pressure and the product isolated as described above for the products of the reaction of cycloöctene dibromide with tetraethylammonium acetate to give 2.17 g. of a colorless liquid, b.p. 50–87° (0.4 mm.), n^{25}D 1.4675. Redistillation of this material through a semimicro column gave: (a) 0.95 g. (45%), b.p. 41° (0.2 mm.), n^{25}D 1.4675, identified as 2-cycloocten-1-yl acetate by hydrolysis and conversion to the phenylurethan; (b) 0.40 g. of intermediate fractions, b.p. 41–82° (0.2 mm.), n^{25}D 1.4675–1.4680; and (c) 0.51 g. (17%) of *cis*-1,2-cycloöctanediol diacetate, b.p. 82° (0.2 mm.), n^{25}D 1.4645. A solution of 464 mg. of (c) in 10 ml. of methanol containing 5 ml. of water and 2 g. of sodium hydroxide was refluxed for 2 hr. After cooling, most of the methanol was removed by warming the mixture under reduced pressure. The residue was diluted with water and extracted continuously for 20 hr. with chloroform to give 235 mg. (80%) of a white solid, m.p. 69–75°. One crystallization from hexane gave 190 mg. of colorless glistening plates of *cis*-1,2-cycloöctanediol, m.p. and mixed m.p. with an authentic sample 78.0–78.5°.

Reaction of *trans*-1,2-Dibromocycloöctane with Silver Acetate at 60°.—To a stirred suspension of 42.5 g. (0.25 mole) of silver acetate in 200 ml. of glacial acetic acid and 20 ml. of acetic anhydride at room temperature was added 25.3 g. (0.095 mole) of cycloöctene dibromide. After 2 hr. at room temperature essentially no reaction had taken place. The mixture was then heated to 60° and held at that temperature for 24 hr. After that period the solids were collected on a filter, washed well with glacial acetic acid, slurried with 20% aqueous nitric acid, again separated by filtration, washed with water and dried, giving 33.7 g. (96%) of silver bromide. The acetic acid filtrates were returned to the reaction flask along with 10 g. of silver acetate and stirred for an additional period of 17 hr. at 60°. No more silver bromide precipitated. About 80% of the acetic acid was removed by warming under reduced pressure, and the remaining residue was poured into water. After thorough extraction of the mixture with ether, the extracts were washed with saturated sodium bicarbonate solution until free from acid. The extracts were dried over anhydrous potassium carbonate and evaporated, leaving a nearly colorless residue. Distillation of the residue gave 8.84 g. (57%) of an unsaturated acetate fraction, b.p. 110–112° (20 mm.), n^{25}D 1.4680–1.4693, and 5.34 g. (26%) of a diacetate fraction, b.p. 95–102° (0.25 mm.), n^{25}D 1.4650.

A sample of the unsaturated acetate fraction was saponified and converted to a mixture of phenylurethans. This mixture (4.53 g.) was chromatographed on 400 g. of grade I alumina in a 30-mm. diameter column, eluting with 4:1 petroleum ether:ether followed by 2:1 petroleum ether:ether. Thirty-two crystalline fractions were obtained. From the first three fractions material of m.p. 92–94° was obtained by repeated crystallization from hexane. A mixed melting point with 4-cycloöcten-1-yl phenylurethan of m.p. 93–94° obtained from another source[10] was undepressed, and the infrared spectra of the two compounds were identical with the exception of a small band at 10.2 μ and minor intensity differences indicating the presence of a small amount of an impurity in the derivative with m.p. 92–94°. Crystallization of the intermediate fractions from either hexane or methanol–water failed to narrow the melting range. From the last fractions, material of m.p. 102–103° was obtained as colorless needles from hexane. No depression in melting point was observed upon admixture of this derivative with an authentic sample of 3-cycloöcten-1-yl phenylurethan, and the infrared spectra of the two samples were found to be identical in detail.

