hydrogen was consumed and on fractional distillation, 65 g. (87%), of *cis*-2-carbethoxycyclohexanol, b.p. 125–217° (27 mm.), n^{25}D 1.4585 (lit.[3] 117–118° (17 mm.)).

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.94; H, 9.47.

Preparation of *cis*-2-Carboxycyclohexanol.—A mixture of 14.5 g. (0.08 mole) of 2-carbethoxycyclohexanol (95% *cis*) and 45 ml. of 25% aq. sodium hydroxide was stirred for 12 hr. The sodium salt of *cis*-2-carboxycyclohexanol acid separated and was filtered. It was dissolved in a small amount of water and the solution made acid to congo red with 10% hydrochloric acid. The aqueous solution was saturated with ammonium sulfate and extracted with ether. The ether-soluble material was recrystallized from a small amount of ether to give 5.4 g. (44%) of the *cis*-acid, m.p. 79–80° (lit.[3] 80–81°).

Preparation of *cis*-2-Carbomethoxycyclohexanol.—To a cooled solution of 5.1 g. (0.035 mole) of *cis*-2-carboxycyclohexanol in 25 ml. of ether was added an ether solution of diazomethane at 0–5°. Fractional distillation gave a quantitative yield of the desired ester, b.p. 87.5–88.5° (3 mm.), n^{25}D 1.4647 (lit.[3] b.p. 105° (14 mm.), n^{25}D 1.4645).

Preparation of *cis*-2-Hydroxymethyl-1-hydroxycyclohexane.—To a solution of 1.44 g. (0.038 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether, we added 5.4 g. (0.034 mole) of *cis*-2-carbomethoxycyclohexanol in an equal volume of ether at such a rate as to maintain slow refluxing. After addition was complete, the mixture was refluxed and stirred for an additional 1.5 hr. The excess lithium aluminum hydride was decomposed with moist ether followed by water and the metal alkoxides with cold dilute sulfuric acid. The aqueous solution was saturated with ammonium sulfate and extracted with ether. Distillation of the resulting glycol yielded a very viscous, colorless oil, b.p. 124° (2 mm.). On standing several hr. the glycol crystallized, m.p. 48–49° (lit.[8] 49–50°).

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.65; H, 10.48.

The di-*p*-nitrobenzoate of *cis*-2-hydroxymethyl-1-hydroxycyclohexane was prepared by the usual procedure for these derivatives, m.p. 133.5–134 (lit.[9] 134°). The mono-*p*-nitrobenzoate, previously unreported, also was isolated, m.p. 95–96°.

Anal. Calcd. for $C_{14}H_{17}O_5N$: C, 60.28; H, 6.14; N, 5.02. Found: C, 59.60; H, 6.03; N, 5.00.

Preparation of *trans*-2-Carboxycyclohexanol.—The mother liquors from the preparation of *cis*-2-carboxycyclohexanol were concentrated *in vacuo* and refluxed with 7.5 *N* potassium hydroxide. The mixture was cooled, acidified to congo red with sulfuric acid and saturated with ammonium sulfate. The aqueous solution was extracted several times with ether. The *trans*-acid was recrystallized from ethyl acetate, m.p. 109–111° (lit.[3] m.p. 111°).

In a similar epimerization 12.1 g. (0.072 mole) of sodium *cis*-cyclohexanol-2-carboxylate was transformed into the *trans*-acid by refluxing with base. The yield was 5.6 g. (54%) of pure *trans*-acid.

Preparation of *trans*-2-Carbomethoxycyclohexanol.—The procedure was identical to that used for the *cis*-ester. Fractional distillation yielded a quantitative amount of the *trans*-methyl ester, b.p. 99.8–101.8° (2 mm.), m.p. 34–35°, n^{25}D 1.4632.

