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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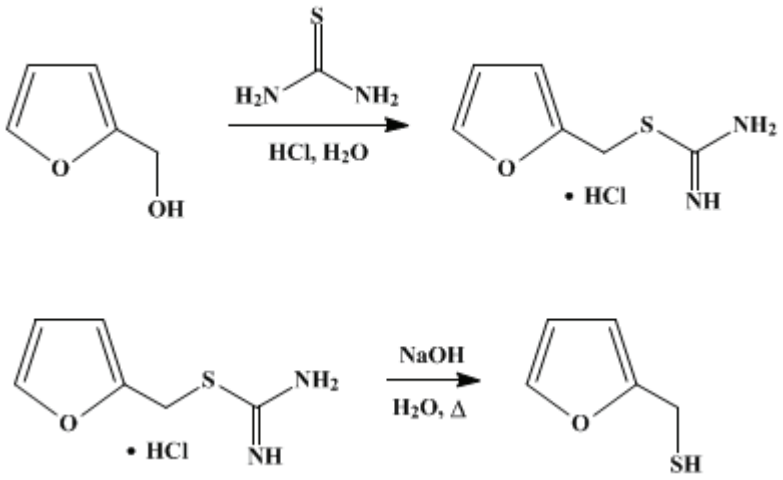
2-FURFURYL MERCAPTAN

[2-Furanmethanethiol]



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1. Procedure

The following operations should be carried out in an effective hood (Note 1).

In a 3-l. round-bottomed flask are placed 380 g. (5 moles) of thiourea (Note 2), 500 ml. of water, and 400 ml. of concentrated hydrochloric acid (12.5*N*) (Note 3). The solid is dissolved by gentle heating, and the solution is cooled to 30°. Furfuryl alcohol (490 g., 434 ml., 5 moles) (Note 4) is added to the reaction mixture. The reaction, which usually commences spontaneously within a few minutes (Note 5), is strongly exothermic and should be controlled by suitable cooling with tap water so as to hold the temperature near 60° (Note 6). When the reaction subsides, cooling is discontinued and the clear, dark green solution is allowed to stand at room temperature for 12 hours.

A solution of 225 g. of sodium hydroxide (Note 3) in 250 ml. of water is poured into the reaction mixture. A heavy brown oil separates, consisting of S-2-furfurylisothiourea, which has already partially decomposed to 2-furfuryl mercaptan. The flask is quickly fitted with a steam-inlet tube and condenser. Steam distillation is continued as long as the distillate contains oily drops. The mercaptan is separated from the aqueous phase by means of a separatory funnel (Note 7) and (Note [*****note*****]). The product is dried with calcium chloride; yield 313–340 g. (55–60%). The 2-furfuryl mercaptan so obtained is of a high degree of purity (Note 9) but can be distilled without decomposition in a nitrogen atmosphere; b.p. 160°/759 mm., 84°/65 mm., n_D^{20} 1.533.

2. Notes

1. The odor of the mercaptan is extremely disagreeable, and the substance in high concentration causes headache. An effective hood is absolutely essential.
2. The checkers employed practical grade thiourea obtained from Matheson, Coleman and Bell, East Rutherford, New Jersey.
3. It is desirable to determine the exact concentration of the hydrochloric acid and the composition of the sodium hydroxide by titration.
4. The checkers employed practical grade furfuryl alcohol obtained from the Eastman Kodak Company.
5. If the reaction does not start, the flask is heated gently until a spontaneous temperature rise sets in.

6. Temperatures above 60° and particularly supplementary refluxing are to be avoided since under these conditions the sensitive furan ring is attacked.
7. The mercaptan is almost insoluble in water, and the aqueous phase contains too little product to justify extraction.
8. It is convenient to use a 2-l. separatory funnel as a receiver during the steam distillation.
9. The checkers found the undistilled product to be essentially pure; n_D^{25} 1.5285. The distilled material was obtained with only mechanical losses; b.p. 84°/65 mm., n_D^{25} 1.5280.

3. Discussion

Furfuryl mercaptan cannot be prepared according to the classical method using furfuryl chloride and potassium sulfide.[2] It has been prepared by reduction of 2-furfuryl disulfide, obtained from furfural and ammonium hydrosulfide.[3] The mercaptan has also been obtained in 33% yield[2] by the reaction of furfuryl chloride with thiourea and subsequent decomposition of the intermediate S-2-furfurylisothiourea according to the general method described in *Organic Syntheses*.[4] In the present method, which has been published previously, the use of the very unstable and difficulty available furfuryl halides is avoided.[5]

The formation of mercaptans directly from alcohols may be applied to the preparation of a large number of mercaptans, but usually much longer reaction periods or higher temperatures and higher concentrations of hydrogen halides are required.[6] Under such conditions the furan ring is destroyed.

References and Notes

1. Danmarks farmaceutiske Højskole, Copenhagen, Denmark.
2. Kirner and Richter, *J. Am. Chem. Soc.*, **51**, 3131 (1929).
3. Staudinger and Reichstein, Can. pat. 283,765 [*C. A.*, **22**, 4537 (1928)].
4. *Org. Syntheses Coll. Vol.* **3**, 363 (1955).
5. Kofod, *Acta Chem. Scand.*, **7**, 1302 (1953).
6. Frank and Smith, *J. Am. Chem. Soc.*, **68**, 2103 (1946).

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

S-2-furfurylisothiourea

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

nitrogen (7727-37-9)

potassium sulfide (1312-73-8)

Furan (110-00-9)

Furfural (98-01-1)

Furfuryl alcohol (98-00-0)

thiourea (62-56-6)

2-Furfuryl mercaptan

2-Furanmethanethiol,
Furfuryl mercaptan (98-02-2)

furfuryl chloride

2-furfuryl disulfide

ammonium hydrosulfide (12135-76-1)