chloric acid and refluxed for 15 minutes. At the end of this period the light brown mixture was poured into 500 ml. of water whereupon 10 g. of brown solid separated. The melting point was 60–61.5°. Recrystallization from 50 ml. of 95% ethanol gave 7.5 g. (77%) of pale yellow crystals, m.p. 62.5–63.5°. A mixed melting point with an authentic sample prepared according to the procedure of Horning and Field[4] showed no depression.

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Synthesis and Identification of Dipropylene Glycol Isomers

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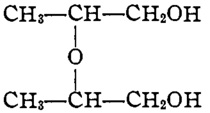
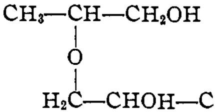
When one mole of propylene oxide is treated with propylene glycol, three isomers of dipropylene glycol may theoretically result.



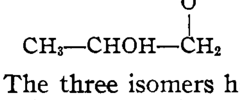
$$\begin{array}{l}\text{CH}_3\text{—CH—CH}_2\text{OH}\\ \quad\;\;|\\ \quad\;\;\text{O}\\ \quad\;\;|\\ \text{CH}_3\text{—CH—CH}_2\text{OH}\end{array}$$

I, 2,2′-oxydi-1-propanol (diprimary alcohol)



$$\begin{array}{l}\text{CH}_3\text{—CH—CH}_2\text{OH}\\ \quad\;\;|\\ \quad\;\;\text{O}\\ \quad\;\;|\\ \text{H}_2\text{C—CHOH—CH}_3\end{array}$$

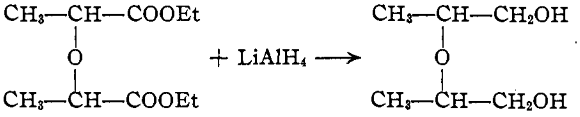
II, 2-(2-hydroxypropoxy)-1-propanol (primary-secondary alcohol)



$$\begin{array}{r}\text{CH}_3\text{—CHOH—CH}_2\\ |\\ \text{O}\\ |\\ \text{CH}_3\text{—CHOH—CH}_2\end{array}$$

III, 1,1′-oxydi-2-propanol (disecondary alcohol)

The three isomers have been prepared and their physical properties determined. The diprimary alcohol I was prepared in 91% yield by the reduction of diethyl dilactate with lithium aluminum hydride.



$$\begin{array}{l}\text{CH}_3\text{—CH—COOEt}\\ \quad\;\;|\\ \quad\;\;\text{O}\\ \quad\;\;|\\ \text{CH}_3\text{—CH—COOEt}\end{array} + \text{LiAlH}_4 \longrightarrow \begin{array}{l}\text{CH}_3\text{—CH—CH}_2\text{OH}\\ \quad\;\;|\\ \quad\;\;\text{O}\\ \quad\;\;|\\ \text{CH}_3\text{—CH—CH}_2\text{OH}\end{array}$$

The synthesis of the primary-secondary isomer (II) was based on the work of earlier investigators[1-4] which showed that addition of propylene oxide to an alcohol with alkaline catalyst yields largely a secondary alcohol. On this basis 1-methoxy-2-propanol[1] was treated with propylene oxide using sodium catalyst to give 1-(2-methoxyisopropoxy)-2-propanol, b.p. 76–78° (10 mm.). This was heated with 48% hydrobromic acid to give methyl bromide and 2-(2-hydroxypropoxy)-1-propanol in 52% yield.

The disecondary isomer (III) was prepared by treating propylene oxide with propylene glycol using sodium as the catalyst. This gave largely the disecondary isomer since propylene oxide reacts much faster with a primary alcohol than with a secondary alcohol. The product was distilled and on recrystallization from diethyl ether melted at 45–46.5°.

A study of infrared absorption curves (Fig. 1) in the region of 8 to 10 μ showed the three isomers to be distinctively different. The compounds were studied in 1% solution of carbon disulfide in 1-mm. cells.

The absorption curve for the ether linkage is designated by E, the primary OH curve by P and the secondary OH curve by S.

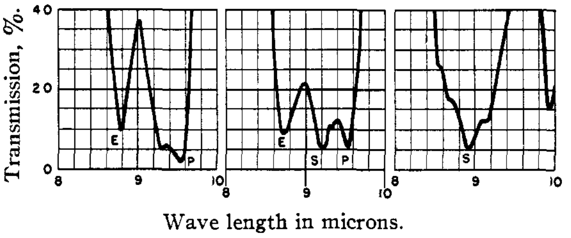


Fig. 1.—Left curve, 2,2′-oxydi-1-propanol; middle curve, 2-(2-hydroxypropoxy)-1-propanol; right curve, 1,1′-oxydi-2-propanol.

Experimental

I. Preparation of 2,2′-Oxydi-1-propanol.—The apparatus consisted of a 5-l., 5-neck flask equipped with a stirrer, thermometer, dropping funnel, nitrogen inlet and reflux condenser. The condenser was vented through a Dry Ice trap and calcium chloride drying tube.