A mixture of 21 mg. of the phenylurethan of m.p. 92–94° and 20 mg. of 3-cycloöcten-1-yl phenylurethan was crystallized from methanol–water to give 31 mg. of colorless needles, m.p. 76–78°. The infrared spectrum of this material was found to be identical in every respect to that of the mixture of phenylurethans, m.p. 73–74°, described in the preceding paper.[2]

Saponification of the diacetate fraction gave the same yields of *trans*-1,2-, 1,4- and *cis*-1,4-cycloöctanediol as reported in the preceding paper.[2]

Ozonolysis of 4-Cycloöcten-1-yl Phenylurethan.[15]—An ethyl acetate solution of 35 mg. of 4-cycloöcten-1-yl phenylurethan,[10] m.p. 93–94°, was ozonized, reduced and treated with phenyl isocyanate as previously described[2] to give 78 mg. (98%) of an octanetriol tris-phenylurethan. Several crystallizations from hexane gave 55 mg. of colorless crystals, m.p. 126.5–128.0°. One further crystallization from methanol–water afforded 38 mg. of 1,4,8-octanetriol tris-phenylurethan, m.p. and mixed m.p. with an authentic sample,[2] 127–128°. The infrared spectra of the two compounds were identical in every respect.

---

(15) Conducted in part by Dr. G. W. Wood.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Proximity Effects. VI. Stereospecific Syntheses of *cis*- and *trans*-1,4-Cycloöctanediols

BY ARTHUR C. COPE AND BURTON C. ANDERSON

RECEIVED MARCH 8, 1957

1,4-Epoxycycloöctane (I) has been prepared by a sequence of reactions beginning with 3,6-epoxycycloheptanecarbonitrile (II and III, *cis* and *trans* isomers). Each of the nitriles was hydrogenated to a single primary amine, but in the synthesis a mixture of amines formed by hydrogenation of a mixture of II and III was employed. The mixture of amines (IV and V) was treated with nitrous acid, and the mixture of alcohols formed was oxidized with N-bromosuccinimide to the ketone IX. Wolff–Kishner reduction of IX yielded I. The 1,4-oxide I was cleaved with acetic anhydride and boron trifluoride to a diacetate, which upon saponification formed *trans*-1,4-cycloöctanediol. The 1,4-oxide I also was cleaved with acetyl bromide, forming *trans*-4-bromocycloöctyl acetate, which was converted into a diacetate by treatment with tetraethylammonium acetate. Saponification of the diacetate yielded *cis*-1,4-cycloöctanediol. The *cis*- and *trans*-1,4-cycloöctanediols obtained by these syntheses proved to be identical with compounds previously prepared by "transannular reactions" from *cis*- and *trans*-cycloöctene, respectively, thereby confirming the structures and stereochemical assignments previously suggested for these compounds.

It has been shown that the solvolysis of *cis*-cycloöctene oxide with formic acid followed by saponification, or hydrolysis of the oxide with dilute hydrochloric acid, forms a 1,4-cycloöctanediol as well as *trans*-1,2-cycloöctanediol.[1] The 1,4-cyclooctanediol formed in this manner tentatively was assigned the *cis* configuration on the basis of a reaction mechanism that was proposed to explain its formation. Later, similar reasoning was used to assign tentatively the *trans* configuration to a 1,4-cycloöctanediol obtained by solvolysis of *trans*-cycloöctene oxide with formic acid followed by saponification.[2] The assignments of configuration to these diols have been confirmed in the

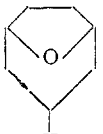
---

(1) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5882 (1952).

(2) A. C. Cope, A. Fournier, Jr., and H. E. Simmons, Jr., *ibid.*, **79**, 3905 (1957).

present work by stereospecific syntheses of *cis*- and *trans*-1,4-cycloöctanediols from *cis*-1,4-epoxycyclooctane (I).

A sample of each of the isomeric 3,6-epoxycycloheptanecarbonitriles[3] (II and III) was hydrogenated to the 3,6-epoxycycloheptanemethylamine (IV and V) of similar configuration (*cis* or *trans*) and the amines were identified as crystalline picrates. Since it appeared that the oxide I could be obtained from either of the isomeric amines, the synthesis described below was carried out using a mixture of amines prepared by hydrogenation of a mixture of the nitriles II and III. The nitriles were obtained by decarboxylating a mixture of the isomeric 1-cyano-3,6-epoxycycloheptanecarboxylic acids in quinoline.[3] In this way a mixture of the amines IV and V was obtained from *cis*-2,5-bis-(hydroxymethyl)-tetrahydrofuran ditosylate in 44% yield.



