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.

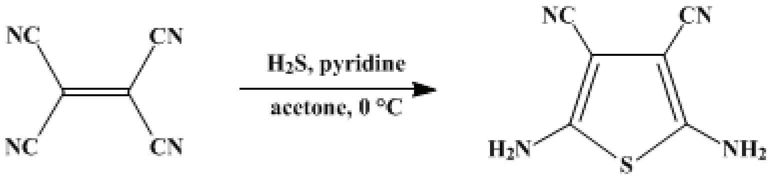
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.039.0008

Organic Syntheses, Coll. Vol. 4, p.243 (1963); Vol. 39, p.8 (1959).

2,5-DIAMINO-3,4-DICYANOTHIOPHENE

[3,4-Thiophenedicarbonitrile, 2,5-diamino-]



Submitted by W. J. Middleton[1]
Checked by James Cason and Ralph J. Fessenden.

1. Procedure

Since carbon disulfide is highly flammable and hydrogen sulfide highly toxic, this reaction should be carried out in a hood, with due precaution against fire. It is also recommended that tetracyanoethylene not be allowed to come into contact with the skin.

A 1-l. three-necked flask is fitted with a sealed mechanical stirrer, a condenser protected by a drying tube, a thermometer, and an inlet tube extending to the bottom of the flask. A solution of 25.6 g. (0.2 mole) of recrystallized tetracyanoethylene (p. 877) in 300 ml. of acetone is placed in the flask, and 300 ml. of carbon disulfide is added. The flask and its contents are cooled to 0° by means of a salt-ice bath. With good stirring, hydrogen sulfide is passed into the reaction mixture at a moderate rate while the temperature is maintained at 0–5°. The solution becomes milky after a few minutes owing to the formation of colloidal sulfur. The hydrogen sulfide addition is continued for about 30 minutes, or until the solution is thoroughly saturated.

The hydrogen sulfide addition is temporarily suspended, and 100 ml. of pyridine is added rapidly in one portion through the condenser as the solution is stirred vigorously (Note 1). The solution becomes clear, and then 2,5-diamino-3,4-dicyanothiophene begins to precipitate immediately. The hydrogen sulfide addition is resumed and is continued for about 30 minutes while the temperature of the reaction mixture is maintained at 0–5°. Finally, the reaction mixture is stirred for an additional 30 minutes at 0–5°, then the yellow precipitate of the thiophene is collected on a Büchner funnel, thoroughly washed with about 500 ml. of acetone, and dried in the air or in a vacuum desiccator. The yield of crude product of yellow or buff color amounts to 30–31 g. (92–95%).

This material is sufficiently pure for most purposes. If a purer product is desired, the crude material is dissolved in 300 ml. of dimethylformamide, 10 g. of activated alumina (48–100 mesh) is added, and the mixture is filtered. The filtrate is heated to 80–90° on a steam bath, then 1 l. of boiling water is added immediately (Note 2). The resultant mixture is cooled in an ice bath, and the light buff crystals of 2,5-diamino-3,4-dicyanothiophene that separate are collected on a Büchner funnel and thoroughly washed with 500 ml. of acetone; weight 26–28 g. (79–85%). The product has no definite melting point but sublimes with some decomposition when heated above 250°.

2. Notes

1. Unless the pyridine is added quite rapidly, some of the product will begin to precipitate before all of the sulfur has dissolved, and the final product will be contaminated with sulfur.
2. This operation should be carried out as rapidly as possible, since prolonged heating in dimethylformamide results in loss of product.

3. Discussion

2,5-Diamino-3,4-dicyanothiophene has been prepared only by the action of hydrogen sulfide or sodium sulfide on tetracyanoethylene or tetracyanoethane.[2] Unlike most aminothiophenes, 2,5-diamino-3,4-dicyanothiophene is very stable and can be stored indefinitely. Its amino groups show the normal reactivity of aromatic amines. For example, they readily condense with aromatic aldehydes to form highly colored bis-anils.[2] Hot 10% sodium hydroxide rearranges 2,5-diamino-3,4-dicyanothiophene to 2-amino-3,4-dicyano-5-mercaptopyrrole.[2]

References and Notes

1. Contribution No. 483 from Central Research Department, Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Delaware.
2. Middleton, Englehardt, and Fisher, *J. Am. Chem. Soc.*, **80**, 2822 (1958).

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

alumina

sodium hydroxide (1310-73-2)

hydrogen sulfide (7783-06-4)

sulfur (7704-34-9)

acetone (67-64-1)

pyridine (110-86-1)

carbon disulfide (75-15-0)

sodium sulfide (1313-82-2)

dimethylformamide (68-12-2)

2,5-Diamino-3,4-dicyanothiophene,
3,4-Thiophenedicarbonitrile, 2,5-diamino- (17989-89-8)

Tetracyanoethylene (670-54-2)

tetracyanoethane

2-amino-3,4-dicyano-5-mercaptopyrrole