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SOME AROMATIC ESTERS OF THE MONOALKYL ETHERS OF ETHYLENE GLYCOL AND DIETHYLENE GLYCOL[1]

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Although a few aromatic esters of the monoalkyl ethers of ethylene glycol ($HOCH_2CH_2OR$) and diethylene glycol ($HOCH_2CH_2OCH_2CH_2OR$) are recorded in the literature, no systematic preparation of such a series of compounds has ever been made. Palomaa[2] has reported the preparation of the benzoates of the monomethyl, monoethyl, monopropyl and monoallyl ethers of ethylene glycol but gives no data for any but the monomethyl compound. Since several of these glycol ethers have recently become commercially available, it has been considered worth while to prepare a series of their benzoates and *p*-nitrobenzoates. These esters are generally liquids of high boiling point. They are insoluble in water but soluble in all common organic solvents. The benzoates are all colorless liquids, the β-methoxy and β-ethoxy compounds possessing characteristic pleasant odors which lessen and almost vanish with the lengthening of the aliphatic side chain.

Benzoylation of the glycol ethers was carried out in pyridine solution according to the following type reactions

$$C_6H_5COCl + HOCH_2CH_2OR = C_6H_5COOCH_2CH_2OR + HCl$$
$$C_6H_5COCl + HOCH_2CH_2OCH_2CH_2OR = C_6H_5COOCH_2CH_2OCH_2CH_2OR + HCl$$

The method was the same as that previously used by Palomaa.[2]

A known quantity of the glycol ether and an excess of dry pyridine were placed together in a flask and an equivalent amount of the acid chloride slowly added from a dropping funnel with continual stirring or shaking. The solid *p*-nitrobenzoyl chloride was first dissolved in a quantity of anhydrous ether. The flask was cooled by ice throughout the course of this addition and the reaction mixture allowed to stand for at least two hours at room temperature. Dilute sulfuric acid (6 *N*) was then added with cooling until the precipitated hydrochloride had dissolved. A separation into two layers was observed. The lower layer was removed in a separatory funnel and the upper, containing the ester, was washed successively with water, dilute sulfuric acid, dilute sodium carbonate solution and then again three times with water. In the case of the *p*-nitro esters, it was necessary to wash the ethereal solution repeatedly with dilute sodium carbonate solution until, upon acidification of the washing solution, no further precipitate of *p*-nitrobenzoic acid was obtained. After drying over anhydrous sodium sulfate the ester was distilled under either atmospheric or diminished pressure.

Experimental

β-Methoxy Ethyl Benzoate.—In order to investigate the reaction of glycol ethers and benzoyl chloride in a medium other than pyridine, 15 g. (0.197 mole) of the mono-

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[1] From a thesis presented by R. C. Conn to the Graduate School of West Virginia University in partial fulfilment of the requirements for the degree of Master of Science, June, 1932.

[2] Palomaa, *Ber.*, **42**, 3873 (1909).

methyl ether of ethylene glycol was dissolved in 40 g. of dry benzene contained in a 500-cc. round-bottomed flask and 28 g. (0.2 mole) of benzoyl chloride added. The flask was fitted with a reflux condenser and heated upon a steam-bath for three hours. The benzene was then removed and the remaining material distilled. After the removal of the unchanged benzoyl chloride, the main portion of the liquid distilled at 252–253° and 744 mm. pressure. The yield was 65%.[3]

The same quantities of glycol ether and benzoyl chloride reacting in 70 g. of pyridine gave a yield of 95%. It was concluded from this that it was better to use pyridine as a medium for such esterifications.

***p*-Nitro β-Methoxy Ethyl Benzoate.**—26.5 g. (0.16 mole) of *p*-nitrobenzoyl chloride was dissolved in 15 cc. of pyridine. The ester was obtained as a yellowish solid which crystallized into almost transparent, rectangular plates and clusters of needles.

***p*-Nitro β-Ethoxy Diethylene Glycol Benzoate.**—Thirty-five grams (0.2 mole) of *p*-nitrobenzoyl chloride was dissolved in 200 cc. of absolute ether and added to 25.3 g. (0.19 mole) of the monoethyl ether of diethylene glycol. The ester was obtained as a yellow amorphous oily solid which could not be crystallized. Analysis showed it to be impure and further purification will be made.

Table I lists the analyses of the compounds prepared. All nitrogen determinations were made by titration with titanous chloride solution.

