



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.

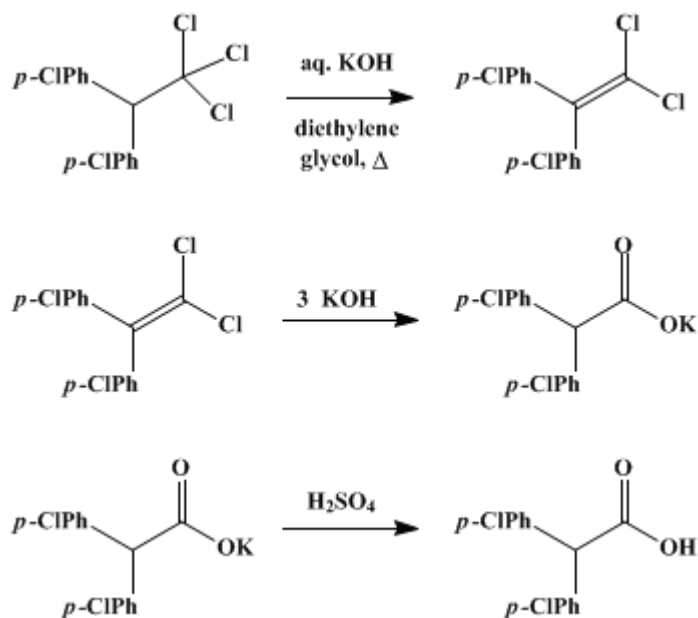
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.270 (1955); Vol. 26, p.21 (1946).

DI-(*p*-CHLOROPHENYL)ACETIC ACID

[Acetic acid, di-(*p*-chlorophenyl)]



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1. Procedure

A mixture of 400 ml. of diethylene glycol (Note 1) and 49.5 g. (0.14 mole) of 1,1-di-(*p*-chlorophenyl)-2,2,2-trichloroethane (Note 2) is placed in a 1-l. three-necked flask fitted with a stirrer, a reflux condenser, and a thermometer. To this is added a solution of 63 g. (1.12 mole) of potassium hydroxide in 35 ml. of water. The mixture is stirred and refluxed for 6 hours at such a rate that the temperature is maintained at 134–137° (Note 3) and (Note 4). The mixture is allowed to cool and, with vigorous stirring, is poured into 1 l. of cold water. The insoluble material is filtered and washed twice with 50-ml. portions of warm water (Note 5). The filtrate is then boiled gently for 5 minutes with 2 g. of Norit; the carbon is removed, the filtrate is acidified to litmus with 20% sulfuric acid (approximately 120 ml.), and then an additional 30 ml. of acid is added. The mixture is cooled to 0–5°; the precipitate is collected by filtration under suction, washed free of sulfate ions with water, and dried at 100–110°. The product is di-(*p*-chlorophenyl) acetic acid melting at 163–165°; it weighs 27–28.5 g. (69–73%). For purification, this material is dissolved in 100 ml. of boiling 95% ethanol, the solution is filtered, and approximately 45 ml. of water is added to the boiling filtrate until it just becomes turbid. The solution is then cooled to 0–5°, and the solid is removed by suction filtration. The material weighs 25–26 g. and melts at 164–166°.

2. Notes

1. Diethylene glycol with a boiling range of 230–270°, from Carbide and Carbon Chemicals Corporation, is satisfactory.
2. A purified grade of 1,1-di-(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) melting at 105–106° should be used. It can be obtained by crystallizing the technical material from ethanol. Thus, 100 g. of technical DDT melting at 81–96°, when crystallized from 550 ml. of 95% ethanol, gave about 70 g. of material melting at 105–106°.
3. The intermediate product, 1,1-di-(*p*-chlorophenyl)-2,2-dichloroethylene,^{1,2} can be isolated readily. The mixture is gradually (7–8 minutes) heated to reflux temperature and is then refluxed 2 minutes. The

mixture is cooled and poured into 1 l. of cold water, and the product is removed by suction filtration, washed well with water, and dried. The yield of crude product melting at 83–86° is 43.5 g. (97%). This may be purified by crystallization from 200 ml. of 95% [ethanol](#); the product weighs 39.5 g. and melts at 86.5–88°.

4. Longer reaction times or higher temperatures favor the formation of [di-\(p-chlorophenyl\) methane](#); see Note 5.

5. The insoluble material consists of silica, [1,1-di-\(p-chlorophenyl\)-2,2-dichloroethylene](#) and a small amount of [di-\(p-chlorophenyl\) methane](#)³ (melting at 54–55° when purified), formed by decarboxylation of the acid.

3. Discussion

[Di-\(p-chlorophenyl\) acetic acid](#) has been made by the action of alcoholic potassium hydroxide on [1,1-di-\(p-chlorophenyl\)-2,2-dichloroethane](#);^{2,4} by the action of [barium hydroxide](#) on DDT in [ethylene glycol](#);⁴ and by the condensation of [chlorobenzene](#) with [glyoxylic acid](#).⁴

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 130](#)
- [Org. Syn. Coll. Vol. 5, 370](#)

References and Notes

1. Zeidler, *Ber.*, **7**, 1181 (1874).
 2. Grummitt, Buck, and Stearns, *J. Am. Chem. Soc.*, **67**, 156 (1945).
 3. Montagne, *Rec. trav. chim.*, **25**, 379 (1906).
 4. White and Sweeney, *Public Health Repts. U. S.*, **60**, 66 (1945).
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Appendix

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

silica

1,1-di-(p-chlorophenyl)-2,2,2-trichloroethane (DDT)

alcoholic potassium hydroxide

[ethanol](#) (64-17-5)

[sulfuric acid](#) (7664-93-9)

[carbon](#),
[Norit](#) (7782-42-5)

[chlorobenzene](#) (108-90-7)

[potassium hydroxide](#) (1310-58-3)

[ethylene glycol](#) (107-21-1)

barium hydroxide (17194-00-2)

glyoxylic acid (298-12-4)

diethylene glycol (111-46-6)

Di-(p-chlorophenyl)acetic acid,
Acetic acid, di-(p-chlorophenyl) (83-05-6)

1,1-di-(p-chlorophenyl)-2,2,2-trichloroethane (50-29-3)

1,1-Di-(p-chlorophenyl)-2,2-dichloroethylene (72-55-9)

di-(p-chlorophenyl) methane (101-76-8)

Di-(p-chlorophenyl) acetic acid

1,1-di-(p-chlorophenyl)-2,2-dichloroethane (72-54-8)