Organic Syntheses

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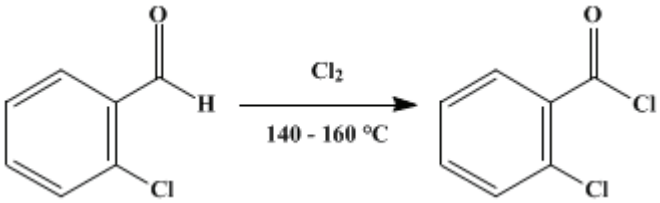
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.009.0034

Organic Syntheses, Coll. Vol. 1, p.155 (1941); Vol. 9, p.34 (1929).

o-CHLOROBENZOYL CHLORIDE

[Benzoyl chloride, *o*-chloro-]



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1. Procedure

In a 3-l. round-bottomed flask, fitted with a thermometer, a reflux condenser, and an inlet tube extending nearly to the bottom, is placed 141 g. (1 mole) of freshly distilled *o*-chlorobenzaldehyde (Note 1). To the upper end of the condenser is attached a tube leading to a flask containing water for the absorption of hydrogen chloride. The reaction vessel and absorption flask are weighed accurately, and a current of chlorine, dried by sulfuric acid, is passed into the aldehyde, the temperature of which is maintained at 140–160°. The rate of the current of gas is so regulated that little or no chlorine escapes. The reaction and absorption flasks are removed and weighed about every three hours. After about fifteen hours (Note 2) the absorption of chlorine at 160° practically ceases.

The total increase in weight (Note 3) amounts to 26–29 g. (75–84 per cent of the theoretical amount). The reaction product is distilled under reduced pressure, when the pure *o*-chlorobenzoyl chloride passes over at 93–95° /10 mm. or 137–139° /60 mm., leaving a small quantity of high-boiling residue which appears to consist mainly of an intermediate compound (Note 2). The yield is 122–126 g. (70–72 per cent of the theoretical amount) (Note 4).

2. Notes

1. Technical *o*-chlorobenzaldehyde of high purity is available. After one distillation under reduced pressure (b.p. 84° /10 mm., 125° /85 mm.), it melts at 7–10°.
2. If the mixture is kept at 125–140°, the reaction requires about thirty hours for completion. When about one-half of the necessary amount of chlorine has been added, the reaction mixture, if allowed to cool, sets to a colorless mass of an addition compound of the aldehyde and acid chloride; this on further chlorination yields *o*-chlorobenzoyl chloride.
3. The increase in weight is distributed between the reaction flask and hydrochloric acid absorption flask in the ratio of about 45: 55.
4. The use of large quantities and vigorous mechanical stirring gives much better yields. Thus, a run of 2665 g. (18.9 moles) of the aldehyde gave a yield of 2700 g. (82 per cent of the theoretical amount.

3. Discussion

o-Chlorobenzoyl chloride can be prepared by the treatment of *o*-chlorobenzoic acid with phosphorus pentachloride[1] or thionyl chloride.[2] The procedure described is based on that for the preparation of benzoyl chloride from benzaldehyde and chlorine.[3]

References and Notes

1. Emmerling, Ber. **8**, 883 (1875); Clark and Bell, Trans. Roy. Soc. Canada, III, **27**, 97 (1933) [C. A. **28**, 3053 (1934)].

2. Meyer, Monatsh. **22**, 427 (1901); Frankland, Carter and Adams, J. Chem. Soc. **101**, 2476 (1912).
3. Wöhler and Liebig, Ann. **3**, 262 (1832).

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

aldehyde

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

benzaldehyde (100-52-7)

benzoyl chloride (98-88-4)

chlorine (7782-50-5)

o-Chlorobenzoyl chloride,
Benzoyl chloride, o-chloro- (609-65-4)

o-chlorobenzaldehyde (89-98-5)

o-Chlorobenzoic acid (118-91-2)