wise. The mixture was allowed to stand overnight and then the solvent was removed at reduced pressure. The residue was dissolved in ether and washed with water. The aqueous layer was saturated with sodium chloride and extracted with ether. The combined ether extracts were dried and concentrated to give 3.98 g (88.5%) of an oil. Glpc analysis on 8-ft 20% LAC-728 at 190° indicated the presence of two components in the ratio 1:3. Analytical samples of the individual ketones were obtained by preparative glpc on the same column. The minor component **12** had mp 29.5-32°; ir (KBr) 1700 (vs), 1190 (m), 1140 (w), 1105 (m), 1090 (s), 1060 (m), 1035 (s), 1005 (w), 960 (w), 945 (m), 860 (w), and 760 cm^{-1} (w); nmr (CCl_4) 1.1-2.3 (m, 6 H), 2.4-3.0 (m, 4 H), 4.15-4.65 (bs, 2 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.32; H, 8.61.

The major component **13** was identical in every respect with the material described below.

9-Oxabicyclo[4.2.1]nonan-2-one (13).—5-Hydroxycyclooctanone (**14**, 7.8 g) was dissolved in glacial acetic acid (75 ml) containing water (25 ml). The solution was heated to 60° and pyridinium bromide perbromide (19.5 g) was added slowly with stirring during 1 hr. When the addition was complete, the solution was left overnight at room temperature. It was then poured into cold water (700 ml) and extracted six times with methylene chloride. The combined extracts were washed twice with water and dried. Removal of the solvent left a viscous brown oil (12.8 g) which was dissolved in methanol and added to a solution of potassium hydroxide (3.0 g) in methanol (20 ml). After 5 min, the solution was poured into cold water (700 ml) and extracted with methylene chloride. The combined extracts were washed with water and dried. Removal of the solvent followed by fractional distillation gave **13**, 3.7 g (47%), bp 76-77.5° (3 mm). A sample of >99% purity was obtained by adsorption chromatography over alumina.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.63; H, 8.57.

Wolff-Kishner Reduction of 9-Oxabicyclo[4.2.1]nonan-2-one (13).—The ketone (1.0 g), potassium hydroxide (1.5 g), hydrazine hydrate (1.0 ml), and diethylene glycol (10 ml) were placed in a flask fitted with a reflux condenser. The mixture was heated in an oil bath at 160° for 2 hr. After cooling, cold water was added and the solution was extracted with ether. The ether solution was washed with water and dried ($MgSO_4$). Cautious removal of the solvent left an oil which was shown by glpc on 2-ft 20% SE-30 to contain components in the ratio 4:1. The individual components were isolated by preparative glpc and identified as 9-oxabicyclo[4.2.1]nonane (**4**) and 4-cycloocten-1-ol (**19**) by comparison of their ir spectra and glpc retention times with those of authentic samples.

Wolff-Kishner Reduction of 9-Oxabicyclo[4.2.1]nonan-3-one (12).—A sample of **12** (24.5 mg) was dissolved in ethylene glycol (0.5 ml) containing 85% hydrazine hydrate (50 μl) and potassium hydroxide (10 mg). The mixture was heated under reflux for 1 hr and then cooled, diluted with water, and extracted with pentane. The pentane solution was dried ($MgSO_4$) and concentrated. The ir spectrum of the residue was identical with that of an authentic sample of 9-oxabicyclo[4.2.1]nonane (**4**). Glpc analysis on a 2-ft 20% SE-30 showed only one component. A sample obtained by preparative glpc had mp 28-30° (lit.[4] mp 31°).

