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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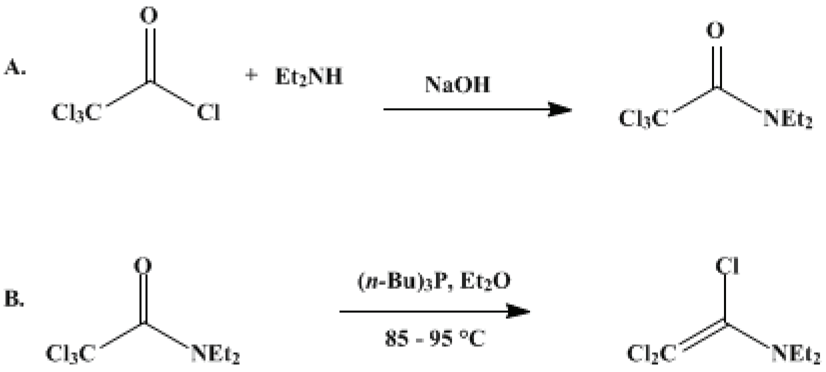
N,N-DIETHYL-1,2,2-TRICHLOROVINYLAMINE

[Vinylamine, 1,2,2-trichloro-N,N-diethyl-]



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1. Procedure

A. *N,N-Diethyl-2,2,2-trichloroacetamide*. A 1-l. three-necked flask equipped with a stirrer and dropping funnel is charged with 73 g. (1.00 mole) of diethylamine, 500 ml. of ether, and a solution of 40 g. (1.00 mole) of sodium hydroxide in 160 ml. of water. The mixture is stirred and maintained at a temperature of −10° to −15° by a bath of Dry Ice and acetone while 200 g. (1.10 moles) of trichloroacetyl chloride is added in the course of 1 hour. The cooling bath is removed, the temperature is allowed to rise to 10°, and the organic layer is separated. The aqueous layer is extracted with two 50-ml. portions of ether. The ether extracts are combined, washed with 50 ml. of 5% hydrochloric acid, two 50-ml. portions of 5% sodium bicarbonate solution, and 50 ml. of water, and dried over magnesium sulfate. The ether is removed by distillation at atmospheric pressure. The residue is distilled through a short indented Claisen still head at reduced pressure. N,N-Diethyl-2,2,2-trichloroacetamide is collected at 77–79°/1.5 mm.; n_{D}^{25} 1.4902–1.4912; weight 183–200 g. (84–92%).

B. *N,N-Diethyl-1,2,2-trichlorovinylamine*. The reaction is carried out in a 500-ml. three-necked flask equipped with an efficient mechanical stirrer, a thermometer, a reflux condenser to which a drying tube containing calcium chloride is attached, and a 250-ml. dropping funnel with a pressure-equalizing tube. The flask is charged with 219 g. (2.00 moles) of N,N-diethyl-2,2,2-trichloroacetamide. A gas-inlet tube is attached to the dropping funnel, and dry nitrogen (Note 1) is passed through the apparatus for 5 minutes with stirring. The gas-inlet tube is removed briefly, 202 g. (2.00 moles) of tri-*n*-butylphosphine (Note 2) is placed in the dropping funnel, the gas-inlet tube is replaced, and nitrogen is passed through the apparatus in a slow stream; the slow flow of nitrogen is continued all during the reaction. The phosphine is added at such a rate that a temperature of 85–90° is reached in 30 minutes (Note 3). The rate of addition is then slowed in order to maintain the temperature within this range. The total addition time is 45–55 minutes.

