

Letters to the Editor

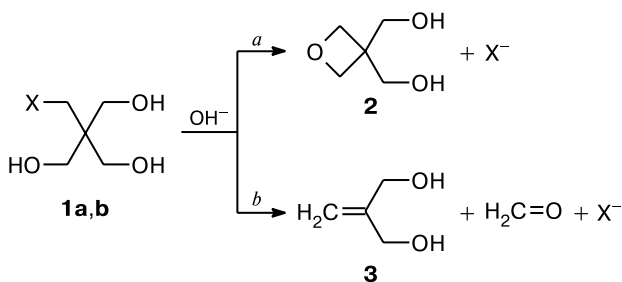
The first example of heterolytic fragmentation of organic nitrates of a heterofunctional series

A. M. Korolev,* L. T. Eremenko, L. V. Meshikhina

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moskovskaya obl., Russian Federation.

Fax: +7 (096) 515 5588. E-mail: elt@icp.ac.ru

The reaction of pentaerythritol mononitrate (**1a**) with a base yields an intramolecular nucleophilic substitution product, *viz.*, 3,3-bis(hydroxymethyl)oxetane (**2**) (heterocyclization, pathway *a*) (this is a new method of its synthesis). An unknown reaction for organic nitrates of a heterofunctional series also takes place, *viz.*, heterolytic fragmentation (Grob's fragmentation,¹ pathway *b*), leading to 2-methylidenepropane-1,3-diol (**3**):



1: X = ONO_2 (**a**), Br (**b**)

First, heterocyclic glycol **2** has been synthesized from bromide **1b**, whereupon the fragmentation product of **3** has not been observed,² this has been obtained later.^{3,4}

A comparison of the reactivities of monosubstituted pentaerythritol derivatives **1a,b** showed that transformations of mononitrate **1a** require more drastic conditions. The yields of heterocyclic glycol **2** in both cases are the same (~70%), the yields of unsaturated glycol **3** in reactions of **1a** and **1b** are 8.5 and 17%, respectively. *O*-Nitration of glycol **3** obtained from **1a** gave the known 2-methylidenepropane-1,3-diol dinitrate(**4**).⁵

Mononitrate **1a** (m.p. 78–79 °C) and bromide **1b** (m.p. 75–76 °C) were obtained according to the known procedures.^{6,7}

3,3-Bis(hydroxymethyl)oxetane (2) and 2-methylidenepropane-1,3-diol (3). *A.* A solution of KOH (6.5 g, 115 mmol) in dry EtOH (95 mL) was added to a stirred solution of compound **1a** (18.1 g, 100 mmol) in dry EtOH (80 mL). The reaction mixture was refluxed for 2 h, cooled, and KNO_3 was filtered off. The filtrate was concentrated, and the residue was distilled *in vacuo* to give compound **3**, yield 0.75 g (8.5%), b.p. 80–82 °C (1 Torr), n_{D}^{20} 1.4755 (Ref. 8: 93–95 °C (2 Torr),³ n_{D}^{20} 1.4758) and compound **2**, yield 8.15 g (69%), b.p. 132–134 °C (1 Torr) (Ref. 2: b.p. 128 °C (0.4 Torr)).

B. Compounds **2** and **3**, identical to those described above, were obtained according to the known procedure³ in yields 70 and 17%, respectively.

2-Methylidene-1,3-propane-1,3-diol dinitrate (4) was obtained upon nitration of compound **3** (from **1a**) according to the known procedure,⁵ b.p. 64–65 °C (1 Torr), n_{D}^{20} 1.4636 (Ref. 5:

b.p. 54–55 °C (0.5 Torr), n_D^{20} 1.4636. According to ^1H NMR and IR data, compound **4** is identical to that described earlier.⁵

This work was financially supported by the International Science and Technology Center (Project № 1550).

References

1. C. A. Grob and W. Baumann, *Helv. Chim. Acta*, 1955, **38**, 594.
2. F. Govaert and M. Beyaert, *Proc. Acad. Sci. Amsterdam*, 1939, **42**, 790.
3. C. H. Issidorides and A. J. Matar, *J. Am. Chem. Soc.*, 1955, **77**, 6382.
4. A. M. S. Odeh, J. A. Usta, and C. H. Issidorides, *Heterocycles*, 1980, **14**, 189.
5. A. M. Korolev, L. T. Eremenko, *Izv. AN SSSR, Ser. khim.*, 1972, 663 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, **21** (Engl. Transl.)].
6. J. Simecek, *Collect. Czech. Chem. Commun.*, 1962, **27**, 362.
7. *Organic Synthesis*, vol. 38, Ed. J. C. Sheehan, J. Wiley and Sons, New York - London, 458.
8. A. Mooradian and J. B. Cloke, *J. Am. Chem. Soc.*, 1945, **67**, 942.

Received July 9, 2002;
in revised form October 16, 2002