



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.

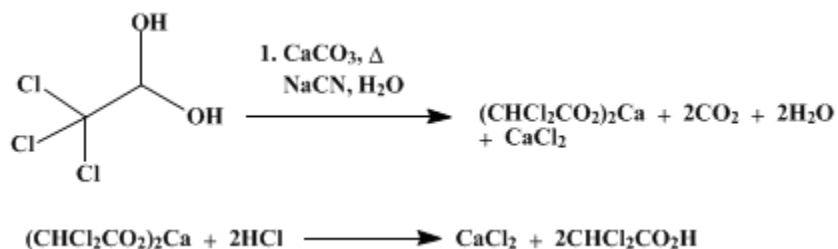
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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DICHLOROACETIC ACID

[Acetic acid, dichloro-]



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1. Procedure

A solution of 250 g. (1.5 moles) of u.s.p. **chloral hydrate** in 450 cc. of warm water (50–60°) is placed in a 3-l. round-bottomed flask bearing a reflux condenser and thermometer (**Note 1**). The condenser is temporarily removed and 152.5 g. (1.52 moles) of precipitated **calcium carbonate** added; this is followed by 2 cc. of **amyl alcohol** (**Note 2**) and a solution of 10 g. of technical **sodium cyanide** in 25 cc. of water. Although the reaction is exothermic, the reaction mixture is heated with a low flame so that it reaches 75° in about ten minutes; at this point heating is discontinued. The temperature continues to rise to 80–85° during five to ten minutes and then drops. As soon as the temperature begins to fall the solution is heated to boiling and refluxed for twenty minutes. The mixture is then cooled to 0–5° in an ice bath, acidified with 215 cc. of concentrated **hydrochloric acid** (sp. gr. 1.18), and extracted with five 100-cc. portions of **ether** (**Note 3**). The combined **ether** extracts are dried with 20 g. of anhydrous **sodium sulfate**, the **ether** is removed by distillation from a steam bath, and the residue is distilled in vacuum from a Claisen flask with a fractionating side arm (**Note 4**). The yield of **dichloroacetic acid**, b.p. 99–104°/23 mm., is 172–180 g. (88–92 per cent of the theoretical amount) (**Note 5**).

2. Notes

1. The amount of **hydrogen cyanide** evolved is small, and the reaction may be carried out in a hood without any special device for removing this gas. The use of mechanical stirring does not improve the results.
2. **Amyl alcohol** is added to decrease the amount of foaming.
3. The emulsion which often forms during the **ether** extraction may be broken by filtering through a fluted filter or with suction.
4. The product decomposes when distilled at atmospheric pressure.
5. The preparation has been carried out with equally good results using double the quantities given above.

3. Discussion

Dichloroacetic acid has been prepared by the chlorination of acetic¹ or chloroacetic² acid, by hydrolysis of **pentachloroethane**,³ from **trichloroacetic acid** by electrolytic reduction⁴ or the action of **copper**,⁵ and by the action of alkali cyanides on **chloral hydrate**.⁶ The method described here is essentially that of Delépine.⁷

References and Notes

1. Müller, Ann. **133**, 159 (1865); Dow Chemical Company, U. S. pat. 1,921,717 [C. A. **27**, 5084

- (1933)].
2. Maumené, Compt. rend. **59**, 84 (1864).
 3. Alais, Froges, and Camargue, Fr. pat. 773, 623 [C. A. **29**, 1437 (1935)].
 4. Brand, Ger. pat. 246,661 [C. A. **6**, 2496 (1912)].
 5. Doughty and Black, J. Am. Chem. Soc. **47**, 1091 (1925); Doughty and Derge, *ibid.* **53**, 1594 (1931).
 6. Wallach, Ann. **173**, 288 (1874); Pucher, J. Am. Chem. Soc. **42**, 2251 (1920); Chattaway and Irving, J. Chem. Soc. **1929**, 1038.
 7. Delépine, Bull. soc. chim. (4) **45**, 827 (1929).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium cyanide (143-33-9)

hydrogen cyanide (74-90-8)

sodium sulfate (7757-82-6)

copper (7440-50-8)

calcium carbonate (471-34-1)

chloral hydrate (302-17-0)

amyl alcohol (71-41-0)

dichloroacetic acid,
Acetic acid, dichloro- (79-43-6)

pentachloroethane (76-01-7)

trichloroacetic acid (76-03-9)