Organic Syntheses

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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

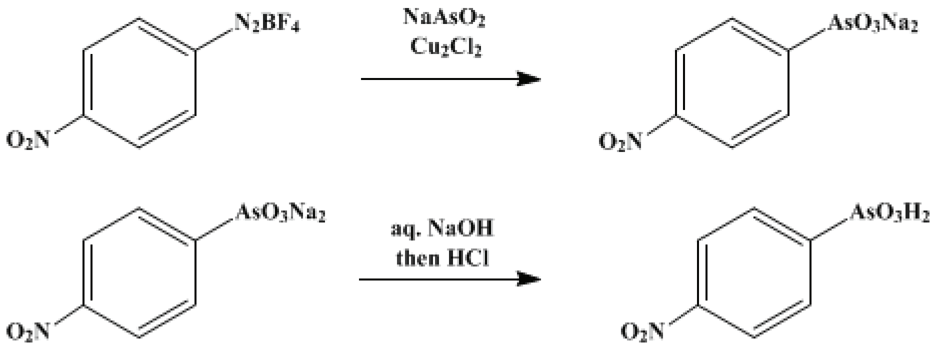
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.026.0060

Organic Syntheses, Coll. Vol. 3, p.665 (1955); Vol. 26, p.60 (1946).

p-NITROPHENYLARSONIC ACID

[Benzenearsonic acid, *p*-nitro-]



Submitted by A. Wayne Ruddy and Edgar B. Starkey.
Checked by Cliff S. Hamilton and Richard E. Benson.

1. Procedure

In a 2-l. beaker provided with an efficient mechanical stirrer, 52 g. (0.4 mole) of sodium metaarsenite and 16 g. (0.4 mole) of sodium hydroxide are dissolved in 600 ml. of water (Note 1) and 6 g. of cuprous chloride is suspended in the solution.

A mixture of 300 ml. of water and the *p*-nitrobenzenediazonium borofluoride[1] obtained from 0.25 mole of *p*-nitroaniline (Note 2) is added during a period of 1 hour to the sodium arsenite solution. The foaming that accompanies the evolution of nitrogen is readily controlled by the occasional addition of small amounts of ether or benzene (Note 3). As the reaction proceeds, 100 ml. of 10% sodium hydroxide solution (0.25 mole) is added in 20-ml. portions. Stirring is continued for another hour, and then the mixture is warmed to 60° for 30 minutes and filtered with suction through a sintered-glass funnel. The residue on the funnel is washed with two 50-ml. portions of water. To the combined filtrate and washings is added concentrated hydrochloric acid (sp. gr. 1.19) until the solution is acid to litmus paper. The mixture is filtered, activated charcoal is added to the filtrate, and the solution is concentrated to about 350 ml. After the hot solution has been filtered with suction, concentrated hydrochloric acid is added until the solution is acid to Congo red paper. The solution is placed in a refrigerator overnight, and the crystals are collected on a Büchner funnel and washed twice with 20-ml. portions of ice water. The combined filtrates and washings are concentrated to about 150 ml., chilled, and filtered. The total quantity of crystals is dissolved in 10% ammonium hydroxide solution; the solution is filtered and again made acid to Congo red paper with concentrated hydrochloric acid. After the solution has been thoroughly chilled (preferably overnight), the *p*-nitrophenylarsonic acid is filtered on a Büchner funnel and washed with small portions of ice water until free of ammonium chloride. After drying, the yellow crystals melt with decomposition at 298–300.° The yield is 44–48.5 g. (71–79%) (Note 4).

