# SYNTHESIS OF 1-BUTENE-3,4-DIOL DINITRATE AND SOME OF ITS DERIVATIVES

## L. T. Eremenko and A. M. Korolev

In preceding communications [1, 2] we have described a general method for preparing the dinitrates of trans- and cis-2-butene-1,4-diol and some of their derivatives. Definite interest attaches to the previously undescribed structural isomer, 1-butene-3,4-diol dinitrate, which contains a secondary nitrate group along with a primary one: CH<sub>2</sub>=CHCHONO<sub>2</sub>CH<sub>2</sub>ONO<sub>2</sub>.



Fig. 1. Thin-layer chromatogram on  $Al_2O_3$  (CHCl<sub>3</sub> solvent, development in iodine vapor): a) mesoerythritol tetranitrate; b) d,*l*-erythritol tetranitrate; c) mixture of mesoand d,*l*-erythritol tetranitrates (control experiment); d) nitration product of erythritol 1,2-dinitrate (erythro- and threo-isomers).

There is an indication in the literature [3] that one cannot obtain the dinitrate of 1-butene-3,4-diol by the reaction of 3,4-dichloro-1-butene with an acetonitrile solution of silver nitrate, although the synthesis of cis- and trans-2butene-1,4-diol dinitrates from the corresponding dichloro derivatives takes place smoothly and in good yield. Under the experimental conditions [3], along with the starting material there was isolated a chlorobutenol nitrate of unknown structure, and also the dinitrate of trans-2-butene-1,4-diol, which, in the author's opinion, appeared in the synthesis products as the result of an allylic rearrangement.

In the present work we describe the synthesis of 1-butene-3,4-diol dinitrate by O-nitration of the corresponding unsaturated glycol. 1-Butene-3,4-diol dinitrate was isolated in high yield and was characterized. The product is a colorless, mobile liquid which distills easily under reduced pressure.

The presence of the terminal double bond in the compound synthesized was identified by its Raman spectrum, from the valence stretching band of the double bond at 1648 cm<sup>-1</sup> and the deformation vibration band of the terminal methylene group at 1423 cm<sup>-1</sup>, and was also confirmed by chemical reactions. Bromination of 1-butene-3,4-diol dinitrate led to formation of 3,4-dibromo-1,2-butanediol dinitrate. Besides this, cis-hydroxylation of the double bond in the synthesized compound with KMnO<sub>4</sub> [1,2] afforded erythritol-1,2-dinitrate. Upon O-nitration of the latter, a mixture of meso- and d,*l*-erythritol dinitrates was isolated, which was demonstrated by thin-layer chromatography (Fig. 1). We did not succeed in securing complete separation of the spots in the chromatogram obtained. However, it is known that the nitrates of various polyhydric alcohols in most cases give very close Rf values [4, 5]. From the mixture of diastereoisomeric erythritol tetranitrates obtained we succeeded in isolating in pure form both meso-

erythritol tetranitrate (mp 61.0-61.3°) and also  $d_{l}$ -erythritol tetranitrate (mp 30-30.5° [1]). Upon acetylation of the erythritol 1,2-dinitrate we also obtained a mixture of 3,4-diacetates of meso- and  $d_{l}$ -erythritol dinitrate. Formation of the nitrate or acetate groups is accompanied by breaking of the O-H bond in the starting hydroxyl-containg molecule; that is, the configuration of the starting molecule remains unchanged. Consequently, the erythritol 1,2-dinitrate from which the mixture of meso- and  $d_{l}$ -erythritol dinitrates was prepared is also a mixture of isomers of this series (erythro- and threo-isomers, respectively).

Actually, the crystalline compound  $-d_{l}$ -erythritol dinitrate (mp 49-50°) was isolated from the mixture of meso- and  $d_{l}$ -erythritol dinitrates. On nitration of this compound,  $d_{l}$ -erythritol tetranitrate was obtained; and on acetylation with acetyl chloride,  $d_{l}$ -erythritol-1,2-dinitrate-3,4-diacetate was obtained. The liquid part of the mixture of meso- and  $d_{l}$ -erythritol dinitrates, which was apparently concentrated erythro isomers, was nitrated to meso-erythritol tetranitrate in high yield.

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We have previously shown that glycerol mononitrate can be prepared by cis-hydroxylation of allyl nitrate [7]. Having available 1-butene-3,4-diol dinitrate, in the present work we have prepared still another partial nitrate with vicinal primary and secondary hydroxyl groups. This permits suggesting that the method of cis-hydroxylation of the nitrates of unsaturated alcohols with terminal double bonds is general and is so far the only one described in the literature for preparing partial nitrates of polyhydric alcohols with the structure indicated.

### EXPERIMENTAL

Synthesis of 1-Butene-3,4-diol Dinitrate (I). To a nitrating mixture of 31.5 g of 100% HNO<sub>3</sub> and 51 g of acetic anhydride at 15-20° was added 11 g of 1-butene-3,4-diol (bp 95-96° at 14 mm;  $n_D^{20}$  1.4630). After stirring for 40 min the reaction mixture was poured into ice water. The organic portion was extracted with ether, washed with water, 5% Na<sub>2</sub>CO<sub>3</sub> solution, and with water once more, and was dried over MgSO<sub>4</sub>. After removal of the ether there was obtained 20.7 g (93%) of I, bp 55-56° (1 mm);  $n_D^{20}$  1.4563;  $d_4^{20}$  1.3398. Found %: C 26.97; H 3.44; N 15.86. MR 36.15.  $C_4H_6O_6N_2$ . Calculated %: C 26.98; H 3.40; N 15.73. MR 36.17.

