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.

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.

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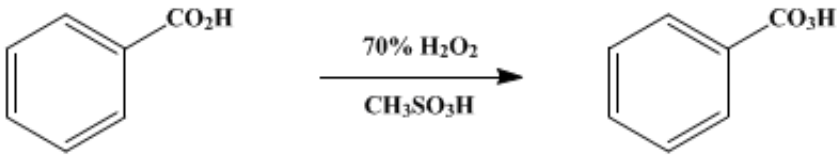
PEROXYBENZOIC ACID



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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].

Caution! All reactions in which 50% or more concentrated hydrogen peroxide is employed must be conducted behind a safety shield. Beakers are recommended as reaction vessels to permit rapid escape of gas and avoidance of pressure build-up in the event of a rapid decomposition. (See (Note 1))

Twenty-two grams (0.45 mole) of 70% hydrogen peroxide (Note 2) is added dropwise with efficient agitation to a slurry or partial solution of 36.6 g. (0.30 mole) of benzoic acid (Note 3) in 86.5 g. (0.90 mole) of methanesulfonic acid (Note 4) in a 500-ml. tall-form beaker. The reaction temperature is maintained at 25–30° by means of an ice-water bath. The reaction is exothermic during the hydrogen peroxide addition, which requires approximately 30 minutes. During this period the benzoic acid completely dissolves.

The solution is stirred for an additional 2 hours and is then cooled to 15°. Fifty grams of chopped ice and 75 ml. of ice-cold saturated ammonium sulfate solution are cautiously added in sequence while the temperature is maintained below 25° during the dilution (Note 5). The contents of the beaker are transferred to a separatory funnel, and the peroxybenzoic acid solution is extracted with three 50-ml. portions of benzene at room temperature (Note 6). The aqueous layer is discarded, and the combined benzene extracts are washed twice with 15 ml. of cold saturated ammonium sulfate solution to ensure complete removal of methanesulfonic acid and hydrogen peroxide, dried over anhydrous sodium sulfate, and filtered. Iodometric titration of an aliquot of the benzene solution (Note 7) indicates that the conversion of benzoic to peroxybenzoic acid is 85–90%. This solution can be used directly for epoxidation or other oxidation reactions without further treatment (Note 8).

2. Notes

1. For a summary of procedures to be followed in the safe handling of hydrogen peroxide and peroxy acids see reference 2, p. 90 and 478.
2. Hydrogen peroxide of this concentration can be obtained from various commercial sources. The submitters have also used 50% and 95% hydrogen peroxide instead of the 70% concentration. With 50% hydrogen peroxide, conversion to peroxybenzoic acid is only about 75%. With 95% peroxide, the reaction proceeds more rapidly and is slightly more exothermic, and conversions of benzoic acid to peroxybenzoic acid are about 90–95% instead of 85–90%. Little advantage is seen in using the more concentrated hydrogen peroxide in the preparation of peroxybenzoic acid except when a high yield of pure crystalline material is needed (Note 7).
3. Benzoic acid of analytical reagent grade is used.
4. Methanesulfonic acid, Eastman Chemicals, practical grade, is satisfactory.
5. Dilution of the methanesulfonic acid is exothermic. Since peroxybenzoic acid has an appreciable solubility in aqueous methanesulfonic acid, dilution and washing are conducted with minimal quantities of saturated ammonium sulfate solution.
6. In the first extraction, 90% of the available peroxybenzoic acid is extracted. The second extraction removes 7%, and the third 2%. The first benzene extract is an approximately 40% solution of peroxybenzoic acid (2.8*M*).
7. A 1-ml. or 2-ml. aliquot of the benzene solution of peroxybenzoic acid is pipetted into an iodine flask, the walls of the flask are rinsed with a small quantity of chloroform, and 15 ml. of acetic acid is added. Two milliliters of a saturated aqueous solution of analytical reagent grade sodium iodide is added. After a reaction period of about 5 minutes, 50–75 ml. of water is added, and the liberated iodine is titrated with 0.1*N* sodium thiosulfate solution (starch indicator). One milliliter of 0.1*N* sodium thiosulfate is equivalent to 0.00691 g. of peroxybenzoic acid.
The analytical method described is also used in following the consumption of peroxybenzoic acid or other peroxy acids during an oxidation reaction; it has also been used in determining the conversion of other carboxylic acids to peroxy acids when solvent extraction has been used in the isolation.
8. If a solvent other than benzene *must* be used in an oxidation reaction, peroxybenzoic acid can be isolated by evaporation of the benzene in an evaporating dish in the hood under a stream of nitrogen gas, or preferably in a rotary evaporator. Evaporation of the solvent from the peroxybenzoic acid solution is preferably conducted as rapidly as possible from a water bath at a temperature below 30°. *Caution! This operation must be carried out behind a good shield. A heavy explosion once occurred during such evaporation of a chloroform solution of perbenzoic acid.*[2] Owing to the volatility of peroxybenzoic acid, some is lost during solvent evaporation; overall recovery of peroxy acid is 70–90%. The crude peroxybenzoic acid obtained as a residue is a pale-yellow mushy solid or liquid if it still contains traces of benzene. The peroxy acid should be stored in a refrigerator if it is not used immediately.
Analytically pure solid peroxybenzoic acid decomposes at the rate of about 2–3% per day at room temperature, but it can be stored for long periods in a refrigerator without significant loss of active oxygen. Crude preparations lose active oxygen more rapidly. Pure peroxybenzoic acid can be obtained readily from peroxybenzoic acid of 90–95% purity by crystallization at –20° from *olefin-free* 3:1 petroleum ether/diethyl ether cosolvent. About 4.5 ml. per gram of crude peroxy acid is needed, and the solution should be seeded at about 5°. From 15 g. of crude peroxy acid, 9–10 g. of the pure acid, m.p. 41–42°, is obtained as long white needles. To obtain reaction products containing 90–95% peroxybenzoic acid, 95% hydrogen peroxide must be used in the preparation.

