perature apparently having no effect on the products obtained. Excess peroxide was then destroyed with "Catalase Sarrett," the solution was diluted to 100 ml. in a volumetric flask and a 10-ml. aliquot was taken for titration studies. Titration and analysis showed an average ratio of one part of sulfuric acid to three parts of total acid. The remaining 90 ml. of solution was neutralized by refluxing with excess barium hydroxide. Precipitated barium sulfate was removed by centrifuging. Carbon dioxide was then bubbled through the solution and the mixture was again centrifuged. This process was repeated until no more barium carbonate precipitate was evident. The solution was concentrated to 15 ml. and again filtered. Final concentration was accomplished at reduced pressure, leaving the barium sulfonate as a sirupy mass. On removal of remaining water in a vacuum desiccator, the salt was obtained as a gray-white powder, in yields ranging from 3.0 g. (14.5%) to 5.0 g. (24%). Analyses for barium indicated that small amounts of inorganic salts were still present. The impure barium 2-hydroxypropanesulfonate was converted to the free sulfonic acid with the calculated amount of sulfuric acid. Treatment with phenylhydrazine in alcohol gave a granular precipitate which on recrystallization from alcohol melted at 132–133°.

Anal. Calcd. for $C_9H_{16}N_2O_4S$: C, 43.53; H, 6.5; N, 11.25; S, 12.91; mol. wt., 248.3. Found: C, 43.25; H, 6.05; N, 11.43; S, 12.96; mol. wt., 250.2.

Part of the barium hydroxypropanesulfonate was converted to a chloropropanesulfonyl chloride with phosphorus pentachloride. The product had a boiling point of 54–55° (1 mm.), $n^{20}D$ 1.4830. The N-methylaniline derivative of this material had a melting point of 57.5–58.5°, corresponding to that of N-methyl-1-propene-1-sulfonanilide (V) as prepared by Autenrieth.[7]

Sodium 2-Hydroxypropane-1-sulfonate (a).—A mixture of 19 g. (0.2 mole) of 1-chloro-2-propanol and 31.5 g. (0.25 mole) of sodium sulfite in 75 ml. of water was heated in a steel hydrogenation-type bomb for 8 hr. at 180°. The reaction mixture was filtered and the solution was evaporated to dryness. Three extractions with 90% ethanol followed by evaporation of the ethanol gave 30 g. of somewhat waxy white solid. This on drying in a vacuum desiccator yielded finally 25 g. (77.2%) of crystalline salt. (b) **Propylene oxide–Sodium Bisulfite Addition Reaction.**—A mixture of 95 g. (0.5 mole) of sodium metabisulfite and 67 g. (1.16 mole) of propylene oxide in 200 ml. of water was stirred at room temperature for 8 hr. and the solution was then evaporated to dryness. The crude product was recrystallized from 90% ethanol and a total of 138 g. (85.2%) of sodium 2-hydroxy-1-propanesulfonate was obtained. A small portion after a second recrystallization from 95% ethanol had a melting point range of 225–227°.

2-Chloro-1-propanesulfonyl Chloride (IX).—This compound was obtained from sodium 2-hydroxy-1-propanesulfonate by treatment with excess phosphorus pentachloride. Yields ranged from 25 to 50% of (IX), b.p. 62–65° (2.5 mm.), $n^{20}D$ 1.4818.

Treatment with N-methylaniline gave N-methyl-1-propene-1-sulfonanilide (V), m.p. 58–59°.

Anal. Calcd. for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20. Found: C, 56.85; H, 6.27.

1-Propene-1-sulfonyl Chloride (X).—A mixture of 32.4 g. (0.2 mole) of sodium 2-hydroxy-1-propanesulfonate and 35 ml. of thionyl chloride was allowed to react at room temperature for two hours and then warmed at 50–70° for a further two hours. It was then poured into water, an excess of sodium carbonate was added and the mixture was evaporated to dryness. Extraction with hot 95% ethanol and removal of ethanol from the extracts left 20 g. of white salt, sodium 1-propene-1-sulfonate. The salt was heated at the steam-cone with 38 g. of phosphorus oxychloride for an hour and the product was worked up as described for other sulfonyl chlorides. On distillation there was obtained some forerun, a main fraction of 8 g. (28%), b.p. 67.5–69° (8 mm.), $n^{20}D$ 1.4756, and some much higher boiling material. Part of the main fraction was converted to the N-methylaniline derivative, m.p. 57–58°, which showed no depression of melting point when mixed with the N-methylaniline derivative made from 2-chloro-1-propanesulfonyl chloride.

2-Chloro-1-propanethiol.—This compound was prepared according to the directions of Davies and Savige[4] by the reaction of propylene sulfide and hydrochloric acid in methanol solution. The compound had a boiling point of 60–62° (82 mm.), $n^{20}D$ 1.4844.

