TABLE I (*Concluded*)

Substance	Boiling point, °C.	Mm.	Refractive index, n_D	Density g./ml.	°C.	Vapor pressure Constants of equation A	A'	B	Deviation,[v] % Max.	Min.
bis-(2-Fluoroethyl) sulfate[h]	80–81	2	1.4177[p]	1.3678	25	9.8117	13.2961	3335.6	0.38	0.22
Ethyl fluorosulfonate[b]	112	755				8.0880	11.4004	2010.7	0.32	0.27
ω-Fluoroacetophenone[h]	79–80	3	1.5309[p]	1.1747	25	9.7533	13.0988	3236.4	0.67	0.45
Methyl γ-fluorothiolbutyrate[h]	54	6	1.4587[p]	1.1135	20	9.233	12.572	2735	2.1	1.6

[a] Submitted by Dr. J. C. Bailar. [b] Submitted by Dr. L. F. Audrieth. [c] These values are from Lange and Krueger (*Ber.*, **65**, 1598 (1932)). [d] Lange and Krueger give d^{25}_4 1.136. [e] Submitted by Dr. R. C. Fuson. [f] The accuracy of this determination may not be better than ±20% due to instability of the compound and its very low volatility. [g] Supplied by Dr. Anton B. Burg. The accuracy for this determination is low, probably −10% due to the fact that the compound would occasionally give a smoke which would fail to condense in the weighing trap. [h] Submitted by Dr. M. S. Kharasch. [i] Price and Jackson (THIS JOURNAL, **69**, 1065 (1947)) give the boiling point as 102°, while Ray and Ray (*J. Indian Chem. Soc.*, **13**, 427 (1936)) give 104°. [j] Swarts (*Bull. soc. chim.*, [3] **15**, 1134 (1896)) gives the density as 1.16126 (15°). [k] It seems doubtful that this material was pure for it was made by alcohol exchange from methyl fluoroacetate. Equipment was not available for doing a precision fractionation on the small sample submitted. Desreux (*Bull. soc. chim. Belg.*, **44**, 258 (1935)) gives the density as 1.0912 (20°). [l] This sample was too small to purify further before use. [m] This material could not be purified beyond this point due to a constant slow decomposition. [n] Submitted by Dr. C. D. Hurd. [o] 23.8°. [p] 20°. [q] 24.2°. [r] 27°. [s] 22°. [t] 25°. [u] 32°. [v] Per cent. deviation of observed points from points calculated from least squares equation.

large mean deviation of 5.3%, which would indicate that the two-constant equation used does not describe the curve satisfactorily. About one-fourth of the compounds show mean deviations of 1 to 5% between the calculated points and the smoothed curves. This may be attributed to difficulty in measurement, for these compounds appeared to undergo slight decomposition in glass apparatus at the higher temperatures, but not at the lower ones, thus giving a distinct curvature to the smoothed curve. 2-Fluoroethyl nitrite underwent a continuous slow decomposition and hence the precision of the measurements is estimated at 10–12%.

Summary

1. The volatility of forty-one fluorine-containing organic compounds has been measured by the transpiration method.

2. The corresponding vapor pressures have been computed from the volatilities and constants for logarithmic equations for both the volatility and vapor pressure have been calculated.

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[CONTRIBUTION FROM ORGANIC RESEARCH LABORATORY, THE DOW CHEMICAL COMPANY]

Synthesis and Identification of Propylene Glycol Phenyl Ethers

BY A. R. SEXTON AND E. C. BRITTON

The observation of Chitwood(1) and others(2,3,4) that reaction of aliphatic alcohols with propylene oxide in the presence of an alkaline catalyst yields a secondary alcohol almost exclusively, and in the presence of an acid catalyst a mixture of the primary and secondary alcohols, has been confirmed by us. In this Laboratory the structures of the primary and secondary alcohols were determined by dehydrogenation to an aldehyde and ketone, respectively, and further confirmed by infrared absorption spectra which show an absorption band for primary alcohols at 9.3–9.6 μ and an absorption for secondary alcohols at 8.9–9.1 μ (Figs. 1 and 3).

In extending the work to cover reaction of phenols with propylene oxide, the infrared absorption spectra indicated that the reaction product using alkaline catalyst was a primary alcohol, which, compared with the similar reaction using aliphatic alcohols, was extremely unusual. To clarify this anomaly, the two possible isomers from the reaction of phenol and propylene oxide have been prepared by other methods and their properties determined.

1-Phenoxy-2-propanol was prepared by (A) the reaction of potassium phenoxide with chloroacetone according to Hurd(5) and (B) by the reaction of phenol with propylene oxide using sodium hydroxide as a catalyst. The ether prepared by method (B) was oxidized catalytically in 80% yields to phenoxyacetone with no aldehyde being detected. The products by both methods had absorption curves corresponding to primary alcohols (Fig. 4), and both had identical properties, namely: b. p. 116–117° (10 mm.) 233° (760 mm.); d^{25}_{25} 1.0610; $n^{25}\text{D}$ 1.5200; α-naphthylcarbamate m. p. 83–84°; N-phenylcarbamate m. p. 85–87°.

2-Phenoxy-1-propanol was prepared (C) from α-phenoxypropionaldehyde according to Stoer-

(1) Chitwood and Freure, THIS JOURNAL, **68**, 680 (1946).

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

(3) Kadesch, THIS JOURNAL, **68**, 41 (1946).

(4) Bartlett, *ibid.*, **70**, 926 (1948).

