1-d, b.p. 77–80°. In another run the yield was 10.9 g. (60%). The combined materials were redistilled to yield 21.0 g. of 1-aminobutane-1-d having b.p. 77–79°, α^{25}_{D} $-0.013 \pm 0.004°$ ($l = 2$), α^{25}_{5461} $-0.015 \pm 0.005°$ ($l = 2$), n^{25}_{D} 1.3967, d^{25}_{4} 0.7471. The infrared spectrum showed a doublet in the C—D region at 4.63 and 4.72 μ.

1-Aminobutane-1,1-d_2.—A portion of the 1-butanol-1,1-d_2 used in this experiment, which had d^{25}_{4} 0.8255 (corresponding to 1.82 ± 0.1 atoms D per molecule), was converted to hydrogen 1-butyl-1,1-d_2 phthalate, which after two crystallizations from benzene–hexane had m.p. 73.0–73.4°. A deuterium analysis[18] showed 1.88 ± 0.03 atoms D per molecule. The alcohol was converted to 1-aminobutane-1,1-d_2 following the procedure described above, in an over-all yield of 69%. A portion of the 1-aminobutane-1,1-d_2 was treated with phenyl isothiocyanate and the resulting N-1-butyl-1,1-d_2-N-phenylthiourea obtained had, after two crystallizations from benzene–heptane, m.p. 64.0–64.3°. Deuterium analysis[18] showed 1.92 ± 0.03 atoms D per molecule. The infrared spectrum of the amine showed a doublet at 4.57 and 4.79 μ.

2-Octyl Tosylate.—To a 500-ml. flask equipped with a calcium chloride drying tube and arranged for magnetic stirring was added 300 ml. of dry pyridine and 33.0 g. (0.25 mole) of 2-octanol, α^{23}_{D} $5.79 \pm 0.01°$ ($l = 2$). The mixture was placed in an ice-bath and 80.0 g. (0.42 mole) of *p*-toluenesulfonyl chloride was added in 40-g. portions, made 15 min. apart. The mixture was stirred in the cold for 1 hr. and placed in a refrigerator for 2 hr. The reaction mixture was poured into 300 ml. of concentrated hydrochloric acid and 500 ml. of water and ice. The organic phase was separated and dried with anhydrous sodium sulfate, yield 56 g. (76% yield) of 2-octyl tosylate.

2-Aminoöctane.—To a solution containing 20.0 g. (0.308 mole) of sodium azide in 260 ml. of methanol and 58 ml. of water pre-heated in a thermostat held at 70° was added 52 g. (0.178 mole) of 2-octyl tosylate. The addition of the tosylate resulted in a small phase separation. After heating and stirring for 24 hr. the mixture was allowed to cool to room temperature and was diluted with 150 ml. of water and poured into 200 ml. of ether. The resulting mixture was treated with 250 ml. of a calcium chloride solution (prepared by dissolving 800 g. of calcium chloride in 2 l. of water). After separating the phases the aqueous phase was extracted three times with 100-ml. portions of ether. The combined ether solutions were dried with calcium chloride.

To a stirred suspension of 50 ml. of dry ether and 7.0 g. (0.184 mole) of lithium aluminum hydride was added dropwise, the ether solution of 2-octyl azide prepared above. The addition was carried out over a period of 1.5 hr. and was accompanied by evolution of nitrogen. The mixture was then refluxed for 1 hr., cooled to room temperature, and treated with an excess of dilute hydrochloric acid. The aqueous phase was separated and was extracted once with 75 ml. of ether. The aqueous phase was then made strongly alkaline with concentrated potassium hydroxide solution and was heated on a steam-bath until all of the inorganic salts dissolved. After cooling to room temperature the mixture was extracted three times with 75-ml. portions of ether. The combined organic phases were dried over magnesium sulfate. After removal of the ether distillation yielded 13.6 g. (59% based on 2-octyl tosylate) of 2-aminoöctane, b.p. 163–164°, α^{23}_{D} $-3.70 \pm 0.02°$ ($l = 2$).

