O-NITRATION OF PRIMARY AND SECONDARY UNSATURATED AND α-EPOXY ALCOHOLS

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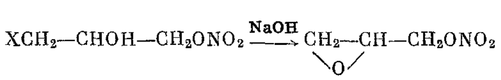
The nitrates of unsaturated and α-epoxy alcohols are interesting compounds synthetically, since, respectively having a double bond and an α-oxide ring, they can be used as starting products for the preparation of various polyfunctional compounds.

The O-nitration of unsaturated alcohols is associated with certain difficulties, since together with the hydroxyl group, the ethylene bond is also capable of reacting with nitric acid. From the few papers on the synthesis of the nitrates of unsaturated alcohols it is known that such nitration can be accomplished if a mixture of concentrated nitric acid and acetic anhydride is used [1, 2]. Based on the data given in [1, 2] the amount of nitric acid in the indicated nitrating mixture varies over a quite wide range. Besides this, in some cases this mixture is diluted with acetic acid or the nitration of the unsaturated alcohol is run in an organic solvent [3]. At times, for the O-nitration of some specific alcohol, a nitrating mixture composition is used that is suitable only for the given case, which naturally does not make the method general.

As regards obtaining α-epoxy nitrates by the O-nitration of the corresponding epoxy alcohols, then here only unsuccessful attempts of accomplishing such a synthesis are known [4]. In addition, in this class of compounds – the α-epoxy nitrates – only the first member of the series, namely glycidol nitrate, is described in the literature. The indicated compound was obtained either from glycerol dinitrate or from the primary nitrate of glycerol monohalohydrin in alkaline medium [5-7].



$$XCH_2{-}CHOH{-}CH_2ONO_2 \xrightarrow{NaOH} \underset{\diagdown O \diagup}{CH_2{-}CH}{-}CH_2ONO_2$$

$X{=}ONO_2$, Hal

Unfortunately, the range of this method is limited to the given example.

In the present paper an attempt was made to find more favorable conditions for running the O-nitration of unsaturated alcohols, and also to ascertain if it is theoretically possible to accomplish the O-nitration of α-epoxy alcohols with retention of the oxide ring. As models of the unsaturated alcohols we selected two alcohols: allyl and methallyl. It was found that an equimolar mixture of concentrated nitric acid and acetic anhydride smoothly nitrates these unsaturated alcohols with retention of the double bond. The synthesized nitrates are easily purified by distillation under reduced pressure. The primary glycerol mononitrate was synthesized from allyl alcohol nitrate using the previously described cis-hydroxylation method [8].

In seeking if the O-nitration of α-epoxy alcohols is possible we postulated that, on the basis of the known common nature in the distribution of the electron density in the α-oxide ring and the double bond, the same nitrating systems as in the case of the unsaturated alcohols can be used to achieve the desired goal. To verify this theory we selected glycidol and α-methylglycidol, which were nitrated with an equimolar mixture of concentrated nitric acid and acetic anhydride to give in good yields glycidol nitrate and α-methylglycidol nitrate. The α-epoxy nitrates are easily purified by distillation under reduced pressure. The structure of glycidol nitrate was confirmed by the elemental analysis and the infrared spectra, and also by the opening of the α-oxide ring with hydrobromic acid to give 3-bromo-1,2-propanediol mononitrate (I). In the synthesis of glycidol nitrate a trace amount (~1%) of glycerol dinitrate acetate was isolated as impurity. The formation of this compound can apparently be explained by an opening of the α-oxide ring by the acetic acid and subsequent O-nitration of the hydroxyl.

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EXPERIMENTAL

Synthesis of Allyl Alcohol Nitrate. With vigorous stirring, 29 g of allyl alcohol was added in drops, at approximately 0°, to a nitrating mixture composed of 38 g of 100% HNO_3 and 61.5 g of acetic anhydride. After additional stirring for 15 min at a temperature not exceeding 10° the reaction mass was poured into ice water. The obtained oil was dissolved in ether, and the ether solution was washed with water, 2% sodium carbonate solution, again with water, and dried over $MgSO_4$. After removal of the solvent we obtained 47.7 g of allyl alcohol nitrate, b.p. 52.5-53° (110 mm); n_D^{20} 1.4175. From [3]: b.p. 106.8°; n_D^{20} 1.417.