Preparation of *trans*-2-Hydroxymethyl-1-hydroxycyclohexane.—The procedure was identical to that used to prepare the *cis*-diol above. A solution of 1.3 g. (0.032 mole) of lithium aluminum hydride in 100 ml. of ether was used to reduce 4.54 g. (0.029 mole) of *trans*-2-carbomethoxycyclohexanol. Fractional distillation yielded 2.4 g. (63%) of a viscous, colorless oil, b.p. 103.5–104° (0.9 mm.), n^{25}D 1.4829, which was shown by comparison of infrared spectrum to be identical with the glycol obtained from the Prins reaction.

The acetonide of *trans*-2-hydroxymethyl-1-hydroxycyclohexane was prepared, b.p. 106–107° (30 mm.), 214–216° (740 mm.), n^{25}D 1.4602.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.60; H, 10.75.

The bis-phenylurethan of *trans*-2-hydroxymethyl-1-hydroxycyclohexanol melted at 159–160.5° (lit.[5] m.p. 160–161).

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[8] S. Siegel, THIS JOURNAL, **75**, 1317 (1953).

[9] M. Mousseron, J. Jullien and F. Winternitz, *Bull. soc. chim. France*, 878 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Epoxyethers. XI. O→O Acyl Migrations with α-Hydroxyacylals

BY CALVIN L. STEVENS AND BERNARD T. GILLIS[1,2]

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1,2-Epoxy-1-methoxy-2-methylpropane (X) was isolated in good yield from the reaction of α-haloisobutyraldehydes with dry sodium methoxide. This epoxyether X reacted with organic acids to form relatively stable α-hydroxyacylals XI (pseudoesters) which readily underwent O → O acyl migration with the loss of alcohol to give esters of α-hydroxyisobutyraldehyde (XIII). At 150°, the 3,5-dinitrobenzoate pseudoester XI eliminated 3,5-dinitrobenzoic acid to form the dioxane derivative IX.

The reaction of an organic acid with an epoxyether has been shown previously to give an α-ketoester. In one example, the intermediate α-hydroxyacylal could be isolated and was shown to undergo irreversible O→O acyl migration to form the α-ketoester and alcohol.[3] Acylals derived from aldehyde epoxyethers were found to be relatively more stable than those from ketone epoxyethers, one being distilled under reduced pressure without decomposition.[4] Since the O→O acyl migration is accompanied by formation of a carbonyl group in α-hydroxyacylals, these compounds provide unique and simple examples for the study of such migrations. The present work demonstrates that the more stable acylals from aldehyde epoxyethers can also be made to undergo acyl migration.

The aldehyde epoxyether chosen for this study was that from isobutyraldehyde. The starting α-chloroaldehyde I was prepared in 60% yield by direct chlorination of isobutyraldehyde using a modification of the method of Brown and Ash.[4,5]

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[2] Abstracted from the dissertation submitted by B. T. Gillis in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Wayne University, 1956.

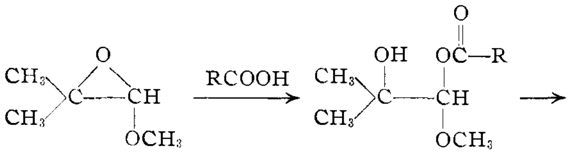
[3] C. L. Stevens and S. Dykstra, THIS JOURNAL, **75**, 5975 (1953).

[4] C. L. Stevens, E. Farkas and B. Gillis, *ibid.*, **76**, 2695 (1954).

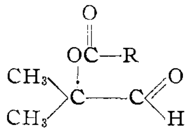
[5] H. C. Brown and A. B. Ash, *ibid.*, **77**, 4019 (1955).

Direct bromination in the presence of calcium carbonate gave 35% of α-bromoisobutyraldehyde.[6,7] The α-haloisobutyraldehydes trimerized either in the presence of a trace of acid or during long standing. The monomeric haloaldehydes were regenerated from their trimers during distillation.