Chlorine Water Oxidation of 2-Chloro-1-propanethiol.—The procedure used was the same as that described for the chlorine water oxidation of propylene sulfide. The product, 2-chloro-1-propanesulfonyl chloride, b.p. 51° (1 mm.), gave N-methyl-1-propene-1-sulfonanilide, m.p. 57–59°, on reaction with N-methylaniline.

MISSOULA, MONTANA

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

Cyclic Polyolefins. XXV. Cycloöctanediols. Molecular Rearrangement of Cycloöctene Oxide on Solvolysis[1]

BY ARTHUR C. COPE, STUART W. FENTON[2] AND CLAUDE F. SPENCER[3]

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Hydroxylation of *cis*-cycloöctene with performic acid, and hydrolysis or solvolysis with formic acid of *cis*-cycloöctene oxide, have been found to yield 1,4-cycloöctanediol in larger amount than the expected product, *trans*-1,2-cycloöctanediol. The structure of 1,4-cycloöctanediol was established by conversion to cycloöctane through the diacetate and cycloöctadiene, and by Oppenauer oxidation to 1,4-cycloöctanedione, which by an intramolecular aldol condensation formed the known ketone, bicyclo[3.3.0]-1(5)-octen-2-one. The molecular rearrangement resulting in formation of the 1,4-glycol is interpreted as a chemical "transannular effect" which permits participation in the solvolysis of the epoxide by a carbon–hydrogen bond that is sterically adjacent because of its location across the compact eight-membered ring. *cis*-1,2-Cycloöctanediol and the eight-membered cyclic acyloin suberoin have been prepared and characterized.

Before cycloöctene from the partial hydrogenation of cycloöctatetraene[4] was available as an intermediate for the synthesis of other eight-membered ring compounds such as 1,3-cycloöctadiene,[5] an investigation of the preparation of 1,2-cycloöctanediols (and 1,3-cycloöctadiene) from the cyclic acyloin suberoin was undertaken. When cyclooctene became available, it was converted into *cis*- and *trans*-1,2-cycloöctanediols. This phase of the work led to discovery of an unusual rearrangement that occurs during the solvolysis of cyclooctene oxide.

The acyloin condensation of dimethyl suberate, under conditions similar to those used for the

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[2] Arthur D. Little Postdoctorate Fellow, 1950–1951.

[3] Abstracted in part from the Ph.D. dissertation of Claude F. Spencer, Massachusetts Institute of Technology, June, 1950.

[4] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[5] A. C. Cope and L. L. Estes, Jr., THIS JOURNAL, **72**, 1128 (1950).

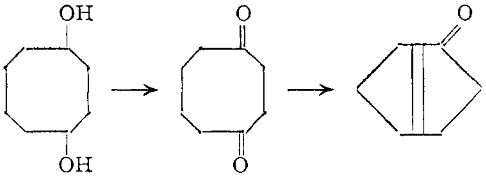
preparation of other macrocyclic acyloins,[6] formed suberoin in 37% yield as a colorless, low-melting solid. Hydrogenation of suberoin in the presence of Raney nickel yielded a mixture of glycols, from which *cis*-1,2-cycloöctanediol was separated by crystallization as leaflets melting at 77.5–79°. Chromatography on alumina of the material remaining in the mother liquors yielded *trans*-1,2-cycloöctanediol as a viscous liquid that was characterized as the crystalline bis-phenylurethan. Both the *cis*- and *trans*-1,2-glycols were obtained more easily from cycloöctene.

Oxidation of cycloöctene with potassium permanganate, hydrogen peroxide and osmium tetroxide, and aqueous sodium chlorate and osmium tetroxide formed crystalline *cis*-1,2-cycloöctanediol in yields of 7.7, 11.4 and 30%, respectively. The *cis* configuration is assigned to the product because these methods of oxidation are known to form *cis*-glycols. *cis*-1,2-Cycloöctanediol was converted into a solid bis-phenylurethan with phenyl isocyanate, and a liquid isopropylidene derivative with acetone in the presence of anhydrous copper sulfate. Evidence for its structure was obtained by rapid quantitative reaction with periodic acid at room temperature, and by oxidation with alkaline permanganate forming suberic acid.

The hydroxylation of cycloöctene with performic acid[7] was expected to form *trans*-1,2-cycloöctanediol. However, after alkaline hydrolysis of the monoformate, extraction and distillation yielded a mixture of products (71.5% calculated as cyclooctanediols) instead of the pure *trans*-1,2-glycol. Crystallization of the mixture was difficult, but it proved to be possible to separate *trans*-1,2-cyclooctanediol as the isopropylidene derivative,[8] formed by treating the mixture with acetone and anhydrous copper sulfate. Subsequent distillation separated the more volatile isopropylidene derivative (30% or 21.5% based on cycloöctene) from a less volatile residue (described below). Acid hydrolysis of the isopropylidene derivative, or treatment with formic acid followed by basic hydrolysis of the formate, yielded *trans*-1,2-cycloöctanediol as a viscous liquid that was characterized as the crystalline bis-phenylurethan (identical with the derivative of the *trans*-1,2-glycol prepared from suberoin) and di-*p*-toluenesulfonate. *trans*-1,2-Cycloöctanediol, like the *cis* isomer, reacted rapidly and quantitatively with periodic acid at room temperature, and formed suberic acid on oxidation with alkaline permanganate.

