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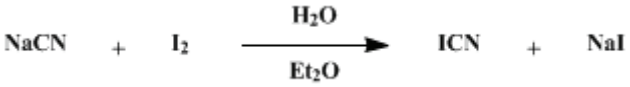
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.032.0029

Organic Syntheses, Coll. Vol. 4, p.207 (1963); Vol. 32, p.29 (1952).

CYANOGEN IODIDE

[Iodine cyanide]



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Checked by R. T. Arnold and H. E. Fritz.

1. Procedure

Caution! Cyanogen iodide is relatively volatile and highly toxic. Therefore, these operations should be conducted in a good hood.

A three-necked 500-ml. flask is surrounded by an ice-water bath and provided with a stirrer and thermometer. Twenty-seven grams (0.55 mole) of sodium cyanide is dissolved in 100 ml. of water, added to the reaction flask, and cooled to 0°. To this, in 3- to 4-g. portions, is added with good stirring a total of 127 g. (0.50 mole) of iodine over a period of 30–40 minutes. A given portion of iodine is not added until the preceding one has reacted almost completely. Ten minutes after the addition of iodine is completed, 120 ml. of peroxide-free ether is added and the mixture is stirred for a few minutes until the precipitated cyanogen iodide has dissolved in the ethereal layer. The entire contents are then transferred to a previously cooled separatory funnel, and the aqueous layer is separated. This aqueous solution is again extracted successively with 100-ml. and 80-ml. portions of cold, peroxide-free ether. The combined ethereal extracts are poured into a 500-ml. round-bottomed flask, and the ether is evaporated under reduced pressure at room temperature. To the slightly brown crude product, which weighs about 90 g., is added 120 ml. of water. A slightly diminished pressure (½ atm.) is maintained while the contents in the closed flask are heated at 50° for 15 minutes with occasional vigorous shaking (Note 1). The mixture is then cooled to 0°, and the crystalline cyanogen iodide is separated from the light yellow mother liquor by suction on a sintered-glass funnel or filter plate (Note 2). The crude product is washed with six 25-ml. portions of ice water, removed from the sintered-glass funnel, and air-dried (in a good hood) for 1 hour at room temperature. Colorless cyanogen iodide weighing about 59 g. (77%) is obtained; m.p. 141–144° (Note 3).

Cyanogen iodide of highest purity may be produced in the following way. The above crude product is dissolved in 150 ml. of boiling chloroform, and the solution is filtered through a plug of glass-wool on a hot-water funnel into a 250-ml. Erlenmeyer flask. This solution, after being cooled at room temperature for 15 minutes, is placed in an ice-salt bath and cooled to −10° (Note 4). By means of suction filtration, the crystalline product is collected on a sintered-glass funnel, washed with three 15-ml. portions of cold chloroform (0°), and freed from the last traces of solvent by being placed on a watch glass and exposed to the atmosphere (in a good hood) at room temperature for 1 hour. Practically colorless needle-shaped crystals weighing 45 g. (59%) are obtained; m.p. 146–147° (Note 3) and (Note 5).

Removal of 100 ml. of chloroform from the above filtrate by means of evaporation under reduced pressure at room temperature and subsequent cooling permits isolation of an additional 2 g. of cyanogen iodide; m.p. 146–147°. The total yield thus becomes 47 g. (62% based on iodine).

2. Notes

1. In this way sodium iodide, soluble in the solution of cyanogen iodide in ether [complex formation of $NaI_2(CN)$], is removed. This complex is avoided in the procedure by Ketelaar and Kruyer[2] in which chlorine is used. The method adopted here is faster and simpler and gives almost the same yield of

purified cyanogen iodide.
2. Contact with filter paper must be avoided.
3. Determinations of the melting point of cyanogen iodide must be made using a sealed capillary which is kept totally immersed in the heating bath.
4. When the chloroform solution is cooled, a small aqueous layer is observed which finally separates as ice. The ice is filtered with cyanogen iodide but melts on the filter plate and is removed with the chloroform used as washing liquid.
5. Owing to the volatility of cyanogen iodide, the yield is slightly dependent on the speed of operation. By the above method sublimation as a means of purification is avoided. If, however, sublimation is desirable, it can be accomplished with appreciable speed only under reduced pressure and at temperatures at which cyanogen iodide is slowly decomposed into iodine and cyanogen. The vacuum must be constantly renewed during the operation.

3. Discussion

Cyanogen iodide has been prepared from mercuric cyanide and iodine,[3] potassium cyanide and iodine,[4] and sodium cyanide and iodine.[5]

References and Notes

1. Universitetets Kemiske Laboratorium, Copenhagen K, Denmark.
2. Ketelaar and Kruyer, *Rec. trav. chim.*, **62**, 550 (1943).
3. Seubert and Pollard, *Ber.*, **23**, 1062 (1890); Woolf, *J. Chem. Soc.*, **1953**, 4121.
4. Grignard and Crouzier, *Bull. soc. chim. France*, [4] **29**, 214 (1921).
5. Moller, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **14**, 3 (1936).

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

ether (60-29-7)

chloroform (67-66-3)

sodium cyanide (143-33-9)

cyanogen

potassium cyanide (151-50-8)

iodine (7553-56-2)

chlorine (7782-50-5)

sodium iodide (7681-82-5)

mercuric cyanide (592-04-1)

Cyanogen iodide,
Iodine cyanide (506-78-5)