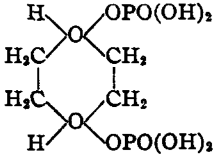
NOTES

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 approximately 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.

Banting Institute
Department of Chemistry
University of Toronto
Toronto, Canada

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The Preparation of Certain Phenolic Esters[1]

By Erwin Baumgarten, Howard G. Walker and Charles R. Hauser

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).

has been found very satisfactory. By this method three new phenolic esters have been prepared on a one to three mole scale.

Ethyl 4-Phenylphenyl Carbonate.—To a solution of 510 g. (3 moles) of 4-phenylphenol in 720 ml. of pyridine (dried over potassium hydroxide pellets) in a 2-liter reaction flask, carrying a reflux condenser, dropping funnel and mercury-sealed "Hershberg" stirrer, there was added, with stirring at 0°, over a period of 30 minutes, 365 g. (3.4 moles) of ethyl chlorocarbonate. A bulky precipitate formed. Stirring was continued for thirty minutes after addition was complete. The reaction mixture was stirred to a paste with 500 ml. of water and filtered under suction; the precipitate was washed with three 200-ml. portions of ice-water prior to fusion *in vacuo*. The fused material was recrystallized from 800 ml. of 95% ethanol. There was obtained 430 g. (60%) of ethyl 4-phenylphenyl carbonate, m. p. 73.2–74.3°. A sample, recrystallized repeatedly from methanol, melted at 73.9–75.0°.

Anal.[6] Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 73.90; H, 5.88.

4-Phenylphenyl Isobutyrate.—The acylation of 255 g. (1.5 moles) of 4-phenylphenol in 360 ml. of pyridine by means of 180 g. (1.7 moles) of isobutyryl chloride as described for ethyl 4-phenylphenyl carbonate gave 294 g. (82%) of 4-phenylphenyl isobutyrate, m. p. 73.2–74.8°. A sample, recrystallized repeatedly from methanol, melted at 74.2–74.8°.

Anal.[6] Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.53; H, 6.80.

Phenyl Isobutyrate.—A solution of 94 g. (1 mole) of phenol in 240 ml. of pyridine was acylated by means of 128 g. (1.2 moles) of isobutyryl chloride essentially as described above. After reaction was complete, the mixture was diluted with water and ether to produce two clear phases. The aqueous phase was extracted with ether and the combined ether phases were dried over anhydrous sodium sulfate followed by "Drierite." After removal of the solvent at atmospheric pressure, the residue was distilled through an eight-inch Vigreux column. Fractions boiling at 60–110° (55 g.) and 110–112° (131 g.) were obtained. The lower boiling fraction was distilled up to 105° at 25 mm. and the residue combined with the fraction boiling at 110–112°. Distillation of the mixture gave 4 g. of a fore-run, b. p. 105–111° at 25.5 mm., and 144 g. (87%) of phenyl isobutyrate, b. p. 111–112.2° at 25.5 mm. A mid-fraction (b. p. 112° at 25.5 mm., const.) was analyzed.

Anal.[6] Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.84; H, 7.32.

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(6) Analysis by T. S. Ma, University of Chicago, Chicago, Illinois.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, NORTH CAROLINA

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The Preparation of 1- and 2-Phenylpyrrole

BY F. F. BLICKE AND J. L. POWERS

Recently we have been able to synthesize relatively large quantities of 1- and 2-phenylpyrrole by means of the procedures reported below.[1]

The apparatus used for the preparation of 1-phenylpyrrole consisted of two round, cast-iron shells with flanges which were clamped together by means of eight short bolts fitted with wing nuts (only two bolts are shown in the drawing); several "cranite" asbestos gaskets placed between the shells prevented leakage.[2] Each of the shells was sixteen inches in diameter and three inches high at the point at which the pipe was attached. Two iron pipes, one inch in diameter, were screwed into the shells as shown in the diagram. The upper, outlet pipe was attached by rubber tubing to a Pyrex glass tube (combustion type) about six feet long which served as a condenser. At the beginning of the process it was found necessary to cool the condenser with wet cloths, but during the end of the operation it was essential, in some instances, to warm the glass tube with a flame to prevent the condensed material from clogging the tube.

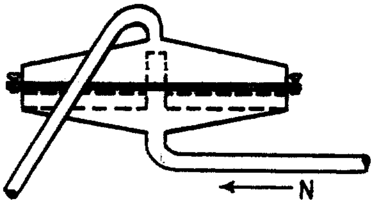

Fig. 1.

The mucic acid salt was placed in a shallow galvanized iron tray. A short, metal tube had been inserted through the center of the tray in order that a stream of nitrogen could be passed through the apparatus.

The apparatus was supported on a tripod, and heated from below with eight Meker burners. Since it was found that rubber tubing attached to the burners melted in a short time, due to the intense heat, it was necessary to unscrew the side arms from the burners and replace them with threaded iron pipes about eighteen inches long.

The upper shell of the apparatus was covered with several removable layers of heavy asbestos, and the whole apparatus was surrounded with a large sheet of the same material.

1-Phenylpyrrole.—In order to prepare the required aniline salt of mucic acid, an intimate mixture of 1116 g. of aniline and 1260 g. of mucic acid was placed in a large evaporating dish, 60 cc. of water added, and the mixture stirred and heated on a steam-bath until it became solid. The material was then pulverized and air-dried.

The salt (396 g.) was placed in the apparatus and the distillate was collected in a 2-liter, round-bottomed flask which contained 110 cc. of concd. hydrochloric acid and 400 cc. of water. The aniline dissolved and the insoluble pyrrole was obtained as a brown, crystalline material. After one-half hour the reaction was complete. The crude material was subjected to steam distillation. The phenylpyrrole separated in the distillate in the form of colorless crystals while a tarry residue remained in the distillation flask. The average yield was 60 g. (42%). The product melted at 58°,[3] and boiled at 230–234°.

2-Phenylpyrrole.—A five-foot length of Pyrex combustion tubing was bent, twenty inches from one end, at a 75° angle, and placed in a combustion furnace. To facilitate the flow of the product through the tube, one end of the furnace was raised about two inches above the level of the laboratory table. Fifty grams of 1-phenylpyrrole were put into a 125-cc. distillation flask in which the usual side arm had been replaced by another 10 cm. long and 9 mm. in thickness, sealed close to the bulb and fitted to the tube by a cork. The tube was heated to a dull red heat, and the pyrrole was distilled through the tube at such a rate that about thirty minutes were required to empty the distillation flask. Since the rearrangement was not complete, the product was distilled through the hot tube two more times.

The material was fractionated, and the recovered 1-phenylpyrrole was subjected to the rearrangement process. From 200 g. of 1-phenylpyrrole there was produced 127 g. (63%) of 2-phenylpyrrole; b. p. 272–278°.[4] A completely colorless product could be obtained only by distillation under reduced pressure; b. p. 151–154° (5 mm.).

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[1] Other methods described during the last few years are those of Allen, Gilbert and Young (*J. Org. Chem.*, **2**, 230 (1937)) and of Adkins and Coonradt (THIS JOURNAL, **63**, 1566 (1941)).

[2] When new gaskets are used, the bolts must be tightened again after the apparatus has become hot.

[3] Köttnitz (*J. prakt. Chem.*, [2] **6**, 148 (1873)) found 62°.

[4] Pictet and Crépieux (*Ber.*, **28**, 1905 (1895)) found 271–272°.