The residue remaining after distilling the isopropylidene derivative of *trans*-1,2-cycloöctanediol from the mixture was crystallized from ethyl acetate, and yielded 36% (25.7% based on cyclooctene) of an isomeric glycol (I) that crystallized as fine needles, m.p. 85–86.5°. This glycol failed to react with periodic acid, showing that it probably was not a 1,2-glycol. Oxidation with aqueous sodium permanganate yielded a mixture containing oxalic acid and adipic acid, indicating a chain of at least six carbon atoms separating the alcoholic hydroxyl groups. The bis-phenylurethan and di-*p*-toluenesulfonate were prepared from I as solid derivatives. Evidence concerning the carbon skeleton of I was obtained by converting the glycol to the diacetate, which was pyrolyzed at 500° and formed a mixture of cycloöctadienes that was reduced quantitatively to cycloöctane. Excluding the unlikely possibility that ring contraction during hydroxylation of cycloöctene might be followed by ring expansion in pyrolysis of the diacetate, this evidence is sufficient to establish the structure of I as a cycloöctanediol other than the *cis*- or *trans*-1,2-diol.

Evidence concerning the orientation of the hydroxyl groups was obtained by oxidation of I by the Oppenauer method, which formed a diketone II that failed to give a ferric chloride enol test (expected to be positive for 1,3-cycloöctanedione). On treatment with dilute sodium hydroxide followed by hydrochloric acid, or directly with concentrated sulfuric acid, the diketone II underwent an intramolecular aldol condensation and formed the known unsaturated ketone, bicyclo-[3.3.0]-1(5)-octen-2-one (III), which was isolated as the semicarbazone. Accordingly the diketone II is 1,4-cycloöctanedione, and the glycol from which it is formed is *cis*- or *trans*-1,4-cycloöctanediol (I).



I II III

Since the formation of a 1,4-glycol by hydroxylation of an olefin with performic acid appeared to be without precedent, evidence was sought concerning the step in the process in which rearrangement occurred. Cycloöctene oxide was prepared from cycloöctene and peracetic acid, and purified by distillation and sublimation, m.p. 56–57°. Fractional distillation and chromatography on both alumina and activated carbon, followed by fractional elution with solvents, failed to separate fractions with significantly different melting points or infrared spectra, indicating that the epoxide was homogeneous. Cycloöctene oxide was hydrogenated to cycloöctanol in 83% yield in the presence of Raney nickel at 125°. This normal behavior on reduction provides evidence that the oxide is a normal 1,2-epoxide. The solvolysis of cycloöctene oxide with formic acid, followed by saponification of the resulting formates, or hydrolysis of the oxide with dilute hydrochloric acid, formed a mixture of glycols similar to the mixture formed from cycloöctene and performic acid. *trans*-1,2-Cycloöctanediol was separated from the mixture as the isopropylidene ketal, after which 1,4-cycloöctanediol (I) was isolated from the residue by crystallization from ethyl acetate in 30% yield. Accordingly the step

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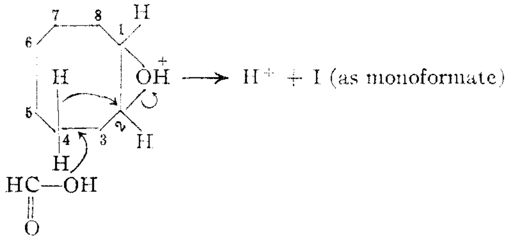
[6] J. L. Hansley, U. S. Patent 2,228,268 (Jan. 14, 1941); *C. A.*, **35**, 2534 (1941); V. Prelog, L. Frenkiel, M. Kobelt and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947); M. Stoll and J. Hulstkamp, *ibid.*, **30**, 1815 (1947); M. Stoll and A. Rouvé, *ibid.*, **30**, 1822 (1947).

[7] D. Swern, *Chem. Revs.*, **45**, 1 (1949), lists the cases in which olefins have been converted into glycols with this reagent.

[8] Both *cis*- and *trans*-1,2-cycloheptanediols are known to form isopropylidene derivatives; J. Böeseken and H. Derx, *Rec. trav. chim.*, **40**, 529 (1921); H. Derx, *ibid.*, **41**, 312 (1922).

in which rearrangement occurs in the conversion of cycloöctene to 1,4-cyclooctanediol is the solvolysis of the epoxide.[9]

A tentative interpretation of the abnormal solvolysis of cyclooctene oxide is based on a hitherto unobserved chemical "transannular effect" for which the proximity of atoms lying across an eight-membered ring may be responsible. In other words, hydrogen atoms that are sterically adjacent to the oxide ring may participate in the displacement reaction in a kind of neighboring group effect for which the conformation of the ring is responsible. According to this interpretation, the 1,4-glycol would be formed by a 1,3-hydride shift in the protonated epoxide, presumably occurring simultaneously with the attack by the solvent at the positively charged carbon in the 4-position, as formulated schematically below. Normal displacement at C_2 with Walden inversion would account for formation of the *trans*-1,2-glycol. Steric hindrance provided by the ring to approach of C_2 by the solvent might retard this "normal" displacement, allowing time for "abnormal" displacement at C_4.



