



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.

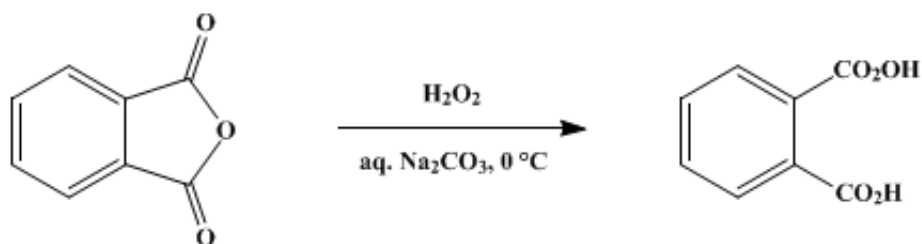
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

MONOPERPHTHALIC ACID

[Phthalic monoperoxy 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].*

In a 1-l. round-bottomed flask equipped with a mechanical stirrer and cooled in an ice-salt bath is placed a solution of 62 g. (0.5 mole) of sodium carbonate monohydrate in 250 ml. of water. This is cooled to 0°, and 69 g. (63 ml., 0.6 mole) of 30% hydrogen peroxide (Note 1) is added in one portion. With the temperature at -5 to 0°, 74 g. (0.5 mole) of phthalic anhydride (Note 1) which has been pulverized to pass a 14-mesh sieve is added (Note 2).

The reaction mixture is stirred vigorously at -5 to 0° for 30 minutes, then the resulting solution or suspension (Note 3) is poured into a 2-l. separatory funnel, shaken with 350 ml. of ether (Note 4), and carefully acidified with an ice-cold solution of 30 ml. of concentrated sulfuric acid in 150 ml. of water. The liberated monoperoxyphthalic acid is extracted into the ether and removed completely from the water by extraction with two more 150-ml. portions of ether. The combined ether extracts are washed with two 200-ml. portions of 40% ammonium sulfate solution and dried overnight in a refrigerator over 50 g. of anhydrous magnesium sulfate.

The peracid content is determined by adding 30 ml. of 20% potassium iodide solution to 2 ml. of the peracid solution and, after 10 minutes, titrating the liberated iodine with 0.1 N thiosulfate. The yield is 71–78 g. (78–86% based on phthalic anhydride).

If crystalline monoperoxyphthalic acid is desired, it may be prepared as described earlier.²

2. Notes

1. Commercial [phthalic anhydride](#) and [hydrogen peroxide](#), both of reagent grade, are used.
2. Fieser and Fieser³ recommend that the [phthalic acid](#) be recrystallized from [benzene](#) rather than pulverized.
3. The sodium salt of monoperphthalic acid may precipitate during the reaction.
4. The [ether](#) may be used, along with a *small amount* of cold water, to effect a quantitative transfer of the suspension from reaction vessel to separatory funnel.

3. Discussion

Monoperphthalic acid has been prepared by hydrolysis of [phthalyl peroxide](#) with [sodium hydroxide](#),⁴ by reaction of [phthalic anhydride](#) with excess alkaline peroxide solution,⁵ by reaction of [phthalic anhydride](#) with [hydrogen peroxide](#),⁶ and by stirring [phthalic anhydride](#) with mildly alkaline peroxide.⁷ The method described here is a slight modification of the last procedure.

The methods of preparation, properties, analysis, and safe handling of monoperphthalic acid have been reviewed.⁸

4. Merits of Preparation

The Böhme procedure^{2,5} for preparing perphthalic acid from [phthalic anhydride](#) and [hydrogen peroxide](#) is sensitive to slight variations in the experimental conditions.^{6,7} The present method gives reproducible yields with quite short reaction times.

References and Notes

1. Shell Development Company, Emeryville, Calif.
2. H. Böhme, *org. Syntheses*, Coll. Vol. **3**, 619 (1955).
3. L. F. Fieser and M. Fieser, *Reagents for Org. Synthesis*, **1**, 820 (1967).
4. A. Baeyer and V. Villiger, *Ber.*, **34**, 764 (1901).
5. H. Böhme, *Ber.*, **70**, 379 (1937); G. B. Bachman and D. E. Cooper, *J. Org. Chem.*, **9**, 307 (1944).
6. E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955).
7. G. B. Payne, *J. Org. Chem.*, **24**, 1354 (1959).
8. D. Swern, "Organic Peroxides," Vol. I, Wiley-Interscience, New York, 1970, p. 424, 489.

Appendix

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

Monoperphthalic acid

Phthalic monoperoxy acid

sodium salt of monoperphthalic acid

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

[Benzene](#) (71-43-2)

[ether](#) (60-29-7)

[sodium hydroxide](#) (1310-73-2)

[potassium iodide](#) (7681-11-0)

phthalic anhydride (85-44-9)

iodine (7553-56-2)

hydrogen peroxide (7722-84-1)

ammonium sulfate (7783-20-2)

phthalic acid (88-99-3)

magnesium sulfate (7487-88-9)

phthalyl peroxide

sodium carbonate monohydrate (5968-11-6)