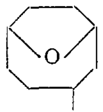
X

II and III, X = C≡N

IV and V, X = CH_2NH_2

VII, X = CH_2OH

VIII, X = CO_2H



X

I, X = H

VI, X = OH

IX, X = =O

Treatment of the mixture of amines with nitrous acid afforded a mixture of olefins (see below) and 3,6-epoxycycloöctanol (VI), probably contaminated with 3,6-epoxycycloheptanemethanol (VII) and 1-methyl-3,6-epoxycycloheptan-1-ol, if this Demjanov rearrangement is analogous to other well-studied cases.[4] The mixture of alcohols was oxidized with N-bromosuccinimide in aqueous acetone. These conditions should cause no change in the tertiary alcohol, 1-methyl-3,6-epoxycycloheptan-1-ol, while the primary alcohol VII would form 3,6-epoxycycloheptanecarboxylic acid (VIII) by further oxidation of the intermediate aldehyde, if it is attacked at all, and the secondary alcohol VI would be oxidized to 3,6-epoxycycloöctanone (IX). The ketone obtained by this oxidation procedure was contaminated with small amounts of hydroxylic compounds as shown by the infrared spectrum of the product.

The impure ketone IX was reduced to the 1,4-oxide I by the Wolff–Kishner method in 57% yield. The oxide I separated from the reaction mixture by steam distillation as it was formed and was purified by heating with molten sodium and redistillation. The distillate crystallized on cooling and melted at 30.8–32.2°. The infrared spectrum of the 1,4-oxide I showed strong absorption at 9.45 μ (absent from the spectrum of *trans*-cyclooctene oxide) and 12.25 μ (absent from the spectrum of *cis*-cycloöctene oxide).[2] These data ensure that the 1,4-oxide I is not present in preparations of these cycloöctene oxides which have been shown to form 1,4-cycloöctanediols on solvolysis.[1,2]

The olefins from the diazotization, a mixture of some or all of the olefins 3,6-epoxycycloöct-1-ene, 4,7-epoxycycloöct-1-ene, 1-methylene-3,6-epoxycycloheptane and 1-methyl-3,6-epoxycyclohept-1-ene, which showed two olefin bands in its infrared spectrum, was hydrogenated to a mixture of I and 1-methyl-3,6-epoxycycloheptane. The infrared spectrum of this mixture showed all the absorption peaks of I as well as several other strong bands. Chromatography of the mixture on silica gel, with elution by benzene–ether mixtures, afforded a partial separation as shown by the infrared spectra of succeeding fractions.

The oxide I was treated with acetic anhydride and boron trifluoride, which should cleave the ether with Walden inversion[5] forming *trans*-1,4-cycloöctanediol diacetate. The cycloöctenyl acetate which also was formed was distilled from the product and the viscous residue was saponified without purification. The glycol formed was chromatographed on alumina and yielded *trans*-1,4-cycloöctanediol (6% from 1,4-epoxycycloöctane), m.p. 89.5–91°, identical with the diol obtained from *trans*-cycloöctene oxide, and tentatively assigned the *trans* structure,[2] as shown by mixed-melting point and a comparison of the infrared spectra, which were identical.

The low-boiling product of this reaction was saponified and converted in good yield to a crystalline phenylurethan, m.p. 93–94°. It was not identical with 2-cycloöcten-1-yl phenylurethan, m.p. 92.5–93.5°, but absorbed 98% of one mole of hydrogen to form cycloöctyl phenylurethan, identical with an authentic sample. The phenylurethan melting at 93–94° has been shown to be 4-cycloöcten-1-yl phenylurethan by ozonization.[6] It is of interest that there was no indication of the presence of the isomeric 3-cycloöcten-1-yl phenylurethan,[7] which also could be formed from the 1,4-oxide I, in this derivative.

The oxide I was cleaved with acetyl bromide and formed 4-bromocycloöctyl acetate, presumably the *trans* isomer,[5] in 40% yield. This product was converted to *cis*-1,4-cycloöctanediol diacetate by treatment with tetraethylammonium acetate in acetone.[8] Saponification of the crude ester followed by chromatography of the product afforded 30% of *cis*-1,4-cycloöctanediol, which was converted in 81% yield to a bis-*p*-nitrobenzoate. Both the glycol and the bis-*p*-nitrobenzoate were identical with the same compounds prepared from *cis*-cycloöctene oxide as shown by melting points, mixed melting points and infrared spectra.