TABLE I

ANALYSIS OF COMPOUNDS

Compound	Calcd. for	Carbon		Hydrogen		Nitrogen			Yield, %
Benzoates		Calcd.	Found	Calcd.	Found	Calcd.	Found		
β-Ethoxy ethyl[a]	$C_{11}H_{14}O_3$								90.0
β-Butoxy ethyl	$C_{13}H_{18}O_3$	70.27	70.54	8.10	7.91				86.0
β-Ethoxy diethylene glycol	$C_{13}H_{18}O_4$	65.56	66.29	7.57	7.80				93.0
β-Butoxy diethylene glycol	$C_{15}H_{22}O_4$	67.55	66.72	8.27	8.05				88.0
p-Nitrobenzoates									
β-Methoxy ethyl	$C_{10}H_{11}O_5N$					6.22	6.24	6.19	95.0
β-Ethoxy ethyl	$C_{11}H_{13}O_5N$					5.86	5.96	5.93	87.5
β-Butoxy ethyl	$C_{13}H_{17}O_5N$					5.24	5.28	5.29	67.4
β-Ethoxy diethylene glycol[b]	$C_{13}H_{17}O_6N$								
β-Butoxy diethylene glycol	$C_{15}H_{21}O_6N$					4.50	4.57	4.52	57.9

[a] Palomaa states that he has prepared this compound but gives no analysis for it nor any of its physical constants. *Mol. wt.* (freezing point in benzene): theoretical, 194; found, 190.4, 190.5. [b] Analysis showed a nitrogen content of 5.4% as compared with a theoretical value of 4.98%. It was concluded that the material was impure.

Table II gives the physical constants determined for all the liquid esters prepared. All boiling points were determined with thermometers certified by the United States Bureau of Standards. Corrections for stem emergence have been made. Refractive indices were determined by means of an Abbé refractometer at 25°. Surface tensions were determined by means

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[3] All yields recorded are given for the ester before distillation and are based upon the quantities of the glycol ether used.

of a du Noüy tensiometer at 26° and Harkins corrections for the ring method applied.

TABLE II

PHYSICAL CONSTANTS OF THE LIQUID ESTERS PREPARED

Compound Benzoates	B. p., °C.	P, mm.	D^{25}_{25}	n^{25}_{D}	γ^{26}
β-Methoxy ethyl	251.6–252.6[a]	738.5	1.0891[b]	1.5040	45.00
β-Ethoxy ethyl	260.0–261.0	738.5	1.0585	1.4969	40.67
β-Butoxy ethyl	156.5–157.0	14.5	1.0277	1.4925	39.86
	131.6–132.6	3.0			
β-Ethoxy diethylene glycol	160.0–161.0	14.5	1.1049	1.5080	43.79
	141.0–143.0	2.0			
β-Butoxy diethylene glycol	179.3–181.3	4.0	1.0407	1.4927	40.35
p-Nitrobenzoates					
β-Methoxy ethyl[c]	158.3–160.3	4.0			
β-Ethoxy ethyl	163.5–164.5	4.0	1.2086	1.5220	44.49
β-Butoxy ethyl	179.0–180.0	3.5	1.1518	1.5125	41.97
β-Ethoxy diethylene glycol[d]	207.0–209.0	4.0			
β-Butoxy diethylene glycol	230.0–232.0	4.0	1.1516	1.5078	41.02

[a] Palomaa gives 254–256° at 760 mm. [b] Palomaa gives 1.1067 at 15°. [c] Solid; crystallized in flat plates and needles; melting point 49.5°. Recrystallized from alcohol and water in white, glistening plates and needles, melting point 50.5°. These melting points were determined by means of a Gerhardt short stem thermometer with the stem completely immersed in the melting point tube. [d] The viscous liquid distillate sets to form an oily, amorphous solid.

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Summary

1. The following new compounds have been prepared and analyzed: β-butoxy ethyl benzoate, β-ethoxy diethylene glycol benzoate, β-butoxy diethylene glycol benzoate, *p*-nitro-β-methoxy ethyl benzoate, *p*-nitro β-ethoxy ethyl benzoate, *p*-nitro β-butoxy ethyl benzoate, *p*-nitro β-butoxy diethylene glycol benzoate.

2. β-Methoxy ethyl benzoate and β-ethoxy ethyl benzoate, compounds previously reported, have been prepared and additional data concerning them obtained.

3. Some of the physical constants of these compounds have been determined.

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