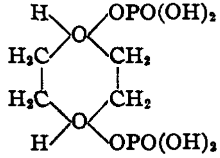
NOTES

Dioxane Diphosphate

By Erich Baer

Dioxane readily forms coördination compounds with several types of organic and inorganic substances. The oxonium salts of sulfuric acid[1] and perchloric acid[2] for example are well known. A phosphate, however, has not been described.[3] In the following the preparation and some of the properties of dioxane diphosphate[4] (I) are reported.



I

Experimental

The dioxane diphosphate (I) is easily obtained in good yields from an 88% aqueous solution of orthophosphoric acid by any one of the following three procedures. (a) Dioxane (one mole) and phosphoric acid (two moles) are mixed and crystallization is induced. The temperature of the mixture rises immediately to approximately 60°. To increase the yield of dioxane diphosphate the mixture is cooled. (b) Dioxane and phosphoric acid in separate containers are kept in a vessel under reduced pressure and at room temperature. The evaporating dioxane is absorbed by phosphoric acid and dioxane diphosphate precipitates. Any excess of absorbed dioxane, which decreases the yield of diphosphate,[5] can be readily removed *in vacuo*. (c) A dry current of air saturated with dioxane at 85° is bubbled through phosphoric acid kept at 100 to 120° until an excess of dioxane has passed into the reaction mixture. The product on cooling thickens to a crystalline sludge.

To isolate the very hygroscopic dioxane diphosphate from the crude reaction mixture obtained by any one of the above methods, the mother liquor is removed either by spreading the thick paste on porous clay plates in a desiccator or by filtering with suction using the rubber sheet technique.[6] The product is dried in a high vacuum over sodium hydroxide. The oxonium salt crystallizes in prisms and is obtained in yields as high as 84%; m. p. 83–87°[7] (sintering at 78°). A recrystallization from ether (10 g. of substance in 20 cc. of dry ether at −60°) does not change this melting point. The diphosphate is readily soluble at 25° in several solvents: water (giving a strongly acid solution), ethyl alcohol, *n*-butyl alcohol, cyclohexanol, benzyl alcohol, acetone, cyclohexanone, acetic acid, ether, dioxane, glycol dimethyl ether, ethyl acetate, trimethyl phosphate, and very slightly soluble or insoluble in benzene, cyclohexane, petrol ether, chloroform and bromoform. Dioxane diphosphate is unstable in water. Its aqueous solution gives all the usual reactions of phosphoric acid and loses dioxane on concentration. The dissociation of the molecular compound in organic solvents has not yet been investigated. *Anal.* Calcd. $C_4H_{14}O_{10}P_2$ (284): C, 16.9; H, 4.93; P, 21.82. Found: C, 16.9; H, 4.84; P, 21.80.

Dioxane diphosphate when kept dry is stable at room temperature. It remains apparently unchanged when heated for a short time in a glass vessel to 150°. Above 175° the substance rapidly turns dark brown and gives off fumes which when condensed form a colorless liquid. This distillate consisting mainly of dioxane [b. p. (756 mm.) 100°, $n^{25}D$ 1.4190] also contains an appreciable amount of acetaldehyde[8] [2,4-dinitrophenylhydrazone m. p. 147°,[9] from chloroform]. If a dry mixture of one mole of dioxane diphosphate with either 2.2 moles of Na_2HPO_4[10] or 1.1 mole of K_3PO_4[10] or 1.1 mole of anhydrous Na_3PO_4[10] is heated in an oil-bath to apptoximately 120 to 130° dioxane distils over in almost the theoretical yield. After redistilling the dioxane over metallic sodium, its refractive index and boiling point are $n^{26}D$ 1.4190, b. p. (751 mm.) 99.5–100.5°. The readily obtainable molecular compound should prove to be a valuable intermediate for the purification of dioxane.

Dioxane diphosphate, which is soluble in many organic liquids, may perhaps be used as a substitute for crystalline phosphoric acid, when a dry solution of phosphoric acid in an organic solvent is required.

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(1) A. Faworski, *J. Russ. Phys.-Chem. Soc.*, **38**, 741 (1906).

(2) C. Smeets, *Natuurw. Tijdschr.*, **19**, 12 (1937).

(3) In spite of an intensive search of the literature no record of the substance could be found. A coördination compound of dioxane with a substituted phosphoric acid, the dioxanate of dimeric glyceraldehyde-1-bromide-3-phosphate has been used successfully where other methods failed to obtain this phosphate in an analytically pure state (Baer and Fischer, *J. Biol. Chem.*, **150**, 226 (1943).

(4) Patent applied for.

(5) Dioxane diphosphate is readily soluble in dioxane.

(6) L. F. Fieser, "Experiments in Organic Chemistry," 2d. ed., 1941, p. 321.

(7) The melting point was taken in a sealed tube. According to Kelley and McCusker (This Journal, **65**, 1307 (1943)) an unsharp melting point seems to be normal for a molecular compound containing a volatile component.

(8) The distillation of dioxane with a small amount of sulfuric acid yields dioxane containing acetaldehyde (Faworski, *loc. cit.*).

(9) Purgotti, reports a m. p. of 147° for acetaldehyde 2,4-dinitrophenylhydrazone, *Gazz. chim. ital.*, **24**, I, 565 (1894).

(10) A slight excess over the amount which is needed to convert all phosphoric acid into NaH_2PO_4 or KH_2PO_4.

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The Preparation of Certain Phenolic Esters[1]

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Phenolic esters have been prepared from the sodium salt of the phenol in aqueous solution and the acid anhydride,[2] from the phenol and anhydride in the presence of the sodium salt of the acid from which the anhydride is derived,[3] and from the phenol and acid chloride in the presence of pyridine with[4] or without[5] an inert solvent. For the preparation of the rather large quantities of certain phenolic esters required in another investigation, the method involving the acylation of the phenol with the acid chloride in pyridine

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(1) This work was supported by a grant from the Duke University Research Council.

(2) Chattaway, *J. Chem. Soc.*, 2495 (1931); Abramovitch and Hauser, This Journal, **64**, 2271 (1942).

(3) Hazlet and Kornberg, *ibid.*, **61**, 3037 (1939).

(4) Hazlet, Hensley and Jass, *ibid.*, **64**, 2449 (1942).

(5) Einhorn and Hollandt, *Ann.*, **301**, 95 (1898); Reichstein, *Helv. chim. acta*, **9**, 800 (1926).