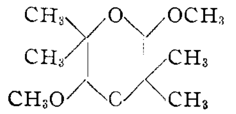
α-Chloroisobutyraldehyde and α-bromoisobutyraldehyde *gave the same* 2,4-dinitrophenylhydrazone when treated with the standard alcoholic 2,4-dinitrophenylhydrazine reagent. The α-chloroisobutyraldehyde derivative previously had been reported[8] to melt at 106°, that of α-bromoisobutyraldehyde at 116°.[9] In the present work, the derivative from both haloaldehydes, m.p. 116°, was found beyond doubt to be α-ethoxyisobutyraldehyde 2,4-dinitrophenylhydrazone. A negative Beilstein test, ultraviolet absorption spectra and carbon–hydrogen analyses supported this conclusion. Recent work of Ramirez[10] has shown that solvolysis of the α-halogen by alcohol occurs in the formation of 2,4-dinitrophenylhydrazones.



X XI



XIII



IX

α-Chloroisobutyraldehyde (I) yielded 82% of α-hydroxyisobutyraldehyde dimethylacetal (II) when allowed to react with sodium methoxide in excess methanol for 1.5 hr. at 50°. The structure of II was proved by preparation of its solid 3,5-dinitrobenzoate derivative III, hydrolysis of the acetal to the aldehyde IV, followed by oxidation to the acid V. This acid was converted to an amide VI which was prepared independently from acetone cyanohydrin.

1,2-Epoxy-1-methoxy-2-methylpropane (X) was obtained in 37% yield from the reaction of α-chloroisobutyraldehyde and dry sodium methoxide in ether. The substitution of diethyl carbitol as solvent increased the yield to 53%, undoubtedly due to increased ease of isolation from the latter solvent.

The epoxyether X was identified by methanolysis to α-hydroxyisobutyraldehyde dimethylacetal in 57% yield. The infrared spectrum of the latter was superimposable on that of II obtained directly from α-chloroisobutyraldehyde. The 3,5-dinitrobenzoate derivatives of the two acetals showed no depression in melting point upon mixing.

When the epoxyether X was allowed to react with 3,5-dinitrobenzoic acid an α-hydroxyacylal XI was formed in 81% yield. The assignment of structure XI to the product of the reaction was based upon the fact that extraction of an ethereal solution with sodium carbonate solution permitted isolation of the acylal from the ether in 90% yield, proving that the acylal was not a complex of acid and epoxyether. An alternate structure, the methyl alcohol hemiacetal of α-hydroxyisobutyraldehyde 3,5-dinitrobenzoate, was eliminated since XI could be oxidized with concentrated nitric acid to give a 98% yield of 3,5-dinitrobenzoic and a 48% yield of α-hydroxyisobutyric acids; authentic α-hydroxyisobutyraldehyde 3,5-dinitrobenzoate gave 60% of α-hydroxyisobutyric acid 3,5-dinitrobenzoate under identical conditions. The fact that the Tollens test failed with XI and that methanol did not react with the aldehyde XIII to give XI provided further evidence against the hemiacetal structure. Spectral data showed the presence of hydroxyl and ester groups and together with the analytical data confirmed structure XI.

A 3,5-dinitrobenzoate acylal corresponding to XI but made from a ketone epoxyether has been shown to undergo O→O acyl migration smoothly at the melting point with the formation of an α-ketoester and alcohol.[3] This acyl migration also took place in an inert solvent at low temperatures.[3] Acylal XI behaved in a totally different manner. When heated above the melting point a change occurred and the resulting mixture partially solidified. The solid was not the aldehyde ester XIII but rather 3,5-dinitrobenzoic acid. When the pyrolysis was conducted under vacuum a second crystalline product could be isolated and shown to be the dioxane IX.

Parham[11] has shown recently that α-hydroxyacetals will undergo acetal interchange with the formation of dioxanes. Using this method IX was synthesized from α-hydroxyisobutyraldehyde dimethylacetal (II) and the crystalline isomer isolated shown to be identical in all respects with IX from the pyrolysis.

The O→O acyl migration of XI could be made to proceed smoothly at room temperature in ether solution with the aid of triethylamine catalyst. The structure of the resulting α-hydroxyisobutyraldehyde 3,5-dinitrobenzoate (XIII) was proved by oxidation to the corresponding acid and by synthesis from the α-hydroxyacetal II.