9-Oxabicyclo[3.3.1]nonan-2-one (17) and 9-Oxabicyclo[5.1.1]-nonan-2-one (18).—4-Hydroxycyclooctanone (**16**, 5.0 g) was dissolved in glacial acetic acid (19 ml) containing water (6 ml). The solution was heated to 60° and pyridinium bromide perbromide (11.1 g) was added slowly with stirring during 15 min. When the addition was complete, the solution was left overnight at room temperature. It was then diluted with cold water (200 ml) and extracted with methylene chloride. The combined extracts were washed with saturated sodium bicarbonate solution and dried. Removal of the solvent left 7.2 g of a brown oil which was then dissolved in methanol (50 ml) and added to a solution of potassium hydroxide (5.0 g) in methanol (35 ml). After 10 min, the volume of the solution was reduced and the residue was dissolved in ether and poured into water (200 ml). The ether layer was separated and the aqueous layer was extracted with an additional 100 ml of ether. The combined extracts were washed with water and dried. Removal of the solvent followed by distillation gave 1.0 g (20%) of a mixture of **17** and **18**, bp 50° (0.3 mm). Glpc analysis on a 5-ft 5% XF-1150 at 148° indicated an isomer ratio of 1:2.5. Separation of the two isomers was achieved by adsorption chromatography on alumina. Elution with methylene chloride–pentane (1:4) gave pure **17** (200 mg) in the first three fractions. Fractions 4-8 (410 mg) contained equal amounts of the two ketones. Finally, elution with 300 ml of methylene chloride gave **18** (300 mg) of 90-95% purity. Further purification was achieved by preparative glpc on an 8-ft 20% LAC-728 at 180°. Ketone **18** had principle ir bands at 1700 (vs), 1050 (s), 1020 (s), 980 (s), 940 (m), and 865 cm^{-1}; mass spectrum major peaks (*m/e*, relative intensity) 140 (17, molecular ion), 84 (45), 83 (46), 68 (45), 55 (100), 41 (100), and 39 (99).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.59; H, 8.80.

Structure Proof of 9-Oxabicyclo[3.3.1]nonan-2-one (17).—A sample of **17** (17 mg) was dissolved in ethylene glycol (250 μl) containing 95% hydrazine (75 μl) and potassium hydroxide (10 mg). The mixture was heated under reflux for 1 hr and then cooled, diluted with water, and extracted with ether. The ether solution was dried ($MgSO_4$) and concentrated. Glpc analysis of the residue on a 2-ft 20% SE-30 showed the presence of 9-oxabicyclo[3.3.1]nonane (**6**) and 4-cycloocten-1-ol (**19**) in the ratio 3:1.

Registry No.—1, 19740-73-9; **2,** 10299-46-4; **5,** 19740-75-1; **8,** 19740-76-2; **9,** 19771-17-6; **12,** 19740-77-3; **13,** 19740-78-4; **17,** 19740-79-5; **18,** 19740-80-8.

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cis,cis-1,5-Cyclooctadiene Diepoxide[1]

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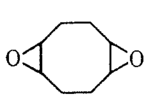
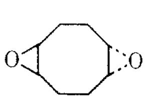
The epoxidation of *cis,cis*-1,5-cyclooctadiene with excess peracid can give *cis*- and/or *trans*-diepoxides **1a** and **b**. The use of perbenzoic acid in this reaction was studied by Criegee and Kerkow,[3] although no experiments concerning the configuration of the product were carried out. We have investigated the stereochemistry of this reaction and have observed some transannular reactions with the diepoxide. A study of the diepoxidation of 1,4-cyclohexadiene revealed that depending on the peracid used, *trans*-1,4-cyclohexadiene diepoxide or mixtures of the *cis* and *trans* isomers were obtained.[4] It appeared possible that changing the peracid would lead to similar effects in the case of *cis,cis*-1,5-cyclooctadiene. However, we found that peracetic acid in acetic acid gave a diepoxide identical in glpc retention time, infrared spectrum, and refractive index with that obtained using perbenzoic acid in chloroform; according to the glpc analysis, performed on various liquid phases, only one isomer of the diepoxide was obtained from both reactions.



1a



1b

The well-established mode of reaction of lithium

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(1) Supported in part by a research grant (GP-1587) from the National Science Foundation.

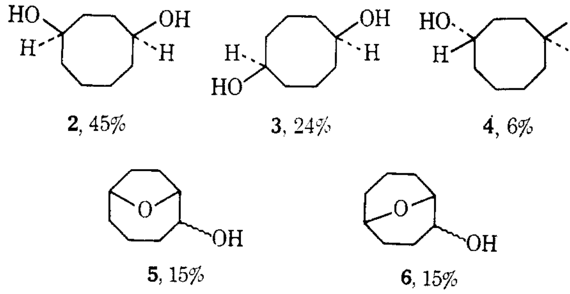
(2) To whom enquiries should be addressed at The Chemistry Department, Queen's University, Belfast, N. Ireland.

(3) Unpublished results of R. Criegee and A. Kerkow. We thank Professor Criegee for an account of this work.

