with organometallic reagents (reactions 8–11) results in products from 1,3 attack rather than

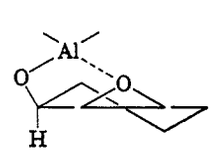
(6) W. A. Patterson, *Anal. Chem.*, **26**, 823 (1954).
(7) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957).
(8) T. Posternack and F. Ravenna, *Helv. Chim. Acta*, **30**, 441 (1947).
(9) H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 221 (1959).
(10) This value was determined at Wayne State University through the courteous service of Professor Norman LeBel.
(11) Method of D. P. Shoemaker and C. W. Garland in "Experiments in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 275–283.
(12) B. Ottar, *Acta Chem. Scand.*, **1**, 283 (1947).
(13) W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, *J. Am. Chem. Soc.*, **86**, 3126 (1964).
(14) E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 106–114.
(15) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).
(16) A. Rosowsky and A. W. Weissberger, "Heterocyclic Compounds with Three and Four Membered Rings," Part I, Vol I, Interscience Publishers, Inc., New York, N. Y., 1964.
(17) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 4137 (1959).
(18) T. J. Howard, *Chem. Ind.* (London), 1899 (1963).

TABLE I
PRODUCTS OBTAINED FROM REACTION OF 1 AND 2 WITH VARIOUS REAGENTS

Reaction no.	Reagent	Yield of product from 	Yield of product from 
1	Aqueous acid	 **13**, 94%	**13**, 95%
2	Aqueous NaOH	**13**, 92%	**13**, 78%
3	48% aqueous HBr	 **14**, 93%	 **15**, 98%
4	NaBr in dimethylformamide	**14**, 68%	**15**, 62%
5	$(CH_3)_2NH$	 **16**, 76%	 **17**, 69%
6	70% aqueous $C_2H_5NH_2$	 **18**, 91%	 **19**, 90%
7	H_2, Pd/C	 **20**, 63 ± 5%  **21**, 37 ± 5% (97%)	No reaction
8	$LiAlH_4$	**20**, 44%	 **22**, 31%
9	$(CH_3)_2Mg$	 **23**, 71%	 **24**, 79%
10	MgI_2	 **25**, 91%	 **26**, 73%
11	CH_3MgI	**25**, 62%	**26**, 42%
12	Na_2S	 **27**, 34%	

1,4 attack. This is reasonable if it is assumed that the organoaluminum or organomagnesium intermediate formed from opening of the first epoxide ring complexes with the remaining epoxide oxygen, *i.e.*, as **28** in reaction 9, thereby preventing ring inversion with subsequent axial attack resulting in 1,3 attack. Such complexes are known to occur with aluminum hydrides[19] and **29** has been suggested to explain the exclusive formation of *cis*-1,2-dihydroxycyclohexane from the re-

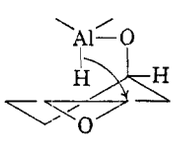

28


29

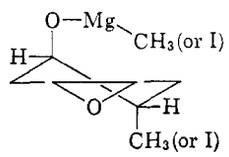
(19) E. L. Eliel and T. J. Brett, *J. Org. Chem.*, **28**, 1923 (1962).

duction of *cis*-3-hydroxycylohexene oxide with $LiAlH_4$.[7] The affinity of magnesium for oxygen is similar to or exceeds that of aluminum.[20]

Reaction of **2** with $LiAlH_4$ results in 1,4 attack whereas reaction with the magnesium reagents (reactions 9–11) results in 1,3 attack. The 1,4 attack in reaction **8** is undoubtedly the result of intramolecular hydride tranfer in **30** being more favorable than an



30



31

intermolecular hydride transfer[21] and is analogous to the formation of *trans*-1,4-cyclohexanediol from reduction of *trans*-4-hydroxycyclohexene oxide with $LiAlH_4$.[22] Intramolecular alkyl (or halogen) transfer would not be expected to occur in **31** since the second alkyl group in dimethylmagnesium or the halogen in methylmagnesium iodide fails to react appreciably even with simple ketones.[23] Consequently, the initial ring-opened product inverts to the more stable diequatorially substituted epoxide prior to the opening of the second epoxide ring which undergoes axial attack to the products resulting from 1,3 attack (reactions 9–11). Formation of the diiodides from reaction of **1** and **2** with CH_3MgI (reaction 12) is similar to the results obtained with 1,5-hexadiene dioxide.[24]

Sodium sulfide in ethanol reacts with **1** (reaction 12) to give 7-thiabicyclo[2.2.1]heptane-2,5-diol[25] (**27**).

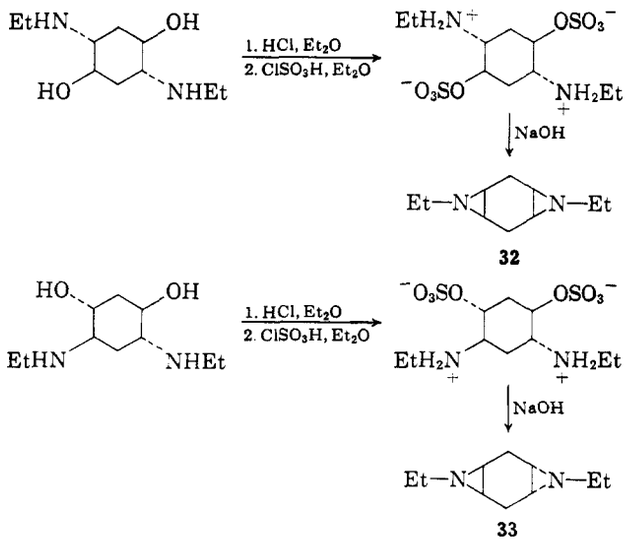
The bisaziridine analogs of **1** and **2** (**32** and **33**, respectively) were readily prepared from the products of ring opening with ethylamine (reaction 6) by known procedures[26,27] as given in Scheme III.