The epoxyether X reacted readily with acetic acid at 0° to give the acylal XI in which R is methyl in 58% yield. This liquid acylal could be distilled under reduced pressure without decomposition. However, when the acylal was heated in the presence of triethylamine catalyst, O→O acetyl migration proceeded smoothly with the evolution of methanol and the formation of α-acetoxyisobutyraldehyde in 79% yield.

Experimental

α-Chloroisobutyraldehyde (I).—In a 500-ml. flask equipped with a dropping funnel, stirrer and reflux condenser protected with a drying tube was placed 72.1 g. (1.0 mole) of isobutyraldehyde. To the aldehyde 135.0 g. (1.0 mole) of freshly distilled sulfuryl chloride was added slowly with agitation to maintain a temperature of 25–40°. After the addition was complete, the reaction was heated for 2 hr.

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[6] H. Erlenmeyer and J. P. Jung, *Helv. Chim. Acta*, **32**, 35 (1949).

[7] I. Heilbron, E. R. H. Jones, R. W. Richardson and F. Sondheimer, *J. Chem. Soc.*, 737 (1949).

[8] A. Krattiger, *Bull. soc. chim. France*, 222 (1953).

[9] P. Z. Bedoukian, THIS JOURNAL, **66**, 1325 (1944).

[10] F. Ramirez and A. F. Kirby, *ibid.*, **75**, 6026 (1953).

[11] W. E. Parham, H. Wynberg and F. L. Ramp, *ibid.*, **75**, 2065 (1953); W. E. Parham and H. E. Reiff, *ibid.*, **77**, 6391 (1955).

and stirred for 4 hr., then flash distilled at 40 mm. pressure at a temperature of 80°. Final distillation through a 15-cm. Vigreux column gave 64 g. (60%) of α-chloroisobutyraldehyde,[8] b.p. 86–89°, n^{25}D 1.4081, d^{25} 1.0199. The product contained 33.2% chlorine (calcd. 33.3%).

A 2,4-dinitrophenylhydrazone derivative of the α-chloroisobutyraldehyde was prepared by the method of Shriner and Fuson,[12] m.p. 116°, and corresponded to α-ethoxyisobutyraldehyde 2,4-dinitrophenylhydrazone, $\lambda_{\max}$ 357 mμ (95% alcohol).

Anal. Calcd. for $C_{12}H_{16}N_4O_5$: C, 48.64; H, 5.44. Found: C, 48.07; H, 5.49.

α-Chloroisobutyraldehyde (18 g., 0.168 mole) was added dropwise with stirring to an excess of concentrated nitric acid. After the evolution of nitrogen dioxide ceased, the remainder of the nitrogen dioxide was aerated from the mixture which then was extracted continuously with ether for 5 days. The ether was removed and the residue was refluxed with excess thionyl chloride for 3 hr. Distillation yielded 16 g. (68%) of α-chloroisobutyryl chloride,[13] b.p. 95–113°. Refractionation of the acid chloride gave a b.p. 111–112.5°, n^{25}D 1.4313, d^{25} 1.1802.

The acid chloride could be converted in 77% yield to the known α-chloroisobutyramide,[14] m.p. 118–119°, and in 79% yield to the known α-chloroisobutyr-*p*-toluidide,[15] m.p. 68–69°.

The α-chloroisobutyraldehyde was trimerized by a trace of acid and the resultant solid trimer[16] melted at 106–107°. The monomeric α-chloroisobutyraldehyde could be regenerated from the trimer by heat and distillation.

α-Bromoisobutyraldehyde.—In a 1-l. flask equipped with condenser, drying tube, stirrer and dropping funnel was placed 150 g. (2.1 moles) of isobutyraldehyde, 200 ml. of carbon disulfide and 250 g. (2.5 moles) of calcium carbonate. Added slowly with agitation was 330 g. (2.06 moles) of bromine. Upon completion of the addition, the reaction mixture was stirred for 4 hr. and the excess bromine destroyed with sodium thiosulfate. The salts were removed by filtration and washed with carbon disulfide and the combined solution dried over anhydrous sodium sulfate. After filtration, the solution was distilled at atmospheric pressure through a 15-cm. Vigreux column to yield 106 g. (35%) of α-bromoisobutyraldehyde, b.p. 108–112°, n^{25}D 1.4567. Redistillation gave b.p. 111–112°, d^{25} 1.4044, n^{25}D 1.4500. The bromine content was 52.6% (calcd. 52.9).