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[18] We are grateful to Dr. N. R. Trenner of Merck and Co. for the deuterium analyses.

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

Proximity Effects. III. *trans*-1,4-Cyclohexanediol from Cyclohexene and Performic Acid

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Hydroxylation of cyclohexene with performic acid has been shown to yield *trans*-1,4-cyclohexanediol (0.03%) and the two stereoisomeric 2,2′-dihydroxydicyclohexyl ethers in addition to 85% of the normal product, *trans*-1,2-cyclohexanediol.

The isolation of *cis*-1,4-cycloheptanediol in 2.4% yield from the products of solvolysis of cycloheptene oxide with dilute hydrochloric acid[2] led us to investigate the hydroxylation of cyclohexene with performic acid, to determine whether products other than the normal *trans*-1,2-glycol were formed. Cyclohexene was treated with a mixture of formic acid and hydrogen peroxide under conditions similar to those described by Roebuck and Adkins.[3] The products isolated were *trans*-1,2-cyclohexanediol (85%), *trans*-1,4-cyclohexanediol (0.03%), 1-methyl-*trans*-1,2-cyclopentanediol (0.37%) and a high-boiling residue (approximately 8%) containing the two stereoisomeric 2,2′-dihydroxydicyclohexyl ethers. These compounds were separated from the mother liquors from crystallization of *trans*-1,2-cyclohexanediol by chromatography on alumina. No other pure compounds were isolated.

trans-1,4-Cyclohexanediol was identified by comparing its infrared spectrum with the spectrum of an authentic sample, and by mixed melting point of the two samples. 1-Methyl-*trans*-1,2-cyclopentanediol was identified by comparison with an authentic sample[4] (infrared spectra and mixed m.p.), and by comparison of the monophenylurethans of the two samples. Vapor phase chromatography of the cyclohexene employed on a column containing silicone oil (Dow Corning 550) and 100–200 mesh Celite in a ratio of 3:7 showed that it contained 0.66% of 1-methylcyclopentene, thus accounting for the formation of 1-methyl-*trans*-1,2-cyclopentanediol derived from this impurity.[5] A second impurity present in the cyclohexene to the extent of 0.20% according to the vapor-phase chromatogram is believed to be methylenecyclopentane; an authentic sample of that hydrocarbon showed identical behavior on vapor-phase chromatography. The structures of the stereoisomeric 2,2′-dihydroxydicyclohexyl ethers are assigned on the basis of elemental analyses, and the isolation of a homolo-

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[1] National Institutes of Health Postdoctoral Fellow, 1955–1956.

[2] A. C. Cope, T. A. Liss and G. W. Wood, *Chemistry and Industry*, 823 (1956).

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

[4] C. J. Maan, *Rec. trav. chim.*, **48**, 332 (1929).

[5] Dehydration of cyclohexanol and isomerization of cyclohexene are known to result in the formation of 1-methylcyclopentene; see H. Adkins and A. K. Roebuck, THIS JOURNAL, **70**, 4041 (1948).

gous ether from the solvolysis of cycloheptene oxide with formic acid.[6]

Formation of *trans*-1,4-cyclohexanediol from cyclohexene may be explained by a variation of the mechanism involving a transannular hydride shift proposed to account for the formation of *cis*-1,4-cycloöctanediol on solvolysis of *cis*-cycloöctene oxide.[7] A 1,3-hydride shift from C_4 to C_2 of the intermediate cyclohexene oxide, opening the oxide ring, with concerted attack of formic acid at C_4 with Walden inversion would lead to *cis*-1,4-cyclohexanediol. Since *trans*-1,4-cyclohexanediol is the observed product, either the epoxide ring opening or the reaction with formic acid at C_4 must occur without Walden inversion. It seems likely that the reaction with formic acid is not completely concerted; in other words, that the carbonium ion at C_4 exists long enough to lead to the more stable *trans*-1,4-glycol with equatorial hydroxyl substituents, rather than the *cis* isomer. Possible conversion of *cis*-1,4-cyclohexanediol to the *trans* isomer during the reaction is unlikely, since the *cis* isomer was recovered unchanged after treatment with formic acid under the conditions of the hydroxylation reaction. *cis*-1,4-Cyclohexanediol is more soluble and lower melting than the *trans* isomer, and may have been present in the reaction mixture and escaped detection.