The structure and stereochemistry of the products listed in Table I were established as follows.

Compound 13.—The nmr spectrum and melting point of this material and its tetraacetate were identical with those previously reported.[28]

Compound 14.—The nmr spectrum in DMSO-d_6 shows absorption for both methylene groups as a triplet (J = 6.3 Hz) at 2.27 ppm indicating the entering bromine atoms must be in a 1,4 relationship. Irradiation of the carbinol hydrogens (broad quartet at 3.81 ppm) with a decoupling frequency of 92.5 Hz collapses the methylene triplet to a doublet and leaves the absorption for the hydrogen atoms on the same carbon atoms as the bromine atoms undisturbed (quartet, J = 6.3 Hz, 4.24 ppm). Irradiation of the methylene absorption with a decoupling frequency of 92.5 Hz

SCHEME III



collapses the carbinol hydrogen absorption to a broad doublet (J = 6.3 Hz). Thus the bromine atoms must be in 1,4 positions and the observed coupling constants are as expected from rapid interconversion of the two equivalent chair conformations of **14**. Similar results are obtained from decoupling experiments with the diacetate of **14**.

Compound 15.—The nmr spectrum of this product shows two methylene absorptions at δ 2.58 (triplet, J = 5.3 Hz) and 1.97 ppm (triplet, J = 5.3 Hz) indicating the bromine atoms to be in 1,3 positions. The diacetate of **15** shows absorption at δ 5.22 (quartet, 2 H, J = 6 Hz, 2 >C*H*OAc), 4.38 (quartet, 2 H, J = 6 Hz, 2 >CHBr), 2.67 (triplet, 2 H, J = 6 Hz (>CBrCH_2-CBr–), 2.23 (triplet, 2 H, J = 6 Hz, >C(OAc)CH_2C(OAc)<), and 2.12 ppm (singlet, 6 H, 2 -$COCH_3$). When the field is irradiated 103 Hz upfield from the 4.38-ppm absorption, this absorption collapses to a doublet (J = 6 Hz). When the field is irradiated 103 Hz downfield from the 2.67-ppm absorption, this absorption collapses to a singlet. The bromine atoms, therefore, must be in 1,3 positions.

Compounds 16–19.—The structures of these products were determined by a comparison of the nmr absorption patterns of these products and their acetate derivatives with the pattern observed for the acetates of **14** and **15**.

Compounds 20–22.—These structures were established by comparison with authentic samples of *cis*- and *trans*-1,3- and -1,4-cyclohexanediols.[29]

Compounds 23 and 24.—These structures were established from the presence of a strong m/e 73 in the mass spectrum ($C_3H_5O_2^+$) and the absence of a strong m/e 71 ($C_4H_7O^+$). Furthermore oxidation produced a diketone shown by infrared and nmr to be a 1,3-diketone (see Experimental Section).

Compound 25.—The 1,3 orientation of the iodine atoms in this product was established by decoupling experiments on the diacetate of **25**. The H_A protons are split into a triplet by H_d and H_b with $J_{A-B} = J_{A-D}$ = 10.5 Hz. The three components of this triplet are further split into a doublet with J_{A-C} = 4 Hz. When the region 152–172 Hz upfield from H_A is ir-

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(25) E. J. Corey and E. Block [*J. Org. Chem.*, **31**, 1663 (1966)] prepared this compound by an alternate route and showed the products from the two routes to be identical.

(26) O. E. Paris and P. E. Fanta, *J. Am. Chem. Soc.*, **74**, 3007 (1952).

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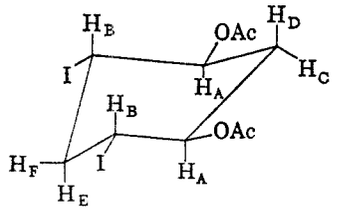
(29) A mixture of *cis*- and *trans*-1,3-cyclohexanediol and a mixture of *cis*- and *trans*-1,4-cyclohexanediol were purchased from Aldrich Chemical Co., Inc., Milwaukee, Wis.



H_A, 5.11 ppm (sextet, 2 H)
H_B, 3.98 ppm (sextet, 2 H)
OAc, 2.08 ppm (singlet, 6 H)
$H_{C,D,E,F}$, 1.3–3.3 ppm (complex multiplet, 4 H)

radiated, the H_C proton in removed and a triplet for H_A–$H_{B,D}$ splitting of 10.5 Hz is observed. When the region 42–52 Hz upfield from H_B is irradiated, the H_F proton is removed and a triplet for H_B–H_{AE} splitting of 10.5 Hz is observed. This pattern is consistent with the assigned stereochemistry resulting from 1,3 attack and is inconsistent with the pattern expected from 1,4 attack which would be similar to that observed for **14**.

Compound 26.—This structure is established from the similarity of the nmr absorption pattern with that of **15**, in particular the presence of absorption for two different methylene groups as triplets at δ 2.1 and 2.7.