A more exact interpretation must await determination of the configuration of I (*cis* or *trans*), and examination of the solvolysis products of cyclooctene oxide that have not been purified or identified and may contain products other than the *trans*-1,2 and 1,4-glycols. The solvolysis of epoxides of other olefins also will be examined to determine whether glycols other than the expected 1,2-glycols are formed.[10]

Experimental[11]

Suberoin.—A 5-l. three-necked flask was equipped with a mercury-sealed Hershberg stirrer and a simple high dilution apparatus,[12] to which was attached a reflux condenser and a Hershberg dropping funnel. Sodium (46 g., 2 g. atoms) was powdered by stirring under 1 l. of refluxing xylene, and a solution of 101 g. (0.5 mole) of dimethyl suberate (b.p. 111–112.5° (2–3 mm.), n^{25}D 1.4305) in 80 ml. of xylene was added through the dilution apparatus over a period of 8 hours in an atmosphere of dry nitrogen, with stirring and refluxing[13] during that period and for 2 hours longer. The mixture was allowed to stand overnight, and then was cooled with an ice-bath. Absolute ethanol (50 ml.) was added to destroy any remaining sodium followed by a solution of 120 g. (2 moles) of glacial acetic acid in 800 ml. of dry ether, added slowly with stirring to neutralize the mixture. The nitrogen atmosphere was maintained to this point. Sodium acetate was separated by filtration and washed well with ether, and the filtrate was concentrated under reduced pressure in a nitrogen atmosphere. The residue was distilled from a Hickman molecular-type pot still at 60–135° (0.5 mm.), and the distillate was fractionated through a 15 × 1-cm. Vigreux column under nitrogen, yielding 26 g. (37%) of suberoin, b.p. 66–71° (1.3 mm.). The nearly colorless product crystallized, and was purified by redistillation and crystallization from a mixture of ether and pentane; b.p. 64° (0.3 mm.), m.p. 37–38.5°.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.58; H, 9.92. Found: C, 66.58; H, 9.95.

Preparation of *cis*- and *trans*-1,2-Cyclooctanediols from Suberoin.—A solution of 3.44 g. of suberoin in 75 ml. of methanol was shaken with hydrogen at room temperature and atmospheric pressure in the presence of 2.5 g. of W-7 Raney nickel catalyst.[14] After 30 minutes, 95.3% of one molar equivalent of hydrogen had been absorbed and the reduction stopped. The catalyst was separated by filtration, and the filtrate was concentrated under reduced pressure. The residue (3.48 g.) was a viscous liquid that partially crystallized. Several crystallizations of a sample (0.97 g.) from ethyl acetate yielded 0.37 g. of *cis*-1,2-cyclooctanediol as white leaflets, m.p. 77.5–79°, and 0.60 g. of a sirup. A solution of the sirup in 10 ml. of chloroform–carbon tetrachloride (2:1 by volume) was placed on a 13.5 × 1.5-cm. column of 48–100 mesh activated alumina, and the column was eluted with 200-ml. portions of the following solvents, from which the indicated weights of liquid residues were obtained: (1) chloroform–carbon tetrachloride (2:1), 0.06 g.; (2) chloroform, 0.19 g.; (3) chloroform–methanol (9:1), 0.34 g. Fractions 2 and 3 were treated with phenyl isocyanate, and both yielded the bisphenylurethan of *trans*-1,2-cyclooctanediol, m.p. 176.5–178.5° after crystallization from ethanol. The derivative gave no depression in mixed melting point with the bisphenylurethan of *trans*-1,2-cyclooctanediol prepared from cyclooctene (described below), while a mixed melting point with the bisphenylurethan of *cis*-1,2-cyclooctanediol (also described below) was depressed to 154–172°.