(4) T. W. Craig, G. R. Harvey, and G. A. Berchtold, *J. Org. Chem.*, **32**, 3743 (1967); H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 221 (1959).

aluminum hydride with epoxides offered a method for determining the stereochemistry of the diepoxide. Normally, the epoxide ring is opened in an S$_N$2-type process. On this basis, **1a** should give *cis*-1,4-and/or *cis*-1,5-cyclooctanediol whereas **1b** should give *trans*-1,4- and/or *trans*-1,5-cyclooctanediol. In this event, reduction of the diepoxide with lithium aluminum hydride in tetrahydrofuran gave a mixture of products (Chart I) from which a cyclooctanediol fraction could be obtained by fractional distillation. The cyclooctanediols, which were inseparable on glpc analysis, were converted into the corresponding ditrifluoroacetates which were separated and identified as derivatives of *cis*-1,4-cyclooctanediol (**2**), *cis*-1,5-cyclooctanediol (**3**), and *trans*-1,4-cyclooctanediol (**4**) by comparison of their glpc retention times and infrared spectra with those of authentic samples.[5] A lower boiling fraction was also isolated from the product mixture and was shown to contain at least three of the four possible isomers of **5** and **6**. A mixture of *endo* **5** and *endo* **6** was synthesized by the method of Moon and Hayes[6] and *endo* **5** was isolated by preparative glpc. Its mass spectrum and glpc retention time were identical with those of the major component (70%) of the mixture of epoxy alcohols obtained from the diepoxide. The presence of *endo* **6** was not definitely established but two other isomers, assumed to be *exo* **5** and *exo* **6**, were isolated by preparative glpc. Their mass spectra (M$^+$ = 142) showed fragmentation patterns almost identical with those of *endo* **5** and *endo* **6**; only slight differences in peak intensities were observed. The results of the lithium aluminum hydride reduction are not completely understood. If the reaction proceeds in the anticipated stereospecific way, then the diepoxide must be a mixture of **1a** and **b**, **1a** being the dominant isomer since *cis* diols were the major products of the reduction. On the other hand, a nonstereospecific reaction involving a small amount of isomerization of one epoxide group to a carbonyl group prior to reduction could account for the small amount of *trans*-diol in the products. The epoxy alcohol *endo* **5** can arise *via* a transannular mechanism in which the oxygen anion resulting from the opening of the first epoxide group reacts with the second epoxide group in the *trans* isomer **1b**; no *exo* isomers can be formed by this mechanism.

Chart I



Catalytic hydrogenation of the diepoxide at room temperature using palladium on carbon as catalyst and a hydrogen pressure of 900 psi gave the products listed in Chart II. Comparisons, similar to those used in the lithium aluminum hydride reduction, revealed that the diol fraction contained *cis* isomers exclusively. The remaining products were identified by comparisons with authentic samples.[7] The isolation of considerable quantities of 4- and 5-hydroxycyclooctanone makes it difficult to assign an exact ratio to the diepoxide although the results confirm that **1a** is the major isomer. In another series of experiments it was established that reduction of the diepoxide with a deficiency of lithium aluminum hydride in ether gave a single epoxy alcohol, assigned *cis* configuration **7**. This alcohol was converted into (a) the crystalline epoxy acetate **8** and (b) the epoxy tosylate **9**. This latter compound on exposure to tetraethylammonium acetate gave the liquid epoxy acetate **10** (Chart III). Comparison of the two epoxy acetates **8** and **10** showed that no trace of one could be found in the crude reaction mixture containing the other under glpc conditions which cleanly separated the two.

