of sodium formate, 3.5 g. of 98–100% formic acid, and 50 mg. of cis-cyclooctene was allowed to stand at room temperature for 24 hr. cis-Cyclooctene was recovered in more than 90% yield and was identified by comparison of its infrared spectrum with that of an authentic sample. Cyclooctyl formate was not detected (gas chromatographic analysis on silicone grease at 155°).

Trifluoroacetolysis of 1 and Subsequent Degradation of Deuterated Cyclooctanol.—The trifluoroacetolysis of 1 was carried out as described for the formolysis at 0° for 3.5 hr. in trifluoroacetic acid–0.5 M sodium acetate. The only trifluoroacetolysis product isolated (after saponification) was partially deuterated cyclooctanol. The procedure used for its isolation and subsequent degradation was that described for the formolysis.

Proximity Effects. XXXVII. Proximity Effects in the Solvolysis of 1-Octene Oxide[1,2]

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Received June 28, 1963

The reaction of 1-octene oxide with trifluoroacetic acid yields small amounts of abnormal products, 1,3-, 1,4-, 1,5-, 1,6-, and 1,7-octanediol, in addition to the normal product, 1,2-octanediol. This may be interpreted as evidence for the operation of a proximity effect in acyclic compounds. From hydroxylation of 1-octene with performic acid or peracetic acid only 1,2-octanediol was isolated.

The reaction of cis-cyclooctene with performic acid gave principally the abnormal product cis-1,4-cyclooctanediol,[3] and the solvolysis of cis-cyclooctene oxide with trifluoroacetic acid gave exclusively products of transannular hydride shifts.[4] To determine whether such a proximity effect was operative in acyclic compounds that could assume conformations similar to those of medium-ring compounds, the solvolysis of 1-octene oxide with trifluoroacetic acid and the hydroxylation of 1-octene with performic and peracetic acid were studied.

In this study several methods were considered which might permit the isolation and identification of extremely small amounts of isomeric octanediols present in a large amount of 1,2-octanediol. The selective formation of a cyclic ketal, used for the separation of trans-1,2-cyclooctanediol and cis-1,4-cyclooctanediol, was not applicable because 1,2-, 1,3-, and 1,4-octanediol formed such ketals on treatment with copper sulfate and acetone. The method which ultimately proved successful was separation of 1,2-octanediol from the reaction product by repeated crystallization and gas chromatography of the diacetates prepared from glycols present in the mother liquor.

The reaction product of 1-octene oxide with trifluoroacetic acid was hydrolyzed and repeatedly recrystallized to separate 1,2-octanediol. Glycols in the mother liquor were converted to diacetates and the diacetates were fractionally distilled. Gas chromatography showed that there were several minor peaks in addition to a major peak due to 1,2-octanediol diacetate. These minor components were 1,3- (0.7%), 1,4- (0.5%), 1,5- (0.3%), 1,6- (0.2%), and 1,7-octanediol diacetate (0.1%).[5] The first four compounds were isolated by gas chromatography and identified by comparison of the infrared spectra with the spectra of authentic samples and by comparison of the retention times with the retention times of authentic samples on four different gas chromatographic columns. The last compound was identified only by comparison of the retention time with an authentic sample on four different gas chromatographic columns.

The small amount of additional material (ca. 1%) was probably a mixture of octenyl acetates on the basis of its analysis and its infrared spectrum, which was similar to that of trans-2-octen-1-yl acetate. Gas chromatography on 1,2,3-tris-(2-cyanoethoxy)-propane showed a broad peak corresponding in retention time to a mixture of cis- and trans-2-octen-1-yl acetate.

Hydroxylation of 1-octene with formic acid and hydrogen peroxide or with peracetic acid and treatment of the products in the manner described above gave only 1,2-octanediol and no detectable amount of any other glycol.

Formation of 1,3-, 1,4-, 1,5-, 1,6-, and 1,7-octanediol can be formulated as the result of 1,2-, 1,3-, 1,4-, 1,5-, and 1,6-hydride shifts in an intermediate carbonium ion resulting from the protonated 1-octene oxide. Alternatively, they may have been formed by a series of 1,2-hydride shifts. It has been shown that trifluoroacetic acid promotes 1,2-hydride shifts.[6] Detection of 1,3-octanediol among the solvolysis products demonstrates that a 1,2-hydride shift has occurred.