These syntheses of *cis*- and *trans*-1,4-cycloöctanediols confirm the configurations previously suggested for these compounds.

Experimental[9]

Hydrogenation of 3,6-Epoxycycloheptanecarbonitrile (II or III), M.p. 87–88°.—In a 335-ml. stainless steel autoclave

---

(3) A. C. Cope and B. C. Anderson, THIS JOURNAL, **78**, 149 (1956).

(4) P. A. S. Smith and D. R. Baer, "The Demjanov and Tiffeneau-Demjanov Ring Expansions," *Org. Reactions*, to be published.

(5) S. Winstein and R. B. Henderson, "Heterocyclic Compounds," edited by R. C. Elderfield, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 29.

(6) A. C. Cope and H. E. Johnson, THIS JOURNAL, **79**, 3889 (1957).

(7) A. C. Cope and G. W. Wood, *ibid.*, **79**, 3885 (1957).

(8) For a similar displacement with Walden inversion see L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4935 (1952).

(9) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses. Infrared spectra were determined with a Baird double beam recording spectrometer, model B, with a sodium chloride prism.

were placed 0.533 g. of 3,6-epoxycycloheptanecarbonitrile,[3] m.p. 87–88°, 30 ml. of methanol and about 1 g. of commercial Raney nickel (washed with methanol). The mixture was cooled in a Dry Ice–acetone-bath and 30 ml. of liquid ammonia was added. The vessel was sealed, pressured to 1650 p.s.i. with hydrogen and rocked and heated at 140° for 1 hr. After cooling, the autoclave was opened, the catalyst was removed by filtration and the solvents were distilled. The residue was diluted with 20 ml. of 10% aqueous potassium hydroxide and extracted with four 25-ml. portions of ether. The ether solution was dried with potassium hydroxide and the ether was distilled. The residue, 0.254 g., was dissolved in 10 ml. of dry ether and a saturated solution of picric acid in ether was added until no further precipitate formed. There was obtained 0.490 g. (34%) of 3,6-epoxycycloheptanemethylamine (IV or V) picrate, which after four crystallizations from ethyl acetate had m.p. 212.3–214.0° dec.

Anal. Calcd. for $C_{14}H_{18}N_4O_8$: C, 45.40; H, 4.90; N, 15.13. Found: C, 45.70; H, 5.20; N, 14.97.

Hydrogenation of 3,6-Epoxycycloheptanecarbonitrile (II or III), M.p. 102.8–103.6°.—Reduction of 0.625 g. of 3,6-epoxycycloheptanecarbonitrile,[3] m.p. 102.8–103.6°, under conditions similar to those described above afforded 0.290 g. of 3,6-epoxycycloheptanemethylamine (IV or V), which was converted to 0.712 g. (42%) of the amine picrate. A sample of this picrate that was recrystallized from ethyl acetate had m.p. 189.2–190.8° dec.

Anal. Calcd. for $C_{14}H_{18}N_4O_8$: C, 45.40; H, 4.90; N, 15.13. Found: C, 45.54; H, 4.79; N, 14.95.

Ethyl 1-cyano-3,6-epoxycycloheptanecarboxylate was prepared as previously described[3]; 200 g. of *cis*-2,5-bis-(hydroxymethyl)-tetrahydrofuran ditosylate yielded 65.4 g. (69%) of a mixture of the isomeric ethyl 1-cyano-3,6-epoxycycloheptanecarboxylates, b.p. 95–111° (0.25 mm.), which partially crystallized.

1-Cyano-3,6-epoxycycloheptanecarboxylic acid was prepared by saponification[3] of the esters described above and afforded 55.5 g. (98%) of a crystalline mixture of the acids which was not further purified.

3,6-Epoxycycloheptanecarbonitriles (II and III).—The mixture of acids (55.5 g.) described above was decarboxylated in quinoline[3] and yielded 34.1 g. (81%) of a waxy semisolid mixture of the nitriles II and III which was not further purified.

3,6-Epoxycycloheptanemethylamine.—The crude nitrile (34.1 g.) obtained from the decarboxylation was hydrogenated by a procedure similar to the one described above for the reduction of 3,6-epoxycycloheptanecarbonitrile, m.p. 87–88°, and afforded 28.3 g. [44% from *cis*-2,5-bis-(hydroxymethyl)-tetrahydrofuran ditosylate] of 3,6-epoxycycloheptanemethylamine, b.p. 104–111.5° (10 mm.), $n^{25}D$ 1.4951–1.5010. A middle fraction showed no absorption characteristic of hydroxylic or carbonyl compounds or nitriles in its infrared spectrum.