***cis*-1,2-Cyclooctanediol (a).**—A solution of 11.0 g. of cyclooctene (n^{25}D 1.4681, prepared by partial hydrogenation of cyclooctatetraene[4,5]) in 50 ml. of acetone was cooled to −20°, and a solution of 15.8 g. of potassium permanganate in 1.5 l. of acetone was added slowly with stirring at −20 to 0° over a period of 12 hours, at a rate at which permanganate did not accumulate in the solution. The manganese dioxide was reduced by addition of saturated aqueous sodium bisulfite with stirring, and most of the acetone was removed by distillation. The residue was poured into 1500 ml. of water, and the solution was made alkaline with sodium carbonate and extracted with six 100-ml. portions of ether. The ether solution was dried over magnesium sulfate and distilled, and yielded 5.0 g. (45%) of recovered cyclooctene. A short path distillation of the residue at 1 mm. yielded 0.96 g. of *cis*-1,2-cyclooctanediol. The aqueous alkaline solution was acidified and extracted with eight 100-ml. portions of ether. Short path distillation of the residue obtained by concentrating the extracts yielded an additional 0.16 g. of the *cis*-1,2-diol, making the total yield 1.12 g. (7.7%); after recrystallization from ethyl acetate the *cis*-1,2-cyclooctanediol melted at 76–79°. Recrystallization from water of the dark solid residue remaining after the second short path distillation yielded 1.84 g. (10.6%) of suberic acid.

(b).—Using the method described by Milas and Sussman[15] for the preparation of *cis*-1,2-cyclohexanediol, 15.1 g. of cyclooctene was added to 100 ml. of *t*-butyl alcohol contain-

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[9] Hydrolysis of *cis*-cyclooctene oxide to a liquid glycol presumed to be the *trans*-1,2-isomer has been reported by K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950), and M. Godchot and G. Cauquil, *Compt. rend.*, **192**, 963 (1931), who report m.p. 182–183° and 166–167°, respectively, for the bis-phenylurethan. We have observed m.p. 176.2–177.4° for *trans*-1,2-cyclooctanediol bis-phenylurethan, and m.p. 186–187.5° for 1,4-cyclooctanediol bis-phenylurethan. Either of these derivatives or a mixture of them might have been isolated in the earlier work, if the glycol was a mixture of isomers similar to the one that we obtained.

[10] The fact that 1,4-cyclooctanediol is formed on hydroxylation of cyclooctene has been communicated to Professor V. Prelog, who has confirmed and extended this observation of a chemical "transannular effect" by studies of the hydroxylation of cyclodecene, to be published soon in *Helv. Chim. Acta.*

[11] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

[12] A. C. Cope and E. C. Herrick, THIS JOURNAL, **72**, 985 (1950).

[13] The flask was heated with an oil-bath. An electric heating mantel caused charring of the gelatinous sodium salt that separated as the reaction progressed.

[14] H. Adkins and H. R. Billica, THIS JOURNAL, **70**, 695 (1948).

[15] N. A. Milas and S. Sussman, *ibid.*, **59**, 2347 (1937). In a model experiment *cis*-1,2-cyclohexanediol was obtained from cyclohexene in 51% yield under these conditions.

ing 5.1 g. (0.15 mole) of hydrogen peroxide and cooled to −5°. Osmium tetroxide (3 ml. of a 0.5% solution in *t*-butyl alcohol) was added, and the solution was allowed to stand for 42 hours at 0 to 5°. The product, isolated by the procedure described above, amounted to 2.24 g. (11.4%) of *cis*-1,2-cycloöctanediol and 0.75 g. of suberic acid. An analytical sample of *cis*-1,2-cycloöctanediol was prepared by recrystallization from ethyl acetate; m.p. 77.5–79°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found: C, 66.81; H, 11.04.

(**c**).—A mixture of 11.0 g. of cycloöctene, 7.6 g. of sodium chlorate, 5 ml. of acetic acid, 50 ml. of water, 100 ml. of dioxane and 5 ml. of 1% osmium tetroxide in *t*-butyl alcohol was heated under reflux for 72 hours.[16] The solution was concentrated under reduced pressure, and the residue was distilled in a short path still. A low boiling fraction of 1.3 g. distilling at a block temperature of 80–100° (0.3 mm.) was separated, followed by 8.6 g. of crude *cis*-1,2-cycloöctanediol, collected at 120–150° (0.3 mm.). Recrystallization from ethyl acetate yielded 4.3 g. (30%) of *cis*-1,2-cyclooctanediol, m.p. 75.8–78°.

cis-1,2-Cycloöctanediol was characterized by oxidation with alkaline permanganate to suberic acid, by rapid oxidation with periodic acid at 25°, which proceeded to the extent of 98.2% within 30 minutes, and by preparation of the following derivatives.

cis-1,2-Cycloöctanediol bis-phenylurethan was prepared by treating the *cis*-glycol with phenyl isocyanate without solvent for 44 hours at room temperature. The crude product was washed with hexane and recrystallized from ethanol; m.p. 175.5–176.8°.

Anal. Calcd. for $C_{22}H_{26}N_2O_4$: C, 69.09; H, 6.85. Found: C, 69.24; H, 6.87.

cis-1,2-Cycloöctanediol isopropylidene ketal was prepared by shaking a solution of 1.44 g. of the *cis*-glycol in 25 ml. of dry acetone with 5.0 g. of anhydrous copper sulfate at room temperature for 48 hours.[17] The mixture was filtered, concentrated, and the residue was distilled through a semimicro column.[18] The yield of *cis*-1,2-cycloöctanediol isopropylidene ketal was 1.23 g. (67%), b.p. 97–98° (10 mm.), $n^{25}\mathrm{D}$ 1.4600.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.52; H, 10.97.