Experimental Section[30]

trans-**4,8-Dioxatricyclo[5.1.0.0^{3,5}]octane** (**2**).—1,4-Cyclohexadiene (10 g, 0.125 mole) was dissolved in 100 ml of $CHCl_3$ and 15 g of anhydrous sodium acetate was added. The mixture was cooled in an ice bath and an excess of commercial peracetic acid solution (30%) was added so as to keep the temperature between 0 and 5°. The mixture was allowed to warm to room temperature with stirring and was held there for 48 hr. The $CHCl_3$ solution was washed with saturated aqueous $Fe_2(SO_4)_3$ solution, saturated aqueous Na_2CO_3 solution, and saturated aqueous NaCl solution. The organic layer was dried (Na_2SO_4) and evaporated to give 12.9 g (89%) of white solid, mp 45–85°, whose nmr spectrum indicated it to be a mixture of 64% **2** and 36% **1**. A similar mixture is obtained in 84% yield from *m*-chloroperbenzoic acid and **3**. Oxidation of **3** with 2 equiv of perbenzoic acid as previously described[4] or with monoperphthalic acid in ethyl ether produced **2** in 50% yield: mp 106.5–107° (lit.[1] mp 106.5–107.5°); $\nu_{max}^{CHCl_3}$ 3010, 1270, and 813 cm^{-1}; nmr (CCl_4), δ 2.33 (br singlet, 4 H, 2 $-CH_2-$) and 3.05 ppm (br singlet, 4 H, four epoxide hydrogens); mass spectrum (70 ev), *m/e* 112, 94, 83, 69, 68, 66, 57, 56, 55, 41, and 39.

Anal. Calcd for $C_6H_8O_2$: C, 64.29; H, 7.14. Found: C, 64.24; H, 7.12.

trans-**4-Hydroxy-5-bromocyclohexene** (**4**).—To 10 g (0.13 mole) of **3** in 50 ml of H_2O and 5 ml of dioxane was added 22 g (0.13 mole) of N-bromosuccinimide[31] in portions with stirring. After 3 hr the solution was extracted with $CHCl_3$. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and saturated aqueous NaCl solution, and dried (Na_2SO_4). Concentration left 14 g (65%) of a colorless oil, bp 109–110° (15 mm), which was shown to be 80% **4** and 20% *trans*-4,5-dibromocyclohexene by gas chromatography with 16% XF1150 on Chromosorb W at 120°. This crude mixture could be used directly in the preparation of **5**. A sample of **4** was purified for analysis by gas chromatography: $\nu_{max}^{CCl_4}$ 3560, 1650, 670 cm^{-1}; nmr ($CDCl_3$), δ 2.5 (multiplet, 4 H, 2 $-CH_2-$), 3.6–4.2 (multiplet, 2 H, >C*H*OHC*H*Br–), and 5.55 ppm (multiplet, 2 H, $-CH{=}CH-$).

Anal. Calcd for C_6H_9BrO: C, 40.68; H, 5.08; Br, 45.19. Found: C, 40.81; H, 5.34; Br, 45.19.

cis-**4,5-Epoxy**-*trans*-**2-bromocyclohexanol** (**5**).—The crude bromohydrin **4** (12.1 g, 0.072 mole) was added to 100 ml of an ether solution containing 0.076 equiv of monoperphthalic acid and the mixture was kept in the dark at room temperature for 24 hr. The solution was filtered and washed with cold saturated aqueous Na_2CO_3, and saturated aqueous NaCl. It was dried and concentrated to give an oil. (The nmr spectrum indicated that the ratio of *cis* to *trans* epoxidation varied from 62:38 to 78:22 in various runs.) The oil was dissolved in ether–hexane and cooled to give crystalline product which could be recrystallized from ether–hexane to give pure **5**: mp 55–56°; $\nu_{max}^{CHCl_3}$ 3550, 3490, 1263, 1065, and 1040 cm^{-1}; nmr ($CDCl_3$), δ 2.0–3.0 (multiplet, 4 H, 2 $-CH_2-$), 3.21 (multiplet, 2 H, two epoxide hydrogens), and 3.7–4.2 ppm (multiplet, 2 H, >C*H*BrC*H*OH–).

Anal. Calcd for $C_6H_9BrO_2$: C, 37.30; H, 4.66; Br, 41.45. Found: C, 37.50; H, 4.89; Br, 41.45.

cis-**4,8-Dioxatricyclo[5.1.0.0^{3,5}]octane** (**1**).—A mixture of **5** (10.0 g, 51.8 mmoles) in 100 ml of 1 *N* aqueous NaOH was stirred 1 hr and extracted with $CHCl_3$; the extracts were dried (Na_2SO_4). Concentration gave 5.6 g (100%) of **1**: mp 59.5–60° (recrystallization from ether–hexane raised this to 60–61°); nmr ($CDCl_3$), δ 2.50 (br quartet, 4 H, J = 17 Hz, 2 $-CH_2$) and 3.09 ppm (br singlet, 4 H, four epoxide hydrogens); mass spectrum (70 ev), *m/e* 112, 94, 83, 69, 68, 66, 57, 41, and 39.

trans,trans-**1,4/2,5-1,2,4,5-Cyclohexanetetrol** (**13**). **From 1. Reaction 1.**—A solution of **1** (454 mg, 4.05 mmoles) in 25 ml of water containing 2 drops of concentrated H_2SO_4 was heated at 45° for 12.5 hr with magnetic stirring. The water was removed *in vacuo* and the residue was recrystallized from 95% ethanol to give 629 mg (94%) of **13**,[4,32] mp 192–194° dec.

Reaction 2.—A solution of **1** (419 mg, 3.72 mmoles) in 20 ml of water brought to pH 10 with sodium hydroxide was stirred at 75° for 12 hr. After neutralization with 5% aqueous HCl the water was evaporated to give a white solid which was recrystallized as above to yield 565 mg (92%) of **13**, mp 194–195° dec.

From 2. Reaction 1.—The procedure was similar to the preparation from **1**: yield, 95%; mp 191–193° dec.

