



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

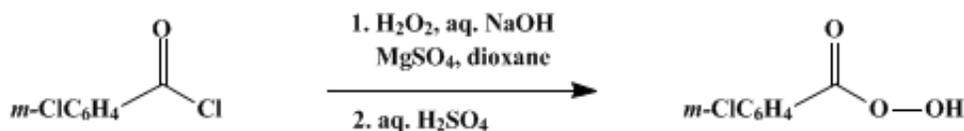
Working with Hazardous Chemicals

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.

m*-CHLOROPERBENZOIC ACID*[Benzenecarboperoxoic acid, 3-chloro-]**

Submitted by Richard N. McDonald¹, Richard N. Steppel, and James E. Dorsey.
 Checked by William N. Washburn and Ronald Breslow.

1. Procedure

*Caution! Reactions and subsequent operations involving peracids and peroxy compounds should be run behind a safety shield. Peroxy compounds should be added to the organic material, never the reverse. For relatively fast reactions, the rate of addition of the peroxy compound should be slow enough so that it reacts rapidly and no significant unreacted excess is allowed to build up. The reaction mixture should be stirred efficiently while the peroxy compound is being added, and cooling should generally be provided since many reactions of peroxy compounds are exothermic. New or unfamiliar reactions, particularly those run at elevated temperatures, should be run first on a small scale. Reaction products should never be recovered from the final reaction mixture by distillation until all residual active oxygen compounds (including unreacted peroxy compounds) have been destroyed. Decomposition of active oxygen compounds may be accomplished by the procedure described in Korach, M.; Nielsen, D. R.; Rideout, W. H. *Org. Synth.* 1962, 42, 50 (*Org. Synth.* 1973, Coll. Vol. 5, 414). [Note added January 2011].*

A 1-l. beaker (Note 1) equipped with a magnetic stirrer is charged with 1.5 g. of magnesium sulfate heptahydrate, 36 g. of sodium hydroxide, 360 ml. of water, 90 ml. of 30% hydrogen peroxide, and 450 ml. of dioxane. This mixture is cooled to 15° with an ice-water bath and by the addition of a small amount of ice to the mixture before 52.5 g. (0.300 mole) of *m*-chlorobenzoyl chloride (Note 2) is added in one portion while vigorous stirring is maintained. Small portions of ice are added to maintain the temperature below 25°. The reaction mixture is stirred at this temperature for 15 minutes, then transferred to a 3-l. separatory funnel. Cold, 20% sulfuric acid (900 ml.) (Note 3) is added to the separatory funnel, the mixture is shaken and separated, and the aqueous layer is extracted with four 200 ml. portions of cold dichloromethane (Note 4). The combined extracts are dried over anhydrous magnesium sulfate, and the dichloromethane is removed under reduced pressure *via* a short-path distillation (Note 5). After most of the solvent has been removed, a white pasty solid remains and the residual solvent is removed under full vacuum for an additional 2 hours or until a white, flaky powder remains. The product weighs approximately 51 g. Sodium thiosulfate analysis indicates 80–85% active oxygen present (Note 6).

2. Notes

1. The checkers used a Pyrex vessel; the submitters utilized a Nalgene beaker, because contact with the glass surface may catalyze the decomposition of the peracid.

2. The *m*-chlorobenzoyl chloride is prepared by refluxing *m*-chlorobenzoic acid, either commercial or recovered, with excess thionyl chloride. Distillation gives the *m*-chlorobenzoyl chloride in high yield, b.p. 112° (11 mm.).²

The recovery of the *m*-chlorobenzoic acid, the by-product from *m*-chloroperbenzoic acid oxidations, is facilitated by using dichloromethane as the solvent since the peracid is very soluble whereas the acid is quite insoluble.