3. Discussion

The methods of preparation, properties, analysis, and safe handling of peroxybenzoic acid have been reviewed.[3] Numerous methods of preparing peroxy acids are described in the literature,[3,4] and many of them have been applied to the synthesis of peroxybenzoic acid. A common way of preparing it has been by the action of sodium methoxide on benzoyl peroxide followed by acidification.[4] The present method is adapted from one in a publication of the submitters.[5]

The preparation of *m*-chloroperoxybenzoic acid is described elsewhere in this series.[6]

4. Merits of the Preparation

The present procedure for peroxybenzoic acid is easier and more reliable than earlier ones. Thus that in an earlier volume of *Organic Syntheses*[4] has been found by the submitters to be difficult to reproduce, and yields are frequently low. The modified procedure of Kolthoff, Lee, and Mairs[7] is an improvement, but it is tedious and indirect.

There are other methods for converting aliphatic acids directly to peroxy acids, but this is the first that converts aromatic acids directly to peroxy acids. With suitable modifications it is applicable to a wide variety of aliphatic and aromatic peroxy acids.[5] The methyl ester may be used in place of highly insoluble acids. Water-insoluble peroxy acids such as *p*-nitroperoxybenzoic acid (an outstanding epoxidizing agent[8]), *p-tert*-butylperoxybenzoic acid, and peroxystearic acid require 90–95% hydrogen peroxide for best results; the procedure is essentially the same *except that greater precautions are necessary with hydrogen peroxide of such high strength*.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 191
- Org. Syn. Coll. Vol. 5, 414
- Org. Syn. Coll. Vol. 5, 900

References and Notes

1. Eastern Regional Research Laboratory, Philadelphia, Pennsylvania.
2. P. Westerhof, private communication.
3. D. Swern, "Organic Peroxides," Vol. **I**, Wiley-Interscience, New York, 1970, p.424, 489.
4. G. Braun, *Org. Syntheses*, Coll. Vol. **1**, 431 (1941).
5. L. S. Silbert, E. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1336 (1962).
6. R. N. McDonald, R. N. Steppel, and J. E. Dorsey, *Org. Syntheses*, **50**, 15 (1970).
7. I. M. Koltoff, T. S. Lee, and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).
8. B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955); M. Vilkas, *Bull. Soc. Chim. France*, 1401 (1959).

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

petroleum ether

acetic acid (64-19-7)

Benzene (71-43-2)

diethyl ether (60-29-7)

chloroform (67-66-3)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

sodium thiosulfate (7772-98-7)

nitrogen (7727-37-9)

Benzoic acid (65-85-0)

iodine (7553-56-2)

sodium methoxide (124-41-4)

hydrogen peroxide,
peroxide (7722-84-1)

sodium iodide (7681-82-5)

ammonium sulfate (7783-20-2)

benzoyl peroxide (94-36-0)

methanesulfonic acid (75-75-2)

Perbenzoic acid,
Peroxybenzoic acid (93-59-4)

peroxystearic acid (5796-86-1)

p-nitroperoxybenzoic acid (943-39-5)

m-chloroperoxybenzoic acid (937-14-4)

p-tert-butylperoxybenzoic acid