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.

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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.

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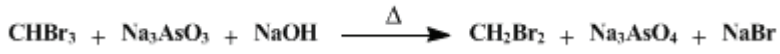
METHYLENE BROMIDE

[Methane, dibromo-]



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1. Procedure

In a 2-l. round-bottomed flask placed on a steam bath and fitted with a stirrer, a separatory funnel, and a reflux condenser is placed 540 g. (1.9 moles) of commercial (88 per cent) bromoform (Note 1). There is then added 10 cc. of a solution of sodium arsenite made by dissolving 230 g. (1.16 moles) of c. p. arsenious oxide and 440 g. (11 moles) of sodium hydroxide in 1.4 l. of water. The mixture is warmed gently to start the reaction, and then the remainder of the sodium arsenite solution is added during about one hour at such a rate that the solution refluxes gently. When the addition is complete, the flask is heated for four hours on the steam bath. The reaction mixture is distilled with steam, the lower layer of methylene bromide separated, and the water layer extracted once with 100 cc. of ether (Note 2). The methylene bromide is dried with 10 g. of calcium chloride and distilled. The yield of slightly yellow liquid boiling at 97–100° is 290–300 g. (88–90 per cent of the theoretical amount).

2. Notes

1. The commercial bromoform used contained 12 per cent of alcohol. Its specific gravity was 2.59/25° as compared with 2.88/25° for pure bromoform.
2. The chief function of the extraction is to collect the fine droplets of methylene bromide which remain in the water layer.

3. Discussion

Methylene bromide can be prepared by the reaction of bromine with methylene iodide.[1] The procedure described is adapted from the preparation of methylene iodide given below, and a like method giving a lower yield has been described.[2]

References and Notes

1. Butlerow, Ann. **111**, 251 (1859).
2. Kocheshkov, J. Russ. Phys. Chem. Soc. **60**, 1191 (1928) [C. A. **23**, 2931 (1929)]; Ber. **61**, 1659 (1928).

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

arsenious oxide

alcohol (64-17-5)

calcium chloride (10043-52-4)

ether (60-29-7)

sodium hydroxide (1310-73-2)

bromine (7726-95-6)

sodium arsenite

Methylene bromide,
Methane, dibromo- (74-95-3)

bromoform (75-25-2)

Methylene iodide (75-11-6)