



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.

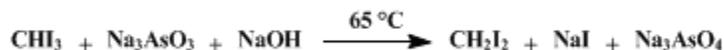
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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METHYLENE IODIDE

[Methane, diiodo-]



Submitted by Roger Adams and C. S. Marvel.

Checked by H. T. Clarke and Katharine Ogden.

1. Procedure

One kilogram (2.5 moles) of **iodoform** (Note 1) is placed in a 5-l. round-bottomed flask fitted with a rubber stopper holding a mechanical stirrer (Note 2), a reflux condenser, a separatory funnel, and a thermometer with bulb immersed in the liquid. To this is added 500 cc. of the **sodium arsenite** solution [prepared from 274 g. (1.38 moles) of c. p. arsenious oxide, 532 g. (13.3 moles) of **sodium hydroxide**, and 2600 cc. of water] (Note 3). Stirring is started, and heat is applied until the temperature of the thermometer reaches 60–65°, where it is held constant during the whole reaction (Note 4). If the temperature is allowed to go much higher, especially at the beginning of the experiment, the reaction becomes too vigorous, and at the same time a little **methyl iodide** is formed. The remainder of the **sodium arsenite** solution is added gradually during the course of one-half hour. The whole mixture is then kept one hour at 60–65° to make sure that the reaction is completed.

The reaction mixture is allowed to cool somewhat (to about 40°) and is filtered with suction in order to remove the mechanical impurities which have come from the technical arsenious oxide and **sodium hydroxide**. The filtrate consists of a clear water solution with a pale yellow oil underneath. It is better not to allow the reaction mixture to cool completely before filtering or else a precipitate of **sodium arsenate** will gradually separate and this will tend to make an emulsion of the **methylene iodide** and hinder filtration and separation. The **methylene iodide** is now separated from the filtrate, dried with a little **calcium chloride**, and then distilled under reduced pressure. Practically all of it (Note 5) comes over as a light straw-colored oil between 106° and 107°/70 mm. (Note 6), the bath being kept at 130–135°. The yield of crude product is 610–660 g. (90–97 per cent of the theoretical amount). On redistillation not more than 10–20 g. is lost. The crude product is quite satisfactory for most purposes.

2. Notes

1. Experiments were made on 100-g. lots of **iodoform**, using varying amounts (between 1 mole and 2 moles) of **sodium arsenite**. The yield is, in general, best when only a very slight excess over 1 mole of arsenious oxide is used. In every case the amount of **sodium hydroxide** employed was that called for by the theory.

In making **methylene iodide** from 100-g. or even 200-g. lots of **iodoform**, the **sodium arsenite** solution may be added all at once. When the runs become larger, however, it is inadvisable to do this, and directions similar to those described above in running 1 kg. of **iodoform** must be used.

2. Mechanical stirring is quite necessary in order to get the best yields in the shortest time.

3. The dilution of the solution makes very little difference, the yields remaining about the same. It is, therefore, better to use as concentrated a solution as possible so that large runs may be made in a comparatively small apparatus. A more concentrated solution, however, than the one advised above is not satisfactory, since too much **sodium arsenate** tends to separate out during the cooling after the **methylene iodide** has formed and causes some trouble in the purification. If **sodium arsenate** does separate, the **methylene iodide** is obtained either by distilling with steam, or by diluting and boiling to dissolve the crystals, this last to be followed by filtering and separating.

4. If the reaction is carried out at refluxing temperature instead of at 60–65°, the yield of product is diminished by 5–10 per cent, the formation of a little **methyl iodide** accounting for the loss.

5. After distillation under reduced pressure, a residue of 1 to 2 g. is left in the flask. When air is admitted to the flask, a single flash of light sometimes occurs. In one case, the thermometer and stopper

were even blown out of the flask. The cause was not determined.
6. The [methylene iodide](#) obtained after distillation under reduced pressure melts at 6°.

3. Discussion

[Methylene iodide](#) can be prepared by the action of iodine,¹ [sodium ethoxide](#),² [hydriodic acid](#),³ and [sodium arsenite](#)⁴ on [iodoform](#). This last method is very simple, and several pounds of pure [methylene iodide](#) may be prepared in a few hours. It can also be prepared from [methylene chloride](#) and [potassium iodide](#),⁵ and in an excellent yield by the oxidation of [iodoacetic acid](#) by [potassium persulfate](#).⁶

References and Notes

1. Hofmann, Ann. **115**, 267 (1860).
 2. Butlerow, Ann. chim. phys. (3) **53**, 313 (1858).
 3. Lieben, Z. Chem. 712 (1868).
 4. Auger, Compt. rend. **145**, 810 (1907); **146**, 1282 (1908); Gutmann, Ber. **52**, 212 (1919).
 5. Perkin and Scarborough, J. Chem. Soc. **119**, 1400 (1921).
 6. Panopoulos and Petzetakis, Chem. Ztg. **54**, 310 (1930).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[arsenious oxide](#)

[calcium chloride](#) (10043-52-4)

[sodium hydroxide](#) (1310-73-2)

[potassium iodide](#) (7681-11-0)

[sodium arsenite](#)

[sodium ethoxide](#) (141-52-6)

[hydriodic acid](#) (10034-85-2)

[Methyl iodide](#) (74-88-4)

[Methylene iodide](#),
[Methane, diiodo-](#) (75-11-6)

[iodoform](#) (75-47-8)

[sodium arsenate](#)

[methylene chloride](#) (75-09-2)

[iodoacetic acid](#) (64-69-7)

potassium persulfate (7727-21-1)

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