335 g. (93–95%).[4] An analytical sample was prepared by recrystallization from water and drying at 110°.

Anal. Calcd. for $C_6H_2O_3SCl_3Na$: C, 25.5; S, 11.3; H, 0.70; Cl, 37.7; Na, 8.13. Found: C, 25.1; H, 0.67; S, 11.1; Cl, 38.0; Na, 8.20.

2,5-Dichloro-4-phenolsulfonic Acid.—A mixture of 141.5 g. (0.5 mole) of the crude sodium salt of 2,4,5-trichlorobenzenesulfonic acid, 43.0 g. (1.07 moles) of sodium hydroxide and 225 ml. of water was heated for two hours at 230° in a stainless-steel autoclave at 150–160 lb. pressure. A sample withdrawn and analyzed for ionic chlorine showed that one atom of chlorine was split off under these conditions. The mixture was removed from the autoclave and treated with 30 ml. of glacial acetic acid. Upon cooling, the precipitate was filtered, washed with ice-cold water and dried; yield 114–115 g. (86–87%). The product is the sodium salt of 2,5-dichloro-4-phenolsulfonic acid. An analytical sample was prepared by recrystallization from water and drying at 110°.

Anal. Calcd. for $C_6H_3O_4Cl_2SNa$: C, 27.2; H, 1.13; S, 12.1; Cl, 26.8; Na, 8.7. Found: C, 27.0; H, 1.02; S, 12.3; Cl, 27.1; Na, 8.6.

2,5-Dichlorophenol.—A mixture of 132 g. (0.5 mole) of the sodium salt of 2,5-dichloro-4-phenolsulfonic acid above and 660 ml. of 70% sulfuric acid was boiled gently for two hours. 2,5-Dichlorophenol was then steam distilled out of the reaction mixture. The product solidified in the receiver in the form of white hard crystalline aggregates, which were filtered and dried at room temperature; yield 58–60 g. (71–73.5%), m.p. 53–55° (lit.[5] 58–59°). The crude product was used without purification in the next step. A sample recrystallized from petroleum ether melted at 58–59°.

2,4,5-Trichlorophenol.—Chlorine was introduced into a solution of 163 g. (1.0 mole) of 2,5-dichlorophenol in 650 ml. of glacial acetic acid at 10–15° until the increase in weight of the reaction mixture was 70–72 g. (corresponding to the combined weights of one atom of chlorine and one mole of hydrogen chloride). The mixture was poured onto 2 kg. of cracked ice and the precipitate washed by decantation with cold water, dilute solution of sodium bisulfite and again with water. The product was then filtered and air-dried; yield 195–200 g. (theory, 197.5 g.), m.p. 56–59°. The crude was used without further purification in the condensation with chloroacetic acid. A sample recrystallized from petroleum ether melted at 65–67° (lit.[6] 68°) and did not depress the melting point of an authentic sample.

2,3,4,6-Tetrachlorophenol was obtained in a nearly quantitative yield by the same procedure as trichlorophenol, using the double amount of chlorine. A recrystallized sample melted at 67–69° (lit.[7] 70°) and did not depress the melting point of an authentic sample.

2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) was obtained by the usual procedure by the condensation of 2,4,5-trichlorophenol with chloroacetic acid in the presence of sodium hydroxide.[7] The product is best isolated in the form of its sparingly soluble sodium salt which is readily purified and obtained colorless by recrystallization from water. The free acid, obtained from the sodium salt purified in this manner, melted at 153° (lit.[9] 153°) and did not depress the melting point of an authentic sample.

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[4] The barium and lead salts of 2,4,5-trichlorobenzenesulfonic acid were prepared by F. Beilstein and A. Kurbatow (*Ann.*, **192**, 231 (1878)). However, the amounts of reagents, the experimental conditions and the yields are not given. The barium salt is isolated by neutralizing the reaction mixture with barium hydroxide, removing barium sulfate by filtration and evaporating of the filtrate to dryness.

[5] G. J. Tiessens, *Rec. trav. chim.*, **50**, 112 (1931).

[6] L. G. Groves, E. E. Turner and G. I. Sharp, *J. Chem. Soc.*, 517 (1929).

[7] R. Pokorny, THIS JOURNAL, **63**, 1768 (1941).

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The Stereochemical Relationship between 2-Butanol and Lactic Acid

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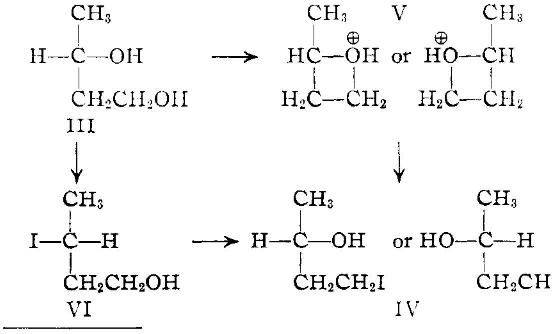
A series of conversions have been effected for redetermining the stereochemical relationship between 2-butanol and lactic acid. As a result, the previously determined relationship has been confirmed.

