



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](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.

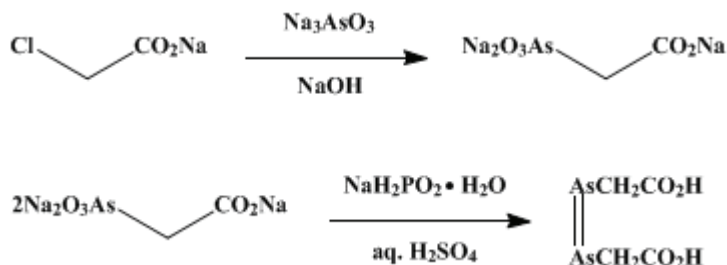
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

*Organic Syntheses, Coll. Vol. 1, p.73 (1941); Vol. 4, p.5 (1925).*

## ARSONO- AND ARSENOACETIC ACIDS

### [Acetic acid, arsono-, and Acetic acid, arsenodi-]



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Checked by Oliver Kamm

### 1. Procedure

(A) *Arsonoacetic Acid*.—One hundred grams (0.51 mole) of powdered arsenious oxide is added to the hot solution obtained by dissolving 160 g. (4 moles) of sodium hydroxide in 300 cc. of water. After the solution has cooled to 20°, 48 g. (0.51 mole) of chloroacetic acid is added. The suspension is well stirred during about five minutes, when a strongly exothermic reaction begins, the temperature rises to 70–75°, and a clear solution results.

The reaction mixture is permitted to stand at room temperature during one hour, or longer if desired (Note 1). The solution is acidified with 160 cc. of glacial acetic acid and, after the temperature has been lowered to 40° by cooling, the precipitated arsenious oxide is filtered off by suction and washed with 50 cc. of water.

The filtrate is poured into a solution containing 185 g. (0.76 mole) of crystallized barium chloride dissolved in 600 cc. of hot water. Barium arsonoacetate,  $\text{Ba}(\text{O}_2\text{CCH}_2\text{AsO}_3)_2$  (hydrated), forms a thick, finely divided precipitate. The mixture is stirred for several minutes and then allowed to stand until the following day, when it is filtered upon a 15-cm. Büchner funnel and washed thoroughly with water (Note 2). The yield of air-dried product is 220 g. (96 per cent of the theoretical amount) (Note 3).

Sodium arsonoacetate is prepared by adding the freshly filtered and washed barium arsonoacetate as obtained above (without drying) to a solution of 108 g. (0.76 mole) of anhydrous sodium sulfate in 500 cc. of hot water. The mixture is mechanically stirred for one hour, the barium sulfate filtered off, and the filtrate concentrated on the steam bath until crystallization commences. Upon cooling and stirring (Note 4), sodium arsonoacetate separates and is filtered by suction, the filtrate being concentrated to obtain a second crop of crystals. The yield of the combined fractions is 100–110 g. (80–88 per cent of the theoretical amount).

(B) *Arsenoacetic Acid*.—A solution of 12.5 g. of sodium arsonoacetate and 30 g. of sodium hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ) in 150 cc. of cold 15 per cent sulfuric acid is allowed to stand at room temperature. After two or three days, the yellow precipitate is filtered off, washed with water, and dried in a vacuum over sulfuric acid or phosphorus pentoxide. A second crop is obtained by allowing the mother liquid to stand for two days longer.

The arsenoacetic acid consists of minute yellow needles, which do not melt below 260° although they undergo considerable decomposition above 200°. The yield is 5 g. (74 per cent of the theoretical amount).

### 2. Notes

1. The reaction between sodium arsenite and chloroacetic acid is very rapid, as may easily be

demonstrated by titrating 1-cc. portions of the solution with 0.1 *N* iodine, according to the usual volumetric method for arsenious acid, before and after the reaction with chloroacetic acid. The excess of sodium arsenite is necessary, as was learned by means of an iodimetric study of the reaction.

2. If the thick paste is not allowed to stand overnight, filtration is more cumbersome and it is extremely difficult to wash the precipitate free from arsenites. With this precaution, it is found that after five washings with 250-cc. portions of water, the final filtrate, as well as the desired barium salt, is practically free from iodine-reducing compounds.

3. The air-dried sample contains 13 per cent of water of hydration, as determined by actual analysis.

4. Stirring is required during the crystallization process, since otherwise the product tends to form a solid cake. The sodium salt is obtained without water of crystallization. Usually it contains a trace of sulfate but this does not interfere with its subsequent use. The sulfate may be removed by recrystallization from water.

### 3. Discussion

Arsonoacetic acid can be prepared by the action of sodium arsenite with sodium chloroacetate followed by isolation as the calcium,<sup>1</sup> lead<sup>2</sup> or barium<sup>3</sup> salt. The procedures described for the preparation of arsono- and arsonoacetic acids have been published.<sup>3</sup>

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### References and Notes

1. Friedr. Bayer and Co., U. S. pat. 1,445,685 [Chem. Zentr. I, 965 (1924)]; Austrian pat. 93,325 [Chem. Zentr. II, 721 (1923)]; Swiss pat. 97,977 [Chem. Zentr. II, 721 (1923)].
2. Ramberg and Ohman, Svensk. Kem. Tids. **36**, 119 (1924) [C. A. **19**, 36 (1925)].
3. Palmer, J. Am. Chem. Soc. **45**, 3023 (1923); Marquez, Anales asoc. quím. argentina **27**, 258 (1939) [C. A. **34**, 4726 (1940)].

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

arsenious acid

#### ARSONO- AND ARSENOACETIC ACIDS

Acetic acid, arsenodi-

arsenious oxide

Arsenoacetic acid

sodium hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ )

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

sodium hydroxide (1310-73-2)

sodium sulfate (7757-82-6)

Acetic acid, arsono-,  
Arsonoacetic acid (107-38-0)

chloroacetic acid (79-11-8)

barium chloride (10361-37-2)

Barium arsonoacetate

Sodium arsonoacetate (27152-51-8)

barium sulfate (7727-43-7)

sodium arsenite

iodine (7553-56-2)

sulfate (14808-79-8)

sodium chloroacetate (3926-62-3)

phosphorus pentoxide (1314-56-3)