2. Notes

1. The sodium arsenite solution may also be prepared by dissolving 39.6 g. (0.2 mole) of arsenious oxide and 32 g. (0.8 mole) of sodium hydroxide in 600 ml. of water.
2. According to the submitters *p*-nitrobenzenediazonium borofluoride may also be prepared as follows: *p*-Nitroaniline (34.5 g.) is dissolved in 63 ml. of concentrated hydrochloric acid (sp. gr. 1.19) and 50 ml. of water. The solution is cooled to 0°, and 17.3 g. of sodium nitrite in 40 ml. of water is added slowly with vigorous stirring. After the diazotization is complete, as indicated by a positive test with starch iodide paper, a solution of 55 g. of sodium fluoborate in 110 ml. of water is added. The thick slurry is stirred for 15 minutes and then filtered with suction and washed with ice water, twice with methanol, and twice with ether. The solid should be sucked as free as possible from liquid after each washing. The

compound may be kept in an evacuated desiccator until needed.

3. The checkers found that the foaming is more readily controlled by amyl alcohol than by the addition of ether or benzene.

4. This is a general method for preparing arylarsonic acids. The melting points and yields of other arsonic acids prepared by the submitters are as follows: phenyl, 156°, 58%; *o*-nitrophenyl, 232–234° dec., 67%; *m*-nitrophenyl, 182°, 47%; *o*-tolyl, 159–160°, 63%; *m*-tolyl, 150°, 54%; *p*-tolyl, 300° dec., 73%; *o*-chlorophenyl, 182°, 52%; *p*-chlorophenyl, above 300°, 63%; *o*-carboxyphenyl, above 300°, 65%; *p*-carboxyphenyl, 232° dec., 67%; *p*-carbethoxyphenyl, 260°, 60%; *p*-acetophenyl, 175°, 70%.

3. Discussion

p-Nitrophenylarsonic acid has been prepared by heating *p*-nitrobenzenediazonium chloride with arsenious acid in hydrochloric acid,[2] by the action of *p*-nitrobenzenediazonium chloride on sodium arsenite,[3] by the action of sodium arsenite on sodium *p*-nitrobenzeneisodiazo oxide,[4] by the diazotization of *p*-nitroaniline in acetic acid in the presence of arsenic chloride and cuprous chloride,[5] and by the reaction of *p*-nitrobenzenediazonium borofluoride with sodium arsenite in the presence of cuprous chloride.[6]

References and Notes

1. *Org. Syntheses* Coll. Vol. **2**, 225 (1943).
2. Bart, Ger. pat. 250,264 [*Frdl.*, **10**, 1254 (1910–12)].
3. Bart, *Ann.*, **429**, 95 (1922).
4. Bart, *Ann.*, **429**, 103 (1922); Jacobs, Heidelberger, and Rolf, *J. Am. Chem. Soc.*, **40**, 1580 (1918).
5. Scheller, U. S. pat. 1,704,106; Fr. pat. 624,028 [*Chem. Zentr.*, **98**, II, 2229 (1927)]; Brit. pat. 261,026; Ger. pat. 624,028 [*Frdl.*, **17**, 2372 (1930)].
6. Ruddy, Starkey, and Hartung, *J. Am. Chem. Soc.*, **64**, 828 (1942).

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

arsenious acid

arsenious oxide

sodium metaarsenite

sodium p-nitrobenzeneisodiazo oxide

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

ammonium chloride (12125-02-9)

sodium hydroxide (1310-73-2)

nitrogen (7727-37-9)

sodium nitrite (7632-00-0)

sodium arsenite

cuprous chloride (7758-89-6)

ammonium hydroxide (1336-21-6)

amyl alcohol (71-41-0)

Phenylarsonic acid (98-05-5)

sodium fluoborate (13755-29-8)

arsenic chloride

p-Nitrophenylarsonic acid,
Benzenearsonic acid, p-nitro- (98-72-6)

p-nitroaniline (100-01-6)

p-nitrobenzenediazonium borofluoride (456-27-9)

p-nitrobenzenediazonium chloride

o-nitrophenylarsonic acid

m-nitrophenylarsonic acid

o-tolylarsonic acid

m-tolylarsonic acid

p-tolylarsonic acid

o-chlorophenylarsonic acid

p-chlorophenylarsonic acid

o-carboxyphenylarsonic acid

p-carboxyphenylarsonic acid

p-carbethoxyphenylarsonic acid

p-acetophenylarsonic acid