Chart II

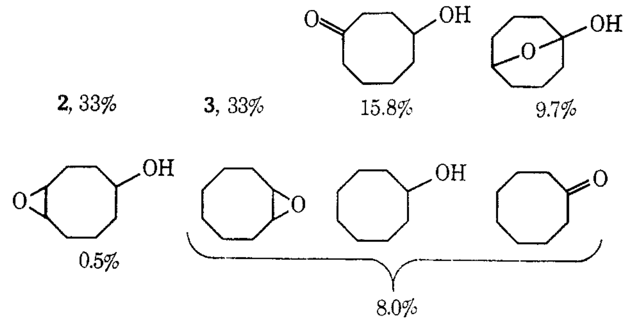
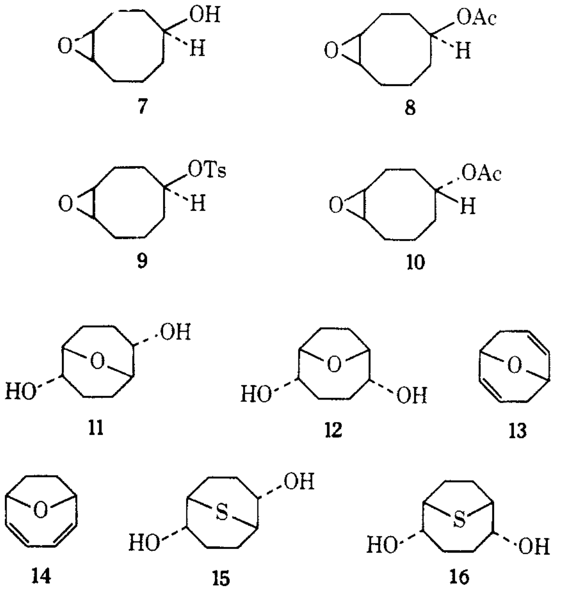


Chart III



Criegee and Kerkow[3] did not obtain the expected tetrols from hydrolysis of the diepoxide with dilute sulfuric acid. Instead, a product was isolated for

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(5) A. C. Cope and B. C. Anderson, *J. Amer. Chem. Soc.*, **79**, 3892 (1957); A. C. Cope and A. Fournier, *ibid.*, **79**, 3896 (1957).

(6) S. Moon and L. Hayes, *J. Org. Chem.*, **31**, 3067 (1966); see also A. C. Cope, M. A. McKervey, and N. M. Weinshenker, *J. Amer. Chem. Soc.*, **89**, 2932 (1967).

(7) We thank Badische Anilin und Soda Fabrik, Ludwigshafen, Germany, for samples of 5-hydroxycyclooctanone (which exists in the hemiketal form) and 4-hydroxycyclooctanone.

which they suggested structure **11**. We repeated the hydrolysis under the same conditions and obtained a product (97.5%), the spectral characteristics of which were consistent with **11** and/or **12**. That the product was a mixture of the two isomers was established by conversion to the ditosylates followed by elimination with potassium hydroxide in triethylene glycol to give a mixture of the epoxy dienes **13** and **14**.[8] Subsequent hydrogenation gave 9-oxabicyclo[4.2.1]nonane (75%) and 9-oxabicyclo[3.3.1]nonane (25%). Hydrolysis of the diepoxide therefore gives **11** and **12**, **12** being the dominant product. The formation of these two products can be explained by a mechanism involving solvolytic opening of one of the epoxide groups in the first step followed by a transannular nucleophilic substitution by one of the hydroxyl groups on the second epoxide group, leading to di-*endo*-epoxydiols.

Transannular reaction also occurred when the diepoxide was treated with sodium sulfide in aqueous ethanol.[9] The product, obtained in 88% yield, analyzed correctly for **15** and/or **16**. That 9-thiabicyclo[4.2.1]nonane-2,5-diol (**16**) was the major component was established by desulfurization with Raney nickel. This reaction gave a complex mixture of products from which three components (representing 80% of the total) were isolated by preparative glpc and identified as 4-hydroxycyclooctanone, 5-hydroxycyclooctanone, and *cis*-1,4-cyclooctanediol (major product). 1,5-Cyclooctanediol was not detected; apparently, 5-hydroxycyclooctanone is the only product of desulfurization of **15**. Although the configurations of the hydroxyl groups in **15** and **16** were not established, they are represented as possessing the *endo* positions since nucleophilic attack by sulfide ion on *cis*-diepoxide **1a** should give this stereochemical result. Berchtold and coworkers[4] have established that the analogous reaction of sodium sulfide with *cis*-1,4-cyclohexadiene bisepoxide gives di-*endo*-7-thiabicyclo[2.2.1]heptane-2,7-diol.

Experimental Section[10]

Epoxidation of *cis*-1,5-Cyclooctadiene.—The diene (15.5 g) was added dropwise to a stirred solution of perbenzoic acid (41.6 g) in chloroform (1350 ml) at −5°. When the addition was completed the solution was allowed to stand at 0° for 5 days. The chloroform solution was then shaken twice with 10% aqueous sodium hydroxide, washed with water, and dried (Na_2SO_4). Removal of the solvent followed by fractional distillation gave 11.4 g (57%) of the diepoxide: bp 64° (0.3 mm); $n^{25}{}_{D}$ 1.4952.