The relative configuration of 2-butanol (I) with respect to lactic acid (II) is particularly important in the scheme of stereochemical relationships since a large number of compounds have been related to lactic acid (and, thereby, glyceraldehyde) through I and its derivatives. Much of the available evidence[1] concerning the relative configurations of I and II is not entirely satisfactory for several reasons, the most cogent of which is the uncertainty associated with one reaction of the series employed.[1a]

This reaction, the conversion of 1,3-butanediol (III) to 4-iodo-2-butanol (IV) by treatment with hydrogen iodide, is unusual in that the primary, rather than the secondary hydroxyl is replaced. The reaction may proceed through a four-membered oxide intermediate (V)[2] leading to inversion or retention of configuration depending on which hydroxyl forms the oxide, or may involve the initial formation of 3-iodo-1-butanol (VI) followed by an exchange reaction of unknown stereochemistry such as that of *t*-butyl iodide and methanol giving *t*-butyl alcohol and methyl iodide.[3,4] In any case, the stereochemistry of the reaction is uncertain and it would be desirable to redetermine the relative configurations of I and II.



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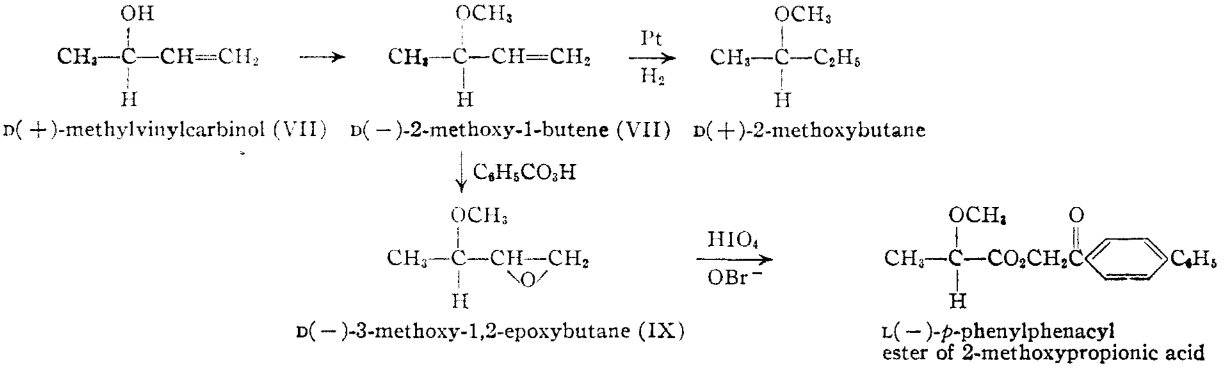
[1] (a) P. A. Levene, A. Walti and H. L. Haller, *J. Biol. Chem.*, **71**, 465 (1927). (b) This relationship has also, in effect, been confirmed by the recently reported conversion of D-mannitol to D(−)-2,3-butanediol (L. J. Rubin, H. A. Lardy and H. O. L. Fischer, THIS JOURNAL, **74**, 425 (1952)). The configurational relationship between D-mannitol and L(+)-lactic acid has been well established, and recently P. J. Leroux and H. J. Lucas, *ibid.*, **73**, 41 (1951), converted D(−)-2,3-butanediol to L(−)-2-butanol with effective inversion of configuration.

[2] W. E. Doering and R. W. Young, *ibid.*, **74**, 2997 (1952).

[3] K. Bauer, *Ann.*, **220**, 163 (1883).

[4] The reaction of the butanediol is currently being investigated in an effort to determine the course of the reaction.

This has now been effected by the following series of reactions. D(+)-Methylvinylcarbinol (VII)[5] was converted to the D(−)-methyl ether (VIII) by treatment with sodium hydride and methyl iodide in ethylene glycol diethyl ether solution. D(−)-VIII was converted to the oxide (IX) by treatment with perbenzoic acid, and then IX was treated with dilute sulfuric acid, periodic acid and strontium hypobromite to give 2-methoxypropionic acid, isolated as the L(−)-*p*-phenylphenacyl ester (X).[6] The infrared spectrum of an acetonitrile solution of (X) prepared by this method was found to be identical with that of authentic X.[6] L(+)-VIII was hydrogenated with platinum in acetic acid to give the L(−)-methyl ether of 2-butanol (XI)[7] identified *via* its infrared spectrum. The results thus obtained are in agreement with those previously obtained.[1]


D(+)-methylvinylcarbinol (VII) D(−)-2-methoxy-1-butene (VII) D(+)-2-methoxybutane

D(−)-3-methoxy-1,2-epoxybutane (IX)

L(−)-*p*-phenylphenacyl ester of 2-methoxypropionic acid

Experimental[8]

