



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

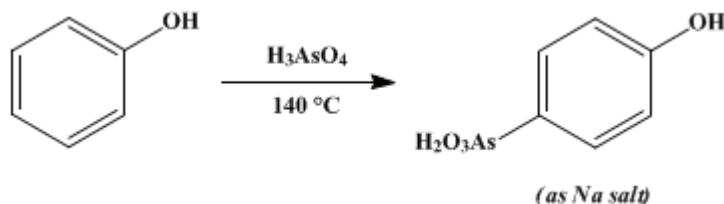
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.490 (1941); Vol. 4, p.65 (1925).

SODIUM *p*-HYDROXYPHENYLARSONATE

[Benzearsonic acid, *p*-hydroxy-, sodium salt]



Submitted by W. G. Christiansen and A. J. Norton.

Checked by Oliver Kamm

1. Procedure

Seven hundred and twenty grams (3.8–4 moles) of sirupy [arsenic acid](#) (75–80 per cent) is boiled in a beaker until the temperature of the acid is 150°; about 120 g. of water is driven off, leaving a sirup containing approximately 95 per cent of [orthoarsenic acid](#), which is then added to 300 g. (3.2 moles) of [phenol](#) in a 1-l. round-bottomed, three-necked Pyrex flask provided with an efficient stirrer, a thermometer, and a connection with a downward condenser. The flask is set in an oil bath which is heated at once to 155–160°, and the stirrer is run at a rate high enough to insure thorough mixing.

When the inside temperature reaches 140°, boiling commences and water with a very little [phenol](#) begins to distil. The distillation is allowed to continue until 60 cc. (one molecular equivalent) of water has been collected; this usually requires one hour, and the inside temperature rises to 146°. The downward condenser is then replaced by a reflux condenser ([Note 1](#)) and the reaction is allowed to continue until a total of four hours has elapsed from the time the contents of the flask first reached 140°. After the return condenser has been attached, the inside temperature declines slowly to 141° or 142° and the reaction mixture becomes thicker and somewhat tarry. After the contents of the flask have been partially cooled, they are poured into 4 l. of water and mechanically stirred; the agitation is continued for a short time in order to break up the tarry material and enable the water to dissolve the hydroxyphenylarsonic acids completely.

Finely ground [barium hydroxide](#) is added gradually to the well-stirred water solution until the material is slightly alkaline to litmus, in order to remove the excess of [arsenic acid](#); when this point is reached, the solution becomes pink. If the procedure is carried out properly, 700–800 g. of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ should suffice ([Note 2](#)). The time required by this method is greater than when a hot solution of [barium hydroxide](#) is used, but the method is more convenient and does not cause such a great increase in volume. After removal of the [barium arsenate](#) by filtration, the mother liquor and washings are treated with [sulfuric acid](#) until the solution contains neither barium nor sulfate ions. When the [barium sulfate](#) has been separated and thoroughly washed ([Note 3](#)), the filtrate is concentrated on a steam bath to about 3 l., neutralized to litmus with [sodium hydroxide](#), filtered, evaporated until the solution becomes well coated with crystals, and then treated with 2.5 volumes of [alcohol](#). After the mixture has cooled in an ice box, the [sodium *p*-hydroxyphenylarsonate](#) is separated, washed with [alcohol](#), and dried in an oven at 80°. A second crop may be secured from the filtrate by concentrating it further and precipitating with [alcohol](#). The total yield of anhydrous [sodium *p*-hydroxyphenylarsonate](#) is 252 g. (33 per cent of the theoretical amount). By proper manipulation, it is possible to obtain as much as 240 g. in the first crop and to have it free from sulfate, arsenate, and [sodium *o*-hydroxyphenylarsonate](#) which is one of the by-products formed in this reaction ([Note 4](#)).

2. Notes

1. When the downward condenser is not replaced by a reflux condenser, the total volume of water that distils is 90–120 cc. and the mass becomes very tarry, owing to the oxidation of [phenol](#) or of some

intermediate substance formed in the reaction. *p*-Hydroxyphenylarsonic acid is not destructively oxidized by hot arsenic acid.

2. In removing the excess arsenic acid with barium hydroxide, the solution should not be permitted to become strongly alkaline, as the barium salt of the hydroxyphenylarsonic acid may commence to separate, thereby decreasing the yield.

3. The filtration of large quantities of barium sulfate is usually tedious; but if filtering carbon is added to the suspension to be filtered and if a mat of this carbon is prepared on the filter by filtering an aqueous suspension of carbon, the barium sulfate may be removed rapidly and completely, even when it is precipitated from cold solutions.

4. When phenol is arsonated with arsenic acid, small amounts of *o*-hydroxyphenylarsonic acid, *p,p'*-dihydroxyphenylarsinic acid, and *o,p'*-di-hydroxyphenylarsinic acid are formed as by-products. As the sodium salts of the secondary acids are soluble in alcohol, they will not appear in the material precipitated by the addition of alcohol. The sodium salt of *o*-hydroxyphenylarsonic acid, although insoluble in alcohol, will not be precipitated if the solution is not concentrated too far before addition of the alcohol. To test the material for the presence of the ortho compound, ferric chloride is added to an aqueous solution of a small amount of the solid; the ortho hydroxy acid gives a deep purple color, whereas the para acid gives no coloration. The sodium salt which is precipitated with alcohol contains water of crystallization, which is driven off by drying at 80°. The product can be purified by dissolving in hot water and adding hot alcohol until a slight permanent turbidity is produced. Upon cooling, the material separates in a crystalline condition. Occasionally, the second crops of sodium *p*-hydroxyphenylarsonate contain small amounts of arsenious oxide which is formed from the arsenic acid during the oxidation mentioned above.

3. Discussion

p-Hydroxyphenylarsonic acid can be prepared by diazotization of arsanilic acid and replacement of the diazo group by hydroxyl;¹ by directly introducing the arsonic group into phenol;² and by diazotization of *p*-aminophenol followed by treatment with sodium arsenite.³

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 75

References and Notes

1. Bertheim, Ber. **41**, 1854 (1908).
2. Friedr. Bayer and Co., Ger. pat. 205,616 [Fr. **9**, 1040 (1908–10)]; Conant, J. Am. Chem. Soc. **41**, 431 (1919); Jacobs and Heidelberger, *ibid.* **41**, 1440 (1919); Christiansen and Norton, *ibid.* **45**, 2188 (1923).
3. Kirkhgof, Korzina, Shevelkin, and Bazuirin, Russ. pat. 23,362 [C. A. **26**, 1946 (1932)].

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

arsenious oxide

hydroxyphenylarsonic acids

Ba(OH)₂·8H₂O

barium salt of the hydroxyphenylarsonic acid

p,p'-dihydroxyphenylarsinic acid

alcohol (64-17-5)

sulfuric acid (7664-93-9)

sodium hydroxide (1310-73-2)

phenol (108-95-2)

Arsanilic acid (98-50-0)

arsenic acid,
orthoarsenic acid (1327-52-2)

barium sulfate (7727-43-7)

sodium arsenite

carbon (7782-42-5)

ferric chloride (7705-08-0)

barium hydroxide (17194-00-2)

barium arsenate

p-aminophenol (123-30-8)

sodium salt (824-79-3)

p-hydroxyphenylarsonic acid (98-14-6)

sodium p-hydroxyphenylarsonate,
Benzearsonic acid, p-hydroxy-, sodium salt (53663-20-0)

sodium o-hydroxyphenylarsonate,
sodium salt of o-hydroxyphenylarsonic acid

o-hydroxyphenylarsonic acid

o,p'-di-hydroxyphenylarsinic acid