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.

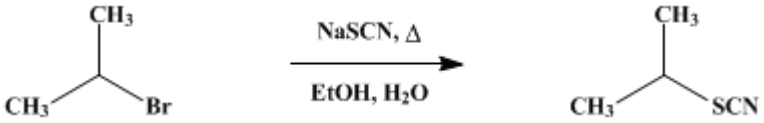
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.011.0092

Organic Syntheses, Coll. Vol. 2, p.366 (1943); Vol. 11, p.92 (1931).

ISOPROPYL THIOCYANATE

[Thiocyanic acid, isopropyl ester]



Submitted by R. L. Shriner
Checked by C. R. Noller

1. Procedure

In a 3-l. round-bottomed flask, fitted with a very efficient mechanical stirrer (Note 1), a reflux condenser, and a 500-cc. separatory funnel, are placed 445 g. (5.5 moles) of sodium thiocyanate (Note 2) and 1250 cc. of 90 per cent ethyl alcohol. The stirrer is started and the mixture is heated to boiling. Then 615 g. (5 moles) of isopropyl bromide (p. 359; Org. Syn. Coll. Vol. I, **1941**, 37) is added slowly during the course of one hour. The mixture is refluxed with stirring for six hours. At the end of this time the precipitated sodium bromide is removed by filtration and washed with 250 cc. of 95 per cent alcohol. As much of the alcohol as possible is then removed by distillation on the steam bath. To the residue in the flask is added 500 cc. of water, and the upper layer of isopropyl thiocyanate is separated. The aqueous layer is extracted with two 100-cc. portions of ether (Note 3). The ether extracts are added to the crude thiocyanate, and the combined product is dried over anhydrous sodium sulfate (Note 4). The dried material is fractionated twice from a modified Claisen flask with a 25-cm. fractionating column. The following fractions are collected: up to 60°; 60–100°; 100–130°; 130–146°; and 146–151°. The last fraction contains the pure product. The yield is 320–345 g. (63–68 per cent of the theoretical amount). By redistilling the alcohol that was removed on the steam bath through an efficient fractionating column (Note 5) until all the alcohol is removed (Note 6), separating the water, and distilling, there is obtained an additional 55–65 g. of product boiling at 146–151°. The total yield is 385–400 g. (76–79 per cent of the theoretical amount). On redistillation of the combined fractions boiling at 146–151°, practically the entire amount distils at 149–151°.

2. Notes

1. A vigorous mechanical stirrer must be used to prevent the precipitated sodium bromide from settling to the bottom and causing bumping.
2. A technical grade of sodium thiocyanate was used. Potassium thiocyanate does not possess any advantages over the sodium salt.
3. If benzene is used to extract the aqueous layer, three fractionations are necessary to obtain the same yields.
4. The sodium sulfate does not remove the water entirely, and in the subsequent fractionation the water layer should be removed by means of a separatory funnel wherever it appears.
5. An eight-bubbler fractionating column of the type described by Clarke and Rahrs[1] was used.
6. Distillation was continued until water began to appear in the lowest bubbler.

3. Discussion

Isopropyl thiocyanate has been prepared by the action of isopropyl iodide on potassium thiocyanate.[2]

References and Notes

1. Clarke and Rahrs, Ind. Eng. Chem. **18**, 1092 (1926).

2. Henry, Ber. **2**, 496 (1869); Gerlich, Ann. **178**, 80 (1875).

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

ethyl alcohol,
alcohol (64-17-5)

Benzene (71-43-2)

ether (60-29-7)

sodium bromide (7647-15-6)

Isopropyl bromide (75-26-3)

sodium sulfate (7757-82-6)

potassium thiocyanate (333-20-0)

isopropyl iodide (75-30-9)

Isopropyl thiocyanate,
Thiocyanic acid, isopropyl ester (625-59-2)

sodium thiocyanate (540-72-7)