After sweeping the flask with nitrogen, 45 g. (1.15 moles) of finely powdered lithium aluminum hydride was added. The flask was cooled in an ice–water-bath. With stirrer going and nitrogen bubbling through, 1500 g. of dry diethyl ether was added slowly. The ice-bath was removed and the mixture refluxed on a water-bath 3 hours to dissolve the lithium aluminum hydride. To this mixture 218 g. (1.08 mole) of dilactic acid diethyl ester[5] in 286 g. of dry diethyl ether was added dropwise over a period of two hours at 15–18°. The temperature was controlled by adding ice to the water-bath. The mixture was then slowly warmed to reflux and held at this temperature for 4 hours.

Fifty grams of ethyl acetate was added dropwise to destroy any unreacted lithium aluminum hydride, followed by slow addition of 250 cc. of water and finally 4–6 moles of 35% hydrochloric acid. The nitrogen was then shut off and the ether distilled off on a steam-bath. The still residue (966 g.) was passed through Dowex-50 cation exchange resin to remove the lithium and aluminum. The filtrate was distilled under vacuum to remove water and hydrochloric acid, and gave 122 g. (0.91 mole) of 2,2′-oxydi-1-propanol boiling at 102° at 5 mm. and at 225.7° at 760 mm. It did not solidify at −40° and had specific gravity 1.0316 (25/25), 1.0018 (60/4); $n^{25}\text{D}$ 1.4410, $n^{60}\text{D}$ 1.4296.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.71; H, 10.52. Found: C, 53.63; H, 10.53.

Its bis-*p*-nitrobenzoate, prepared in 86.5% yield, melted at 142–143°.

Anal. Calcd. for $C_{20}H_{20}N_2O_9$: N, 6.48. Found: N, 6.54.

Its bis-triphenylmethyl ether, prepared in 70% yield,[6] melted at 131–132°.

Anal. Calcd. for $C_{44}H_{42}O_3$: C, 85.40; H, 6.84. Found: C, 85.2; H, 7.0.

II. Synthesis of 2-(2-Hydroxypropoxy)-1-propanol.—The apparatus was the same as described under I. Nine hundred grams (10 moles) of 1-methoxy-2-propanol[1] and 4 g. of metallic sodium were added to the flask. The mixture was heated to 80° and 406 g. (7 moles) of propylene oxide was added dropwise at 80–100° over a period of 4 hours. The mixture was distilled on a 1¼″ × 4′ column packed with 3/16″ KA2S stainless steel saddles at a 10/1 reflux ratio to give 430 g. (2.9 moles) of 1-(2-methoxyisopropoxy)-2-propanol, b.p. 76–78° (10 mm.). Two moles of this was mixed with 3 moles of 48% hydrogen bromide and refluxed at 80–108° until no more methyl bromide was liberated. The methyl bromide (88.5% of theory) was collected in a Dry Ice trap. The residue was passed through a bed of Amber-

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(1) H. C. Chitwood and B. T. Freure, THIS JOURNAL, **68**, 680 (1946).

(2) R. G. Kadesch, *ibid.*, **68**, 41 (1946).

(3) P. D. Bartlett, *ibid.*, **70**, 926 (1948).

(4) A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R*), **14**, 1038 (1944).

(5) Pierre Vieles, *Ann. chim.*, [11] **3**, 143 (1935).

(6) Prepared according to M. K. Seikel and E. H. Huntress, THIS JOURNAL, **63**, 593 (1941).

lite IR4B anion exchange resin to remove the excess hydrogen bromide. The filtrate was distilled under vacuum to remove the water, and 139 g. (1.04 mole) of 2-(2-hydroxypropoxy)-1-propanol, b.p. 96–96.5° (4 mm.), 224° (760 mm.), were obtained. This is a 52% yield based on alcohol taken. The substance did not solidify at −40°. It possessed the following properties: sp. gr. 1.0229 (25/25), 0.9925 (60/4); $n^{25}\text{D}$ 1.4391, $n^{60}\text{D}$ 1.4283.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.71; H, 10.52. Found: C, 53.68; H, 10.45.

Its bis-*p*-nitrobenzoate, prepared in 85% yield, melted at 83–84°.

Anal. Calcd. for $C_{20}H_{20}N_2O_9$: N, 6.48. Found: N, 6.40.

III. **Preparation of 1,1′-Oxydi-2-propanol.**—The apparatus was the same as used in I above. Twenty moles (1520 g.) of propylene glycol and 16 g. of sodium metal were added to the flask under a nitrogen blanket and the mixture was heated to 105°. Twenty moles (1160 g.) of propylene oxide was added dropwise at 105–144° over a period of 3.5 hours. The mixture was distilled as in II above and 1092 g. (8.15 moles) of 1,1′-oxydi-2-propanol; b.p. 113–114° (10 mm.), 222.2° (760 mm.), yield 47.5%, was obtained. On recrystallizing from ether this material melted at 45–46.5°. It had the following properties: sp. gr. 0.9878 (60/4), $n^{60}\text{D}$ 1.4284.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.71; H, 10.52. Found: C, 53.70; H, 10.50.

