



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.

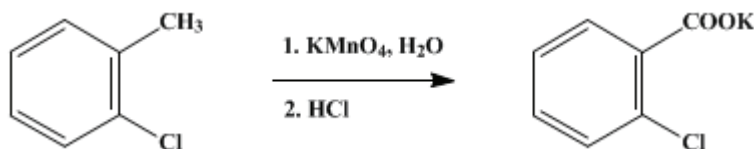
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.135 (1943); Vol. 10, p.20 (1930).

o-CHLOROBENZOIC ACID

[Benzoic acid, *o*-chloro-]



Submitted by H. T. Clarke and E. R. Taylor.
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1. Procedure

In a 12-l. flask fitted with stirrer and reflux condenser are placed 600 g. (3.8 moles) of [potassium permanganate](#), 7 l. of water, and 200 g. (1.6 moles) of *o*-chlorotoluene ([Org. Syn. Coll. Vol. I, 1941, 170](#)). The mixture is slowly heated to boiling ([Note 1](#)) with continual stirring until the permanganate color has disappeared. This requires three to four hours. The condenser is now set downward for distillation, and the mixture is distilled, with constant stirring, until no more oil passes over with the water. The unattacked *o*-chlorotoluene thus obtained amounts to 25–30 g. The hot mixture is filtered with suction and the cake of hydrated [manganese dioxide](#) washed with two 500-cc. portions of hot water. The combined filtrate is concentrated ([Note 2](#)) to about 3.5 l.; if it is not entirely clear it may be clarified by the use of 1–2 g. of [decolorizing carbon](#). It is now, while still hot, acidified by cautiously adding 250 cc. of concentrated [hydrochloric acid](#) (sp. gr. 1.19) with continual agitation. When the mixture is cool the white precipitate of *o*-chlorobenzoic acid is filtered and washed with cold water. The dry weight is 163–167 g. (76–78 per cent of the theoretical amount, based on the amount of *o*-chlorotoluene actually oxidized) of a very nearly pure ([Note 3](#)) product melting at 137–138°. For purification this may be recrystallized from 600 cc. of [toluene](#), when 135–140 g. of a product melting at 139–140° is obtained. Further crops can be obtained by concentrating the mother liquor.

2. Notes

1. If the mixture is heated too rapidly the reaction may be violent at the outset; it can be controlled by laying wet towels upon the upper part of the flask.
2. This concentration is satisfactorily carried out on the steam bath under reduced pressure ([Org. Syn. Coll. Vol. I, 1941, 427](#)).
3. It is important to use pure *o*-chlorotoluene in this preparation; otherwise the *o*-chlorobenzoic acid may be contaminated with isomeric acids which are very difficult to remove. The *o*-chlorotoluene therefore should be prepared from pure *o*-toluidine or *o*-chlorotoluenesulfonic acid. Directions for the purification of technical *o*-chlorobenzoic acid are to be found on [p. 16](#).

3. Discussion

The only practical methods of preparing *o*-chlorobenzoic acid consist in the oxidation of *o*-chlorotoluene and the replacement of the amino group in [anthranilic acid](#) by a chlorine atom. Both methods have been fully discussed by Graebe,¹ who recommends the former for the preparation of relatively large quantities. The oxidation of *o*-chlorotoluene by permanganate was originally described by Emmerling.²

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 15](#)
- [Org. Syn. Coll. Vol. 3, 28](#)

References and Notes

1. Graebe, Ann. **276**, 54 (1893).
 2. Emmerling, Ber. **8**, 880 (1875).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

hydrochloric acid (7647-01-0)

potassium permanganate (7722-64-7)

decolorizing carbon (7782-42-5)

toluene (108-88-3)

manganese dioxide (1313-13-9)

o-Chlorotoluene (95-49-8)

Anthranilic Acid (118-92-3)

o-toluidine (95-53-4)

o-Chlorobenzoic acid,
Benzoic acid, o-chloro- (118-91-2)

o-chlorotoluenesulfonic acid