A sample of a similar mixture, purified by redistillation, had b.p. 53–54° (0.30 mm.) and $n^{25}D$ 1.4953.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.27; H, 10.58; N, 10.14.

Diazotization of 3,6-Epoxycycloheptanemethylamine (IV and V).—3,6-Epoxycycloheptanemethylamine, 27.0 g., was dissolved in a solution of 17.3 g. of 85% phosphoric acid in 125 ml. of ice-water. The slightly cloudy solution was extracted with ether to remove any neutral impurities, a solution of 13.2 g. of sodium nitrite in 30 ml. of water was added and the solution was allowed to stand for 16 hr. The greenish organic layer which had formed was extracted with ether. The solution was heated at 100° for 1 hr., cooled and extracted with two 100-ml. portions of ether, and the processes of heating and extraction were repeated twice in the same way. Phosphoric acid (1.7 g.) was added, then 1.6 g. of sodium nitrite, and the solution was heated at 100° for 1 hr., cooled and extracted with two 100-ml. portions of ether. The heating and extraction were repeated, the extract was dried with potassium carbonate and distilled. When it was found that the high-boiling residue from this operation was less than 1 g., all of the ether extracts were combined and dried with potassium carbonate and the ether was distilled. The residue was fractionated through a semi-micro column, affording an olefin fraction, b.p. 54–59.5° (11 mm.), and an alcohol fraction, b.p. 60–83° (0.30 mm.). The olefins amounted to 4.95 g. or 22% of the theoretical amount; the alcohols amounted to 11.6 g. or 43%.

N-Bromosuccinimide Oxidation of the Alcohol Mixture.—The alcohol fraction from the nitrous acid reaction, 11.6 g., was dissolved in 400 ml. of reagent acetone and 40 ml. of water. N-Bromosuccinimide (36 g.) was added, and the solution was allowed to stand for 19.5 hr. During the course of the reaction the mixture turned gradually from colorless to orange and back to colorless again. The reaction mixture was neutralized with saturated sodium bicarbonate solution, and the excess N-bromosuccinimide was destroyed with sodium thiosulfate solution. The acetone was distilled, and the solution was cooled and extracted with nine 50-ml. portions of chloroform. The combined extracts were dried with potassium carbonate and the chloroform was distilled. Fractionation through a semi-micro column afforded 9.23 g. or 81% of the theoretical amount of a product, b.p. 58° (1.40 mm.) to 64° (0.18 mm.), $n^{25}D$ 1.4872–1.4933. All fractions gave precipitates with 2,4-dinitrophenylhydrazine reagent. Refractionation of this product through a 30 × 0.8-cm. semi-micro column with a spinning band afforded 6.64 g. (58%) of a product, b.p. 56–61° (0.7 mm.), $n^{25}D$ 1.4893–1.4906. The infrared spectrum of this product showed a small hydroxyl band.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.11; H, 8.80.

1,4-Epoxycycloöctane (I).—The slightly impure ketone described above, 5.65 g., was placed in a Claisen distilling flask with 7.0 g. of solid potassium hydroxide, 5.0 ml. of hydrazine hydrate and 50 ml. of diethylene glycol. The mixture was heated under reflux for 1 hr., and then a mixture of water and the 1,4-oxide I was distilled slowly for 1.5 hr., after which 5.0 ml. of water was added and distilled over the course of 1 hr. Another addition of water followed by distillation gave a clear distillate, indicating that the reaction was complete. The distillates were combined, the water solution was made strongly acidic with hydrochloric acid and the product was extracted with three 20-ml. portions of petroleum ether. The combined extracts were dried with sodium hydride, filtered and the solvent was distilled. Sodium (about 0.5 g.) was added, and the mixture was heated in a flask attached to a semi-micro column until the sodium had melted and this temperature was maintained for 15 minutes. Distillation yielded 2.82 g. (57%) of 1,4-epoxycycloöctane, b.p. 89–95° (53 mm.). The later fractions crystallized when cooled. A middle fraction had b.p. 94° (53 mm.), $n^{25}D$ 1.4720, m.p. 30.8–32.2°.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.44; H, 11.29.

