



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.

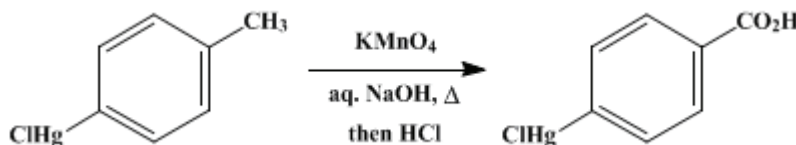
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.159 (1941); Vol. 7, p.18 (1927).

***p*-CHLOROMERCURIBENZOIC ACID**

[Benzoic acid, *p*-chloromercuri-]



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1. Procedure

Five hundred grams (1.5 moles) of crude *p*-tolylmercuric chloride (p. 519) and 720 g. (4.6 moles) of potassium permanganate are added to a solution of 1200 g. (30 moles) of sodium hydroxide in 18 l. of water contained in a large enameled pail (or similar vessel) placed on a 15-cm. Fletcher burner and provided with a mechanical stirrer. The mixture is stirred and heated as near boiling as possible for fifteen minutes. The highest temperature conveniently obtainable is 95°. The tolylmercuric chloride dissolves (Note 1), forming the sodium salt of *p*-hydroxymercuribenzoic acid. The solution is cooled somewhat and alcohol is added to react with the excess of potassium permanganate (250 cc. is generally required to completely decolorize the solution). The manganese dioxide thus precipitated is removed by filtering with suction (Note 2). The filtrate should be clear and colorless. (If it is green, not enough alcohol has been added.)

After the filtrate has become thoroughly cool (Note 3), it is acidified with hydrochloric acid, about 1700 cc. of technical concentrated acid being necessary. The precipitated *p*-chloromercuribenzoic acid is difficult to filter because of its flocculent character. It is best to allow it to stand at least overnight and then filter by suction after siphoning most of the clear supernatant liquid. The acid retains much water and should be dried at 110° (Note 4). The yield is 350–420 g. (61–74 per cent of the theoretical amount). The crude acid may be purified by reprecipitation with hydrochloric acid from a solution in sodium hydroxide (Note 5). The crude acid is sufficiently pure for the preparation of *p*-iodobenzoic acid (p. 325). It can be used for this purpose without drying.

2. Notes

1. The chief impurity in the *p*-tolylmercuric chloride is mercurous chloride, which is converted to the oxide and remains in the manganese dioxide precipitate.
2. In filtering the manganese dioxide from the strongly alkaline solution, it is best to support the filter paper by means of a cloth which is cut to fit the funnel and placed under the filter paper.
3. It is necessary that the filtrate be cooled at least to 20° before acidifying to avoid the splitting of the carbon-mercury linkage.
4. The caked acid loses water very slowly, even at 110°. Since the chief use of the acid is in preparing the *p*-halogen compounds (p. 325), it need not be dried, but can be mixed with water while still wet.
5. The pure acid melts at 273°.¹

3. Discussion

p-Chloromercuribenzoic acid can be prepared by the oxidation of *p*-tolylmercuric chloride² and by heating the corresponding boric acid,³ (HO)₂BC₆H₄CO₂H, with mercuric chloride.

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 1, 325*

References and Notes

1. Nesmeyanov and Makarova, J. Gen. Chem. (U.S.S.R.) **1**, 1162 (1931) [C. A. **26**, 5295 (1932)].
 2. Whitmore and Woodward, J. Am. Chem. Soc. **48**, 534 (1926).
 3. Michaelis, Ann. **315**, 35 (1901).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

corresponding boric acid

p-halogen compounds

hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

potassium permanganate (7722-64-7)

mercuric chloride (7487-94-7)

tolylmercuric chloride,
p-tolylmercuric chloride (539-43-5)

manganese dioxide (1313-13-9)

mercurous chloride (7546-30-7)

p-Chloromercuribenzoic acid,
Benzoic acid, p-chloromercuri- (59-85-8)

sodium salt of p-hydroxymercuribenzoic acid

p-iodobenzoic acid (619-58-9)