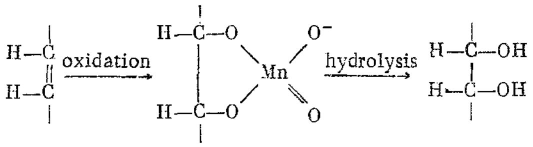
A NEW VARIANT OF THE WAGNER OXIDATION OF UNSATURATED COMPOUNDS

L. T. Eremenko and A. M. Korolev

UDC 542.943+547.423

The Wagner [1] oxidation of unsaturated compounds is one of the principal methods of cis-hydroxylation of the double bond. Studying the oxidation of nitrates of unsaturated alcohols to the corresponding partial nitrates with vicinal hydroxyl groups [2-5], we established that the Wagner method of oxidation in the form in which it is described in the literature [1, 6, 7] has a number of important defects. Its main inconvenience consists of the need to work with very large volumes of reaction mixture, containing much water and often with various auxiliary substances, which in overall complexity considerably hinders the process of isolating the glycol obtained. The purpose of the present work is to develop a new, more convenient variant of hydroxylating a double bond with potassium permanganate. For this purpose we chose as model starting compounds the nitrates of unsaturated alcohols which we have already examined: allyl nitrate [3] and the dinitrates of the isomeric butenediols, containing the double bond both within the carbon chain [2, 4] and also at the end of the chain [5].

In connection with the problem set, it is necessary to consider the role of all components used in this reaction. The mechanism of oxidation by potassium permanganate to glycols, by analogy with the action of another cis-hydroxylating agent – osmium tetroxide – is suggested to be the following [8]



(1)

It is known that both oxygen atoms in the glycol come from the potassium permanganate [9], and water is not only a solvent for the potassium permanganate but also participates in the reaction itself. Since many unsaturated compounds are insoluble in water, they are initially dissolved in an organic solvent and an aqueous solution of potassium permanganate is added to the cooled solution. When ethyl alcohol is used as the solvent, magnesium sulfate is introduced into the solution to reduce the alkalinity of the reaction medium, which is capable of oxidizing ethyl alcohol (the insoluble magnesium hydroxide is precipitated). Among the other auxiliary agents, one must note the use of sodium bisulfite solution and dilute sulfuric acid to convert the precipitated lower valence manganese compounds and the magnesium hydroxide into a soluble state. Thus, except for the potassium permanganate and water, all the remaining reagents do not participate in the main process of oxidation of the unsaturated compounds, and, in principle, can be eliminated from the reaction. To do this, it is necessary, primarily, to select such a solvent for the unsaturated compound (in our case, the nitrate of the unsaturated alcohol) as will not be oxidized by potassium permanganate, and to find the optimum necessary amount of water. Acetone satisfies almost ideally the requirement of the first part of the problem. To solve the second part, it is necessary that the amount of water in the reaction mixture should be a minimum, but sufficient for the hydrolysis of the intermediate compound [see Scheme (1)] and, besides this, should be such that the solubility of potassium permanganate in the acetone–water system will be the greatest possible. In connection with the latter requirement, it must be noted that potassium permanganate dissolves considerably better in aqueous acetone than in the individual components of this

---

Institute of Chemical Physics, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 147-149, January, 1970. Original article submitted June 30, 1969.

system [10]. Thus, in the acetone–water system which we chose (volume ratio, 7:1) potassium permanganate dissolves four times as well as in acetone, and is twice as soluble as in water.

As a result of the research conducted, we have developed a new variant of the Wagner oxidation of nitrates of unsaturated alcohols. Its essence consists in adding dry, finely ground potassium permanganate, which, as it dissolves, almost at once goes over into completely insoluble brown lower valence manganese compounds, to an aqueous acetone solution of the unsaturated compound; the brown compounds are separated from the practically colorless filtrate. Using this method, we have succeeded in considerably simplifying the process of isolating the glycol obtained and appreciably shortening the reaction time. In the new oxidation variant, the volume of the reaction mixture is reduced several-fold: per gram of reacting compounds (olefin and potassium permanganate), instead of 20-25 ml of solvent with a water content of up to 80% [1-7] there is needed 3-4 ml of solvent containing 15% water; besides this, the temperature for performing the reaction is raised from –20° to about 0-15°. It must be noted that hereupon the yields of the glycols – partial nitrates of polyhydric alcohols – are increased by 10-15%, and amount to 73-80%. Only in the case of preparing glycerin mononitrate do the yields remain identical (76%).