Performic Acid Oxidation of Cycloöctene.—A procedure described for the oxidation of cyclohexene to *trans*-1,2-cyclohexanediol[19] was used, except that the product (after basic hydrolysis of the monoformate) was extracted with four 100-ml. and three 50-ml. portions of chloroform. The product obtained from 55.2 g. of cycloöctene, 60 ml. of commercial 35% hydrogen peroxide and 300 ml. of 87% formic acid was distilled without any attempt at fractionation and amounted to 51.5 g. (corresponding to 71.5% of cycloöctanediols) of a very viscous liquid, b.p. 97–125° (0.2–0.5 mm.).

trans-1,2-Cycloöctanediol isopropylidene ketal was prepared by shaking a solution of 28.4 g. of the above mixture in 300 ml. of dry acetone with 30 g. of anhydrous copper sulfate at room temperature for 22 hours. The mixture was filtered, the filtrate was concentrated, and the residue was distilled through a semi-micro column, yielding 11.0 g. (30% from the crude mixture of glycols) of *trans*-1,2-cycloöctanediol isopropylidene ketal, b.p. 66.5–67° (1.3 mm.), $n^{25}\mathrm{D}$ 1.4585.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.44; H, 10.68.

1,4-Cycloöctanediol was isolated from the distillation residue, which was dissolved in 25 ml. of ethyl acetate and cooled to 0°. The colorless, crystalline 1,4-diol that separated was recrystallized from ethyl acetate and obtained in a yield of 10.3 g. (36% from the crude mixture of glycols) as fine needles, m.p. 85–86.5°; mixed melting point with *cis*-1,2-cycloöctanediol, 55–65°. Evidence for the structure of the 1,4-diol is presented below.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found: C, 66.72; H, 11.11.

A semi-solid mixture (8 g. or 28% of the crude mixture calculated as $C_8H_{16}O_2$) obtained by concentration of the ethyl acetate mother liquors and short path distillation of the residue at 0.35 mm. with a heating block temperature of 100–133°, is being examined further to determine whether it contains other isomeric cycloöctanediols.

trans-1,2-Cycloöctanediol was obtained by heating a 2.0-g. sample of the isopropylidene ketal with 10 ml. of 85% formic acid for 2 hours at 100°, concentrating the solution, and shaking the residue with 15 ml. of 20% aqueous sodium hydroxide for 30 minutes. The product was extracted with 25 ml. of chloroform, and the extract was dried over magnesium sulfate. The solution was concentrated and the residue was distilled through a semimicro column, yielding 1.4 g. (89%) of *trans*-1,2-cycloöctanediol as a viscous, colorless liquid that failed to crystallize; b.p. 93–94° (0.5 mm.), $n^{25}\mathrm{D}$ 1.4980.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found: C, 66.90; H, 11.35.

Hydrolysis of a 5.7-g. sample of the isopropylidene ketal by heating under reflux for four hours with 100 ml. of water containing a few drops of hydrochloric acid was incomplete; 2.7 g. of the ketal steam distilled on concentrating the solution and was recovered from the distillate. *trans*-1,2-Cyclooctanediol (1.7 g.) was extracted from the aqueous residue with chloroform and distilled as described above. Another sample of *trans*-1,2-cycloöctanediol with the same physical properties was obtained by saponification of 0.56 g. of the bis-phenylurethan (described below) by heating under reflux with 25 ml. of 20% alcoholic potassium hydroxide for 23 hours.

trans-1,2-Cycloöctanediol was characterized by oxidation to suberic acid with alkaline permanganate, oxidation with periodic acid at 25°, which was complete within 20 minutes with reduction of 99.9% of the calculated quantity of the oxidizing agent, and by preparation of the bis-phenylurethan.

trans-1,2-Cycloöctanediol bis-phenylurethan was prepared by warming the *trans*-1,2-diol briefly with phenyl isocyanate and allowing the mixture to stand overnight. The crude solid product was washed with hexane and recrystallized from ethanol; m.p. 176.2–177.4°, and mixed m.p. with *cis*-1,2-cycloöctanediol bis-phenylurethan, 154–163°.

Anal. Calcd. for $C_{22}H_{26}N_2O_4$: C, 69.09; H, 6.85. Found: C, 69.16; H, 7.12.

Cycloöctene Oxide.—Commercial 40% peracetic acid[20] (125 ml.), to which 25 g. of sodium acetate trihydrate had been added to neutralize the sulfuric acid present, was added dropwise during 45 minutes with vigorous stirring to 55 g. of cycloöctene. The reaction temperature was maintained at 27–29° with an ice-bath. The mixture was cooled to 0°, neutralized with 40% sodium hydroxide, and extracted with three 200-ml. portions of ether. The extracts were dried over magnesium sulfate, concentrated, and the residue was distilled through a 20 × 1.8-cm. column packed with glass helices. The yield of cycloöctene oxide, b.p. 90–93° (37 mm.), m.p. 52.5–56.5°, was 54.2 g. (86%). Cycloöctene oxide was purified by sublimation under reduced pressure as needles melting at 56–57°, with a very characteristic odor. Homogeneity of the epoxide was established by chromatography on alumina and on activated carbon followed by fractional elution with pentane–ether, and also by fractional distillation. Comparison of the melting points and infrared spectra of the various fractions showed no significant differences.

