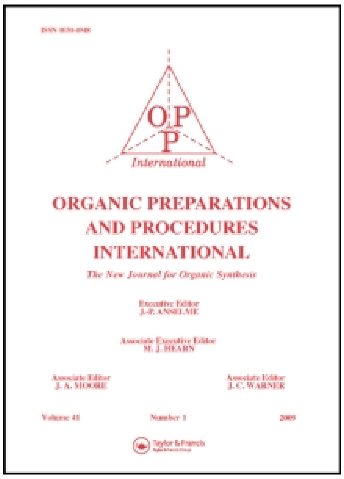

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# PREPARATION OF PHOSPHANILIC ACID (p-AMINOBENZENEPHOSPHONIC ACID)

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# PREPARATION OF PHOSPHANILIC ACID

## (p-AMINOBENZENEPHOSPHONIC ACID)

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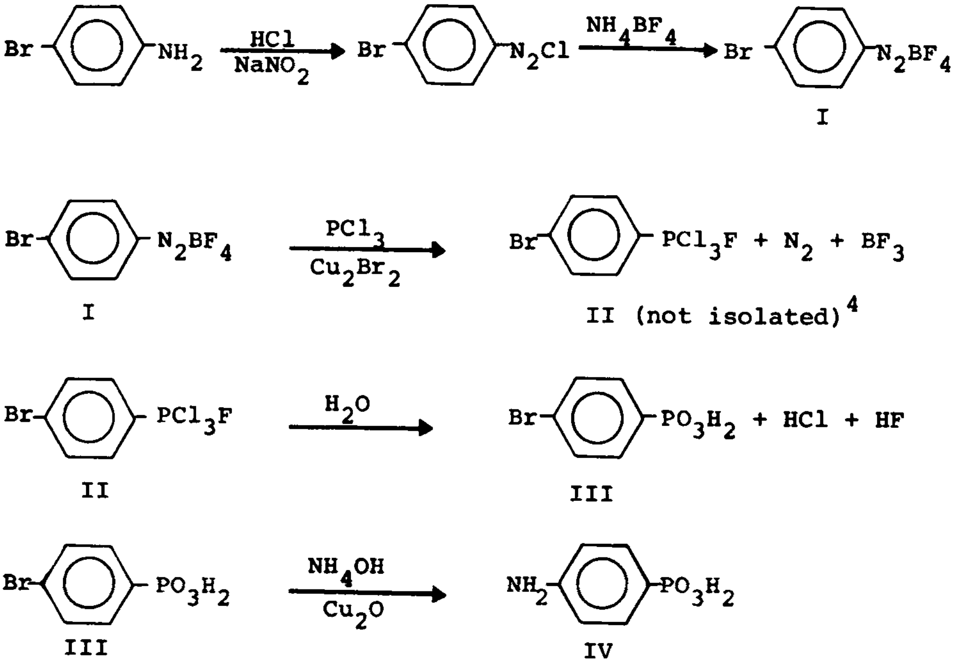

Need for a considerable quantity of phosphanilic acid led us to review the literature and to select those reactions which appeared most suitable for preparative work[4,5,6,7]. Other syntheses can be found in references 4b, 8, and 9.

## Experimental

p-Bromobenzenediazonium Fluoborate (I). - To a 3 l., 3-necked flask equipped with mechanical stirrer and 250 ml. dropping funnel are placed 248 ml. (3.0 moles) of concentrated hydrochloric acid, 248 ml. of water, and 172 g. (1.0 mole) of p-bromoaniline.[10] A thermometer is inserted beneath the surface of the liquid. The mixture is cooled to 0°, then an ice-cold solution of 69.2 g. (1.0 mole) of sodium nitrite in 100 ml. of water is added, with stirring over a period of 0.5 hour, while the temperature of the solution is kept at 0-5°. The dropping funnel is removed, an ice-cold slurry of 140 g. (1.34 moles) of ammonium fluoborate (technical) in 480 ml. of water is added through the open neck of the flask over a period of 30 minutes.

Precipitated I is stirred at 0° for 1 hour, suction-filtered, and washed successively with 100 ml. of ice-cold 5% ammonium fluoborate solution, 120 ml. of ice-cold absolute methanol, and two 200-ml. portions of ice-cold anhydrous ether. The solid is dried on the filter as thoroughly as possible after each washing, then transferred to clean filter paper, broken up with a spatula. Paper and solid are placed on a wire screen and allowed to dry overnight under the hood.[11] The yield is 210-222 g. (78-82%).

p-Bromobenzenephosphonic Acid (III). - To a 3 l., 3-necked flask (Hood) equipped with a sealed stirrer, a thermometer placed beneath the surface of the mixture, and a gas outlet tube 10-12 mm. in diameter connected to a gas absorption trap[3] are placed 222 g. (0.82 mole) of I, 1020 ml.

of anhydrous ethyl acetate, and 16.5 g. of cuprous bromide. To the stirred mixture is added 113 g. (71.6 ml., 0.82 mole) of phosphorus trichloride. Reaction occurs spontaneously after an induction period of 30-35 minutes. Evidences of reaction are a color change of gray to reddish-brown, vigorous gas evolution, and a temperature rise to about 35°.[12] Stirring is continued for 2 hours.