After all the phosphine has been added, the water bath is replaced by a heating mantle, and the reaction mixture is held at 85–95° for one additional hour and cooled to room temperature. The nitrogen-inlet tube, dropping funnel, and reflux condenser are removed, and the reaction flask is fitted with a 15 × 150-mm. Vigreux column for distillation under reduced pressure. The reaction mixture is then distilled (Note 4). The pot temperature rises from 94° to 150° during the distillation, and the crude N,N-diethyl-1,2,2-trichlorovinylamine, weight 151–164 g., is collected at 73–120°/8–11 mm. Redistillation of the crude vinylamine through a 20 × 400-mm. column packed with glass helices affords 140–150 g. (69–74%) of pure N,N-diethyl-1,2,2-trichlorovinylamine, b.p. 78–79°/18 mm., n_{D}^{25} 1.4857–1.4867 (Note 5) and (Note 6).

2. Notes

1. Tri-*n*-butylphosphine reacts exothermically with atmospheric oxygen to form tri-*n*-butylphosphine oxide.
2. Tri-*n*-butylphosphine obtainable from Westvaco Mineral Products, 161 East Forty-second St., New York City, can be used without further purification.
3. Because this reaction is very exothermic, the phosphine should be added cautiously.
4. The reaction and the initial distillation should be carried out on the same day.
5. As N,N-diethyl-1,2,2-trichlorovinylamine reacts rapidly with atmospheric moisture, it should be stored under nitrogen, preferably in a refrigerator.
6. If desired, the tri-*n*-butylphosphine oxide can be recovered by continuing the distillation. Crude tri-*n*-butylphosphine oxide distils at 115–118°/1–2 mm. (pot temperature 125–135°). The pure phosphine oxide[2] distils at 94–95°/0.03 mm.; m.p. 64.6–66.6°; yield 135–159 g. (62–73%). *Caution! The reaction mixture should not be distilled to dryness.* There should be a residue of about 40–50 ml.

3. Discussion

N,N-Diethyl-1,2,2-trichlorovinylamine has been prepared by the action of trimethyl, triethyl, or triisopropyl phosphite or triphenylphosphine on N,N-diethyl-2,2,2-trichloroacetamide.[3] These methods require a reaction temperature of 150–160° and several distillations in order to obtain a pure product. Consequently, the yields of the vinylamine are lower than by the present procedure.[3]

4. Merits of Procedure

The procedure has also been applied to the synthesis of N,N-dimethyl-1,2,2-trichlorovinylamine from trichloroacetamide (60% yield),[3] and it probably is a general means of preparing N,N-dialkyl-1,2,2-trichlorovinylamines. The reaction is an unusual one involving reduction of the amide and halogen migration and is of theoretical interest.

N,N-Diethyl-1,2,2-trichlorovinylamine undergoes certain reactions which involve the 1-chlorine atom. Acids and alcohols are converted to their respective chlorides. Aniline converts the vinylamine to N,N-diethyl-N'-phenyl-2,2-dichloroacetamidine.[3]

References and Notes

1. Organic Chemicals Division, Monsanto Chemical Co., St. Louis, Mo.
2. G. M. Kosolapoff, *J. Am. Chem. Soc.*, **72**, 5508 (1950).
3. A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 903 (1960).

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

hydrochloric acid (7647-01-0)

ether (60-29-7)

aniline (62-53-3)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

oxygen (7782-44-7)

nitrogen (7727-37-9)

diethylamine (109-89-7)

magnesium sulfate (7487-88-9)

trichloroacetamide (594-65-0)

phosphine (7723-14-0)

N,N-Diethyl-2,2,2-trichloroacetamide

vinylamine (593-67-9)

N,N-dimethyl-1,2,2-trichlorovinylamine

triisopropyl phosphite (116-17-6)

Triethyl phosphite (122-52-1)

triphenylphosphine (603-35-0)

phosphine oxide

N,N-Diethyl-1,2,2-trichlorovinylamine,
Vinylamine, 1,2,2-trichloro-N,N-diethyl- (686-10-2)

trichloroacetyl chloride (76-02-8)

trimethyl phosphite (121-45-9)

tri-n-butylphosphine (998-40-3)

tri-n-butylphosphine oxide (814-29-9)

N,N-diethyl-N'-phenyl-2,2-dichloroacetamidine