

SHORT
COMMUNICATIONS

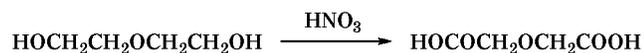
Oxidation of Diethylene Glycol with Nitric Acid

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It is known that nitric acid is capable of splitting ether bonds to give carboxy groups [1] and that aliphatic alcohols react with HNO_3 to afford alkyl nitrates [2]. Diethylene glycol can react with nitric acid at both the ether bond and the hydroxy groups. We performed oxidation of diethylene glycol with 85% nitric acid at 25–30°C. The reaction was exothermic and was accompanied by evolution of nitrogen oxides. In 1.5–2 h after mixing of the reactants, colorless crystals began to separate. The product was identified as diglycolic acid.



Presumably, the reaction involves intermediate formation of diethylene glycol dinitrate which is unstable at elevated temperature [2]. The presence of O_2NO groups reduces the nucleophilicity of the ether bond, so that the latter remains unchanged under the given conditions. This reaction provides a convenient procedure for preparation of diglycolic acid: The procedure is fairly simple and it utilizes accessible starting compounds. The known methods for preparation of diglycolic acid are based on dehydration of glycolic acid above 200°C or transformations of haloacetic acids [3].

Diethylene glycol, 15.7 g (0.15 mol), was added with stirring at 25–30°C to 56.7 g of 85% nitric acid (0.9 mol of HNO_3). The temperature was maintained by cooling with cold water. The reaction was accompanied by evolution of nitrogen oxides. When the entire amount of diethylene glycol was added and

heat evolution was over (~2 h), the mixture was kept for 12–14 h at 20°C, and the product was filtered off and dried at 60°C. Yield 18.6 g (85%). mp 148°C (from water) [3]. IR spectrum, ν , cm^{-1} : 1720 (C=O), 2400–3200 (COOH). ^1H NMR spectrum, δ , ppm: 4.2 s (4H, CH_2), 7.0 br.s (2H, OH).

Reproducible results were obtained with enlarged amounts of the reactants (by several times). In some cases, a seed should be added to initiate crystallization. In order to increase the yield of the product, it is advisable to cool the reaction mixture below 0°C.

We used diethylene glycol A containing 99.5% of the main substance and 97% nitric acid of technical grade which was diluted with water to a required concentration.

The ^1H NMR spectrum was recorded on a Tesla-497 spectrometer (100 MHz) at room temperature using acetone- d_6 as solvent and HMDS as internal reference. The IR spectrum was measured on a UR-20 instrument.

REFERENCES

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2. Orlova, E.Yu., *Khimiya i tekhnologiya brizantnykh vzryvchatykh veshchestv* (Chemistry and Technology of High Explosives), Moscow: Oborongiz, 1960, pp. 301, 329.
3. *Beilsteins Handbuch der organischen Chemie*, H, vol. 3, p. 234.