Repetition of the epoxidation using peracetic acid (1.4 equiv) in acetic acid containing sodium acetate gave a mixture of unreacted diene (16%), the monoepoxide (51%), and the diepoxide (14%). The monoepoxide had bp 64–66° (6 mm).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.62; H, 9.92.

The diepoxide had bp 65–72° (*ca.* 0.35 mm); mp 25–27°; ir (CCl_4) 915 cm^{-1}; nmr ($CDCl_3$) 2.95 (m, 4 H), 1.92 (m, 8 H); mass spectrum (80 eV) *m/e* no molecular ion species at 140 but peaks in order of decreasing intensity occurred at 41, 67, 68, 39, 55, and 79. Glpc analysis, performed on a variety of liquid phases, showed a single peak.

Reduction of the Diepoxide with Lithium Aluminum Hydride.—To a stirred suspension of lithium aluminum hydride (45 g) in tetrahydrofuran (650 ml) was added dropwise a solution of the diepoxide (45 g) in tetrahydrofuran (300 ml). The mixture was stirred at room temperature for 42 hr and at reflux temperature for 4 hr after which aqueous methanol was added. After the addition of chloroform, the mixture was filtered and the solid residue was washed with chloroform and acetone. The combined organic solutions were dried ($MgSO_4$) and concentrated at reduced pressure. Distillation of the residue gave 41 g of an oil (89% yield, calculated for cyclooctanediol), bp 100–113° (0.15–0.3 mm). Glpc analysis on an 8-ft 20% silicon rubber at 150° showed the presence of three components—A (9%), B (15%), and C (75%)—in order of increasing retention time. Samples of each were obtained by preparative glpc. Component A, which had a very short retention time compared with B and C, was not investigated further. Component B was further partially resolved into three compounds by glpc on an 8-ft 5% XF-1150 at 160°. The major compound of this mixture was found to be identical with a sample of *endo* **5**, prepared by the method of Moon and Hayes.[6]

A sample of component C (cyclooctanediols) was purified by preparative glpc and analyzed.

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.30; H, 11.02.

Ditrifluoroacetates of C.—To a solution of C (90 mg) in pyridine (2 ml) was added trifluoroacetic anhydride (2 ml) at 0°. The mixture was stirred at room temperature for 30 min, poured into cold dilute hydrochloric acid, and extracted with ether. The ether solution was washed with saturated sodium bicarbonate solution and dried ($MgSO_4$). Removal of the solvent gave an oil from which *trans*-1,4-cyclooctanediol ditrifluoroacetate, *cis*-1,5-cyclooctanediol ditrifluoroacetate, and *cis*-1,4-cyclooctanediol ditrifluoroacetate were isolated by preparative glpc on a 12-ft 5% XF-1150 at 120° and identified by comparison of their retention times and spectral properties with those of authentic samples.[5]

Catalytic Hydrogenation of the Diepoxide.—A solution of the diepoxide (3 g) in ethyl acetate (150 ml) was hydrogenated at room temperature with a hydrogen pressure of 900 psi and 10% palladium on charcoal (1.5 g) as catalyst. The solution was filtered, concentrated to a volume of 20 ml, and analyzed by glpc on an 8-ft 20% silicon rubber at 150°. The diol fraction was isolated by preparative glpc and shown to contain *cis*-1,4-cyclooctanediol and *cis*-1,5-cyclooctanediol by conversion to the ditrifluoroacetates as described above. The remaining products are listed in Chart II.

4,5-Epoxycyclooctanol (7).—Reduction of the diepoxide with lithium aluminum hydride in ether as previously described[11] gave a mixture containing unreacted diepoxide, epoxy alcohol **7**, and a trace of diol. The epoxy alcohol was purified by fractional distillation.

4,5-Epoxycyclooctyl Acetate (3).—To a solution of **7** (200 mg) in dry pyridine (2 ml) was added acetic anhydride (0.75 ml) at room temperature. After 46 hr, water was added and the mixture was extracted with three 20-ml portions of ether. The ether solution was washed with water and dried ($MgSO_4$). Removal of the solvent gave a solid which was homogeneous on glpc analysis on a 10-ft 20% LAC-728. Recrystallization from pentane gave 210 mg (80%) of the crystalline epoxy acetate **8**: mp 66.5–67°; ir (CCl_4) 1740, 1250, and 1025 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.04; H, 8.77.