Reaction 2.—The procedure was similar to the preparation from **1**: yield, 78% mp 196–197° dec. The nmr spectrum and melting point of **13** and its tetraacetate derivative agreed with the literature values.[32]

trans,trans-**1,4/2,5-2,5-Dibromo-1,4-cyclohexanediol** (**14**). **Reaction 3.**—To a solution of **1** (488 mg, 4.35 mmoles) in 50 ml of $CHCl_3$ was added 1.5 g (9 mmoles) of 48% aqueous HBr. This was stirred at 45° for 14 hr. A white solid appeared after approximately 10 min and was collected after completion of the reaction. Recrystallization from water gave 1.11 g (93%) of white needles: mp 161.2–162°; ν_{max}^{KBr} 3455, 3360, 2908, 1445, 1378, 1345, 1310, 1720, 1245, 1198, 1174, 1056, 1048, 973, 960, 828, 668, and 650 cm^{-1}; nmr (acetone-d_6), δ 3.94 (doublet, 2 H, $-OH$, collapses to a singlet on addition of HCl gas), 3.2–3.8 (multiplet, 4 H, 2 >C*H*Br and 2 >C*H*OH), and 1.79 ppm (triplet, 4 H, J = 5.5 Hz, 2 $-CH_2-$).

Anal. Calcd for $C_6H_{10}Br_2O_2$: C, 26.30; H, 3.67; Br, 58.34. Found: C, 26.25; H, 3.68; Br, 58.54.

Reaction 4.—Anhydrous sodium bromide (1.15 g, 11.2 mmoles) was added to a solution of **1** (615 mg, 5.5 mmoles) in 25 ml of of anhydrous dimethylformamide. The solution was stirred under N_2 for 19 hr at 50°, 0.62 ml of glacial acetic acid was added, and the solvent was removed by evaporation *in vacuo*. The white residue was sublimed at 180° (0.2 mm) to give 1.02 g (68%) of white cubes, mp 159–162°.

From *cis*-**4,5-Epoxy**-*trans*-**2-bromocyclohexanol** (**5**).—To a solution of **5** (600 mg, 3.11 mmoles) in 20 ml of $CHCl_3$ was added 0.55 g (3.2 mmoles) of 48% aqueous HBr and the mixture was stirred at 45° for 12 hr. The resultant white solid was collected and dried to give 785 mg (93%) of white cubes, mp 161–162° recrystallized from water.

trans,trans-**1,4/2,5-2,5-Dibromo-1,4-cyclohexanediol Diacetate.**—The diol **14** (154 mg, 0.536 mmole) was dissolved in 6 ml of anhydrous pyridine and 0.124 ml (1.3 mmoles) of anhydrous acetic anhydride. The mixture was rapidly heated and refluxed for 5 min and then cooled to room temperature and poured into

(30) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with Perkin-Elmer Model 237 and Model 337 recording spectrophotomers fitted with sodium chloride prisms and grating, respectively. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 11MS. The microanalyses were performed by Dr. S. M. Nagy and his associates and by Galbraith Laboratories, Inc. The nmr spectra were determined with a Varian A-60 spectrometer and the data are in parts per million using tetramethylsilane as an internal standard at 0.00 ppm. The decoupling results were obtained with a Varian Model V-6058 decoupler attachment and are all recorded at 500-cps sweep width. The variable temperature nmr data were obtained with a Varian Model V-6040 attachment. The mass spectra were determined with a CEC Model 21-130 mass spectrometer at 70 ev.

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(32) (a) G. E. McCasland and E. C. Horswill, *ibid.* **76**, 1654 (1954); (b) G. E. McCasland, J. Furuta, L. F. Johnson, and J. N. Shoolery, *J. Org. Chem.*, **28**, 894 (1963).

ice water. Concentration of the solution under vacuum gave 181 mg (92%) of a white solid. Sublimation at 85° and 0.4 mm gave white cubes: mp 104–106°; $\nu_{max}^{CHCl_3}$ 2960, 1745, 1425, 1360, 1220, 1035 cm^{-1}; nmr ($CDCl_3$), δ 5.08–5.34 (multiplet, 2 H, >C*H*OAc), 4.08–4.37 (multiplet, 2 H, >C*H*Br), 2.30–2.60 (multiplet, 4 H, –CH_2–), and 2.06 ppm (singlet, 6 H, 2 –C(=O)CH_3).

Anal. Calcd for $C_{10}H_{14}Br_2O_2$: C, 33.53; H, 3.94; Br, 44.65. Found: C, 33.46; H, 3.78; Br, 44.75.

trans,trans-**1,4/2,5-2,4-Dibromo-1,5-cyclohexanediol (15). Reaction 3.**—The product was prepared from 308 mg of **2** and 1.2 g of 48% aqueous HBr as described for the preparation of **14**: yield, 905 mg (98%); mp 174.5–175.1°; ν_{max}^{KBr} 3450, 3350, 2950, 2910, 1450, 1370, 1320, 1218, 1198, 1177, 1083, 1062, 1043, 988, 953, 861, 822, 783, 662, and 550 cm^{-1}; nmr (dimethyl sulfoxide-d_6, δ 5.42 (doublet, 2 H, J = 5 Hz, –O*H*, collapses to a singlet on addition of HCl gas), 3.7–4.33 (multiplet, 4 H, 2 >C*H*Br and 2 >C*H*OH), 2.58 (triplet, 2 H, J = 5.3 Hz, –CH_2–), and 1.97 ppm (triplet, 2 H, J = 5.3 Hz, –CH_2–).

Anal. Calcd for $C_6H_{10}Br_2O_2$: C, 26.30; H, 3.67; Br, 58.34. Found: C, 26.20; H, 3.68; Br, 58.13.

