



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

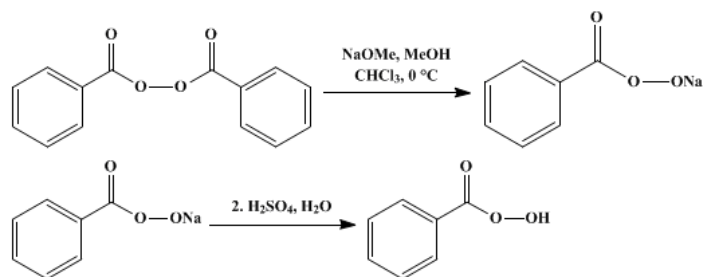
The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The 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.

PERBENZOIC ACID



Submitted by Géza Braun
Checked by C. R. Noller and Poe Liang.

1. Procedure

Caution! Reactions and subsequent operations involving peracids and peroxy compounds should be run behind a safety shield. 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].

See the discussion in Org. Synth. 1973, Coll. Vol. 5, 900 with regard to potential hazards associated with this procedure.

In a 500-cc. Erlenmeyer flask (Note 1), 5.2 g. (0.22 gram atom) of sodium is dissolved in 100 cc. of absolute methyl alcohol with moderate cooling. The resulting solution of sodium methoxide (Note 2) is cooled to -5° in a freezing mixture. A solution of 50 g. (0.21 mole) of pure commercial benzoyl peroxide (m.p. 104°) (Note 3) in 200 cc. of chloroform (Note 4) is prepared, cooled to 0° , and added without delay to the sodium methoxide solution (Note 2) with shaking and cooling at such a rate that the temperature does not rise above 0° . The mixture is kept for four or five minutes in an ice-salt bath with continuous shaking; it turns milky, but no precipitate appears. The reaction mixture is now transferred to a 1-l. separatory funnel, and the sodium perbenzoate is extracted with 500 cc. of water containing much chopped ice (Note 5). The chloroform layer is then separated and the aqueous layer is extracted twice with 100-cc. portions of cold chloroform to remove the methyl benzoate. The aqueous solution contains the sodium salt of perbenzoic acid. The perbenzoic acid is liberated by the addition of 225 cc. of cold 1 *N* sulfuric acid and is removed from solution by extracting three times with 100-cc. portions of cold chloroform (Note 6). The united chloroform solutions are washed twice with 50-cc. portions of water, and the chloroform layer is carefully separated.

The volume of the moist (milky) chloroform solution is about 308 cc., and iodometric titration indicates that it contains 23.5–24.5 g. of perbenzoic acid (82.5–86 per cent of the theoretical amount) (Note 7), (Note 8), and (Note 9). Water is the only impurity present in the moist solution; the solution may therefore be used as such for oxidations that are to be carried out in the presence of water.

To obtain crystalline perbenzoic acid, the moist chloroform solution is dried with a small amount of anhydrous sodium sulfate for an hour (Note 6). Then the sodium sulfate is removed by filtration and washed with dry chloroform; from the filtrate the chloroform is completely removed under reduced pressure while carbon dioxide is introduced through a capillary tube. The white or pale yellow residue is dried for several hours under 10 mm. pressure at $30\text{--}35^{\circ}$. The yield is 22–23 g. of crystalline mass which contains several per cent less active oxygen than the theoretical owing to a slight contamination with benzoic acid (Note 8) and (Note 9). The perbenzoic acid is very soluble in the usual organic solvents, such as chloroform, ether, ethyl acetate; it is slightly soluble in cold water and in cold ligroin.

2. Notes

1. All the glassware used in the preparation should be carefully cleaned. Either cork or thoroughly cleaned rubber stoppers may be used.

2. Sodium methoxide is preferred to sodium ethoxide because it is more soluble in the excess of alcohol and it does not precipitate provided that the solution is not cooled below -5° . If sodium ethoxide is used the sodium perbenzoate precipitates immediately as a white powder when the sodium ethoxide is added to the chloroform solution of benzoyl peroxide. With sodium methoxide the solution turns milky, but no precipitate appears.

3. The commercial (Eastman) benzoyl peroxide may be used if it gives a colorless or pale yellow chloroform solution; otherwise it should be recrystallized from a small amount of hot chloroform. It should always be analyzed before use, since the melting point is not a safe criterion of purity. The following method of analysis is convenient and satisfactory:

In a 300-cc. Erlenmeyer flask, 0.5 g. of benzoyl peroxide is dissolved in 15 cc. of chloroform. The solution is cooled to -5° , and 25 cc. of 0.1 *N* ice-cold sodium methoxide solution is added at once with cooling and shaking. After four to five minutes at -5° , 100 cc. of iced water, 5 cc. of 10 per cent sulfuric acid, and 2 g. of potassium iodide in 20 cc. of 10 per cent sulfuric acid are added in the order mentioned with violent stirring. The liberated iodine is titrated with 0.1 *N* sodium thiosulfate solution. One cubic centimeter of 0.1 *N* sodium thiosulfate solution is equivalent to 0.0121 g. of benzoyl peroxide.