4,5-Epoxycyclooctyl Tosylate (9).—To a solution of **7** (1.6 g) in dry pyridine (10 ml) was added *p*-toluenesulfonyl chloride (2.5 g). The solution was left at room temperature for 60 hr. Dilution with cold water followed by filtration gave a white solid which was recrystallized from pentane to give 1.53 g (46%) of epoxy tosylate **9**: mp 94.5–96°; nmr (CCl_4) 7.50 (q, 4 H), 4.41–4.82 (m, 1 H), 3.00–1.05 (m, 12 H), 2.44 (s, 3 H).

Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.80; H, 6.80; S, 10.80. Found: C, 60.65; H, 6.74; S, 10.66.

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(8) A more convenient route to **13** and **14** is described in a forthcoming publication by A. C. Cope, M. A. McKervey, and N. M. Weinshenker.

(9) Other transannular routes to sulfur-bridged cyclooctyl compounds have been described by E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966), and E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, 1669 (1966).

(10) Melting points were taken on a Thomas–Hoover melting point apparatus and are uncorrected. Boiling points are uncorrected. Glpc analyses were performed using an F & M Model 720 instrument. Liquid phases are abbreviated in the following way: SE-30, silane gum rubber; TCEP, 1,2,3-tris(2-cyanoethoxy)propane; XF-1150, GE-fluorisilicone, LAC-728, diethyleneglycol succinate. Nmr spectra were recorded on a Varian A-60 spectrometer and chemical shifts are expressed in δ values relative to tetramethylsilane. Microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

(11) A. C. Cope, R. S. Bly, M. M. Martin, and R. C. Petterson, *J. Amer. Chem. Soc.*, **87**, 3111 (1965).

4,5-Epoxycyclooctyl Acetate (10).—Tetraethylammonium acetate (5.10 g) was added to a solution of 9 (1.15 g) in dry acetone (40 ml) and the mixture was heated under reflux for 46 hr. Removal of the solvent at reduced pressure gave a semisolid which was treated with water (80 ml) and extracted with ether. The ether extracts were washed with water, dried ($MgSO_4$), and concentrated to an oil (0.62 g). Glpc analysis showed the presence of three components, two of which had retention times similar to that of 4,5-epoxycyclooctene. The third component, which had a retention time close to that of epoxy acetate **8**, was obtained by preparative glpc: ir (CCl_4) 1740, 1250, 1035, and 1020 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.02; H, 8.68.

Glpc analysis of a mixture of **8** and **10** showed that these isomers were cleanly separated on a 10-ft 20% LAC-728.

Hydrolysis of the Diepoxide.—A mixture of the diepoxide (10 g) and 0.02 *N* sulfuric acid (100 ml) was heated on a steam bath for 20 hr. After cooling, solid sodium bicarbonate was added followed by sodium chloride. Continuous extraction with ethyl acetate for 12 hr then gave 11 g (97%) of a solid. A sample collected by preparative glpc had mp 60–85°, mol wt (mass spectrometry), 158.19.

Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.33; H, 8.90.

Ditosylates of 11 and 12.—To a cold solution of the crude diol mixture (3.1 g) in pyridine (30 ml) was added *p*-toluenesulfonyl chloride (8.2 g). The mixture was stirred at room temperature for 4 hr and was then poured into cold water. The precipitated solid was collected by filtration and dissolved in benzene. The benzene solution was washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate, and water, and dried ($MgSO_4$). Removal of the solvent gave an oil 8.7 g (97%) which solidified on standing, mp 117–125°. Thin layer chromatography indicated the presence of two components. A sample had mp 153° after three recrystallizations from ethyl acetate–hexane.

Anal. Calcd for $C_{22}H_{26}O_7S_2$: C, 56.63; H, 5.62. Found: C, 56.62; H, 5.60.