Reaction 4.—The product was prepared from 610 mg of **2** and 2.5 g of NaBr as described for the preparation of **18**: yield, 915 mg (62%); mp 172–173°.

trans,trans-**1,4/2,5-2,4-Dibromo-1,5-cyclohexanediol Diacetate.**—The product was prepared from 1.76 g of diol **15** by the same procedure as the preparation of **19**: yield, 1.77 g (87%); mp 82.5–83.5°; $\nu_{max}^{CHCl_3}$ 2960, 1740, 1434, 1370, 1220, 1050, 900, and 875 cm^{-1}; nmr ($CDCl_3$), δ 5.22 (quartet, 2 H, J = 6 Hz, 2 >C*H*OAc), 4.38 (quartet, 2 H, J = 6 Hz, 2 >C*H*Br), 2.67 (triplet, 2 H, J = 6 Hz, –CH_2–), 2.23 (triplet, 2 H, J = 6 Hz, –CH_2–), and 2.12 ppm (singlet, 6 H, 2 –C(=O)CH_3).

Anal. Calcd for $C_{10}H_{14}Br_2O_4$: C, 33.53; H, 3.94; Br, 44.65. Found: C, 33.78; H, 3.96; Br, 44.78.

trans,trans-**1,4/2,5-2,5-Bisdimethylamino-1,4-cyclohexanediol (16).**—An autoclave glass liner containing **1** (1.148 g, 10.2 mmoles) was cooled in a Dry Ice bath, partially filled with excess anhydrous dimethylamine, placed in an autoclave, and filled to a pressure of 290 lb/in.^{2} with N_2. The chamber was heated at 97° for 17.5 hr (470 lb/in.^{2}). The autoclave was cooled to room temperature and vented. The residual oil was short-path distilled at 123° (0.45 mm) to give 1.71 g of a viscous orange oil which was crystallized from benzene–hexane to give 1.57 g (76%) of product: mp 103–104°; $\nu_{max}^{CHCl_3}$ 3600, 3400, 2950, 2865, 2825, 2780, 1455 cm^{-1}; nmr ($CDCl_3$), δ 3.95 (quartet, 2 H, J = 6 Hz, 2 >C*H*OH), 3.42 (singlet, 2 H, –O*H*), 2.7 (singlet and quartet, 14 H, 2 >C*H*–N(CH_3)$_2$), and 1.8 ppm (multiplet, 4 H, 2 –CH_2).

Anal. Calcd for $C_{10}H_{22}N_2O_2$: C, 59.37; H, 10.96; N, 13.85. Found: C, 59.54; H, 10.90; N, 13.75.

trans,trans-**1,4/2,5-2,5-Bisdimethylamino-1,4-cyclohexanediol Diacetate.**—Diol **16** (543 mg, 2.69 mmoles) was dissolved in 8 ml of anhydrous pyridine and 0.50 ml (5.4 mmoles) of anhydrous acetic anhydride. The solution was refluxed for 10 min, cooled to room temperature, and added to ice water. The mixture was concentrated under vacuum and chloroform was added. The organic layer was separated, washed with water, and dried (Na_2SO_4). Evaporation gave 605 mg (78%) of white crystals. Sublimation at 58° (0.4 mm) gave white cubes: mp 81–82°; ν_{max}^{KBr} 2980, 2960, 2940, 2840, 2800, 1740, 1460, 1380, 1250, 1207, 1068, 1050, 1038, 940, 903, 878, 858, 733, and 600 cm^{-1}; nmr ($CDCl_3$), δ 5.2 (multiplet, 2 H, >C*H*OAc), 2.5 (multiplet, 2 H, 2 >C*H*NMe$_2$), 2.3 (singlet, 12 H, 2 –N(CH_3)$_2$), 2.08 (singlet, 6 H, 2 –C(=O)CH_3), and 1.8 ppm (multiplet, 4 H, 2 –CH_2–).

Anal. Calcd for $C_{14}H_{22}N_2O_4$: C, 58.71; H, 9.15; N, 9.78. Found: C, 58.77; H, 8.92; N, 9.92.

trans,trans-**1,4/2,5-2,4-Bisdimethylamino-1,4-cyclohexanediol (17)** was prepared from **2** (1.1148 g, 10.2 mmoles) in 69% yield after recrystallization from benzene–hexane by the same procedure described for **16** (autoclave at 109° and 320 lb/in.^{2}): mp 104–105°; $\nu_{max}^{CHCl_3}$ 3620, 3430, 2950, 2878, 2845, 2796, 1468, 1270, 1210, 1070, and 1040 cm^{-1}; nmr ($CDCl_3$), δ 3.92 (multiplet, 2 H, 2 >C*H*OAc), 3.58 (singlet, 2 H, –O*H*), 2.31 (multiplet, 2 H, 2 >C*H*NMe$_2$), 2.24 (singlet, 12 H, 2-N(CH_3)$_2$), and 1.8 ppm (multiplet, 4 H, 2 –CH_2–).

Anal. Calcd for $C_{10}H_{22}N_2O_2$: C, 59.37; H, 10.92; N, 13.85. Found: C, 59.18; H, 11.03; N, 13.89.

trans,trans-**1,4/2,5-2,4-Bisdimethylamino-1,5-cyclohexanediol** diacetate was prepared in 59% yield by the same procedure as the diacetate of **16**: mp 68.5–70°; $\nu_{max}^{CHCl_3}$ 2960, 2842, 2791, 1735, 1470, 1378, 1260, 1100, 1030, and 780 cm^{-1}; nmr ($CDCl_3$), δ 5.18 (multiplet 2 H, 2 >C*H*OAc), 2.5 (multiplet, 2 H, 2 >C*H*NMe$_2$), 2.26 (singlet, 12 H, –N(CH_3)$_2$), 2.03 (singlet, 6 H, 2 –C(=O)CH_3), and 1.8 ppm (multiplet, 4 H, 2 –CH_2).