(5) Hurd and Perletz, *ibid.*, **68**, 38 (1946).

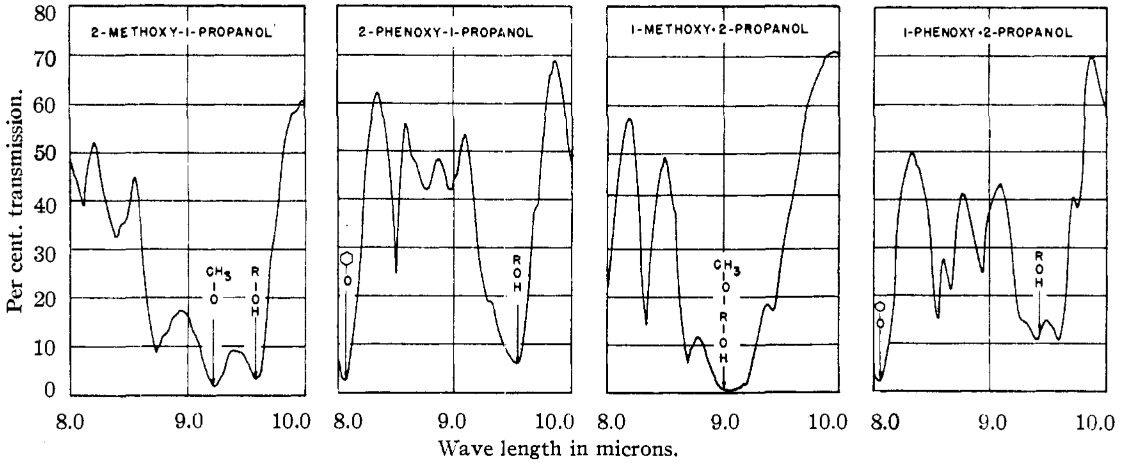

Fig. 1. Fig. 2. Fig. 3. Fig. 4.

Infrared examination of propylene glycol ethers: primary OH = 9.3–9.6 μ; secondary OH = 8.9–9.1 μ; tertiary OH = 8.3–8.6 μ; CH_3O = 9.2 μ; C_6H_5O = 8.0–8.2 μ.

mer[6] and (D) by treating phenol with propylene oxide using benzenesulfonic acid as a catalyst and separating the two isomers by careful fractionation.

The ether prepared by both methods gave absorption curves corresponding to a primary alcohol (Fig. 2) and identical properties, namely: b. p. 120° (10 mm.) 244° (760 mm.); d^{25}_{25} 0.9830; n^{25}_{D} 1.4760; α-naphthylcarbamate m. p. 113–115°; N-phenylcarbamate m. p. 50–52°.

Infrared curves of several other ethers prepared by treating substituted phenols with propylene oxide in the presence of sodium hydroxide gave curves corresponding to Fig. 4.

Since the secondary alcohol group in 1-phenoxy-2-propanol was not revealed by its infrared absorption spectra, it is evident that this method should be used with greater caution when dealing with 1-aryloxy-2-alkanols and 2-aryloxy-1-alkanols.

Experimental

Preparation of 1-Phenoxy-2-propanol. Method A.—This was prepared by the method of Hurd[5] from chloroacetone and phenol.

Method B.—One mole (94 g.) of phenol, 1.1 moles (63.8 g.) of propylene oxide, and 0.8 g. of 50% sodium hydroxide were placed in a rocking bomb and heated four hours at 150°. The product on distillation gave 137 g. boiling at 116–117° (10 mm.), corresponding to a 90% yield based on the phenol; d^{25} 1.0610, n^{25}_{D} 1.5200, α-naphthylcarbamate m. p. 83–84°, N-phenylcarbamate m. p. 85–87°.

Preparation of 2-Phenoxy-1-propanol. Method C.—α-Phenoxypropionaldehyde was prepared according to Stoermer.[6] The aldehyde was reduced with hydrogen over platinum oxide giving 100% yield of 2-phenoxy-1-propanol, b. p. 120° (10 mm.), d^{25} 0.9830, n^{25}_{D} 1.4760, α-naphthylcarbamate m. p. 113–115°, N-phenylcarbamate m. p. 50–52°.

Method D.—Sixty-five moles of phenol and 300 g. of benzenesulfonic acid were placed in a 1-liter 4-neck flask equipped with a stirrer, reflux condenser, thermometer and separatory funnel for introducing the oxide below the surface of the liquid. The mixture was heated with stirring to 100° and 70 moles of oxide added dropwise at such a rate as to maintain slow reflux. After the oxide was all added, heating and stirring were continued until refluxing ceased. The acid was neutralized with sodium hydroxide and the mixture flash distilled to remove tar. The distillate was washed with 10% sodium hydroxide to remove the unreacted phenol and propylene glycol. Due to the formation of tar and propylene glycol only a 6.5% yield of mixed isomers was obtained. The glycol ether was refractionated and consisted of 51% primary alcohol isomer and 49% secondary alcohol isomer.

Properties of the primary alcohol herein produced were the same as in method C.

Acknowledgment.—We are indebted to Dr. Norman Wright for supplying the infrared analyses and curves.

Summary

The reaction of phenols with propylene oxide in the presence of an alkaline catalyst gives secondary alcohol ethers and in the presence of an acid catalyst both primary and secondary ethers are obtained.

Infrared absorption curves are presented showing a comparison of aliphatic and aromatic glycol ethers.

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(6) Stoermer, *Ann.*, **312**, 271–272 (1900).