The α-bromoisobutyraldehyde was trimerized in the same manner as the α-chloroisobutyraldehyde to yield a white solid,[17] m.p. 129–130°. The monomeric α-bromoisobutyraldehyde could be generated from the trimer by distillation.

A 2,4-dinitrophenylhydrazone derivative of the α-bromoisobutyraldehyde was prepared by the method of Shriner and Fuson[12] and melted at 116°. A mixture melting point determination with the derivative obtained from α-chloroisobutyraldehyde was undepressed.

α-Hydroxyisobutyraldehyde Dimethylacetal (II).—To 200 ml. of anhydrous methanol was added 6.5 g. (0.28 g. atom) of freshly cut sodium metal. After the sodium was completely dissolved, the sodium methoxide solution was cooled to 0° and 30 g. (0.282 mole) of α-chloroisobutyraldehyde was introduced over a period of 5 minutes. The reaction mixture was heated at 50° with stirring for 1.5 hr. The precipitated salt was removed by centrifugation and washed once with ether. The solutions were combined and distilled through a 30-cm. tubular column at atmospheric pressure to yield 31 g. (82%) of α-hydroxyisobutyraldehyde dimethylacetal, b.p. 148–149°, d^{25} 0.9694, n^{25}D 1.4123.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.70; H, 10.51. Found: C, 53.42; H, 10.55.

α-Hydroxyisobutyraldehyde Dimethylacetal 3,5-Dinitrobenzoate (III).—To 8.36 g. (0.036 mole) of 3,5-dinitrobenzoyl chloride in excess anhydrous pyridine was added 4.88 g. (0.036 mole) of α-hydroxyisobutyraldehyde dimethylacetal. The reactants were heated and then poured onto cracked ice. A solid resulted which was filtered, dissolved in ether, extracted with sodium bicarbonate and saturated sodium chloride solution and then poured through anhydrous sodium sulfate. The ether was removed and 7.2 g. (61%) of α-hydroxyisobutyraldehyde dimethylacetal 3,5-dinitrobenzoate, m.p. 70–71°, was obtained. Recrystallization from a methanol–water mixture raised the melting point to 71–72°.

Anal. Calcd. for $C_{13}H_{16}N_2O_8$: C, 47.56; H, 4.91. Found: C, 47.81; H, 5.20.

α-Hydroxyisobutyraldehyde 3,5-Dinitrobenzoate (IV).—The acetal III (0.86 g., 0.0026 mole) and 14 ml. of concentrated hydrochloric acid were mixed and warmed. To this mixture was added 5 ml. of water and the reaction was heated 30 minutes on a steam-bath. The reaction mixture was then poured onto cracked ice from which 0.39 g. (53%) of α-hydroxyisobutyraldehyde 3,5-dinitrobenzoate, m.p. 140–142°, was isolated. An analytical sample melted at 143–144°.

Anal. Calcd. for $C_{11}H_{10}N_2O_7$: C, 46.81; H, 3.57. Found: C, 46.57; H, 3.58.

A 2,4-dinitrophenylhydrazone derivative of the aldehyde was prepared according to the directions of Shriner and Fuson,[12] m.p. 174–175° (dec).

Anal. Calcd. for $C_{17}H_{14}N_6O_{10}$: C, 44.16; H, 3.06. Found: C, 43.72; H, 3.42.

α-Hydroxyisobutyric Acid 3,5-Dinitrobenzoate (V).—Two grams (0.007 mole) of α-hydroxyisobutyraldehyde 3,5-dinitrobenzoate was placed in excess concentrated nitric acid and the mixture heated on a steam-bath until oxides of nitrogen were no longer evolved. After this time (3 hr.) the reaction mixture was poured onto cracked ice and solidified. The solid was dissolved in sodium bicarbonate solution, acidification of which yielded 1.27 g. (60%) of α-hydroxyisobutyric acid 3,5-dinitrobenzoate, m.p. 149–150°.