Synthesis of Glycerol 1-Mononitrate. With stirring, a solution of 12.5 g of potassium permanganate and 9.5 g of $MgSO_4$ in 250 ml of water was added dropwise at approximately −20° to a solution of 10.2 g of allyl alcohol nitrate in 180 ml of ethyl alcohol. Then in sequence were added a water solution, containing 18.5 g of sodium bisulfite, and 4 N H_2SO_4 solution. The reaction mass was filtered, the filtrate was evaporated in vacuo, and the residue was treated with acetone. The solution was dried over $MgSO_4$. After removal of the solvent we obtained 10.4 g of glycerol 1-mononitrate, m.p. 57-58° (from ether). From [5]: m.p. 58-59°. Found %: C 26.40; H 4.91; N 10.35. $C_3H_7O_5N$. Calculated %: C 26.28; H 5.15; N 10.22.

Synthesis of Methallyl Alcohol Nitrate. With stirring, 10 g of methallyl alcohol (b.p. 94°; n_D^{20} 1.4167) was added dropwise at approximately −20° to a nitrating mixture composed of 17 g of 100% HNO_3 and 27.5 g of acetic anhydride. After additional stirring for 15 min at a temperature not exceeding 10° the product was isolated in the same manner as described above for allyl alcohol nitrate. We obtained 14.9 g of methallyl alcohol nitrate, b.p. 43° (50 mm); n_D^{20} 1.4147; d_4^{20} 1.0448. Found %: C 40.42; H 6.04; N 11.99. MR 28.05. $C_4H_7O_3N$. Calculated %: C 41.03; H 6.03; N 11.96. MR 28.14.

Synthesis of Glycidol Nitrate. With stirring, 11 g of glycidol [b.p. 55° (10 mm); n_D^{20} 1.4353] was added dropwise at approximately −10° to a nitrating mixture composed of 16 g of 100% HNO_3 and 26 g of acetic anhydride. After stirring for 20 min the reaction mixture was poured into ice water. The organic layer was separated, and the water-diluted reaction mass was neutralized with sodium carbonate, in which connection an additional amount of product separated, which together with the previously obtained substance was combined with the ether extracts from the neutralized reaction mass. The ether solution was washed with 10% sodium carbonate solution, then with water, and dried over $MgSO_4$. After removal of the ether, followed by vacuum-distillation of the residue, we obtained 15.2 g of glycidol nitrate, b.p. 56-58° (8 mm); n_D^{20} 1.4365; d_4^{20} 1.3186. Found %: C 30.19; H 4.17; N 11.71. MR 23.64. $C_3H_5O_4N$. Calculated %: C 30.26; H 4.23; N 11.76. MR 23.71.

The residue from the distillation (did not distill at 146° and 1 mm) was a thick oil (0.4 g; n_D^{20} 1.4728), which based on the elemental analysis corresponds to glycerol dinitrate acetate. Found %: C 26.85; H 3.55; N 12.79. $C_5H_8O_8N_2$. Calculated %: C 26.79; H 3.60; N 12.50.

Reaction of Glycidol Nitrate with Hydrobromic Acid. With stirring, 4 g of glycidol nitrate was added dropwise at 0° to 12.5 ml of 40% hydrobromic acid. After stirring for 10 min the reaction mass was saturated with ammonium sulfate, extracted with ether, and the ether extracts were dried over $MgSO_4$. After removal of the solvent we obtained 4.4 g of 3-bromo-1,2-propanediol nitrate (I): n_D^{20} 1.4983; d_4^{20} 1.7609. Found %: C 18.09; H 3.19; N 6.88; Br 39.95. MR 33.31. $C_3H_6O_4NBr$. Calculated %: C 18.02; H 3.02; N 7.00; Br 39.96. MR 33.23.

Synthesis of α-Methylglycidol Nitrate. The compound was obtained from 1.7 g of α-methylglycidol [b.p. 72° (45 mm); n_D^{20} 1.4267] using the directions for the preparation of glycidol nitrate. After vacuum-distillation we obtained 2.3 g of α-methylglycidol nitrate, b.p. 61-62° (8 mm); n_D^{20} 1.4333; d_4^{20} 1.2696. Found %: C 36.04; H 5.35; N 10.48. MR 28.15. $C_4H_7O_4N$. Calculated %: C 36.09; H 5.30; N 10.52. MR 28.35.

CONCLUSIONS

1. A new variation was developed for the O-nitration of unsaturated alcohols.

2. It was shown that the O-nitration of α-epoxy alcohols with retention of the oxide ring is theoretically possible.

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