



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.

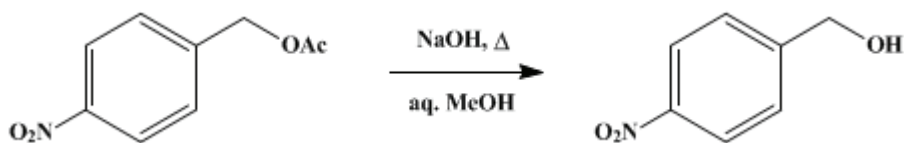
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.652 (1955); Vol. 24, p.81 (1944).

***p*-NITROBENZYL ALCOHOL**

[Benzyl alcohol, *p*-nitro]



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

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1. Procedure

A solution of 218 g. (1.12 moles) of *p*-nitrobenzyl acetate (p. 650) in 500 ml. of hot methanol is prepared in a 2-l. flask. To the hot solution is added 380 g. (1.43 moles) of a 15% solution of sodium hydroxide. The alkali should be added slowly at first with shaking to prevent too vigorous boiling. After standing for 5 minutes, the mixture is poured with vigorous hand stirring into 4.5 kg. of a mixture of cracked ice and water. The precipitate is collected on a Büchner funnel and recrystallized from 3 to 3.7 l. of hot water with the aid of 15 g. of Norit. The alcohol is dried at 60° to 65° in an oven for several hours and bottled (Note 1). The yield of slender, nearly colorless needles amounts to 110–121 g. (64–71%); the product melts at 92–93° (Note 2).

2. Notes

1. The product turns yellow if it is spread out to dry in the air.
2. The submitters report that *p*-iodobenzyl alcohol can be prepared in a similar manner, and that it is unnecessary to isolate the acetate. A mixture of 148 g. of *p*-iodobenzyl bromide, 52 g. of potassium acetate, and 750 ml. of 95% ethanol is refluxed for 8 hours, cooled, and filtered from the salt. To the filtrate is added 33.6 g. of potassium hydroxide, and the solution is refluxed for 6 hours. It is then diluted with 2 l. of water, and the oil taken up in 500 ml. of chloroform. After concentration to 150 ml. and chilling, *p*-iodobenzyl alcohol crystallizes. It is filtered and the solid rinsed with petroleum ether; the rinse added to the mother liquor causes the separation of an additional amount of *p*-iodobenzyl alcohol. The combined yield is 95–100 g. (81–86%); the product melts at 70–72°.

3. Discussion

p-Nitrobenzyl alcohol has been secured by the oxidation of *p*-nitrotoluene electrolytically¹ or chemically,² by the reduction of *p*-nitrobenzaldehyde with formaldehyde in alkaline solution,³ and by the hydrolysis of the acetate.^{4,5} *p*-Iodobenzyl alcohol has been prepared by hydrolysis of *p*-iodobenzyl bromide and *p*-iodobenzyl acetate.^{6,7}

References and Notes

1. Elbs, *Ber.* (Ref.), **29**, 1122 (1896).
2. Dieffenbach, Ger. pat. 214,949 [*Frdl.*, **9**, 156 (1908–10)].
3. B. M. Bogoslovskii and Z. S. Kazakova, *Zhur. Priklad. Khim.*, **21**, 1183 (1948) [*C. A.*, **43**, 6182 (1949)].
4. Beilstein and Kuhlberg, *Ann.*, **147**, 343 (1868).
5. Basler, *Ber.*, **16**, 2715 (1883).
6. Mabery and Jackson, *Ber.*, **11**, 56 (1878).
7. Jackson and Mabery, *Am. Chem. J.*, **2**, 251 (1880).

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

petroleum ether

ethanol (64-17-5)

methanol (67-56-1)

sodium hydroxide (1310-73-2)

formaldehyde (50-00-0)

chloroform (67-66-3)

Norit (7782-42-5)

potassium hydroxide (1310-58-3)

potassium acetate (127-08-2)

p-Nitrobenzaldehyde (555-16-8)

p-iodobenzyl acetate

p-Nitrobenzyl alcohol,
Benzyl alcohol, p-nitro (619-73-8)

p-nitrotoluene (99-99-0)

p-Nitrobenzyl acetate (619-90-9)

p-iodobenzyl alcohol (18282-51-4)

p-iodobenzyl bromide (16004-15-2)