The infrared spectrum of this compound was free of hydroxyl and carbonyl bands (Fig. 1).

***trans*-1,4-Cycloöctanediol.**—1,4-Epoxycycloöctane, 0.95 g., 1.5 g. of acetic anhydride and 0.1 ml. of boron trifluoride etherate were heated on a steam-bath for 90 minutes, cooled and diluted to a volume of 50 ml. with ether. The ether solution was washed with two 20-ml. portions of water, dried overnight with anhydrous magnesium sulfate and the ether was distilled. The residue was placed in a flask attached to a semi-micro column, and 0.47 g. (37%) of material boiling in the range of the cycloöctenyl acetates was distilled. (Characterization of this material is described below.) The residue in the distilling flask was saponified by heating in methanol (15 ml.) with sodium hydroxide (1.0 g.) for 90 minutes. The methanol was distilled, the residue was taken up in water and the water solution was extracted continuously with chloroform overnight. Distillation of the extract afforded 0.16 g. of high-boiling residue which was chromatographed on Brockmann Grade III alumina.

Fractions 1–3 were eluted with benzene and amounted to 0.025 g.; fractions 4–15 were eluted with benzene–ether mixtures (0.002 g.); fractions 16–28 were eluted with 0.5% methanol–99.5% ether (0.009 g.); fractions 29–45 were eluted with 1% methanol–99% ether (0.066 g.); fractions 46–56 were eluted with 2% methanol–98% ether (0.002 g.); and fractions 57 and 58 were eluted with 50% methanol–50% ether (0.002 g.).

Fractions 29–45 contained 0.066 g. or 6% of the theoretical amount of crystalline *trans*-1,4-cycloöctanediol. A sample recrystallized twice from ethyl acetate had m.p. 89.5–91° (hot-stage) and did not depress the melting point (90.5–91.5°) of *trans*-1,4-cycloöctanediol that was identical with a sample prepared from *trans*-cycloöctene.[2] The in-

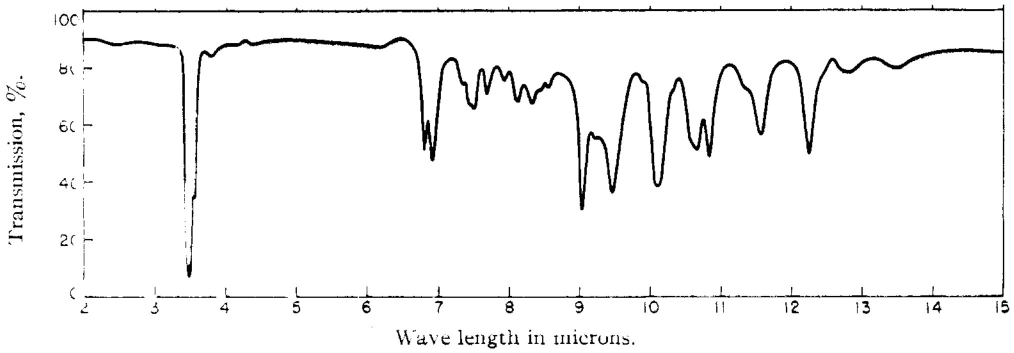


Fig. 1.—Infrared absorption spectrum of 1,4-epoxycycloöctane as a solution (100 mg./ml.) in carbon tetrachloride in the region 2–8μ and in carbon disulfide in the region 8–16μ.

frared spectra of these compounds determined at 1% concentration in a potassium bromide pellet were superimposable.

The other fractions, which did not crystallize, were discarded. There was no indication that they contained the easily crystallized *cis*-1,4-cycloöctanediol.

Treatment of the Low-boiling Fraction.—A mixture of 0.47 g. of the cycloöctenyl acetate fraction, 5.0 ml. of methanol and 2.0 g. of potassium hydroxide was heated under reflux for 40 minutes, and the mixture was then diluted with water. Extraction of the product with ether and fractionation of the dried extracts afforded 0.28 g. (79%) of an unsaturated alcohol. This material was treated with 0.4 g. of phenyl isocyanate, and when the mixture had solidified, the excess phenyl isocyanate was distilled under reduced pressure. Chromatography of the product on alumina afforded 0.472 g. (87%) of a product which was homogeneous. A sample purified by recrystallization from methanol–water had m.p. 93–94°.

