[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH AND THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF PITTSBURGH]

ALKYL ETHERS OF ETHYLENE GLYCOL

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Introduction

During the progress of a research on the influence, in general, of the addition of hydroxyl groups to physiologically active compounds it became necessary to prepare a series of mono-alkyl ethers of ethylene glycol. It appears, from a search of the literature, that the method of Palomaa,[3] which is an improved adaptation of the earlier methods of Wurtz[4] and Demole,[5] is the most satisfactory hitherto described. Good yields of the methyl and ethyl ethers are obtainable, but the time required and the difficulties of procedure are considerable. One to two days are necessary for the preparation of the sodium derivatives of glycol, from which the ethers are subsequently made by boiling with alkyl iodides.

The possibility of preparing such ethers by reaction between the easily prepared sodium alcoholates of the monohydric alcohols and either ethylene oxide or ethylene chlorohydrin suggested itself as a simplification of the older methods. Both of these reactions have been applied with the results recorded below.

Results of a pharmacodynamic study of these compounds will be reported elsewhere.

Experimental Part

For the reactions with ethylene oxide (Method A) one molecular proportion of sodium was dissolved in the proper alcohol, the flask placed on a balance, and 1.1 moles of gaseous ethylene oxide passed into the solution at such a rate as to keep the temperature between 35° and 40°. The flask was corked and allowed to stand for about two hours, after which time the contents were poured into water and extracted several times with ethyl ether. The ethereal solution was dried over sodium sulfate, the ether removed, and the residue distilled and fractionated.

The procedure with ethylene chlorohydrin (Method B) was as follows. One mole of sodium was dissolved in the alcohol, the solution cooled and 1.1 moles of anhydrous chlorohydrin gradually added. After about a half hour, the mixture was heated on a water-bath until neutral, the sodium chloride filtered off, and the filtrate distilled and fractionated.

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[3] Palomaa, (a) *Ber.*, **35**, 3299 (1902); (b) **42**, 3873 (1909).

[4] Wurtz, *Ann. chim.*, [3] **55**, 429 (1859).

[5] Demole, *Ber.*, **9**, 745 (1876).

The yields by both processes A and B are affected adversely by the presence of water in the reagents.

TABLE I

GLYCOL ETHERS PREPARED

Glycol ether	Formula	Boiling point °C.	Boiling point Mm.	Yield by method A %	Yield by method B %	d^{15}_{15}	Analysis Calc. C %	Analysis Calc. H %	Analysis Found C %	Analysis Found H %
Mono-methyl[a]	.....	124.5	743	26	35	....	...	...	...	...
Mono-ethyl[b]	.....	134.8	743	50	60	....	...	...	...	...
Mono-*iso*propyl	$C_5H_{12}O_2$	144	743	31	25	0.9115	57.64	11.61	57.35	11.46
Mono-propyl[c]	$C_5H_{12}O_2$	150	743	50	40	.9141	57.64	11.61	57.85	11.94
Mono-*iso*butyl	$C_6H_{14}O_2$	158.8	743	42	36	.8950	60.96	11.94	60.41	11.75
Mono-butyl	$C_6H_{14}O_2$	170.6	743	40	30	.9011	60.96	11.94	61.03	12.02
Mono-amyl	$C_7H_{16}O_2$	181	745	42	30	.8926	63.58	12.20	63.43	12.38

[a] Ref. 3 b, p. 3874. Palomaa gives b. p., 124.9° (768 mm.).

[b] Palomaa gives b. p., 134.7–134.9° (748 mm.).

[c] Prepared by Palomaa but not analyzed.

Summary

1. A simple method for the preparation of alkyl ethers of ethylene glycol has been developed.
2. Several new compounds in this series have been prepared.

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THE SPECIFIC HEATS OF TRINITROTOLUENE, TETRYL, PICRIC ACID AND THEIR MOLECULAR COMPLEXES[1]

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At the suggestion of Dr. C. E. Munroe of the National Research Council, the Explosives Chemical Laboratory of the Bureau of Mines has undertaken the determination of some of the hitherto undetermined constants of explosive compounds.

The only data on the specific heats of the substances covered by this paper are those by Prentiss[4] on the mean specific heats of trinitrotoluene and tetryl as determined by the method of mixtures.

Method of Determination

The liquid oxygen calorimeter first described by Dewar[5] was used. The apparatus consisted of a small Dewar flask of about 50cc. capacity,

[1] Published by permission of the Director, U. S. Bureau of Mines.

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[4] Prentiss, "Specific Heats and Thermal Diffusivities of Certain Explosives," *Army Ordnance*, vol. **4**, 1923, pp. 117, 184, 242.

[5] Dewar, *Chem. News*, **92**, 181 (1905).