Anal. Calcd for $C_{14}H_{26}N_2O_4$: C, 58.71; H, 9.15; N, 9.78. Found: C, 58.95; H, 9.31; N, 10.04.

trans,trans-**1,4/2,5-2,5-Bisethylamino-1,4-cyclohexanediol (18).**—A solution of **1** (2.60 g, 25 mmoles) in 35 ml of 70% aqueous ethylamine at 55° was stirred for 3 days. The solvent was removed under vacuum and a small amount of acetone was added to induce crystallization. The product was dried in a vacuum desiccator: yield, 4.8 g (91%); $\nu_{max}^{CHCl_3}$ 3650, 3600, 3330, 2960, 2940, 2850, 1458, 1378, 1345, 1285, 1105, and 1025 cm^{-1}; nmr (D_2O), δ 4.7 (singlet 4 H, 2 –O*H* and 2 >N*H*), 1.4–4.0 (complex, poorly resolved multiplets, 12 H), and 1.05 ppm (triplet, 6 H, J = 7 Hz, 2 –CH_3).

Anal. Calcd for $C_{10}H_{22}N_2O_2$: C, 59.37; H, 10.96; N, 13.85. Found: C, 59.55; H, 10.96; H, 13.82.

4,8-Diethyl-*cis*-4,8-diazatricyclo[5.1.0.0^{3,5}]octane (32).—Into a stirred suspension of **18** (500 mg, 2.48 mmoles) in 225 ml of dry ethyl ether was bubbled gaseous HCl with occasional cooling in an ice bath. The HCl salt precipitated as the gas was added. Excess chlorosulfonic acid was added over 0.5 hr and the suspension was stirred for 21 hr. The sulfate ester was filtered and dried: yield, 650 mg (79%); mp 228–230° dec.

The sulfate ester (5.0 g, 15.1 moles) was dissolved in 30 ml of hot water and added dropwise to 50 ml of a 30% aqueous NaOH solution at 80°. The mixture was stirred for 0.5 hr, cooled, and extracted with ether. The aqueous solution was stirred at 80° for 1 hr more and extracted with ether. The ether extracts were combined, dried (NaOH), and evaporated. The residue was short-path distilled to give 0.48 g (22%) of product: bp 90–92° (12 mm); ν_{max}^{CHCl} 2960, 2935, 2907, 2625, 1450, 1350, 1287, 1240, 1140, 1092, 1037, and 940 cm^{-1}; nmr ($CHCl_3$), δ 2.13 (multiplet, 8 H, 4 –CH_2–) and 1.03 ppm (multiplet, 10 H, 2 –CH_3 and four azeridine hydrogens); mass spectrum, m/e 122, 108, 96, 68, 56, and 28.

Anal. Calcd for $C_{10}H_{18}N_2$: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.07; H, 11.01; N, 16.72.

trans,trans-**1,4/2,5-2,4-Bisethylamino-1,5-cyclohexanediol (19)** was prepared as the monohydrate in 90% yield from 2.1 g of **2** by the same procedure described for **18**: mp 92–93° (EtOAc); ν_{max}^{KBr} 3400, 3265, 3170, 2975, 2900, 2860, 1675, 1490, 1455, 1380, 1260, 1137, 1007, 1075, 1035, 976, and 840 cm^{-1}; nmr (dimethyl sulfoxide-d_6), δ 2.0–4.2 (complex multiplets, 14 H, 2 –CH_3CH_2–NHC*H*C*H*OH and H_2O), 1.68 (quartet, 4 H, J = 6 Hz, 2 –CH_2–), and 1.06 ppm (triplet, 6 H, J = 7 Hz, 2 –CH_3).

Anal. Calcd for $C_{10}H_{22}N_2O_2 \cdot H_2O$: C, 54.51; H, 10.98; N, 12.72. Found: C, 54.60; H, 10.98; N, 12.63.

4,8-Diethyl-*trans*-4,8-diazatricyclo[5.1.0.0^{3,5}]octane (33).—The sulfate ester was prepared in 75% yield from 3.0 g of **19** by the same procedure described in the preparation of **32**, mp 184–192° dec, and converted by the same procedure to **33** in 21% yield: bp 110° (14 mm); $\nu_{max}^{CHCl_3}$ 2950, 2915, 2885, 2800, 1470, 1449, 1428, 1408, 1380, 1345, 1330, 1250, 1083, and 860 cm^{-1}; nmr ($CDCl_3$), δ 2.15 (quartet, 4 H, J = 7 Hz, 2 >NCH_2–CH$_2$CH–), 1.94 (br singlet, 4 H, 2 >CHCH_2–), 1.18 (br singlet, 4 H, >C*H*N<), and 1.03 (triplet, 6 H, J = 7 Hz, 2 –CH_3); mass spectrum, m/e 123, 121, 110, 96, 81, 71, 68, 56, and 41.

Anal. Calcd for $C_{10}H_{18}N_2$: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.47; H, 11.02; N, 16.90.

Hydrogenation of 1. Reaction 7.—A solution of **1** (982 mg, 8.76 mmoles) in 75 ml of anhydrous ethyl acetate was placed in a 300-ml autoclave liner and 0.4 g of prereduced 10% Pd/C catalyst[33] was added. The mixture was kept under 1400 lb/in.^{2} of hydrogen at room temperature for 36 hr. The solution was filtered and the solvent removed under reduced pressure to obtain 954 mg (97%) of the diol mixture. The diol mixture was acetylated by the same procedure as that used to acetylate **14** and the mixture was found by gas chromatographic analysis (12 ft × 1/8 in. i.d. column containing 5% 1,2,3-tris(2-cyanoethoxy)-propane on washed neutral Chromosorb P, 80–100 mesh, column temperature 145°) to consist of 65 ± 5% *cis*-1,3-cyclohexanediol diacetate and 27 ± 5% *cis*-1,4-cyclohexanediol diacetate by comparison with authentic samples.

