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.

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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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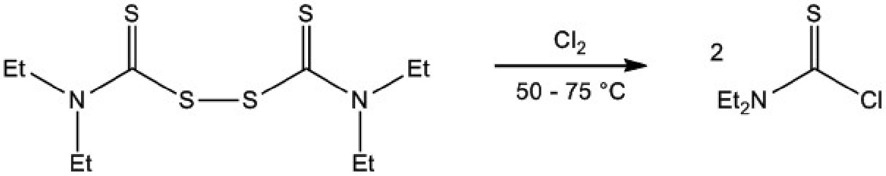
DIETHYLTHIOCARBAMYL CHLORIDE

[Carbamoyl chloride, diethylthio-]



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1. Procedure

A 200-ml. three-necked flask, equipped with a mechanical stirrer arranged to permit escape of gas, a thermometer, and a gas-inlet tube 10 mm. in diameter (Note 1), is placed in a vessel to which cooling water may be added. The entire apparatus is placed in a well-ventilated hood (Note 2). The flask is charged with 74 g. (0.25 mole) of dry (Note 3), molten (70°) tetraethylthiuram disulfide (Note 4). The molten mass is stirred vigorously, and chlorine is passed through a safety trap and is introduced below the surface of the liquid through the inlet tube. The reaction is exothermic, and the temperature is held at 70–75° by adjusting the rate of chlorine addition and by surrounding the reaction flask with cold water. After approximately 6 g. of chlorine has been absorbed, the temperature is lowered to 50–55° and held in this range for the remainder of the chlorination (Note 5). When about 90% of the theoretical amount of chlorine has been added, sulfur begins to precipitate and the reaction mass changes from a clear yellow-to-red solution to a cloudy yellow mixture. The reaction is considered complete when 18 g. (0.25 mole) of chlorine has been absorbed (measured by gain in weight of the reaction mixture). The time required for the chlorination is about 40 minutes.

The crude reaction product at 50° consists of a reddish yellow upper layer of diethylthiocarbamyl chloride saturated with sulfur (Note 6) and a viscous lower layer of amorphous sulfur saturated with diethylthiocarbamyl chloride. The mechanical stirrer is replaced by a 6-in. glass-helix-packed column arranged for distillation. A magnetic stirrer is used throughout the distillation. The diethylthiocarbamyl chloride is distilled under reduced pressure, b.p. 80–85°/1 mm. (Note 7) and (Note 8), m.p. 48–51°. The yield is 71–72 g. (94–95%) (Note 9) and (Note 10).

2. Notes

1. A tube of smaller diameter may be used, but a tube 10 mm. in diameter is recommended to minimize plugging.
2. The hood serves to carry away unabsorbed chlorine and diethylthiocarbamyl chloride vapors. The fumes are irritating to the eyes, nose, and throat and may have other injurious physiological effects.
3. The quality of the product depends to a large extent upon the purity of the tetraethylthiuram disulfide used. Since the yield is decreased in proportion to the quantity of water present, reagents used should be dry. Dry Sharples Tetraethylthiuram Disulfide No. 163 was found to be satisfactory without further purification.
4. An alternative method is to add chlorine to a solution or suspension of tetraethylthiuram disulfide in an inert liquid medium such as carbon tetrachloride. If the quantity and nature of the solvent are such as to dissolve the diethylthiocarbamyl chloride, most of the liberated sulfur can be separated mechanically and the chloride isolated by distillation after evaporation of the solvent.
5. As the chlorination progresses, the melting point of the reaction mass becomes lower so that after about one-third of the theoretical quantity of chlorine has been added the temperature may be dropped to 50°, which is approximately the melting point of the final product. The low temperature is desirable because there is less danger of overheating at the point of entry of the chlorine.

6. If the crude product is held at 50–55° for 6–8 hours, approximately 70% of the theoretical amount of free sulfur precipitates and may be separated by decantation and filtration. The remaining 30% of the theoretical quantity of sulfur remains in solution in the diethylthiocarbamyl chloride.

7. Good fractionation is not necessary, and a better product can usually be obtained by a rapid distillation than by a slow distillation at a high reflux ratio. A column with a 6- or 8-in. packed section gives a sufficiently pure product for most purposes.

The distillation may be carried out at higher pressures with only slightly more decomposition. At a pressure of 13–14 mm. diethylthiocarbamyl chloride distils at 117–120°. If the pot temperature is above 140° decomposition becomes appreciable, and at 160–190° a vigorous decomposition occurs, especially when a relatively large amount of sulfur is present.

8. The crude diethylthiocarbamyl chloride need not be distilled if sulfur does not interfere in the reaction for which the chloride is to be used and if sulfur can be readily separated from the product. At approximately 105° all the sulfur liberated by the chlorination of tetraethylthiuram disulfide will dissolve in the diethylthiocarbamyl chloride, forming a homogeneous product which may be used on the basis of 100% conversion of the disulfide to the chloride.

9. The submitters used a scale 10 times larger than that given here and obtained yields of 89–94%.

10. The submitters have prepared the following thiocarbamyl chlorides by the chlorination of the corresponding disulfides: dimethylthiocarbamyl chloride, b.p. 90–95° /0.5 mm., m.p. 42.5–43.5°, carbon tetrachloride reaction medium; diisopropylthiocarbamyl chloride, m.p. 69–71°, benzene reaction medium; diisobutylthiocarbamyl chloride, m.p. 46–48°, no solvent.

3. Discussion

Billeter prepared diethylthiocarbamyl chloride[2] and other carbamyl chlorides[3,4] by the reaction of the appropriate amine hydrochloride with thiophosgene. Free amines also have been used in this reaction.[5] Diethylthiocarbamyl chloride has been obtained from the reaction of trichloromethanesulfenyl chloride with sodium diethyl dithiocarbamate.[6] The present procedure represents an adaptation of the Ritter process.[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 824

References and Notes

1. Pennsylvania Salt Manufacturing Company, Wyndmoor, Pennsylvania.
2. Billeter, *Ber.*, **26**, 1681 (1893).
3. Billeter, *Ber.*, **20**, 1629 (1887).
4. Mazzara, *Gazz. chim. ital.*, **23**, I, 37 (1893) [*Chem. Zentr.*, **64**, I, 647 (1893)].
5. American Cyanamid Co., Brit. pat. 683,141 [*C. A.*, **48**, 1446 (1954)].
6. Zbirovsky and Ettel, *Chem. listy*, **52**, 95 (1958) [*C. A.*, **52**, 16335 (1958)].
7. Ritter, U. S. pat. 2,466,276 [*C. A.*, **43**, 5038 (1949)].

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

Benzene (71-43-2)

carbon tetrachloride (56-23-5)

sulfur (7704-34-9)

chlorine (7782-50-5)

Thiophosgene (463-71-8)

Diethylthiocarbamyl chloride,
Carbamoyl chloride, diethylthio- (88-11-9)

tetraethylthiuram disulfide (97-77-8)

dimethylthiocarbamyl chloride (16420-13-6)

diisopropylthiocarbamyl chloride

diisobutylthiocarbamyl chloride

trichloromethanesulfenyl chloride (594-42-3)

sodium diethyl dithiocarbamate (20624-25-3)