However, the following argument suggests that a series of 1,2-shifts would give a different distribution of products. The total amount of the abnormal products is less than 2%. Using 2% as a representative amount of 1,2-hydride shift in secondary cations, it may be estimated that the amounts of 1,3-, 1,4-, 1,5-, 1,6-, and 1,7-octanediol formed by successive 1,2-shifts in the reaction of 1-octene oxide would be 2, 0.04, 0.0008%.... Experimentally, the yields of isomeric octanediols does not decrease this sharply. Accordingly, one-step hydride shifts appear to explain our results more satisfactorily.

Experimental[7]

cis-2-Octen-1-ol.—Commercial 2-octyn-1-ol (Farchan Research Laboratories) was hydrogenated in methanol using 1.5% palladium chloride on calcium carbonate as catalyst, giving cis-2-octen-1-ol, n^{25}D 1.4465 (lit.[8,9] n^{20}D 1.44609).

The alcohol was treated with acetic anhydride in pyridine, giving cis 2-octen-1-yl acetate, n^{25}D 1.4348.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.27; H, 10.54.

(1) Supported in part by a research grant (NSF-G5055) of the National Science Foundation.

(2) Paper XXXVI: *J. Am. Chem. Soc.*, **85**, 3747 (1963).

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(5) The percentages are based on 1-octene oxide.

(6) P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 5834 (1960).

(7) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses. Footnote 24 of A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959), describes the conditions and equipment used for gas chromatography.

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trans-2-Octen-1-ol.—*trans*-2-Octenoic acid (Aldrich) was treated with lithium aluminum hydride in ether, yielding 1-octanol and *trans*-2-octen-1-ol. The latter was isolated by gas chromatography (silicone oil at 180°); n^{25}D 1.4440 (lit.[8] n^{25}D 1.44464, n^{25}D 1.4400[10]).

The alcohol was treated with acetic anhydride in pyridine, affording *trans*-2-octen-1-yl acetate.[8,11]

1,2-Octanediol.—Hydroxylation of 1-octene with formic acid and 30% hydrogen peroxide gave 1,2-octanediol[12] (84%), b.p. 80–95° (0.25 mm.), n^{25}D 1.4435–1.4460.

1,2-Octanediol bis-phenylurethan, recrystallized from pentane, had m.p. 60–62°.

Anal. Calcd. for $C_{22}H_{28}O_4N_2$: C, 68.73; H, 7.34; N, 7.29. Found: C, 68.85; H, 7.45; N, 7.45.

1,3-Octanediol Diacetate.—*trans*-2-Octen-1-ol was treated with peracetic acid followed by lithium aluminum hydride, giving a mixture of 1,2- and 1,3-octanediol. Treatment directly with acetic anhydride and pyridine gave a mixture of diacetates, which were separated and isolated by gas chromatography (TCEP at 145°). 1,2-Octanediol diacetate was identified by comparison (infrared spectrum and retention time) with an authentic sample. 1,3-Octanediol diacetate had n^{25}D 1.4295.

Anal. Calcd. for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.47; H, 9.35.

1,4-Octanediol Diacetate.—Addition of *n*-propylmagnesium bromide to furfural followed by gas phase dehydration over alumina at 400° gave 2-(1-butenyl)-furan (56%).[13,14] Hydrogenation of this material over Raney nickel at 130° and 1600 p.s.i. gave 2-*n*-butyltetrahydrofuraa,[15] which was cleaved with acetic anhydride in the presence of boron trifluoride etherate to give 1,4-octanediol diactate,[16] b.p. 66–74° (0.03 mm.), n^{25}D 1.4300–1.4313. The diacetate was hydrolyzed with potassium hydroxide to 1,4-octanediol (94%), b.p. 72–75° (0.025 mm.), n^{25}D 1.4519–1.4522.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.70; H, 12.41. Found: C, 66.05; H, 12.45.

1,4-Octanediol bis-phenylurethan, recrystallized from pentane–hexane, had m.p. 85–88°.

Anal. Calcd. for $C_{22}H_{28}O_4N_2$: C, 68.73; H, 7.34; N, 7.29. Found: C, 69.07; H, 7.31; N, 7.48.

1,5-Octanediol, prepared by the method of Paul,[17] gave a bis-phenylurethan, m.p. 69–70°, after recrystallization from pentane–hexane.

Anal. Calcd. for $C_{22}H_{28}O_4N_2$: C, 68.73; H, 7.34; N, 7.29. Found: C, 68.89; H, 7.44; N, 7.28.

