



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.

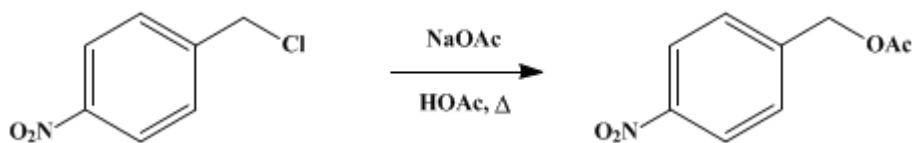
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.650 (1955); Vol. 24, p.79 (1944).

***p*-NITROBENZYL ACETATE**

[Acetic acid, *p*-nitrobenzyl ester]



Submitted by W. W. Hartman and E. J. Rahrs.

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1. Procedure

A mixture of 250 g. (1.46 moles) of *p*-nitrobenzyl chloride, 225 g. (2.74 moles) of fused sodium acetate, and 375 g. (6.25 moles) of glacial acetic acid is refluxed for 8–10 hours in a 2-l. flask heated by an oil bath, the temperature of which is maintained at 160–170° (Note 1). After this time the bath is allowed to cool to about 125°, and the acetic acid is removed by distillation under reduced pressure. Care must be taken not to reduce the pressure too rapidly in the early stages of the distillation. As the distillation slows down, the pressure is further reduced until it reaches 50 mm. or lower, and the temperature is slowly raised to 160°. From 2.5 to 3 hours is required for the complete removal of the acetic acid. About 500 ml. of water is added, and the hard cake is broken up with a stirring rod (Note 2).

The entire contents of the flask are then transferred to a 1.5-l. beaker and stirred with a mechanical stirrer for about 30 minutes or long enough to break up all the lumps. The finely divided material is filtered on a Büchner funnel and washed with 200 ml. of cold water. The above process of washing, stirring, and filtering is repeated twice. The product is then transferred to a 1.5-l. beaker, and 500 ml. of methanol is added and heated to boiling in order to effect solution. The hot solution is filtered through a heated Büchner funnel and allowed to cool slowly. When the solution has cooled to 20°, the product is collected on a filter and air-dried. This first crop consists of yellow needles which melt at 74–77° and weigh 215–225 g. The filtrate is evaporated to 100 ml. and cooled. An additional 25–30 g. of solid separates. Both crops are again washed with cold water and recrystallized from 500 ml. of hot methanol. The first crop from this second crystallization weighs 210–218 g. and melts at 77–78°. Evaporation of the filtrate to 100 ml. and cooling yield an additional 15–18 g. of acetate which is purified by recrystallization from methanol; about 12 to 15 g. of product is obtained. The combined yield of pale yellow crystals which melt at 77–78° amounts to 222–233 g. (78–82%).

2. Notes

1. *p*-Nitrobenzyl chloride obtained from the Eastman Kodak Company was used.
2. The hard cake may be removed by the addition of 500 ml. of boiling water; the ester melts and forms an oily layer. The molten ester solidifies in small lumps when the flask is cooled rapidly in an ice bath while the molten mixture is stirred vigorously. Purification in this manner by repeating the process two or three times does not seem to produce better results than purification with cold water.

3. Discussion

p-Nitrobenzyl acetate has been prepared by the action of ethanolic potassium acetate on *p*-nitrobenzyl chloride¹ or bromide,² and by the nitration of benzyl acetate.^{3,4}

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 652

References and Notes

1. Grimaux, *Zeit. für Chem.*, **1867**, 562.
 2. Reid, *J. Am. Chem. Soc.*, **39**, 130 (1917).
 3. Beilstein and Kuhlberg, *Ann.*, **147**, 340 (1868).
 4. Hurd, Fancher, and Bonner, *J. Org. Chem.*, **12**, 369 (1947).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

acetic acid (64-19-7)

methanol (67-56-1)

sodium acetate (127-09-3)

bromide (24959-67-9)

acetate

potassium acetate (127-08-2)

benzyl acetate (140-11-4)

p-nitrobenzyl chloride (100-14-1)

p-Nitrobenzyl acetate,
Acetic acid, p-nitrobenzyl ester (619-90-9)