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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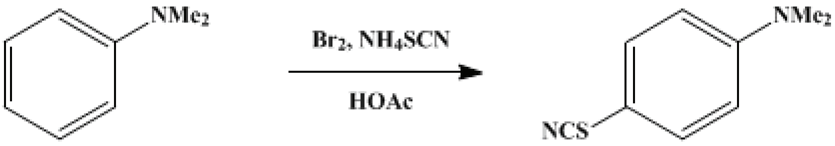
p-THIOCYANODIMETHYLANILINE

[Aniline, N,N-dimethyl-*p*-thiocyano-]



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1. Procedure

A solution of 60.5 g. (0.5 mole) of dimethylaniline and 80 g. (1.05 moles) of ammonium thiocyanate in 250 cc. of glacial acetic acid, contained in a 1-l. beaker, is cooled to 10–20° in a bath of ice and water. The solution is stirred mechanically while a solution of 80 g. (25.7 cc., 0.5 mole) of bromine in 100 cc. of glacial acetic acid is added dropwise, over a period of twenty to thirty minutes, and the temperature is kept below 20° (Note 1) and (Note 2). After all the bromine has been added the reaction mixture is removed from the cooling bath and, after standing at room temperature for ten minutes, is poured into 5–6 l. of water. Most of the *p*-thiocyanodimethylaniline separates as a pale yellow solid (Note 3), which is collected on a suction filter and washed with water. After drying in air it weighs 50–55 g. and melts at 71–73°. An additional 10–15 g. of less pure product is obtained by making the filtrate alkaline to litmus; this requires about 1250 cc. of 20 per cent sodium hydroxide. The two fractions are combined, dissolved in about 1.2 l. of boiling ligroin (b.p. 90–100°), and filtered rapidly through a large fluted filter in a heated funnel. The product separates from the filtrate in the form of long yellow needles, and crystallization is completed by thorough chilling. The melting point of the purified product is 73–74°, and the total yield is 56–60 g. (63–67 per cent of the theoretical amount) (Note 4).

2. Notes

1. At higher temperatures a considerable quantity of a yellow thiocyanogen polymer is formed which contaminates the product.
2. Toward the end of the addition a heavy precipitate begins to accumulate on the walls of the beaker; this should be dislodged occasionally with a spatula.
3. *p*-Thiocyanodimethylaniline is a weak base, and its salts are easily hydrolyzed.
4. An additional 4–5 g. of low-melting product may be recovered by evaporation of the mother liquor.

3. Discussion

p-Thiocyanodimethylaniline has been prepared from dimethylaniline and thiocyanogen,[1] chlorothiocyanogen,[2] ammonium thiocyanate and bromine,[3], [4] or lead thiocyanate and iodobenzene dichloride.[5] Thiocyanation of aromatic amines and phenols has also been accomplished electrolytically.[4], [6]

References and Notes

1. Söderbäck, Ann. **419**, 275 (1919).
2. Lecher and Joseph, Ber. **59**, 2603 (1926).
3. Likhosherstov and Petrov, J. Gen. Chem. (U.S.S.R.) **3**, 183 (1933) [C. A. **28**, 1677 (1934)].
4. Helwig, U. S. pat. 1,816,848 [C. A. **25**, 5355 (1931)].
5. Neu, Ber. **72**, 1505 (1939).

6. Fichter and Schönmann, Helv. Chim. Acta **19**, 1411 (1936).

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

ligroin

thiocyanogen

acetic acid (64-19-7)

ammonium thiocyanate (1762-95-4)

sodium hydroxide (1310-73-2)

bromine (7726-95-6)

dimethylaniline (121-69-7)

chlorothiocyanogen

iodobenzene dichloride (2401-21-0)

lead thiocyanate

p-THIOCYANODIMETHYLANILINE,
Aniline, N,N-dimethyl-p-thiocyano- (7152-80-9)