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.

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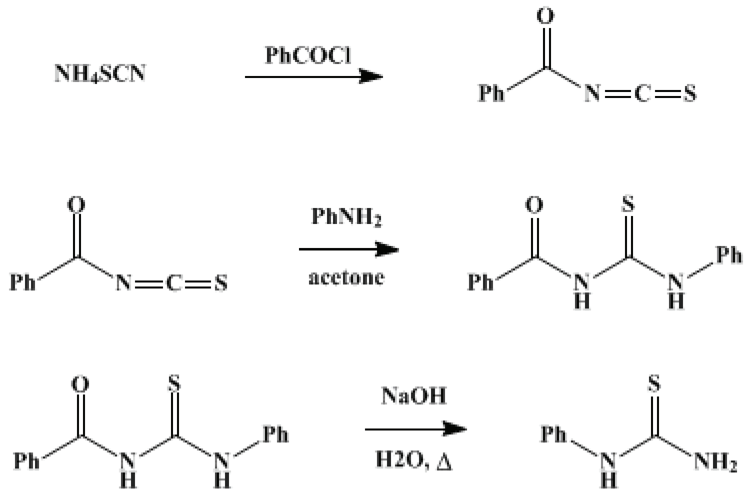
α-PHENYLTHIOUREA

[Urea, 1-phenyl-2-thio-]



Submitted by Robert L. Frank and Paul V. Smith[1].
Checked by Richard T. Arnold and Sherman Sundet.

1. Procedure

In a 500-ml. three-necked flask fitted with a reflux condenser, a mechanical stirrer, and a 100-ml. dropping funnel are placed 17 g. (0.22 mole) of ammonium thiocyanate and 100 ml. of dry acetone (Note 1). Through the dropping funnel is added, with stirring, 28.2 g. (0.2 mole) of benzoyl chloride. After the addition is complete, the mixture is refluxed for 5 minutes. Then a solution of 18.6 g. (0.2 mole) of aniline in 50 ml. of dry acetone is added at such a rate that the solution refluxes gently. The mixture is poured carefully with stirring into 1.5 l. of water, and the resulting yellow precipitate (α-benzoyl-β-phenylthiourea) is separated by filtration. The crystals are heated for 5 minutes with a boiling solution of 30 g. of sodium hydroxide in 270 ml. of water. After the removal of a small amount of insoluble material by filtration, the solution is acidified with concentration hydrochloric acid and then made slightly basic with ammonium hydroxide. Upon standing, the solution deposits the crystalline product. The yield of oven-dried material (m.p. 151–153°) is 25.8 g. (85%). Recrystallization from ethanol yields 23.2 g. (76%) of white plates melting at 152.5–153°.

2. Notes

1. The acetone is dried for at least 48 hours over anhydrous calcium sulfate (Drierite) and distilled just before it is used.

3. Discussion

α-Phenylthiourea has been prepared by the action of ammonium thiocyanate,[2] thiocyanic acid,[3] thiuramdisulfide,[4] or silicon thiocyanate[5] on aniline; by the action of ammonium thiocyanate on aniline hydrochloride;[6] by the action of ammonia on phenyl isothiocyanate,[7] 1-phenyl-2-thiobiuret,[8] thiocarbanilide,[9] phenyldithiocarbamazide,[10] or phenyl isothiocyanate hexasulfide;[11] by the addition of hydrogen sulfide to monophenylcyanamide;[12] by the decomposition of salts of phenyldithiocarbamic acid in the presence of lead carbonate,[13] ammonium polysulfide,[14] or ammonium carbonate;[15] by the reaction of thiophosgene, aniline, and ammonia;[16] and by the action of hydrazine hydrate on phenyldithiobiuret.[17]

The preparation of α-phenylthiourea by the procedure described herein has not been reported, although Douglass and Dains[18] have applied the method to the preparation of various substituted phenyl derivatives.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 700

References and Notes

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

phenyl isothiocyanate hexasulfide

ammonium polysulfide

α-Phenylthiourea

α-benzoyl-β-phenylthiourea

salts of phenyldithiocarbamic acid

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ammonium carbonate (506-87-6)

ammonia (7664-41-7)

ammonium thiocyanate (1762-95-4)

aniline (62-53-3)

sodium hydroxide (1310-73-2)

hydrogen sulfide (7783-06-4)

aniline hydrochloride (142-04-1)

calcium sulfate (7778-18-9)

acetone (67-64-1)

benzoyl chloride (98-88-4)

Thiophosgene (463-71-8)

ammonium hydroxide (1336-21-6)

hydrazine hydrate (7803-57-8)

PHENYL ISOTHIOCYANATE (103-72-0)

Urea, 1-phenyl-2-thio- (103-85-5)

thiocarbanilide (102-08-9)

thiocyanic acid (463-56-9)

thiuramdisulfide

silicon thiocyanate

1-Phenyl-2-thiobiuret (53555-72-9)

phenyldithiocarbamazide

monophenylcyanamide

phenyldithiobiuret

lead carbonate