



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.

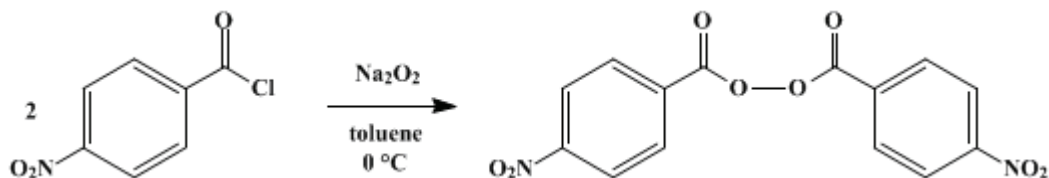
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.649 (1955); Vol. 23, p.65 (1943).

***p*-NITROBENZOYL PEROXIDE**

[Peroxide, bis(*p*-nitrobenzoyl)]



Submitted by Charles C. Price and Edwin Krebs.
Checked by R. L. Shriner and C. H. Tilford.

1. Procedure

A 600-ml. beaker containing 100 ml. of water and equipped with an efficient stirrer, a thermometer, and a 200-ml. separatory funnel is immersed in an ice-water bath. When the temperature of the water has fallen to 0–5°, 10 g. (0.13 mole) of [sodium peroxide](#) ([Note 1](#)) is added. Then, with vigorous stirring, a solution of 37 g. (0.2 mole) of [p-nitrobenzoyl chloride](#) in 100 ml. of dry [toluene](#) is added dropwise over a period of about 30 minutes. After the mixture has been stirred for an additional 1.5 hours, the precipitate is filtered and washed with 200 ml. of cold water ([Note 2](#)). The yield of [p-nitrobenzoyl peroxide](#) is 28.5–29 g. (86–88%). It melts at 155–156°.

The product may be recrystallized most conveniently by dissolving it as rapidly as possible ([Note 3](#)) in 500 ml. of dry [toluene](#) which has been preheated to 80–85°. As soon as the solid is completely dissolved (2–3 minutes of stirring), the solution is filtered through a warm Büchner funnel and the filtrate is immediately cooled in an ice-water bath. The yield of very pale yellow glistening needles is 25 to 26 g. (86–89% recovery); they melt at 156° with vigorous decomposition ([Note 4](#)).

2. Notes

1. In a parallel experiment in which 25 g. of [sodium peroxide](#) was used, the precipitate was not the peroxide but evidently consisted of sodium *p*-nitroperbenzoate.
2. [p-Nitrobenzoic acid](#) may be recovered by acidification of the filtrate.
3. Excessive heating during recrystallization leads to extensive decomposition of the peroxide.
4. By a procedure similar to that described for [p-nitrobenzoyl peroxide](#), the following peroxides have been prepared: [m-nitrobenzoyl peroxide](#) (m.p. 136–137°) in 90% yield; [anisoyl peroxide](#) (m.p. 126–127°) in 86–89% yields; [p-bromobenzoyl peroxide](#) (m.p. 144°) in 73% yield; and [3,4,5-tribromobenzoyl peroxide](#) (m.p. 186°) in 40% yield.¹ The procedure is not satisfactory for preparation of [acetylsalicylyl peroxide](#), which is more conveniently prepared by action of [hydrogen peroxide](#) upon an [acetone](#) solution of the acid chloride.

3. Discussion

[p-Nitrobenzoyl peroxide](#),² as well as [m-nitrobenzoyl peroxide](#)² and [anisoyl peroxide](#),³ have been prepared in about 50% yields from the acid chlorides and an [acetone](#) solution of [hydrogen peroxide](#), in the presence of a basic substance such as [pyridine](#), [sodium acetate](#), or [sodium hydroxide](#). [m-Nitrobenzoyl peroxide](#) has also been prepared by nitration of [benzoyl peroxide](#) with cold concentrated [nitric acid](#),⁴ or with a cold⁵ or hot² mixture of nitric and sulfuric acids.

References and Notes

1. Price, Kell, and Krebs, *J. Am. Chem. Soc.*, **64**, 1104 (1942).

2. Vanino and Uhlfelder, *Ber.*, **33**, 1046 (1900).
 3. Vanino and Uhlfelder, *Ber.*, **37**, 3624 (1904).
 4. Brodie, *J. Chem. Soc.*, **17**, 271 (1864).
 5. Vanino, *Ber.*, **30**, 2004 (1897); Gelissen and Hermans, *Ber.*, **58**, 285 (1925).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

sodium p-nitroperbenzoate

sodium acetate (127-09-3)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

acetone (67-64-1)

pyridine (110-86-1)

toluene (108-88-3)

hydrogen peroxide (7722-84-1)

sodium peroxide

benzoyl peroxide (94-36-0)

anisoyl peroxide

3,4,5-tribromobenzoyl peroxide

acetylsalicylyl peroxide

p-NITROBENZOIC ACID (62-23-7)

p-Nitrobenzoyl chloride (122-04-3)

p-Nitrobenzoyl peroxide,
Peroxide, bis(p-nitrobenzoyl) (1712-84-1)

m-nitrobenzoyl peroxide

p-bromobenzoyl peroxide