Anal. Calcd. for $C_{15}H_{19}NO_2$: C, 73.43; H, 7.81; N, 5.71. Found: C, 73.55; H, 7.89; N, 5.57.

Hydrogenation of the Phenylurethan, M.p. 93–94°.—In a micro hydrogenation apparatus were placed 15 ml. of 95% ethanol and 0.40 g. of 10% palladium-on-carbon hydrogenation catalyst. After the catalyst and solvent had equilibrated with the hydrogen atmosphere, a sample (0.0307 g.) of the phenylurethan described above was added. When the reduction was complete, after absorption of 98% of one molar equivalent of hydrogen, the solution was filtered and the ethanol was distilled. There was obtained 0.031 g. of a product, m.p. 53–56.5°. Recrystallization from aqueous methanol afforded cycloöctyl phenylurethan, m.p. 55.6–56.6°, alone or admixed with an authentic sample. The infrared spectra of the hydrogenation product and the authentic sample were identical. As noted earlier, the phenylurethan with m.p. 93–94° now has been identified as 4-cycloöcten-1-yl phenylurethan by ozonization.[6]

***cis*-1,4-Cycloöctanediol.**—1,4-Epoxycycloöctane (1.01 g.) and 1.5 g. of acetyl bromide were heated on a steam-bath for 1 hr. The brown mixture was cooled and poured into water. The product was extracted with ether, and the ethereal extract was washed with water, saturated sodium bicarbonate solution and again with water. The extract was dried and fractionated. There was obtained 0.79 g. or 40% of *trans*-4-bromocycloöctyl acetate, b.p. 90–95° (0.17 mm.), $n^{25}\text{D}$ 1.4980–1.4994. This product was dissolved in a solution of 0.90 g. of tetraethylammonium acetate monohydrate in 25 ml. of reagent acetone and the solution was heated under reflux for 4 hr. The acetone was distilled, water was added and the product was extracted with three 25-ml. portions of ether. The extracts were combined and dried with magnesium sulfate. The solvent was distilled, and the residue obtained was saponified by heating in methanol (25 ml.) with potassium hydroxide (2.0 g.) for 30 minutes. The methanol was distilled, 20 ml. of water was added and the mixture was extracted continuously with chloroform for 24 hr. Distillation of the solvent afforded 0.30 g. of viscous residue which was chromatographed on activity III alumina.

Fractions 1–14 were eluted with benzene–ether mixtures and amounted to 0.010 g.; fractions 15–18 were eluted with ether (0.005 g.); fractions 18–27 were eluted with 1% methanol–99% ether (no material); fractions 28–47 were eluted with 2% methanol–98% ether (0.137 g.); fractions 48–52 were eluted with 10% methanol–90% ether (0.007 g.); fractions 53–56 were eluted with 30% methanol–70% ether (no material).

Fractions 28–52 crystallized on evaporation of the solvent, and contained only one compound as shown by melting points and mixed melting points. A middle fraction after two recrystallizations from ethyl acetate melted at 83.0–84.5° alone or admixed with *cis*-1,4-cycloöctanediol prepared from *cis*-cycloöctene.[1] The yield of 0.144 g. was 31% from *trans*-4-bromocycloöctyl acetate.

Fractions 1–18 did not crystallize and were discarded.

***cis*-1,4-Cycloöctanediol Bis-*p*-nitrobenzoate.**—A portion (0.0549 g.) of the above glycol was treated with *p*-nitrobenzoyl chloride in pyridine under conditions previously described,[10] and the product was purified by chromatography on alumina. The yield of *cis*-1,4-cycloöctanediol bis-*p*-nitrobenzoate was 0.136 g. (81%), and after two recrystallizations from ethyl acetate the compound melted at 161.5–162.7° alone or admixed with the corresponding ester prepared from *cis*-1,4-cycloöctanediol obtained from *cis*-cycloöctene.[1]

The infrared spectra of the *cis*-1,4-glycol and its bis-*p*-nitrobenzoate were identical with the spectra of the same compounds prepared from *cis*-cycloöctene.

CAMBRIDGE, MASSACHUSETTS

---

[10] A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, THIS JOURNAL, **79**, 3900 (1957).