Anal. Calcd. for $C_{11}H_{10}N_2O_8$: C, 44.30; H, 3.38. Found: C, 43.94; H, 3.45.

Treatment of the acid (0.5 g.) with thionyl chloride followed by ammonia gave 0.40 g. (80%) of the α-hydroxyisobutyramide 3,5-dinitrobenzoate (VI), m.p. 177–178°.

Anal. Calcd. for $C_{11}H_{11}N_3O_7$: C, 44.44; H, 3.73. Found: C, 44.60; H, 3.97.

Acetone Cyanohydrin 3,5-Dinitrobenzoate.—Acetone cyanohydrin (5 g., 0.06 mole), 26.9 g. (0.117 mole) of 3,5-dinitrobenzoyl chloride and 10 ml. of anhydrous pyridine were mixed and heated on a steam-bath for 2 hr. From the reaction 14.88 g. (89%) of acetone cyanohydrin 3,5-dinitrobenzoate (VII), m.p. 125–126°, was isolated.

Anal. Calcd. for $C_{11}H_9N_3O_6$: C, 47.32; H, 3.25. Found: C, 46.86; H, 3.35.

Hydrolysis of 1.0 g. (0.00358 mole) of the above nitrile was accomplished in sulfuric acid solution to give 0.56 g. (53%) of α-hydroxyisobutyramide 3,5-dinitrobenzoate, m.p. 168–172°. Recrystallization from ethanol resulted in a solid, m.p. 178–179°, whose infrared absorption spectrum was superimposable with the amide obtained from the parent acid. A mixture melting point of the two amides was undepressed.

2,2,5,5-Tetramethyl-3,6-dimethoxy-*p*-dioxane (IX).—α-Hydroxyisobutyraldehyde dimethylacetal (12 g., 0.0894 mole) and a drop of sulfuric acid were heated to 100°. From the reaction 3.3 ml. of methanol, n^{25}D 1.3270, was collected. The remaining material in the flask solidified at room temperature and amounted to 8.54 g. of 2,2,5,5-tetramethyl-3,6-dimethoxy-*p*-dioxane, m.p. 58–61°. The infrared spectrum of this compound had no hydroxyl or carbonyl absorption. A small sample sublimed at room temperature and 1 mm. pressure to give an analytical sample, m.p. 61–62°.

Anal. Calcd. for $C_{10}H_{20}O_4$: C, 58.79; H, 9.87. Found: C, 59.01; H, 9.54.

1,2-Epoxy-1-methoxy-2-methylpropane (X).—Two procedures were used. Procedure A was essentially the same as reported[4] for the reaction of α-chlorobutyraldehyde and sodium methoxide. From 25 g. of α-chloroisobutyraldehyde there was obtained 8.78 g. (37%) of 1,2-epoxy-1-methoxy-1-methylpropane, b.p. 93–94°, d^{25} 0.9036, n^{25}D 1.3889.

Procedure B.—Dry sodium methoxide was prepared from

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[12] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

[13] M. S. Kharasch and H. C. Brown, THIS JOURNAL, **62**, 298 (1940).

[14] C. L. Stevens, T. K. Mukherjee and V. Traynelis, *ibid.*, **78**, 2264 (1956).

[15] C. L. Stevens and J. C. French, *ibid.*, **76**, 4398 (1954).

[16] M. A. Brochet, *Ann. chim.*, [7] **10**, 352 (1897).

[17] A. Franke, *Monatsh.*, **21**, 206 (1900).

11.5 g. (0.5 g. atom) of sodium. Diethyl carbitol was added to the dry finely powdered methoxide and the resulting slurry was cooled to 0°. To this slurry was added 39.5 g. (0.37 mole) of α-chloroisobutyraldehyde, and the reaction mixture was heated for 1.5 hr. at 50° with agitation. The product was distilled directly from the reaction mixture at 10 mm. pressure and 50° into a receiver cooled in a Dry Ice–acetone mixture. Final distillation through a 30-cm. tubular column at atmospheric pressure gave 19.97 g. (53%) of the epoxyether, b.p. 92–93°, n^{25}D 1.3885.