***cis*-1,3-Cyclohexanediol from 1. Reaction 8.**—To an ethyl ether solution containing 0.60 g of $LiAlH_4$ was added **1** (1.24 g, 11

(33) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 685.

mmoles) and the mixture was refluxed 18 hr. The excess hydride was decomposed by the addition of EtOAc followed by 1 *N* NaOH at 0°. The ether was removed under vacuum and the residue extracted with four 25-ml portions of hot EtOAc. The EtOAc extracts were combined, washed with saturated aqueous NaCl, dried, and concentrated to a white solid which was recrystallized from acetone to obtain 0.55 g (44%) of diol, mp 83–84° (lit.[34] mp 83–84°), bisphenylurethan mp 212–213° (lit.[35] mp 213°).

trans-1,4-Cyclohexanediol from 2. **Reaction 8.**—This compound was prepared in 31% yield from 32.2 mg of **2** by the procedure described for *cis*-1,3-cyclohexanediol, mp 139–140° (lit.[36] mp 140–141°), dibenzoate mp 148–149° (lit.[36] mp 149–150°).

trans,trans-1,5/2,4-2,4-Dimethyl-1,5-cyclohexanediol (23).—A halide-free ethereal dimethylmagnesium solution[37] (80 ml, 1.6 *N*, 64 mmoles) was added to **1** (698 mg, 6.22 mmoles) and the solution was refluxed for 7 days under N_2 with occasional addition of dry ether. A mixture of saturated aqueous NH_4Cl and 5% aqueous HCl was added, the water layer was made acidic, and it was extracted with ether. The ether extracts were combined, dried (Na_2SO_4), and evaporated to give 630 mg (71%) of product which was recrystallized from acetone: mp 135–136°; ν_{max}^{KBr} 3200, 2970, 2955, 2940, 2873, 1460, 1378, 1348, 1279, 1232, 1092, 1068, 1045, 1018, 1001, 955, and 700 cm^{-1}; nmr (dimethyl sulfoxide-d_6), δ 4.3 (multiplet, 2 H, 2 >C*H*OH), 3.31 (singlet, 2 H, 2 -O*H*), and 0.7–1.6 ppm (multiplet, 12 H, 2 $-CH_2-$ and 2 >C*H*CH_3); mass spectrum (70 ev), *m/e* 126, 111, 108, 97, 93, 85, 83, 73, 71, 58, and 55.

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.69; H, 11.36.

The diacetate was prepared from 250 mg of diol in 78% yield by the same procedure reported for the preparation of **14**: bp 103° (0.6 mm); $\nu_{max}^{CHCl_3}$ 2960, 2940, 2870, 1730, 1520, 1455, 1378, 1250, and 972 cm^{-1}; nmr ($CDCl_3$), δ 4.3–4.9 (sextet, 2 H, J = 11, 5 Hz, 2 >C*H*OAc), 2.13 (singlet, 6 H, 2 $-C(=O)CH_3$), 1.1–2.45 (multiplet, 6 H, 2 $-CH_2CH-$), and 0.92 ppm (doublet, 6 H, 2 >CHCH_3).

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.01; H, 8.81.

cis-4,6-Dimethyl-1,3-cyclohexanedione.—The diol **23** (207 mg, 1.44 mmoles) was added to 15 ml of anhydrous acetone, 8 *N* Jones reagent[38] was added dropwise until a yellow color remained, and the solution was filtered repeatedly with a Büchner funnel until colorless. The solvent was removed under vacuum to give 181 mg of a pale green oil which crystallized on standing. Sublimation gave 162 mg (74%) of white needles: mp 112–113° (lit.[39] mp 114°); $\nu_{max}^{CHCl_3}$ 2975, 2940, 2850, 1730, 1704, 1600, 1465, and 1380 cm^{-1}; nmr ($CDCl_3$) δ 7.7 and 3.47 (singlets, 2 H, $-COCH_2CO-$ and COC*H*=CO*H*), 2.5 (multiplet, 4 H, >C*H*-CH_2CH-), and 1.2 ppm (doublet, 6 H, 2 >CHCH_3); mass spectrum (70 ev), *m/e* 140, 112, 97, 69, 56, 41, and 39.

trans,trans-1,4/2,5-2,4-Dimethyl-1,5-cyclohexanediol (24) was prepared in 79% yield from 770 mg of **2** by the same procedure used to prepare **23**: mp 107–108°; ν_{max}^{KBr} 3420, 3365, 2970, 2940, 2910, 2880, 1470, 1440, 1340, 1200, 1042, 1024, 1003, 903, 740, 612, and 536 cm^{-1}; nmr (dimethyl sulfoxide-d_6), δ 4.32 (doublet, 2 H, 2 -O*H*), 3.43 (multiplet, 2 H, >C*H*OH), 1.5 (triplet, 2 H, HOCHCH_2CHOH), 1.41 (multiplet, 2 H, $CH_3CHCH_2CHCH_3$), and 0.87 ppm (doublet, 6 H, 2 $-CH_3$); mass spectrum (70 ev), *m/e* 126, 111, 84, 73, 71, 58, 55, and 41.

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.63; H, 11.29.

The diacetate was prepared in 77% yield from 328 mg of the piol by the same procedure used to prepare **14**: bp 81° (0.3 mm); $\nu_{max}^{CHCl_3}$ 2950, 2910, 1725, 1455, 1372, 1225, 1102, 1020, 975, and 820 cm^{-1}, nmr ($CDCl_3$), δ 4.5 (quartet, 2 H, J = 6.5 Hz, 2 >CHOAc), 1.67 (singlet, 6 H, 2 >COCH_3), 0.9–2.0 (multiplet, 6 H, 2 $-CH_2-$ and 2 >C*H*CH_3), and 0.65 ppm (doublet, 6 H, 2 $-CH_3$).