The described variant of the Wagner oxidation also gives positive results in the case of other unsaturated compounds. Thus, trans-1,4-dibromo-2-butene is smoothly hydroxylated to d,*l*-1,4-dibromo-2,3-butanediol by this method.*

EXPERIMENTAL

Synthesis of meso-Erythritol 1,4-Dinitrate (I) (typical experiment). To a solution of 10 g of cis-2-butene-1,4-diol in 70 ml of acetone and 10 ml of water (85% aqueous acetone) was added 8.9 g of finely ground $KMnO_4$ in small portions, at a temperature of about 15°, with vigorous stirring, over a period of 40-60 min. As the potassium permanganate dissolved, it went over almost at once into completely insoluble brown lower valence manganese compounds. The precipitate was filtered off, it was washed with acetone (3 × 10 ml), and the practically colorless filtrate was evaporated under vacuum. Toward the end of solvent removal the residue crystallized readily; mp 87-88°. There was obtained 9.5 g (80%) of (I), mp 91-91.5° (platelets from dichloroethane). Found: C 22.79; H 3.75; N 13.37%. $C_4H_8O_8N_2$. Calculated: C 22.65; H 3.80; N 13.21%. The compound which we had previously synthesized [2] had mp 89-90° (from water).

Synthesis of d,*l*-Erythritol 1,4-Dinitrate (II). Upon reaction of a solution of 19.6 g of trans-2-butene-1,4-diol dinitrate in 140 ml of acetone and 20 ml of water with 17.4 g of $KMnO_4$ at a temperature of about 0° by the method given above there was obtained 18.1 g (77.5%) of (II), mp 80-81° (needles from dichloroethane). A mixed mp test using a sample of (II) which had been prepared previously [4] gave no mp depression.

Synthesis of meso- and d,*l*-Erythritol 1,2-Dinitrates (erythro- and threo-isomers) (III). At the end of the reaction of 8.9 g of $KMnO_4$ with 10 g of 1-butene-3,4-diol dinitrate in a solution of 70 ml acetone plus 10 ml water, at about 0°, the filtrate from separation of the precipitate was evaporated under vacuum; the residue was extracted with ether, and the extract was dried over $MgSO_4$. The ether solution was passed through a column containing Al_2O_3 and was then evaporated. There was obtained 8.7 g (73%) of (III), n_D^{20} 1.4818. The product is hygroscopic. Found: N 13.40%. $C_4H_8O_8N_2$. Calculated: N 13.21%.

Upon keeping, the 1,2-dinitrate of d,*l*-erythritol (the threo-isomer) crystallizes, mp 46-47°; this mp agrees with previously obtained data [5]. Found: N 13.36%. $C_4H_8O_8N_2$. Calculated: N 13.21%.

The liquid portion of (III) is the 1,2-dinitrate of meso-erythritol (the erythro-isomer) [5].

Synthesis of Glycerin-1-mononitrate (IV). From 15 g of alkyl nitrate dissolved in 100 ml of acetone and 15 ml of water, plus 23 g of $KMnO_4$, at about –5°, by the procedure described for (I), there was obtained 15.1 g (76%) of (IV), mp 57-58° (from ether). Found: N 10.31%. $C_3H_7O_5N$. Calculated: N 10.22%.

CONCLUSIONS

In the case of preparing a series of partial nitrates of polyhydric alcohols we have worked out a new, simpler, and more convenient variant of the Wagner oxidation of unsaturated compounds.

---

*This part of the work was performed jointly with G. I. Slepko, V. R. Linde, and A. M. Uzenska.

LITERATURE CITED

1. E. E. Wagner, Zh. Russk. Fiz.-Khim. Obshchestva, 20, 72 (1888).
2. L. T. Eremenko and A. M. Korolev, Izv. Akad. Nauk SSSR, Ser. Khim., 1436 (1966).
3. L. T. Eremenko and A. M. Korolev, ibid., 1142 (1967).
4. L. T. Eremenko and A. M. Korolev, ibid., 1125 (1968).
5. L. T. Eremenko and A. M. Korolev, ibid., 2110 (1968).
6. M. G. Griner, Compt. Rend., 117, 553 (1893).
7. I. Thiele, Ann., 308, 383 (1899).
8. J. S. Pode and W. A. Waters, J. Chem. Soc., 717 (1956).
9. K. B. Wiberg and K. A. Saegebarth, J. Am. Chem. Soc., 79, 2822 (1957).
10. W. Herz and K. Knoch, Z. Anorg. und Allgem. Chem., 41, 319 (1904).