9-Oxabicyclo[4.2.1]nonane and 9-Oxabicyclo[3.3.1]nonane.—To a solution of potassium hydroxide (1.4 g) in triethyleneglycol (6 ml) in a flask fitted with a condenser set for distillation was added the crude ditosylate mixture (2.0 g). The flask was heated for 30 min with a flame and a mixture of the epoxydienes **13** and **14** (0.6 g) was collected in a cold trap. The mixture was dissolved in ethyl acetate and hydrogenated during 12 hr at room temperature using Adams catalyst. The catalyst was removed by filtration and the filtrate was concentrated at reduced pressure. Preparative glpc of the residue gave 9-oxabicyclo[4.2.1]nonane (75%) and 9-oxabicyclo[3.3.1]nonane (25%), identified by spectral comparisons with authentic samples.

Reaction of the Diepoxide with Sodium Sulfide.—A solution of the diepoxide (2.8 g) in ethanol (20 ml) was mixed with a solution of sodium sulfide (4.8 g) in 50% aqueous ethanol (40 ml) and the mixture was heated under reflux for 14 hr. The mixture was cooled, diluted with water, and extracted with ethyl acetate. The extract was dried (Na_2SO_4) and concentrated to give a mixture of **15** and **16**, 3.1 g (88%), as a solid. Recrystallization from benzene–ethyl acetate gave colorless needles, mp 179°. A sample which was sublimed at 120° (0.5 mm) had mp 175–176°. Thin layer chromatography indicated the presence of both isomers. The major isomer **16**, mp 174°, could be obtained pure by adsorption chromatography of the mixture on alumina.

Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10; S, 18.40. Found: C, 55.12; H, 8.05; S, 18.33.

Desulfurization of 15 and 16 with Raney Nickel.—A solution of of the above mixture of **15** and **16** (1.5 g) in 95% ethanol was stirred and heated under reflux with excess W_2 Raney nickel for 15 hr. The catalyst was removed by filtration and the filtrate analyzed by glpc on an 8-ft 20% silicon rubber column at 150°. The three major components (representing 80% of the total) were isolated and identified as 4-hydroxycyclooctanone, 5-hydroxycyclooctanone, and *cis*-1,4-cyclooctanediol.

Registry No.—**1a,** 19740-81-9; **8,** 19740-82-0; **9,** 19740-83-1; **10,** 19740-84-2; **11,** 19771-18-7; **11** (ditosylate), 19740-85-3; **12,** 19740-86-4; **12** (ditosylate), 19740-87-5; **15,** 19740-88-6; **16,** 19740-89-7; *cis,cis*-1,5-cyclooctadiene monoepoxide, 19740-90-0.

Purification of Hydrocarbon Solvents with a Silver Nitrate Column

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Hydrocarbon solvents of the utmost purity were required in a research program dealing with the properties of niobium and tantalum halides in nonaqueous systems. The usual procedures and combinations of procedures for purifying these liquids were tried with little success.

The predominant impurities in commercial and reagent grades of saturated hydrocarbon solvents are olefinic and aromatic compounds. One method[2a] for the removal of these impurities involves washing the hydrocarbon with a nitrating mixture of sulfuric and nitric acids followed by several washings with sulfuric acid, water, and finally with sodium bicarbonate solution. Alternatively, the hydrocarbon can be passed through silica gel columns.[2b,3,4] Maclean, Jencks, and Acree[4] demonstrated that several passes are necessary to obtain reasonably pure solvent by this latter method; their sample of purified cyclohexane had an absorbance of 0.4 in a 1.0-cm cell at 220 mμ. The data of Mair and Farziati[3b] indicate that the yield of pure solvent is equal approximately to the mass of silica gel used in their purification procedure. In our work distillation from solutions containing niobium pentachloride as outlined by Fairbrother, *et al.*,[5] was found to add an impurity which interfered with the measurements being made; a similar phenomenon was observed with the sulfuric acid treatment referred to above. Hydrocarbon solvents which were pure enough for our purposes were not obtained after repeated and frustrating attempts to apply the above methods.

Solid silver nitrate as an adsorbent for the hydrocarbon impurities was then investigated. Reports in the literature indicate that silver nitrate on alumina has been used in columns for the separation of olefinic mixtures in both liquid–solid[6-8] and gas–solid[9-11] partition chromatography; silver nitrate on alumina and on silica gel has been used in thin layer chromatography[12,13] for the separation of unsaturated compounds.

Columns filled with silver nitrate on alumina have been used in our study for the facile preparation of

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