Synthesis of 3,4-Dibromobutane-1,2-diol Dinitrate. A solution of 4.2 g of Br<sub>2</sub> in 10 ml of CHCl<sub>3</sub> was added dropwise, with stirring, to a solution of 4.0 g of I in 10 ml of CHCl<sub>3</sub>, at a temperature of about 0°. The reaction mixture was kept at 0-10° for 30 h, and at about 20° for 40 h. After removal of the solvent and excess bromine there was obtained 7.3 g (96%) of 3,4-dibromobutane-1,2-diol dinitrate, bp 97-99° (0.5 mm);  $n_D^{20}$  1.5275;  $d_4^{20}$  2.0002. Found %: C 14.13; H 1.62; N 8.44; Br 47.43. MR 51.98. C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>N<sub>2</sub>Br<sub>2</sub>. Calculated %: C 14.22; H 1.79; N 8.29; Br 47.29. MR 52.07.

Synthesis of Erythritol 1,2-Dinitrate (Erythro- and Threo-isomers) (II). To a solution of 30 g of I in 300 ml of ethanol, with stirring at about 20°, was added dropwise a solution of 20.4 g of KMnO<sub>4</sub> and 15.3 g of MgSO<sub>4</sub> in 420 ml of water. The reaction mixture was filtered, the filtrate was evaporated under vacuum, the residue was extracted with ether, and the extract was dried over MgSO<sub>4</sub>. There was obtained 22.9 g (64.5%) of II;  $n_D^{20}$  1.4805;  $d_4^{20}$  1.5127. Found %: C 23.01; H 4.06; N 13.23. MR 39.89. C<sub>4</sub>H<sub>8</sub>O<sub>8</sub>N<sub>2</sub>. Calculated %: C 22.65; H 3.80; N 13.21. MR 39.68.

On storage in the cold, the erythritol 1,2-dinitrate begins to partially crystallize. The crystalline portion is the 1,2-dinitrate of d,*l*-erythritol (the threo-isomer, III), mp 49-50°. Found %: N 14.39.  $C_4H_8O_8N_2$ . Calculated %: N 13.21.

The liquid portion is meso-erythritol 1,2-dinitrate (the erythro-isomer, IV) with an impurity of III dissolved in it.

Synthesis of Erythritol Tetranitrate [Meso- (V) and d, l- (VI) isomers]. To a nitrating mixture of 3.8 g of 100% nitric acid and 6.1 g of acetic anhydride at about 15° was added 2.45 g of II. After stirring for 40 min, the reaction mixture was poured onto chopped ice. The organic portion was dissolved in ether, washed with water, with 1% Na<sub>2</sub>CO<sub>3</sub> solution, and with water again, and the ether solution was dried over MgSO<sub>4</sub>. There was obtained 3.1 g (89%) of (V+VI) (R<sub>f</sub> = 0.71 and 0.64, respectively, see Fig. 1). The crystalline part was removed and washed with cold ether. There was obtained 1.2 g of V, mp 61-61.3° (from CCl<sub>4</sub>) [2, 6]. The liquid part was treated at room temperature with CCl<sub>4</sub>. Compound VI was isolated from the solution on cooling, mp 30-30.5° [1].

Synthesis of Meso-erythritol Tetranitrate, (V). Similarly, upon reaction of a nitrating mixture composed of 3 g of 100% HNO<sub>3</sub> and 4.9 g of acetic anhydride with 1.99 g of IV (containing some III as impurity) there was obtained 2.47 g (87.5%) of V, mp 61-61.3° (from  $CCl_4$ ).

Synthesis of d,*l*-Erythritol Tetranitrate (VI). Upon reaction of a nitrating mixture from 3.8 g of 100%  $HNO_3$  and 6.1 g of acetic anhydride with 0.23 g of III there was obtained 0.30 g (92%) of VI, mp 30-30.5°.

<u>Synthesis of Erythritol-1,2-dinitrate-3,4-diacetate (Erythro- and Threo-isomers).</u> To 10.5 ml of CH<sub>3</sub>COCl was added 1.55 g of II. After 10 min the excess CH<sub>3</sub>COCl was removed under vacuum. There was obtained 2.01 g (93%) of erythritol-1,2-dinitrate-3,4-diacetate (erythro- and threo-isomers);  $n_D^{20}$  1.4580;  $d_4^{20}$  1.3819 (after passage over a layer of Al<sub>2</sub>O<sub>3</sub>). Found %: C 32.70; H 3.88; N 9.66. MR 58.48. C<sub>8</sub>H<sub>12</sub>O<sub>10</sub>N<sub>2</sub>. Calculated %: C 32.44; H 4.08; N 9.46. MR 58.30.

Synthesis of d,*I*-Erythritol-1,2-dinitrate-3,4-diacetate (VII). To 3 ml of CH<sub>3</sub>COCl was added 0.47 g of III. After the vigorous evolution of HCl had ceased, the reaction mixture was heated for 20 min at about 40°. The excess CH<sub>3</sub>COCl was removed under vacuum. Compound VII (0.65, quantitative yield) was obtained;  $n_D^{20}$  1.4600 (after passage over a layer of Al<sub>2</sub>O<sub>3</sub>). Found %: C 32.13; H 3.88; N 9.40. C<sub>8</sub>H<sub>12</sub>O<sub>10</sub>N<sub>2</sub>. Calculated %: C 32.44; H 4.08; N 9.46.

## CONCLUSIONS

1. 1-Butene-3,4-diol dinitrate, a starting material for preparing a number of meso- and  $d_{l}$ -erythritol derivatives, has been prepared.

2. The possibility of preparing partial nitrates of polyhydric alcohols containing vicinal primary and secondary hydroxyl groups has been demonstrated in the case of synthesis of the diastereoisomeric 1,2-dinitrates of erythritol by cis-hydroxylation of 1-butene-3,4-diol dinitrate.

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