



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.

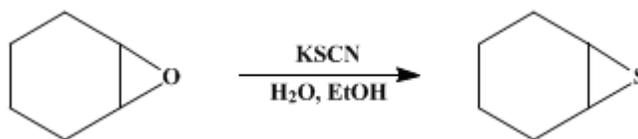
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.232 (1963); Vol. 32, p.39 (1952).

CYCLOHEXENE SULFIDE

[7-Thiabicyclo[4.1.0]heptane]



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1. Procedure

Ninety-eight grams (1 mole) of cyclohexene oxide (Note 1) is divided into two approximately equal portions; one portion is added to a solution of 121 g. (1.25 moles) of potassium thiocyanate in 100 ml. of water and 75 ml. of 95% ethanol. After standing for 3–4 hours (Note 2) the clear solution is transferred to a 1-l. flask equipped with a mechanical stirrer. The second portion of oxide is added, and the resulting solution is stirred vigorously for 36 hours at room temperature. The supernatant layer and the aqueous phase are then decanted from the precipitated potassium cyanate into a 1-l. separatory funnel. The potassium cyanate is rinsed with 50 ml. of ether, which is subsequently added to the separatory funnel and used to extract the cyclohexene sulfide. The ether extract is washed twice with 50-ml. portions of saturated sodium chloride solution and then dried over anhydrous sodium sulfate. The excess ether is removed on the steam bath, and the residual liquid is distilled under reduced pressure through an 18-in. Vigreux column while the distillate is being cooled in ice. The main fraction boils at 71.5–73.5°/21 mm. (69–71°/19 mm.) (Note 3); n_D^{25} 1.5306–1.5311. A fore-run, boiling up to 71.5°/21 mm., yields more of the product on redistillation. The total yield of cyclohexene sulfide is 81.5–83.5 g. (71–73%).

2. Notes

1. The cyclohexene oxide (b.p. 129–134°) was prepared from 2-chlorocyclohexanol.²
2. During this time a temperature rise of about 5° occurs.
3. Cyclohexene sulfide can be stored at about 5° in a closed container for at least a month without apparent decomposition.

3. Discussion

Cyclohexene sulfide has been prepared by the action of thiourea, potassium thiocyanate, or ammonium thiocyanate on cyclohexene oxide,³ by the hydrolysis of S-(*trans*-2-hydroxycyclohexyl) thiuronium sulfate in sodium carbonate solution,⁴ and by the alkaline hydrolysis of 2-mercaptopcyclohexyl acetate or 2-acetylmercaptocyclohexyl acetate.⁵

The method described above is a modification of that of Snyder, Stewart, and Ziegler.⁶

References and Notes

1. University of Wisconsin, Madison, Wisconsin.
2. *Org. Syntheses Coll. Vol. 1*, 185 (1941).
3. Culvenor, Davies, and Pausacker, *J. Chem. Soc.*, **1946**, 1050.
4. Bordwell and Andersen, *J. Am. Chem. Soc.*, **75**, 4959 (1953).
5. Harding, Miles, and Owen, *Chem. & Ind. (London)*, **1951**, 887.
6. Snyder, Stewart, and Ziegler, *J. Am. Chem. Soc.*, **69**, 2672 (1947).

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

ethanol (64-17-5)

ether (60-29-7)

ammonium thiocyanate (1762-95-4)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

2-Chlorocyclohexanol (1561-86-0)

Cyclohexene oxide (286-20-4)

potassium thiocyanate (333-20-0)

potassium cyanate (590-28-3)

thiourea (62-56-6)

Cyclohexene sulfide,
7-Thiabicyclo[4.1.0]heptane (286-28-2)

2-mercaptocyclohexyl acetate

2-acetylmercaptocyclohexyl acetate

S-(trans-2-hydroxycyclohexyl)thiuronium sulfate