The 1,5-octanediol diacetate had n^{25}D 1.4291.

Anal. Calcd. for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.43; H, 9.57.

1,6-Octanediol.—The reaction of ω-carboethoxyvaleryl chloride, b.p. 124–125° (16 mm.) (prepared from ethyl hydrogen adipate[18]), with diethylcadmium in benzene in the manner described by Cason[19] yielded ethyl 6-ketooctanoate[20] (35%), b.p. 113–128° (2 mm.), n^{24}D 1.4311.

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(20) H. Adkins and C. Scanley, *J. Am. Chem. Soc.*, **73**, 2854 (1951).

Treatment of ethyl 6-ketooctanoate with lithium aluminum hydride in ether at room temperature gave 1,6-octanediol, n^{25}D 1.4550.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.71; H, 12.41. Found: C, 65.64; H, 12.31.

1,6-Octanediol diacetate, prepared by the acetic anhydride-pyridine method, had n^{25}D 1.4299.

Anal. Calcd. for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.71; H, 9.72.

7-Ketooctanoic Acid.—2-Acetylcyclohexanone was treated with potassium hydroxide solution in a manner previously described[21] to give 7-ketooctanoic acid, b.p. 123–125° (0.4 mm.), n^{25}D 1.4455.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.43; H, 9.00.

1,7-Octanediol.—Treatment of 7-ketooctanoic acid with lithium aluminum hydride in ether at room temperature gave 1,7-octanediol,[22] n^{25}D 1.4515, which was converted to 1,7-octanediol diacetate,[22] n^{25}D 1.4290 (lit. n^{21}D 1.4374).

Solvolysis of 1-Octene Oxide.—1-Octene oxide (20 g.), homogeneous by gas chromatography (silicone oil at 150°), was added dropwise to 200 g. of trifluoroacetic acid at 0°. The solution was allowed to stand at 0–5° for 4 hr. and then was neutralized by slow addition of 1 l. of 10% sodium carbonate solution with cooling and stirring. The mixture was extracted with ether and the ether extracts were washed with water and dried over magnesium sulfate. The crude product (39 g.) obtained by evaporation of the ether was stirred overnight at room temperature with a solution of 40 g. of sodium hydroxide in 100 ml. of water and 100 ml. of methanol. From the hydrolysis mixture 22.3 g. (99%) of the crude glycol was obtained. Six recrystallizations from pentane gave 15 g. of pure 1,2-octanediol. The glycol mixture from the mother liquors (5.5 g.) was treated with acetic anhydride in pyridine and the resulting mixture of diacetates was distilled and analyzed by gas chromatography. The yields of the solvolysis products, based on 1-octene oxide, were 90% 1,2-octanediol, 0.7% 1,3-octanediol, 0.5% 1,4-octanediol, 0.3% 1,5-octanediol, 0.2% 1,6-octanediol, and 0.1% 1,7-octanediol (all except the first isolated as the diacetates). All of the diacetates except 1,7-octanediol diacetate were collected by gas chromatography and identified by comparison of their infrared spectra with those of authentic samples as well as by comparison of retention times on four different gas chromatographic columns (silicone oil at 180°, 1,2,3-tris-(2-cyanoethoxy)-propane at 160°, Carbowax 20M at 200°, and polyethylene glycol phthalate at 180°). 1,7-Octanediol diacetate was identified by comparison of its retention time with that of an authentic sample on these four columns. No 2,3-octanediol diacetate was detected.

Hydroxylation of 1-Octene.—A mixture of 120 ml. of 90% formic acid, 37 ml. of 30% hydrogen peroxide, and 20.2 g. of 1-octene (99.56% pure)[23] was heated at 40–50° for 20 hr. The solvent was distilled under reduced pressure and the residue was heated at 40–50° for 16 hr. with 45 g. of potassium hydroxide in 275 ml. of ethanol. The solution was concentrated and extracted with chloroform and the chloroform extracts were washed with water and dried over magnesium sulfate. Evaporation of the chloroform left 23.7 g. (80%) which after six recrystallizations from pentane gave 15 g. of 1,2-octanediol. Gas chromatographic analysis (silicone oil at 190°) of the diacetates prepared as described previously from the mother liquors showed that only 1,2-octanediol diacetate was present. Repetition of the hydroxylation of 1-octene with peracetic acid gave the same result.

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(23) We are indebted to Dr. F. D. Rossini for this material.