



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.

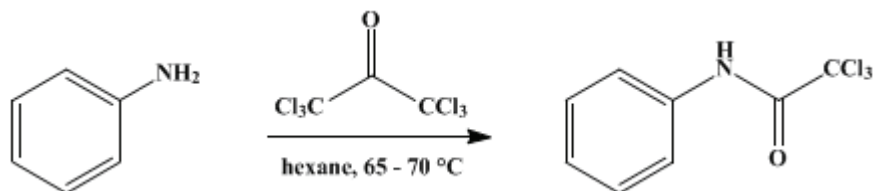
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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α,α,α -TRICHLOROACETANILIDE

[Acetanilide, α,α,α -trichloro-]



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1. Procedure

Into a 1-l. three-necked flask, fitted with a mechanical stirrer, a reflux condenser, a thermometer (Note 1), and a dropping funnel, is placed a solution of 265 g. (1 mole) of hexachloroacetone (Note 2) in 400 ml. of hexane (Note 3). To the stirred solution is added, dropwise, 93 g. (1 mole) of aniline (Note 4) over a period of 35–40 minutes. During this time the temperature rises to about 55°. After the addition is complete, stirring is continued at 65–70° for 45 minutes.

The hot solution is poured into a 1-l. beaker and cooled to 0–5°. The solid is collected on a filter and air-dried; it weighs 208–218 g. (87–91%) and melts at 90–92°. One recrystallization from 400 ml. of 90% ethanol (Note 5) yields 160–165 g. (67–69%) (Note 6) of product melting at 92.5–93.0° (Note 7). A second crop of 9–16 g. (4–7%), m.p. 93.5–95.5°, can be obtained by concentrating the filtrate to 200 ml. and cooling (Note 8).

2. Notes

1. The thermometer and the reflux condenser are fitted to a two-necked adapter.
2. Commercial hexachloroacetone (Allied Chemical Corporation) was distilled and the fraction boiling at 93–97°/24 mm. was used.
3. Technical grade hexane suffices.
4. Technical grade aniline was purified by simple distillation and the light-yellow distillate was used directly.
5. The 90% ethanol was prepared by adding 22 ml. of water to 378 ml. of 95% ethanol.
6. The submitter reports a 76–81% yield of product melting at 94–96°.
7. The melting point is raised to 93.5–94.0° by carefully washing the product on a Büchner funnel with 50 ml. of iced 90% ethanol.
8. The submitter has applied this procedure successfully to several amines² (see Table I).

TABLE I

Amine	Yield of N-Trichloroacetylamine, %	M.p., °C*
3-Chloroaniline	93	101
4-Chloroaniline	97	125–127
2-Toluidine	83	98
3-Toluidine	79	102–103
4-Toluidine	70	115
4-Fluoroaniline	83	96
Benzidine	65	301 (dec.)
Benzylamine	84	87–90
2-Phenylethylamine	97	117–120
Ammonia	96	141

Dimethylamine	89	b.p. 110–111°/16 mm.
2-Aminothiazole	80	196–198 (dec.)

*All melting points are uncorrected.

3. Discussion

Trichloroacetanilide has been prepared from hexachloroacetone and aniline,³ from trichloroacetyl chloride and aniline,⁴ by the action of aniline magnesium iodide on ethyl trichloroacetate,⁵ by heating N-phenyltrichloroacetimidyl chloride with dilute methanol,⁶ and from trichloroacetic acid and aniline in the presence of phosphorus oxychloride⁷ or dicyclohexylcarbodiimide,⁸ and from trichloroacetyl diethyl phosphonate and aniline.⁹

References and Notes

1. Allied Chemical Corp., P.O. Box 405, Morristown, New Jersey.
2. Unpublished results.
3. Ch. Cloez, *Ann. Chim. Phys.*, **9** (6), 204 (1886).
4. W. E. Judson, *Ber.*, **3**, 783 (1870).
5. F. Bodroux, *Compt. Rend.*, **140**, 1598 (1905).
6. J. von Braun, F. Jostes, and R. W. Munch, *Ann.*, **453**, 133 (1927).
7. F. A. Berti and L. M. Ziti, *Arch. Pharm.*, **285**, 372 (1952).
8. A. Benzas, C. Egnell, and P. Freon, *Compt. Rend.*, **252**, 896 (1961).
9. A. N. Pudovik, T. K. Gazizov, and A. P. Pashinkin, *Ah. Obschch. Khim.*, **38**, 12 (1968).

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

N-phenyltrichloroacetimidyl chloride

trichloroacetyl diethyl phosphonate

ethanol (64-17-5)

ammonia (7664-41-7)

methanol (67-56-1)

aniline (62-53-3)

Phosphorus Oxychloride (21295-50-1)

dimethylamine (124-40-3)

benzylamine (100-46-9)

benzidine (92-87-5)

trichloroacetic acid (76-03-9)

2-phenylethylamine (64-04-0)
4-Toluidine (106-49-0)
hexane (110-54-3)
ethyl trichloroacetate (515-84-4)
dicyclohexylcarbodiimide (538-75-0)
trichloroacetyl chloride (76-02-8)
 α,α,α -Trichloroacetanilide,
Trichloroacetanilide,
Acetanilide, α,α,α -trichloro- (2563-97-5)
hexachloroacetone (116-16-5)
N-Trichloroacetylamine
3-Chloroaniline (108-42-9)
4-Chloroaniline (106-47-8)
2-Toluidine (95-53-4)
3-Toluidine (108-44-1)
4-Fluoroaniline (371-40-4)
2-Aminothiazole (96-50-4)
aniline magnesium iodide