4. The chloroform (u. s. p. grade) used in the preparation can be recovered by careful drying with anhydrous sodium sulfate and subsequent fractional distillation and used over and over again. The by-product is methyl benzoate, which is purified by vacuum distillation.

5. The preparation should be carried out as quickly as possible; the temperature must be kept around 0° by the addition of chopped ice, especially before the free acid is liberated from the sodium salt. Failure to observe this precaution leads to very uncertain results, whereas under correct conditions the yield of perbenzoic acid is invariably as high as 82–86 per cent of the theoretical amount.

6. After the perbenzoic acid is liberated with sulfuric acid, it may be extracted from the aqueous solution with any appropriate organic solvent (e.g. ether or ethyl acetate). Even if concentrated solutions of perbenzoic acid are required, it is better to apply the amount of solvent specified (or more) and then to concentrate the solution under reduced pressure at a temperature not above $30\text{--}35^{\circ}$. The solution may, but need not, be dried before concentration. Anhydrous sodium sulfate is the only satisfactory drying agent. Calcium chloride sometimes causes a sudden decomposition of the peracid.

7. The yield is calculated on the benzoyl peroxide content of the material used. These directions are equally satisfactory for the preparation of perbenzoic acid on a smaller or larger scale. Experiments in which the amount of benzoyl peroxide used ranged from 10 to 250 g. gave an average yield of 85 per cent of the theoretical. However, amounts from 25 to 50 g. are preferred because the

experiments can easily be completed in a short time.

8. The perbenzoic acid thus prepared is fairly stable, especially when kept in the dark in a cold place. A sample kept in moist chloroform solution showed the following change in active oxygen:

1 cc. of the solution required:

Immediately after preparation..... 13.2 cc. of 0.1 N Na₂S₂O₃

After 21 days at 2° in the dark..... 12.5 cc. of 0.1 N Na₂S₂O₃

After 5 days more at room temperature..... 7.8 cc. of 0.1 N Na₂S₂O₃

9. The amount of active oxygen is estimated by iodometric titration. One or two grams of sodium iodide is dissolved in 50 cc. of water, and then about 5 cc. of glacial acetic acid and 5 cc. of chloroform are added. To this mixture a chloroform solution of perbenzoic acid is added with violent shaking. The iodine liberated is titrated with 0.1 N sodium thiosulfate solution, of which 1 cc. is equivalent to 0.0069 g. of perbenzoic acid.

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3. Discussion

Perbenzoic acid can be prepared by the action of sodium methoxide¹ or ethoxide² on benzoyl peroxide followed by acidification with dilute sulfuric acid; from benzoyl chloride, hydrogen peroxide, and sodium peroxide;³ and from benzaldehyde and acetic anhydride in acetone and an atmosphere of oxygen.⁴

The procedure described above, which is taken from *Org. Syn.* **13**, 86, is a considerable improvement in ease of manipulation, time required, and yield obtained, over that given in the original *Collective Volume I*, 422. Chloroform is a better solvent than ether or toluene for benzoyl peroxide. A further improvement is the substitution of sodium methoxide for sodium ethoxide. Sodium methoxide is much more soluble in the excess of alcohol, and the sodium perbenzoate remains in solution, thus assuring a quantitative conversion.

The directions in the original *Collective Volume I*, 422, contain two errors. The amount of sodium specified (23 g.) is twice the correct amount, and the percentage yield, stated as 90, is only 65.

This preparation is referenced from:

- *Org. Syn. Coll. Vol.* 1, 494
- *Org. Syn. Coll. Vol.* 5, 904
- *Org. Syn. Coll. Vol.* 5, 900

References and Notes

1. Braun, *J. Am. Chem. Soc.* **51**, 239 (1929).
2. Baeyer and Villiger, *Ber.* **33**, 858, 1569 (1900); Levy and Lagrave, *Bull. soc. chim.* (4) **37**, 1597 (1925); Pummerer and Reindel, *Ber.* **66**, 336 (1933).
3. Bergmann and Witte, *Ger. pat.* 409,779 [*Chem. Zentr.* I, 1911 (1925)]; Brooks and Brooks, *J. Am. Chem. Soc.* **55**, 4310 (1933).
4. Jorissen and Van der Beek, *Rec. trav. chim.* **45**, 245 (1926).

Appendix

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

ligroin

sodium perbenzoate

sodium salt of perbenzoic acid

peracid

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ethyl acetate (141-78-6)

methyl alcohol (67-56-1)

ether (60-29-7)

acetic anhydride (108-24-7)

chloroform (67-66-3)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

potassium iodide (7681-11-0)

sodium thiosulfate (7772-98-7)

Benzoic acid (65-85-0)

carbon dioxide (124-38-9)

benzaldehyde (100-52-7)

iodine (7553-56-2)

acetone (67-64-1)

sodium methoxide (124-41-4)

benzoyl chloride (98-88-4)

toluene (108-88-3)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

hydrogen peroxide (7722-84-1)

sodium peroxide

sodium iodide (7681-82-5)

methyl benzoate (93-58-3)

benzoyl peroxide (94-36-0)

Perbenzoic acid (93-59-4)

sodium salt (824-79-3)

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