

From the author's experience and the paper by Redemann and Dunn it appears that benzoyl-aminomalonic ester should find general use in the synthesis of α -amino acids.

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The 3-Nitrophthalates of the Mono Ethers of Ethylene and Diethylene Glycol

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The problem of identifying the monoethyl ether of ethylene glycol (Cellosolve) arose here recently and was successfully solved by the use of the 3-nitrophthalic anhydride reagent proposed by Nicolet and Sachs² for the identification of alcohols. The work has now been extended to the other commercially available monoethers of ethylene glycol ("Cellosolve" series), and of diethylene glycol ("Carbitol" series).

The ethers were obtained from the Carbide and Carbon Chemicals Corporation, and were purified by fractional distillation. A constant boiling fraction was taken, the boiling points and refractive indices checking with recorded values.

The procedure followed for the preparation of the acid 3-nitrophthalate esters of these ether alcohols was essentially that recommended by Nicolet and Sachs.

The anhydride was heated with an excess of the ether alcohol at the boiling point of the latter until all of the anhydride had dissolved and then for fifteen minutes longer. In the cases of those liquids having boiling points above 150°, toluene was added to avoid higher temperatures which cause decomposition of the esters formed; the toluene was then removed by distillation under reduced pressure. The oily layer of ester was then extracted with hot water to remove the unreacted reagents. It was then treated with a hot mixture of water and the least amount of ethyl alcohol necessary to effect complete solution. This solution was allowed to cool slowly with frequent scratching to induce crystallization. The initial crystallization was generally very slow, periods of standing for several days in a refrigerator sometimes being required. Recrystallization was con-

(1) Taken from a Thesis submitted to the Faculty of Purdue University by Mr. Veraguth in partial fulfillment of the requirements for the Degree of Master of Science.

(2) Nicolet and Sachs, *THIS JOURNAL*, **47**, 2348 (1925); see also the further work of Dickinson, Crosson and Copenhaver, *ibid.*, **59**, 1094 (1937).

tinued until a constant melting point was obtained, generally three to five recrystallizations. Toluene was found to be a better solvent for recrystallization of the monophenyl ether of ethylene glycol than the water-alcohol mixtures.

Molecular weights of the derivatives were determined by titrating, with standard alkali, a solution containing 0.5 g. of the ester in 50% alcohol, using phenolphthalein as indicator. The melting points were taken with standard Anschütz thermometers in a mechanically stirred bath.

White crystalline derivatives were obtained from the monomethyl, monoethyl, monobutyl and monophenyl ethers of ethylene glycol and from the monomethyl ether of diethylene glycol but not from the monobenzyl ether of ethylene glycol or from the monoethyl or monobutyl ethers of diethylene glycol.

The 3-nitrophthalates obtained from the monoethyl ether of ethylene glycol and from the monomethyl ether of diethylene glycol crystallize with one molecule of water. Their water of crystallization was determined by drying a weighed amount of the ester in a vacuum at 100° over anhydrous magnesium perchlorate (Fischer drying pistol). The percentages of water found were 5.89 and 5.83, the calculated values being 5.98 and 5.43, respectively.

TABLE I
3-NITROPHthalATES OF MONO ALKYL ETHERS OF ETHYLENE GLYCOL

Alkyl	3-Nitrophthalates	
	M. P., °C.	Mol. wt. Calcd. Found
Methyl	128.4-129.0	269 268 \pm 1
Ethyl	118.0-118.6	283 284 \pm 3
Ethyl (monohydrate)	94.2-94.5	301 302 \pm 4
Butyl	121.0-120.6	311 311 \pm 1
Phenyl	112.0-113.0	331 330 \pm 2

The 3-nitrophthalate monohydrate of the monomethyl ether of diethylene glycol was also a white crystalline solid and melted at 87-90°. The anhydrous 3-nitrophthalate melted at 91.4-92.2° and was found to have a molecular weight of 313 \pm 1, as compared with the calculated value of 313. All attempts to induce the liquid reaction products from the monobenzyl ether of ethylene glycol ("Benzyl Cellosolve") and the monoethyl and monobutyl ethers of diethylene glycol ("Carbitol" and "Butyl Carbitol," respectively) to crystallize failed.

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