When 28.5 g. (0.188 mole) of α-bromoisobutyraldehyde was treated with sodium methoxide following procedure B, 8.15 g. (42.5%) of the epoxyether was obtained, b.p. 91–96°, n^{25}D 1.3884.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.79; H, 9.87; OCH_3, 30.3. Found: C, 59.05; H, 10.04; OCH_3, 30.2.

To 3.65 g. (0.0357 mole) of the epoxyether in 20 ml. of anhydrous ether and 3.42 g. (0.107 mole) of anhydrous methanol at −30° was added a drop of hydrochloric acid. The reaction was then warmed slightly on a steam-bath. After cooling the flask to room temperature, the hydrochloric acid was neutralized with excess solid sodium carbonate. The reaction mixture was filtered and distilled. The α-hydroxyisobutyraldehyde dimethylacetal obtained amounted to 2.72 g. (57%), b.p. 63–64° (25 mm.), n^{25}D 1.4122. The infrared spectrum of this material was superimposable on that of the acetal obtained from α-chloroisobutyraldehyde.

When 1.0 g. of the above acetal was permitted to react with 3,5-dinitrobenzoyl chloride in pyridine, 1.16 g. (48%) of the 3,5-dinitrobenzoate derivative was isolated, m.p. 70–71°. A mixture melting point determination with the authentic material obtained from α-chloroisobutyraldehyde was not depressed.

1-Methoxy-2-methylpropane-1,2-diol 1-(3,5-Dinitrobenzoate) (XI).—To 5.3 g. (0.052 mole) of epoxyether X in anhydrous ether was added 10.9 g. (0.052 mole) of 3,5-dinitrobenzoic acid in anhydrous ether. The reaction mixture was allowed to stand overnight. The ethereal solution was dried over anhydrous sodium sulfate and filtered. The ether was partially removed, the solution cooled to a sirup, a small amount of petroleum ether (30–60°) was added and upon scratching the product solidified to yield 13.18 g. (81%) of 1-methoxy-2-methylpropane-1,2-diol 1-(3,5-dinitrobenzoate), m.p. 84–85°.

Anal. Calcd. for $C_{12}H_{14}N_2O_8$: C, 45.86; H, 4.49; OCH_3, 9.87. Found: C, 45.46; H, 4.32; OCH_3, 9.99.

When 50 mg. of 1-methoxy-2-methylpropane-1,2-diol 1-(3,5-dinitrobenzoate) was placed in 50 ml. of ether and extracted with three 15-ml. portions of cold 5% sodium carbonate, no solid was obtained on acidification of the carbonate layer. Upon evaporation of the ether layer, addition of petroleum ether (30–60°) and cooling, there was obtained 45 mg. of the unchanged acylal, m.p. 81–83°. A mixture melting point with material melting 83–84° was not depressed.

Treatment of 7.74 g. (0.0246 mole) of the α-hydroxyacylal with excess nitric acid for 3 hr. on the steam-bath until oxides of nitrogen were no longer evolved gave two acids. The reaction mixture was poured onto cracked ice and filtered to give 5.10 g. (98%) of 3,5-dinitrobenzoic acid, m.p. 203–204°. The acidity of the remaining solution was reduced to *p*H 5, and the solution was continuously extracted with ether for 3 days. The ether was removed in part, the solution dried with anydrous sodium sulfate and product crystallized from a benzene–ether mixture to yield 1.22 g. (47.5%) of α-hydroxyisobutyric acid, m.p. 79°. A mixture melting point determination with the authentic hydroxy acid was undepressed. The infrared spectra of the two samples were superimposable.