Hydrogenation of a solution of 5.0 g. of cycloöctene oxide in 5 ml. of ethanol at 125° in the presence of 0.5 g. of Raney nickel at 1900–1500 p.s.i. was complete in 1 hour, and yielded 4.24 g. (83%) of cycloöctanol, b.p. 92–93° (12 mm.), $n^{25}\mathrm{D}$ 1.4842, m.p. 24.3–24.5°, identified by its infrared spectrum and by oxidation to cycloöctanone with chromic acid.

Solvolysis of Cycloöctene Oxide with Formic Acid.—A mixture of 5.03 g. of cycloöctene oxide and 25 ml. of 85% formic acid was heated under reflux for 30 minutes. The excess formic acid was removed under reduced pressure, and the viscous residue was shaken with 50 ml. of 10% sodium hydroxide for 1 hour. The product was extracted with

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[16] A hydroxylation procedure similar to one used for hydroxylation of maleic and fumaric acid by M. Zelikoff and H. A. Taylor, This Journal, **72**, 5039 (1950).

[17] Based on a procedure for preparing isopropylidene derivatives of 1,2-glycols described by C. Niemann and C. D. Wagner, *J. Org. Chem.*, **7**, 230 (1942).

[18] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

[19] A. Roebuck and H. Adkins, *Org. Syntheses*, **28**, 35 (1948).

[20] Obtained from the Becco Sales Corporation, Buffalo, N. Y.

chloroform, and the extract was dried over magnesium sulfate and concentrated. The residue was distilled and yielded 4.6 g. of a mixture of cycloöctanediols, b.p. 120–130° (0.18 mm.), which was separated by the procedure described above for the mixture obtained by oxidation of cycloöctene with performic acid. The yield of *trans*-1,2-cycloöctanediol isopropylidene ketal was 1.42 g. (19%), b.p. 60–62° (1.1 mm.), n^{25}D 1.4584. The residue remaining after distillation of the ketal was crystallized from ethyl acetate and yielded 1.7 g. (30%) of 1,4-cycloöctanediol, m.p. 84.6–86.2°. Any other isomeric cycloöctanediols that may have been present in the crystallization mother liquors were not isolated.

The same products were formed by hydrolysis of cyclooctene oxide with boiling 1% hydrochloric acid, and were isolated in the manner described above.

Structure of 1,4-Cycloöctanediol.—1,4-Cycloöctanediol, m.p. 85–86.5°, prepared by performic acid oxidation of cycloöctene or by solvolysis of cycloöctene oxide with formic acid, failed to react at all with periodic acid during 24 hours under conditions that resulted in quantitative oxidation of *cis*- and *trans*-1,2-cycloöctanediols in 20 to 30 minutes. A solution of 0.72 g. of the 1,4-diol in 15 ml. of water was oxidized by addition of 2.0 g. of sodium permanganate trihydrate as a 2% aqueous solution with stirring over a period of 45 minutes at 0–20°. The excess permanganate and manganese dioxide were reduced with sulfur dioxide at 0°, and the solution was acidified with hydrochloric acid and extracted continuously with ether for 14 hours. A mixture of acids (0.83 g.) remained as a residue after distillation of the ether, and was separated into two fractions by sublimation under reduced pressure: (1) oxalic acid, 0.20 g., m.p. 186–189° (dec.), and m.p. and mixed m.p. with oxalic acid hydrate 99–100° after recrystallization from water; (2) adipic acid, recrystallized from water, 0.41 g., m.p. and mixed m.p. with an authentic sample 152–153°.

1,4-Cycloöctanediol bis-phenylurethan was prepared by warming the 1,4-diol with a slight excess of phenyl isocyanate for a short time and allowing the mixture to stand overnight. The solid product was washed with petroleum ether and recrystallized from benzene and from ethanol; m.p. 186–187.5°; mixed m.p. with *cis*-1,2-cycloöctanediol bis-phenylurethan, 154–172°; mixed m.p. with *trans*-1,2-cyclooctanediol bis-phenylurethan, 159–180°.

Anal. Calcd. for $C_{22}H_{26}N_2O_4$: C, 69.09; H, 6.85; mol. wt., 382. Found: C, 69.01; H, 7.11; mol. wt., 354 (Rast method in camphor).