3-Methoxy-1-butene (VIII).—3-Hydroxy-1-butene[5] (14.4 g., 0.2 mole, $[\alpha]^{25}\mathrm{D}$ +18.05°, d^{25} 0.830) was added to 6 g. (20% excess) of sodium hydride in 100 ml. of redistilled anhydrous ethylene glycol diethyl ether. After the initial exothermic reaction had subsided, 33 g. (20% excess) of methyl iodide was added with stirring. The solution was cooled, treated with water, and the organic layer was separated and dried over anhydrous sodium sulfate. Distillation through a 14″ "Helipak" packed column gave 8 g. of 3-methoxy-1-butene (VIII) (50%), b.p. 53–55°, $n^{25}\mathrm{D}$ 1.3794, d^{25} 0.753, $[\alpha]^{25}\mathrm{D}$ −22.55°; $M\mathrm{D}$, calcd. 26.44, found 26.56.

Anal. Calcd. for $C_5H_{10}O_2$: C, 69.72; H, 11.70. Found: C, 69.62; H, 11.74.

3-Methoxy-1,2-epoxybutane (IX).—To a solution of 0.15 mole of perbenzoic acid in 280 ml. of chloroform was added 6 g. (0.07 mole) of VIII ($[\alpha]^{25}\mathrm{D}$ −22.55°). After three days, the solution was washed with 10% sodium hydroxide solution and dried over sodium sulfate. Most of the chloroform was distilled through an 18-cm. Vigreux column and the residue distilled through a 75-cm. concentric tube column giving 3.9 g. (56%) of 3-methoxy-1-epoxybutane (IX), b.p. 117–118°, $n^{25}\mathrm{D}$ 1.4030, d^{25} 0.936, $[\alpha]^{25}\mathrm{D}$ −4.87°; $M\mathrm{D}$, calcd. 27.08, found 26.77.

Anal. Calcd. for $C_5H_{10}O_3$: C, 58.80; H, 9.87. Found: C, 58.35; H, 9.94.

***p*-Phenylphenacyl Ester of 2-Methoxypropionic Acid (X).**—To a solution of 0.66 g. (6.5 mm.) of IX ($[\alpha]^{25}\mathrm{D}$ −4.87°), in 20 ml. of water was added 2 ml. of 1 *N* sulfuric acid. After 12 hours, 0.4 g. of barium carbonate was added and the solution was filtered. To the filtrate was added 8 ml. of 1 *N* periodic acid solution. After two hours at room temperature, titration for periodic acid indicated 87% of the theoretical uptake. The solution was made just basic to phenolphthalein with barium hydroxide solution. After filtration, 8 g. of strontium carbonate and 3 g. of bromine were added. The 2-methoxypropionic acid was isolated as the *p*-phenylphenacyl ester (X) by the procedure of Wolfrom, *et al.*,[6] and had $[\alpha]^{25}\mathrm{D}$ −5.0° (*c* 2.2, benzene).

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.76; H, 6.23.

The identity of the *p*-phenylphenacyl ester was confirmed by comparison of the infrared absorption spectrum of this material (in acetonitrile solution) with authentic (±) ester prepared by the procedure of Wolfrom, *et al.*[6] The (±) ester had m.p. 109–110°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.68; H, 6.28.

Hydrogenation of 3-Methoxy-1-butene (VIII).—Quantitative hydrogenation of 4.0 g. of VIII ($[\alpha]^{25}\mathrm{D}$ +18.22°) with platinum in acetic acid was followed by neutralization and heptane extraction. Distillation through a 14″ "Helipak" packed column gave 3.2 g. (80%) of 2-methoxybutane (XI), b.p. 60–62°, $n^{25}\mathrm{D}$ 1.3702, d^{25} 0.740,[9] $[\alpha]^{25}\mathrm{D}$ − 7.54°; $M\mathrm{D}$ calcd. 26.93; found 26.91. The infrared spectrum of XI was identical with that of an authentic sample.

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[5] Resolved by the procedure of J. Kenyon and D. R. Snellgrove, *J. Chem. Soc.*, **127**, 1174 (1925).

[6] The method of M. L. Wolfrom, R. U. Lemieux, S. M. Olin and D. I. Weisblat, THIS JOURNAL, **71**, 4057 (1949) was employed. These workers obtained the (−) *p*-phenylphenacyl ester from (+) lactic acid.

[7] D(+)-2-Butanol has been shown to give the D(+)-methyl ether. D. S. Tarbell and M. C. Paulson, *ibid.*, **64**, 2842 (1942); R. Rometsch and W. Kuhn, *Helv. Chim. Acta*, **29**, 1483 (1946).

[8] Melting points and boiling points are corrected. Analyses were performed by F. Schwarzkopf, T. Hutton and R. Wade. Rotations were determined on the pure liquid in a 1-dm. tube unless otherwise noted.

[9] Reference 2 reported b.p. 61–63°, $n^{25}\mathrm{D}$ 1.3702, d^{25} 0.737.