Its bis-*p*-nitrobenzoate, prepared in 96% yield, melted at 150–151°.

Anal. Calcd. for $C_{20}H_{20}N_2O_9$: N, 6.48. Found: N, 6.42.

Its bis-triphenylmethyl ether, prepared[6] in 75% yield, had m.p. 145–146°.

Anal. Calcd. for $C_{44}H_{42}O_3$: C, 85.40; H, 6.84. Found: C, 85.07; H, 6.84.

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The Iodine Complexes of Polyalkylbenzenes[1]

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In recent papers, Mulliken has proposed structures for the benzene complexes with silver ion[2] and with iodine.[2,3] His structure for the Ar·Ag$^+$ complex with the silver ion in the region between and somewhat above two carbon atoms in the aromatic ring, makes plausible the observation that continued methyl substitution in the ring eventually leads to a decrease in stability of the complex. (The association constant of silver ion with mesitylene is smaller than that with the xylenes or with toluene,[4] a result which is opposite to the normal inductive effect.) This decrease in stability may occur when there are no longer available two adjacent unsubstituted carbon atoms to serve as a site for the silver ion.[2] The fact that the complex with durene is more stable than that with mesitylene[5] is still in accord with this hypothesis.

Mulliken considered several structural possibilities for the Ar·I_2 complex. These are as follows (where the roman numerals and the capital letters in parentheses designate the models in references 2 and 3, respectively): the iodine molecule located along an edge or corner of the benzene ring with the iodine axis either in the plane of the ring (II or T and L), or perpendicular to the plane of the ring (III or E), or inclined to the plane of the ring (O); the iodine axis coinciding with the sixfold symmetry axis of benzene with the two iodine atoms on the same side of the benzene plane (IV or A), or on opposite sides of the benzene plane (V); the iodine molecule located with its center on the sixfold axis of symmetry of the aromatic ring, with the iodine axis being parallel and slightly above the plane of the aromatic ring (I or R). Of these possibilities, the one favored most strongly by Mulliken on the basis of spectroscopic and electrostatic principles is model R (or I). With this model it would be difficult to imagine that the methyl groups in polymethylbenzenes could interact sterically with the iodine molecule, as they apparently do with the silver ion, and one would expect hexamethylbenzene to be a stronger base toward iodine than any of the other methylbenzenes.[6] The results published recently by Andrews and Keefer[5] on the interaction of of polyalkylbenzenes with iodine and with iodine monochloride show that this is actually the case. Working independently in this Laboratory we also found this to be true, and our results on the interaction of several polyalkylbenzenes with iodine offer interesting comparison with the data of Andrews and Keefer.

The equilibrium constant of the complex, K, and the molar extinction coefficient of the complex, ϵ_c, were determined from the equation first derived by Benesi and Hildebrand.[7]

$$\frac{(I_2)l}{d_c} = \frac{1}{K\epsilon_c} \times \frac{1}{N_a} + \frac{1}{\epsilon_c}$$

The notation for this equation is similar to that which has been employed by Andrews and Keefer.[8] Plots of $(I_2)/d_c$ *versus* $1/N_a$ (based on at least four points for each aromatic compound) gave straight lines. Since ϵ_c and K are sensitively dependent upon the line drawn through the experimental points, the equation for the line was determined by the method of least squares and the values of ϵ_c and

TABLE I

WAVE LENGTHS OF MAXIMUM ABSORPTION, MOLAR EXTINCTION COEFFICIENTS AND EQUILIBRIUM CONSTANTS OF IODINE–AROMATIC COMPLEXES IN CARBON TETRACHLORIDE AT ROOM TEMPERATURE

Aromatic cpd.	λ_{max}, mμ	$\epsilon_c \times 10^{-3}$	K
Benzene	295	14.7	1.60[a]
Mesitylene	332	10.2	5.96[a]
Isodurene	339	8.70	6.87
Pentamethylbenzene	355	7.77	9.72
Hexamethylbenzene	371	6.69	15.2
Hexaethylbenzene	375	4.57	4.58

[a] H. A. Benesi and J. H. Hildebrand (ref. 7) report for benzene λ_{max} 297 mμ, ϵ_c 15.4 × 10^3, K 1.72; and for mesitylene λ_{max} 333 mμ, ϵ_c 9.3 × 10^3, K 7.2.

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(1) From the B.S. honor's thesis of Donald Robert Virzi submitted to the chemistry department, University of Illinois, June, 1952.

(2) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

(3) R. S. Mulliken, *ibid.*, **72**, 600 (1950).

(4) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 5034 (1950).

(5) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952)

(6) In a private discussion, Professor Mulliken agreed with this prediction.

(7) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

(8) L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 4077, 5170 (1950); *ibid.* **73**, 462 (1951).