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.25, 63.11; H, 8.79, 8.74.

trans,trans-1,5/2,4-2,4-Diiodo-1,5-cyclohexanediol (25). From 1. **Reaction 10.**—Magnesium turnings (0.45 g, 18.8 g-atoms) were added to 100 ml of ethyl ether freshly distilled from $LiAlH_4$. To this was added 4.8 g of I_2 and the solution was refluxed until MgI_2 formation was complete as evidenced by the formation of a pale yellow color (~4 hr). The epoxide **1** (974 mg, 8.68 mmoles) in 45 ml of ethyl ether was added over 1.5 hr at reflux under nitrogen. The solution was refluxed an additional 3 hr and an aqueous solution of NH_4Cl and 5% HCl was added until the aqueous layer remained acidic. The aqueous layer was extracted with ether. The ether extracts were combined, dried (Na_2SO_4), and evaporated to give 2.37 g (73%) of product which was recrystallized from water: mp 184–185°; ν_{max}^{KBr} 3420, 3200, 2945, 2875, 1640, 1450, 1350, 1310, 1260, 1140, 1100, 1083, 1022, 976, and 522 cm^{-1}; nmr (dimethyl sulfoxide-d_6), δ 5.28 (doublet, 2 H, J = Hz, 2 -O*H*), 3.34–4.18 (multiplet, 4 H, 2 -C(OH)*H*C(I)*H*-) and 1.2–3.0 ppm (multiplet, 4 H, 2 $-CH_2-$).

Anal. Calcd for $C_8H_{10}I_2O_2$: C, 19.58; H, 2.74; I, 68.98. Found: C, 19.76; H, 2.73; I, 69.02.

From 1. **Reaction 11.**—Methyl iodide (8.0 g, 54.5 mmoles) was added to a dry ether suspension of 2.0 g (83.4 g-atoms) of clean Mg turnings in 150 ml of ether. After the Grignard reagent had formed, **1** (1.3 g, 11.6 mmoles) in 50 ml of ether was added slowly. The solution deposited a white solid as it was stirred under N_2 at reflux for 48 hr. A saturated aqueous NH_4Cl solution was slowly added and the aqueous layer was acidified with 5% HCl. The aqueous layer was extracted with ether. The ether layers were combined, washed with aqueous $NaHCO_3$ and NaCl, and dried (Na_2SO_4). Evaporation of the solvent gave 2.57 g (62%) of product which was recrystallized from water, mp 184–185° dec. The infrared spectrum of this was identical with that of the product prepared from MgI_2 (reaction 10).

The diacetate was prepared from 133 mg of diol by the same procedure described for the preparation of **14**: mp 111–112° (from hexane); ν_{max}^{KBr} 2940, 1750, 1740, 1370, 1250, 1088, 1040, and 903 cm^{-1}; nmr ($CDCl_3$), δ 5.0 (sextet, 2 H, J = 11 and 5 Hz, 2 >C*H*OAc), 3.9 (sextet, 2 H, J = 11 and 5 Hz, 2 >C*H*I), 2.9 (multiplet, 4 H, 2 $-CH_2-$), and 2.08 ppm (singlet, 6 H, 2 $-COCH_3$).

Anal. Calcd for $C_{10}H_{14}I_2O_4$: C, 26.57; H, 3.12; I, 56.14. Found: C, 26.65; H, 3.18; I, 56.11.

trans,trans-1,4/2,5-2,4-Diiodo-1,5-cyclohexanediol (26). From 2. **Reaction 10.**—This compound was prepared in 73% yield from 1.0 g of **2** by the same procedure used to prepare **25**, from **1** and MgI_2: mp 164–165° (from H_2O); ν_{max}^{KBr} 3470, 3390, 2950, 2895, 1445, 1350 (t), 1172 (d), 1080, 1028, 981, 772, and 629 cm^{-1}; nmr (dimethyl sulfoxide-d_6), δ 5.6 (doublet, 2 H, 2 -O*H*), 4.2 (multiplet, 4 H, 2 >C*H*I and 2 >C*H*OH), 2.7 (triplet, 2 H, J = 6 Hz, $-CH_2-$), and 2.1 ppm (triplet, 2 H, J = 6 Hz, $-CH_2-$).

Anal. Calcd for $C_8H_{16}I_2O_2$: C, 19.58; H, 2.74; I, 68.98. Found: C, 19.41; H, 2.71; I, 69.32.

From 2. **Reaction 11.**—The product was prepared in 42% yield from 2.39 g of **2** by the same procedure described for the preparation of **25** from **1** and CH_3MgI, mp 164–165°. The infrared and nmr spectra were identical with those of the product from reaction 10.

2,5-Bis-*endo*-hydroxy-7-thiabicyclo[2.2.1]heptane (27).—A solution of **1** (1.0 g, 8.94 mmoles) in 25 ml of absolute ethanol and a solution of $Na_2S \cdot 9H_2O$ in 50 ml of 1:1 aqueous ethanol were added simultaneously to 25 ml of refluxing ethanol and the mixture was refluxed 13 hr. The solvent was removed under vacuum, dilute acetic acid was added to neutrality, and the residue was extracted with ethyl ether. The ether extracts were combined, washed with brine, and dried (Na_2SO_4). Evaporation of the solvent *in vacuo* gave an oil which crystallized on standing. Recrystallization from benzene and sublimation gave 447 mg (34%) of **27**, mp 233–235°.[25]

Desulfurization of 65 mg of **27** with excess W-2 Raney nickel[40] in ethanol gave *cis*-1,4-cyclohexanediol in 81% yield, mp 107–109° (lit.[41] mp 108–110°). The infrared spectrum was identical with that previously reported (Sadtler No. 17179).

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