



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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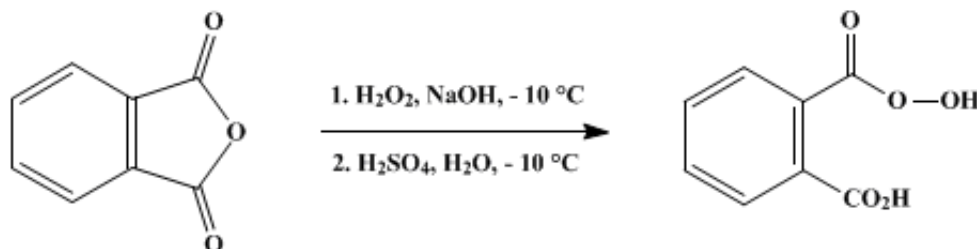
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

MONOPERPHTHALIC ACID

[Phthalic monoperacid]



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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 275 g. (250 ml., approximately 1 mole) of 15% sodium hydroxide solution. This is cooled to -10° (Note 1), and 115 g. (105 ml., approximately 1 mole) of 30% hydrogen peroxide which has been similarly cooled is added in one portion. The heat of reaction causes the temperature to rise markedly. When the temperature has again dropped to -10° , 75 g. (0.5 mole) of phthalic anhydride which has been pulverized to pass a 40-mesh sieve is added as quickly as possible while the contents are stirred vigorously in the freezing mixture (Note 2) and (Note 3). As soon as all the anhydride has dissolved, 250 ml. (0.5 mole) of 20% sulfuric acid which has been previously cooled to -10° , but not frozen (Note 4), is added.

The acid solution is filtered without suction through glass wool into a 2-l. separatory funnel and extracted once with 500 ml. of ether, then three times with 250-ml. portions of the same solvent. The combined ether extracts are shaken out with three 150-ml. portions of 40% ammonium sulfate solution and dried for 24 hours, preferably in a refrigerator, over 50 g. of anhydrous sodium sulfate.

If the ether is evaporated under reduced pressure (Note 5), crystalline monoperphthalic acid is obtained. It is more convenient, however, to use the ether solution directly (Note 6). Its peracid content is determined by adding to 2 ml. of the solution 30 ml. of 20% potassium iodide solution and titrating the iodine after 10 minutes with 0.05 N thiosulfate solution. The yield is 60–65 g. (65–70% based on the phthalic anhydride) (Note 7).

2. Notes

1. If the solutions are cooled to -10° , little oxygen is evolved and the yields of peracid are good. If the reaction is carried out at 0° , a large amount of oxygen is evolved and the yields are poor.
2. Commercial phthalic anhydride may be used directly. If excessive decomposition occurs, however, the anhydride should be purified by distillation under reduced pressure.
3. The anhydride is added in large portions or, better, in one portion.
4. The decisive factor in the success of this preparation is the time interval between the addition of the anhydride and the acidification of the reaction mixture. All the anhydride should dissolve, but prolonged stirring results in excessive oxygen evolution. The quicker the anhydride dissolves, and the smaller the oxygen evolution, the better the yield of the peracid. Hence, stirring must be vigorous.
5. If crystalline monoperphthalic acid is desired, it may be prepared conveniently as follows: The dried ether solution is placed in a distilling flask equipped with a capillary tube connected with a drying tube, and the flask is connected with the water pump. The ether is evaporated at the pressure thus obtained without the application of heat (ice will form on the flask) to a thin syrup (approximately 150 ml.). The syrup is transferred to an evaporating dish and the flask rinsed with a small amount of dry ether, the washings being added to the syrup. The remainder of the ether is then evaporated in a vacuum desiccator over concentrated sulfuric acid. For good results in this preparation the drying must be very thorough, for only 1% of water in the ether solution will be more than sufficient to destroy the entire amount of peracid.
6. If ether is not suitable for the oxidation reactions in which the peracid is to be used, the material can be dissolved in another solvent after removal of the ether. An excellent solvent for monoperphthalic acid oxidations is dioxane, and a solution of the peracid in dioxane is readily prepared by adding dioxane to the dried ether extract and then removing the ether under reduced pressure at 15° . The dioxane must be peroxide-free.¹
7. As originally submitted, this preparation was on one-fifth the scale indicated here. However, the checkers have had no difficulty with the larger-scale preparation. It has been reported² that an 86% yield of monoperphthalic acid results when a single ether extraction is employed. In the modified procedure, 40% alkali was employed, and crushed ice was added directly for cooling.

3. Discussion

Monoperphthalic acid has been prepared by hydrolysis of phthalyl peroxide with sodium hydroxide³ and by shaking phthalic anhydride with excess alkaline peroxide solution.³ The method described here is a modification of the latter process.⁴

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 805
- Org. Syn. Coll. Vol. 6, 482

References and Notes

1. Eigenberger, *J. prakt. Chem.*, (2) **130**, 75 (1931).
 2. Bachman and Cooper, *J. Org. Chem.*, **9**, 307 (1944).
 3. Baeyer and Villiger, *Ber.*, **34**, 764 (1901).
 4. Böhme, *Ber.*, **70**, 379 (1937).
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Appendix

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

Monoperphthalic acid

Phthalic monoperacid
sulfuric acid (7664-93-9)
ether (60-29-7)
sodium hydroxide (1310-73-2)
sodium sulfate (7757-82-6)
oxygen (7782-44-7)
potassium iodide (7681-11-0)
phthalic anhydride (85-44-9)
iodine (7553-56-2)
hydrogen peroxide,
peroxide (7722-84-1)
thiosulfate
ammonium sulfate (7783-20-2)
dioxane (123-91-1)
phthalyl peroxide