3. The cold 20% [sulfuric acid](#) solution is made by adding concentrated [sulfuric acid](#) (180 ml.) to crushed ice followed by the addition of more ice until the required volume is reached, *i.e.*, 900 ml. The acid solution is kept cold in an ice bath until required. The [dichloromethane](#) is also precooled before use.
4. Iodometric titration of the moist extracts indicates approximately 51 g. of [m-chloroperbenzoic acid](#) present. A 4.0-ml. aliquot of the solution requires approximately 20 ml. of a 0.1000 *N* solution of [sodium thiosulfate](#). To prepare the sample, 10 ml. of 10% [sodium iodide](#) and 5 ml. of [acetic acid](#) are added to the 5-ml. aliquot, and the mixture is diluted to 50 ml. The dark red solution is titrated to a pale yellow. At this point 1 ml. of starch solution is added and the titration continued to the end point, *i.e.*, a change from dark blue to clear.

$$\text{Total weight of peracid} = \frac{N_{\text{Na}_2\text{S}_2\text{O}_3} \cdot V_{\text{Na}_2\text{S}_2\text{O}_3(\text{ml.})} \cdot V_{\text{total extract (l.)}} \cdot 86.29}{V_{\text{aliquot (ml.)}}}$$

5. The [dichloromethane](#) solvent should be removed as rapidly as possible because contact with glass and heat cause decomposition of the peracid. A convenient method for the removal of the solvent involves a short-path vacuum distillation using a 2-l. distillation flask and trapping the solvent at dry ice or liquid [nitrogen](#) temperatures. The pressure should be reduced slowly at first and at least three traps used to minimize the amount of solvent introduced into the vacuum pump. Adjustment of a stopcock located between the first and second traps will help to control this problem. The distillation flask is placed in a water bath maintained between 25° and 35° so that the rate of solvent evaporation is quite rapid. Removal of the solvent over prolonged periods and drying of the solid peracid by excessive heating results in drastic losses of active [oxygen](#). *m*-Chloroperbenzoic, once isolated, is stable over long periods of time when stored in polyethylene containers and refrigerated.
6. Iodometric titration of the solid product involves the use of 0.2-g. samples of the peracid and the procedure in ([Note 4](#)).

$$\text{Percent peracid} = \frac{N_{\text{Na}_2\text{S}_2\text{O}_3} \cdot V_{\text{Na}_2\text{S}_2\text{O}_3(\text{ml.})} \cdot 0.8629}{\text{Weight of sample}}$$

3. Discussion

This method is an extension of the reported perhydrolysis of certain other acid chlorides and anhydrides.³ Although *m*-chloroperbenzoic acid is commercially available, this preparation requires only a short reaction time and simple equipment, and it affords high yields of this relatively stable and useful peracid. The [dichloromethane–dioxane](#) extracts can be stored and used directly for many peroxidations, in which case the total preparation time should not exceed 2 hours.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 904](#)
- [Org. Syn. Coll. Vol. 6, 403](#)

References and Notes

1. Department of Chemistry, Kansas State University, Manhattan, Kansas 66502.
 2. R. M. Herbst and R. R. Wilson, *J. Org. Chem.*, **22**, 1142 (1957).
 3. Y. Ogata and Y. Swaki, *Tetrahedron*, **23**, 3327 (1967).
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Appendix

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

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

acetic acid (64-19-7)
sodium hydroxide (1310-73-2)
thionyl chloride (7719-09-7)
oxygen (7782-44-7)
sodium thiosulfate (7772-98-7)
nitrogen (7727-37-9)
hydrogen peroxide (7722-84-1)
sodium iodide (7681-82-5)
dichloromethane (75-09-2)
magnesium sulfate (7487-88-9)
dioxane (123-91-1)
magnesium sulfate heptahydrate (10034-99-8)
m-Chloroperbenzoic acid,
Benzenecarboperoxoic acid, 3-chloro- (937-14-4)
m-chlorobenzoic acid (535-80-8)
m-chlorobenzoyl chloride (618-46-2)