Experimental[8]

Hydroxylation of Cyclohexene.—Freshly distilled cyclohexene (200 g.) was treated with 1100 ml. of 88% formic acid and 300 ml. of 30% hydrogen peroxide as described by Roebuck and Adkins.[3] After removing volatile compounds by warming under reduced pressure, the residue was saponified by the addition of 200 g. of sodium hydroxide in 350 ml. of water. Water (approximately 300 ml.) was added, and the mixture was extracted six times with chloroform. Continuous extraction of the aqueous solution for 24 hr. removed an additional 3.0 g. of organic material, while further extraction removed no more. The extracts were combined, dried over magnesium sulfate, and concentrated. The solid residue (261 g.) on crystallization from benzene afforded 235 g. of pure *trans*-1,2-cyclohexanediol, m.p. 103–104°. The residue from the mother liquors (22.7 g.) was distilled under reduced pressure, giving 13.8 g. of distillate, b.p. 145–155° (30 mm.). Crystallization of the distillate from benzene gave 6.75 g. of *trans*-1,2-cyclohexanediol and 7.03 g. of residue from the mother liquors. The residue was dissolved in 100 ml. of ether and adsorbed on 500 g. of alumina in a column 50 mm. in diameter. Elution with ether–methanol (99:1, 4.25 l.) removed 2.0 g. of a mixture of the 2,2′-dihydroxydicyclohexyl ethers. Further elution with the same solvent gave *trans*-1,4-cyclohexanediol, which after one crystallization from benzene weighed 82 mg. (0.03%) and had m.p. 138–143°. Recrystallization from benzene raised the melting point to 142–143°. Mixed melting point with an authentic sample showed no depression, and the infrared spectra of the two samples were identical in every respect. Continued elution with ether–methanol (49:1, 3.5 l.) gave 1.05 g. (0.37%) of an oil, and ether–methanol (4:1, 1.5 l.) removed an additional 3.50 g. of *trans*-1,2-cyclohexanediol.

The oily fraction from the chromatogram was distilled, and yielded a solid distillate, m.p. 55–60°, raised to 62–64° by two crystallizations from benzene. The infrared spectrum of this compound was identical with the spectrum of an authentic sample of 1-methyl-*trans*-1,2-cyclopentanediol, m.p. 62–64° (reported[4] m.p. 65°). A portion of the distillate was treated with excess phenyl isocyanate at 100° for 15 min. The excess reagent was removed by warming at 0.05 mm., and the residue was crystallized several times from benzene to give a monophenylurethan (presumably through reaction of the secondary alcohol group), m.p. 166–166.5°, which was not depressed on admixture with the same derivative prepared from the authentic glycol.

Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.48; H, 7.37; N, 6.01.

The 2,2′-dihydroxydicyclohexyl ether fraction from another similar hydroxylation of cyclohexene (in which the residues from the mother liquors were not distilled) was separated into two crystalline isomers by chromatography on alumina and elution with ether–methanol (99:1). The isomer that was eluted first formed clusters of minute colorless needles on crystallization from hexane, m.p. 124.2–124.8°.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.48; H, 10.48.

The second isomer formed colorless plates on crystallization from hexane, m.p. 125.2–126.0°, depressed to less than 114° on mixture with the first isomer.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.15; H, 10.37.

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[6] A. C. Cope and W. N. Baxter, THIS JOURNAL, **76**, 279 (1954).

[7] A. C. Cope, S. W. Fenton and C. F. Spencer, *ibid.*, **74**, 588 (1952).

[8] Melting points are corrected and boiling points are uncorrected. Alumina used for chromatography was "Merck acid washed" and was determined to have activity II on the Brockmann scale. We are indebted to Dr. S. M. Nagy and his associates for analyses.