1,4-Cycloöctanediol di-*p*-toluenesulfonate was prepared by adding 3.6 g. of *p*-toluenesulfonyl chloride with cooling to a solution of 1.25 g. of the 1,4-diol in 10 ml. of dry pyridine. The mixture was allowed to stand at room temperature overnight, and poured into 75 ml. of iced 3 *N* hydrochloric acid. The product was extracted with three 75-ml. portions of ether, which were combined, dried over magnesium sulfate, and concentrated under reduced pressure. The colorless liquid residue (3.66 g.) was crystallized from methanol, and yielded 2.83 g. (72%) of the ditosylate as colorless needles, which after recrystallization from methanol melted at 96.5–98.5° (dec., introduced at 94°).

Anal. Calcd. for $C_{22}H_{28}O_6S_2$: C, 58.38; H, 6.24. Found: C, 58.47; H, 6.27.

1,4-Cycloöctanediol diacetate was prepared by heating 2.61 g. of the 1,4-diol and 2.5 g. of anhydrous sodium acetate with 6 ml. of acetic anhydride at 50° for 3 hours. The mixture was poured onto ice, neutralized with saturated sodium bicarbonate solution, and the product was extracted with 50 ml. of ether. The extract was dried over magnesium sulfate, concentrated, and the residue was distilled in a short path still at 0.07 mm. with a heating block temperature of 100°; yield 4.08 g. (98%), u^{25}D 1.4631.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.38; H, 8.83.

A 3.78-g. sample of the diacetate was pyrolyzed at 500° in a slow stream of nitrogen by introduction over a period of 1.5 hours into a vertically mounted tube containing a 50 × 1.0-cm. heated section packed with glass helices. The condensate that was collected in a trap cooled with Dry Ice was washed with sodium bicarbonate solution and extracted with pentane. The solution was dried over sodium sulfate, concentrated and the residue was distilled through a semi-micro column, yielding 1.46 g. (81%) of a mixture of cycloöctadienes, n^{25}D 1.4895–1.4930. A fraction with n^{25}D 1.4922 was analyzed.

Anal. Calcd. for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 89.11; H, 11.28.

Hydrogenation of a solution of 0.520 g. of the mixture of dienes in 7 ml. of acetic acid in the presence of 0.1 g. of prereduced platinum oxide was complete in 3 hours and 95% of two molar equivalents of hydrogen was absorbed. The product was isolated by a procedure described previously[21] and amounted to 0.491 g. (91%) of cycloöctane, b.p. 73–74° (90 mm.), n^{25}D 1.4557, m.p. 8–9.5° (indicating 98% purity) and mixed m.p. with an authentic sample, 9.5–10.4°. The sample of cycloöctane was also identified by its infrared spectrum.

1,4-Cycloöctanedione was obtained by heating a mixture of 7.2 g. of 1,4-cycloöctanediol, 10.8 g. of *p*-benzoquinone, 1.0 g. of aluminum isopropoxide and 250 ml. of toluene under reflux for 14 hours. The mixture was cooled, filtered to separate hydroquinone, concentrated, and the residue was distilled in a short path still at 0.05 mm. with a bath temperature of 60–175°. The distillate was collected in a receiver cooled with Dry Ice, and fractionated through a semi-micro column. The yield of 1,4-cycloöctanedione, b.p. 75–75.5° (1 mm.), was 1.08 g. (15%). The diketone gave a negative enol test with ferric chloride.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.82; H, 8.94.

The 1,4-cycloöctanedione derived from the 1,4-diol was characterized by conversion into the known semicarbazone of bicyclo[3.3.0]-1(5)-octen-2-one.[22] A 70-mg. sample of the diketone was added to 2% aqueous sodium hydroxide, and allowed to stand at 26° for 8 hours. The dark mixture was extracted with three 20-ml. portions of ether, and the extracts were concentrated. The residue was treated with 15 ml. of 10% hydrochloric acid for 1 hour at room temperature and 3 hours at 70°. The mixture was neutralized with sodium bicarbonate and steam distilled. To the distillate (200 ml.) was added 0.1 g. of semicarbazide hydrochloride and 0.15 g. of sodium acetate trihydrate. The mixture was heated on a steam-bath for 20 minutes and cooled to 0° overnight and the crystalline bicyclo[3.3.0]-1(5)-octen-2-one semicarbazone was separated and recrystallized from aqueous ethanol; m.p. and mixed m.p. with an authentic sample, 237–238.5° (dec.). Infrared spectra of Nujol mulls of the two semicarbazone samples were identical within experimental error.

A 140-mg. sample of 1,4-cycloöctanedione was treated with 0.3 ml. of concentrated sulfuric acid at 0° for 1 hour and 70° for 20 minutes, after which the mixture was neutralized, steam distilled, and bicyclo[3.3.0]-1(5)-octen-2-one semicarbazone was isolated from the distillate (20 ml.) by the procedure described above in a yield of 87 mg. (48%).

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[21] A. C. Cope and F. A. Hochstein, THIS JOURNAL, **72**, 2517 (1950).

[22] A. C. Cope and W. R. Schmitz, *ibid.*, **72**, 3059 (1950).