Pyrolysis of 1-Methoxy-2-methylpropane-1,2-diol 1-(3,5-Dinitrobenzoate).—In a molecular still, 4.5 g. (0.014 mole) of the solid α-hydroxyacylal was placed under a pressure of 5 mm. and heated. The acylal melted cleanly and when the temperature reached 135°, vigorous bubbling occurred and the melt resolidified. After 0.5 hr. the solid residue dissolved in a bicarbonate solution and upon reacidification yielded 2.58 g. (85%) of 3,5-dinitrobenzoic acid, m.p. 203–204°. A mixture melting point determination with authentic acid showed no depression. The distillate from the pyrolysis amounted to 1.05 g. (73%) of semi-solid 2,2,5,5-tetramethyl-3,6-dimethoxy-*p*-dioxane, which probably contained both *cis* and *trans* isomers. Recrystallization from petroleum ether yielded an analytical sample, m.p. 61–62°. The infrared absorption of this compound and the compound obtained by pyrolysis of the α-hydroxyisobutyraldehyde dimethylacetal were identical.

Anal. Calcd. for $C_{10}H_{20}O_4$: C, 58.79; H, 9.87. Found: C, 58.60; H, 9.68.

Rearrangement of 1-Methoxy-2-methylpropane-1,2-diol 1-(3,5-Dinitrobenzoate).—To 5 g. (0.016 mole) of 1-methoxy-2-methylpropane-1,2-diol 1-(3,5-dinitrobenzoate) dissolved in ether was added a catalytic amount of triethylamine. After the solution remained at room temperature overnight, white crystals had formed. The solid was filtered and amounted to 4.08 g. (90%) of α-hydroxyisobutyraldehyde 3,5-dinitrobenzoate, m.p. 143–144°. A mixture melting point determination with authentic material from hydrolysis of α-hydroxyisobutyraldehyde dimethylacetal 3,5-dinitrobenzoate was not depressed.

Into a 10-ml. erlenmeyer flask was placed 0.5 g. (0.0016 mole) of the solid acylal in anhydrous benzene, and the solution was heated for 4 hr. Upon evaporating off the benzene an oil formed which was cooled, scratched and solidified. Ligroin and acetone were added and the solution was cooled to yield a white solid, 0.13 g. (29%), of the α-hydroxyisobutyraldehyde 3,5-dinitrobenzoate, m.p. 141–143°. A mixture melting point with the material above was not depressed, m.p. 142–143°.

1-Methoxy-2-methylpropane-1,2-diol 1-Acetate (XI).—Ten grams (0.0978 mole) of epoxyether was dissolved in 70 ml. of anhydrous ether, cooled to 0°, and 5.87 g. (0.0978 mole) of pure acetic acid in 20 ml. of anhydrous ether was added. The reaction mixture was stoppered, placed in a desiccator, and permitted to stand in the refrigerator overnight. The mixture was then extracted with three 20-ml. portions of cold saturated sodium bicarbonate and dried over anhydrous sodium sulfate. After filtration and removal of the ether under vacuum, the liquid acylal was distilled. The yield was 9.27 g. (58.4%) of 1-methoxy-2-methylpropane-1,2-diol 1-acetate, b.p. 84–85° (13 mm.), d^{25} 1.0454, n^{25}D 1.4187.

Anal. Calcd. for $C_7H_{14}O_4$: C, 51.83; H, 8.70; OCH_3, 19.13. Found: C, 51.59; H, 8.97; OCH_3, 19.16.

Rearrangement of 1-Methoxy-2-methylpropane-1,2-diol 1-Acetate.—The liquid α-hydroxyacylal (5 g., 0.0308 mole) and 0.5 ml. of triethylamine were heated to 90° for 3 hr. The temperature was then raised to 105° and methanol and the triethylamine were collected until approximately the theoretical amount of methanol had been removed. The residue was then distilled at reduced pressure to yield 3.17 g. (79%) of α-acetoxyisobutyraldehyde, b.p. 79–81° (50 mm.), d^{25} 1.0155, n^{25}D 1.4093.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 54.86; H, 8.09.

A 2,4-dinitrophenylhydrazone derivative melted at 113–114°. *Anal.* Calcd. for $C_{12}H_{14}N_4O_6$: C, 46.44; H, 4.54. Found: C, 46.20; H, 4.82.

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