The gas absorption trap is removed and a dropping funnel without a connecting ₮ joint placed in the open neck. The opening allows the gases evolved to escape. Then 205 ml. of water is added from the funnel to the stirred solution *cautiously* so that the temperature does not exceed 60° (about 2 hours). The hydrolyzed mixture is steam distilled until 4 l. of distillate is collected. The residual solution is cooled to 0° and solid IIIa is suction filtered. The black, tarry residue remaining in the flask is extracted with 100 ml. of boiling water and this extract is added to the filtrate from IIIa.

Solid IIIa is washed with 75 ml. of ice-cold water. The original filtrate, the filtrate from the wash water and the 100-ml. extract of the tarry residue are combined and evaporated on the steam bath until crystals appear on the surface. The mixture is cooled to 0°, suction filtered, and the solid (IIIb) is washed with 50 ml. of ice-cold water.

Solids IIIa and IIIb are combined, dissolved in 1.6 l. of boiling water, then filtered hot. A trace of insoluble solid (*bis*-(p-bromobenzene)phosphinic acid[4c]) is discarded. The filtrate is cooled at 0°, the product filtered, the filtrate is evaporated to one-half its volume, cooled to 0°, and suction filtered. These steps are repeated until the final evaporated mixture has a volume of about 25 ml. Each batch of crystals is dried in a vacuum desiccator for 4 hours and the melting point taken. Crystals melting 194° or higher are used directly in the next step. Less pure material is crystallized from hot concentrated hydrochloric acid; weight ratio of acid-to-solid is about 20/1. Use acid-resistant filter paper, e.g., glass fiber paper, Hurlbut Paper Co. When recrystallized material melts 194° or higher, it is combined with the other products for the next step. The yield of p-bromobenzenephosphonic acid (III) is 90-102 g. (47-53%), lit.[4c] m.p. 201-202°.

Phosphanilic Acid (IV). - To a 3 l., 3-necked, round-bottomed flask equipped with mechanical stirrer and reflux condenser are added 102 g. (0.43 mole) of III, 77 g. (0.54 mole) of freshly prepared cuprous oxide[13] and 1710 ml. (26.2 moles) of concentrated ammonium hydroxide. The mixture is heated on a steam bath (Hood) for 10 hours with stirring, then transferred to a 2-liter beaker and hydrogen sulfide is passed in rapidly for 30 minutes to precipitate copper sulfide[14]. The mixture is warmed to 70-80° and suction filtered. Hydrogen sulfide is passed into the filtrate for an additional 15 minutes, the solution is again warmed and suction filtered.

The filtrate is concentrated on a steam bath until crystallization just starts. Twenty drops of concentrated ammonium hydroxide is added to the filtrate; it then is filtered hot (70-80°), cooled to room temperature, and acidified with 25%

hydrochloric acid (70 ml. concd. acid diluted to 110 ml.; about 100 ml. needed) to a pH of 3 (pH paper) to precipitate IV. The product is suction filtered, the filtrate is acidified to pH 2, and the additional precipitated solid is collected on the same filter. The solid is washed with 75 ml. of ice-cold water. The solid is transferred to a 500 ml. Erlenmeyer flask, 200 ml. of hot 95% alcohol is added, the mixture is gently boiled for 2-3 minutes, then suction filtered hot.

Crude IV is purified by dissolving it in a solution of 360 ml. of water and 240 ml. of concentrated hydrochloric acid; 0.6 g. of Norit is added. The mixture is gently boiled for 15 minutes with stirring, then suction filtered. The filtrate is treated with Norit, boiled, etc., two more times. Then 10 N sodium hydroxide (about 280 ml.) is added to the filtrate until the pH is 3 to precipitate IV. The product is suction filtered, washed with 75 ml. of ice-cold water, and dried in a vacuum desiccator for 4 hours. The product melts 239-240° with decomposition, if the melting point bath is pre-heated to 235°; lit.[6] m.p. 245°. The yield is 48-56 g. (71-75%), and the overall yield based on p-bromoaniline is 28-32%.

I.R. spectrum (KBr, 1 mg./100 mg. KBr): 2100-3000 $cm.^{-1}$ (broad, s), 1550-1620 (m), 1130 (s), 1030 (s), 940 (s), 850 (m).

The preparation was run at least twice, independently, by NV and by RFT.

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10. p-Bromoaniline should not melt below 62-64°. Crystallization from 60% ethanol may improve low-melting p-bromoaniline.

11. I should be used in the next step not later than the day after it is prepared because it may decompose. Absorption of water and a tightly packed condition make it less stable.

12. Have an ice bath ready. If the temperature goes above 40°, cool the flask. Although no uncontrollable reaction was encountered in several runs, this reaction may be violent with other fluoborates.[4]

13. Cuprous oxide is prepared by dissolving 200 g. of copper sulfate crystals and 60 g. of glucose in 400 ml. of warm water. The solution is brought to boiling and a cold solution of 80 g. of sodium hydroxide in 240 ml. of water is added. The precipitated blue cupric hydroxide changes quickly to yellow cuprous oxide. As soon as this reaction is complete, as shown by the color change, the mixture is quickly cooled in an ice bath, suction filtered as dry as possible, then dried in a vacuum desiccator for 30 minutes. The cuprous oxide is used immediately.

14. Hydrogen sulfide may be obtained from a commercial tank or from a ferrous sulfide-hydrochloric acid generator. The gas from the generator is passed through a saturated solution of barium hydroxide, then through glass wool.

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