



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.

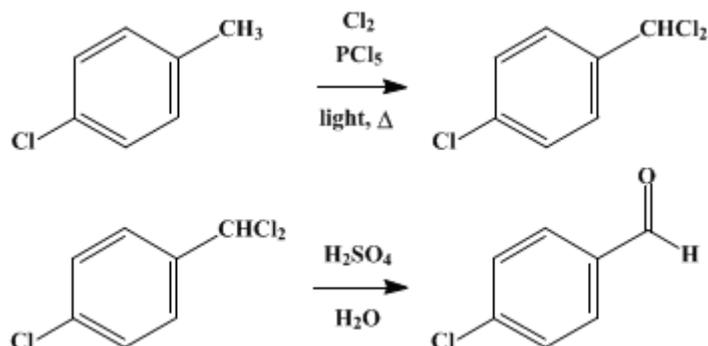
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.133 (1943); Vol. 12, p.12 (1932).

***p*-CHLOROBENZALDEHYDE**

[Benzaldehyde, *p*-chloro-]



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1. Procedure

A 500-cc. two-necked, round-bottomed flask is provided with an air-cooled reflux condenser, 2 cm. in diameter and filled for a length of 60 cm. with 5–6 mm. glass pearls or rings (Note 1). Chlorine is to be introduced by means of a 4-mm. glass tube, inserted through a cork in a neck of the flask, extending close to the bottom of the flask and provided with a small bulb with fine perforations to break up the gas stream into small bubbles. The large quantities of hydrogen chloride formed can be disposed of by means of a gas absorption trap.

Into the tared flask are placed 126.5 g. (1 mole) of *p*-chlorotoluene (Org. Syn. Coll. Vol. I, 1941, 170) and 3.8 g. of phosphorus pentachloride. The flask is heated in a bath kept at 160–170° (Note 2), and while illuminated with direct sunlight or with an unfrosted 100-watt tungsten lamp a rapid stream of chlorine is introduced directly from a cylinder until the gain in weight is 55–66 (Note 3).

The pale yellow or yellow-green product is then transferred to a 4-l. wide-mouthed bottle containing 400 cc. of concentrated sulfuric acid, and stirred vigorously (Hood) for five hours (Note 4). The viscous mixture is then transferred to a separatory funnel and allowed to stand overnight, after which the lower layer (Note 5) is run slowly, with stirring, into a 3-l. beaker three-quarters filled with cracked ice. The cream-colored solid obtained when the ice has melted is filtered by suction, washed with water, pressed dry on the funnel, and divided into three equal parts. Each portion is dissolved in a minimum of ether, and the ether solution is repeatedly shaken with 2 per cent sodium hydroxide solution until acidification of the washings gives no precipitate of *p*-chlorobenzoic acid (Note 6).

After removal of the ether by distillation on a steam bath, the residue is distilled under diminished pressure from a Claisen flask. The yield of *p*-chlorobenzaldehyde distilling at 108–111°/25 mm. and melting at 46–47° is 76–84 g. (54–60 per cent of the theoretical amount).

2. Notes

1. The glass packing reduces the tendency of the stream of hydrogen chloride to carry away *p*-chlorotoluene as a spray.

If only one run is to be made, good-quality corks are satisfactory. If several runs are made, it is recommended that the corks be impregnated with sodium silicate solution to prevent excessive corrosion by the hydrogen chloride and chlorine.

2. The bath contains either oil or graphite.

3. The time required was four and one-half hours. In a larger run by the submitter, in which 750 g. of *p*-chlorotoluene and 23 g. of phosphorus pentachloride were used, the time required for a gain in weight of

330–360 g. was six to ten hours.

4. Vigorous stirring is necessary to prevent undue foaming. Most of the [hydrogen chloride](#) is evolved early in stirring.

5. The waxy upper layer is discarded.

6. The yield of [p-chlorobenzoic acid](#) is about 20 g. From the larger runs, starting with 750 g. of [p-chlorotoluene](#), the yield of acid averaged 260 g.

3. Discussion

[p-Chlorobenzaldehyde](#) can be prepared from [p-chlorobenzyl chloride](#) or [p-chlorobenzyl bromide](#) with aqueous [lead nitrate](#);¹ from [p-chlorotoluene](#) and [chromyl chloride](#);² by the hydrolysis of [p-chlorobenzal chloride](#);³ from [p-aminobenzaldehyde](#) by diazotization and subsequent treatment with [cuprous chloride](#);⁴ from [p-chlorophenylmagnesium bromide](#) and [ethyl orthoformate](#);⁵ from [p-chlorobenzyl chloride](#) with [hexamethylenetetramine](#) and subsequent hydrolysis;⁶ by conversion of [p-chlorobenzonitrile](#) to the iminochloride which is then hydrolyzed;⁷ by the action of [carbon monoxide](#) and [aluminum chloride](#) on [chlorobenzene](#);⁸ and by the action of [sodium carbonate](#) on [2,5-dichlorobenzenesulfonyl-4-chlorobenzoylhydrazine](#).⁹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 200](#)

References and Notes

1. Beilstein and Kuhlberg, *Ann.* **147**, 352 (1867); Jackson and White, *Am. Chem. J.* **3**, 30 (1881).
2. Law and Perkin, *J. Chem. Soc.* **93**, 1636 (1908).
3. Erdmann and Kirchhoff, *Ann.* **247**, 368 (1888); Erdmann and Schwechten, *ibid* **260**, 63 (1890); *Kaeswurm, Ber.* **19**, 742 (1886).
4. Von Walther and Raetze, *J. prakt. Chem. (2)* **65**, 258 (1902).
5. Bodroux, *Bull. soc. chim. (3)* **31**, 587 (1904).
6. Mayer and English, *Ann.* **417**, 78 (1918).
7. Stephen, *J. Chem. Soc.* **127**, 1874 (1925).
8. Boehringer and Sons, *Ger. pat.* 281,212 (*Chem. Zentr.* **1915**, I, 178).
9. McFadyen and Stevens, *J. Chem. Soc.* **1936**, 584.

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

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

[hydrogen chloride](#) (7647-01-0)

[ether](#) (60-29-7)

[sodium hydroxide](#) (1310-73-2)

[phosphorus pentachloride](#) (10026-13-8)

[carbon monoxide](#) (630-08-0)

sodium silicate

sodium carbonate (497-19-8)

chlorobenzene (108-90-7)

aluminum chloride (3495-54-3)

chlorine (7782-50-5)

lead nitrate (10099-74-8)

cuprous chloride (7758-89-6)

p-Chlorotoluene (106-43-4)

Ethyl orthoformate

hexamethylenetetramine (100-97-0)

chromyl chloride

2,5-dichlorobenzenesulfonyl-4-chlorobenzoylhydrazine

p-chlorophenylmagnesium bromide

p-Chlorobenzaldehyde,
Benzaldehyde, p-chloro- (104-88-1)

p-chlorobenzyl chloride (104-83-6)

p-chlorobenzoic acid (74-11-3)

p-chlorobenzyl bromide (622-95-7)

p-chlorobenzal chloride (13940-94-8)

p-Aminobenzaldehyde (17625-83-1)

p-chlorobenzonitrile (623-03-0)