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.

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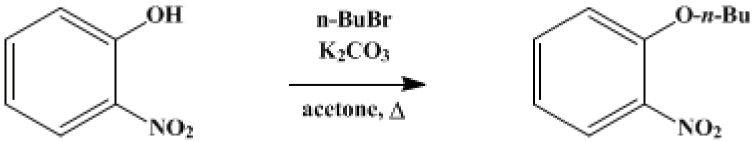
o-*n*-BUTOXYNITROBENZENE

[Ether, butyl *o*-nitrophenyl]



Submitted by C. F. H. Allen and J. W. Gates, Jr..
Checked by W. E. Bachmann and G. Dana Johnson.

1. Procedure

A mixture of 28 g. (0.2 mole) of *o*-nitrophenol (Note 1), 30 g. (0.22 mole) of *n*-butyl bromide, 28 g. (0.2 mole) of anhydrous potassium carbonate, and 200 ml. of dry acetone in a 1-l. round-bottomed flask is refluxed on a steam bath for 48 hours (Note 2). At the end of this time the acetone is distilled from the mixture, 200 ml. of water is added to the residue, and the product is extracted with two 100-ml. portions of benzene. The combined benzene extracts are washed with three 100-ml. portions of 10% sodium hydroxide, the benzene is removed by distillation at ordinary pressure, and the residual oil is distilled under reduced pressure. The yield of product boiling at 118–121°/1 mm. (Note 3) is 29–31 g. (75–80%) (Note 4) and (Note 5).

2. Notes

1. A technical grade of *o*-nitrophenol was used; the yield is no better with the pure material. In place of *n*-butyl bromide, a corresponding amount (36.8 g.) of the iodide can be used with no change in yield.
2. The checkers shook the flask occasionally during the first 1.5 hours in order to prevent caking of the contents.
3. The boiling point is 126–129°/2 mm. and 171–172°/19 mm.
4. Other nitrophenyl ethers can be prepared in a similar manner and in essentially the same yields. When the size of the run was increased to 2 moles, the yields were increased to 85–90%. The hexyl derivatives require 72 hours for reaction.
The boiling points of some ethers prepared by the present procedure are as follows: *m*-*n*-butoxynitrobenzene, 120–124°/2 mm.; *p*-*n*-butoxynitrobenzene, 150–154°/5 mm.; *p*-isopropoxynitrobenzene, 283–286°/760 mm.; *o*-*n*-hexyloxynitrobenzene, 145–148°/1 mm.; *p*-*n*-hexyloxynitrobenzene, 170–174°/5 mm.
5. The alkoxyanilines are obtained readily by reduction of the alkoxynitrobenzenes in alcohol in the presence of Raney nickel catalyst (see p. 63). The boiling points of some of these are as follows: *m*-*n*-butoxyaniline, 120–124°/2 mm.; *p*-*n*-butoxyaniline, 135–138°/5 mm.; *p*-isopropoxyaniline, 145–147°/20 mm.; *p*-*n*-hexoxyaniline, 155–158°/5 mm.

3. Discussion

The present procedure, which avoids the preparation of the salts of the phenols, is of general utility. It was first used by Claisen[1] for allyl ethers. *o*-*n*-Butoxynitrobenzene has been prepared in a similar manner previously.[2] The *m*-nitro- and *p*-nitrobutoxybenzenes have been obtained by alkylation of the phenol salts.[3,4,5] The corresponding amines have been prepared previously by reduction of the nitro compounds by means of iron and water[2] and by stannous chloride and hydrochloric acid.[4]

References and Notes

1. Claisen and Eisleb, *Ann.*, **401**, 39, 59 (1913).

2. Li and Adams, *J. Am. Chem. Soc.*, **57**, 1567 (1935).
3. Hodgson and Clay, *J. Chem. Soc.*, **1933**, 661.
4. Gutekunst and Gray, *J. Am. Chem. Soc.*, **44**, 1742 (1922).
5. Profft, *Deut. Chem. Ztg.*, **2**, 194 (1950).

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

p-n-hexoxyaniline

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

iron (7439-89-6)

n-butyl bromide (109-65-9)

stannous chloride

Raney nickel (7440-02-0)

acetone (67-64-1)

o-nitrophenol (88-75-5)

iodide (20461-54-5)

o-n-hexyloxynitrobenzene

o-n-BUTOXYNITROBENZENE,
Ether, butyl o-nitrophenyl (7252-51-9)

m-n-butoxynitrobenzene

p-n-butoxynitrobenzene (7244-78-2)

p-isopropoxynitrobenzene (26455-31-2)

m-n-butoxyaniline

p-n-butoxyaniline (4344-55-2)

p-isopropoxyaniline (7664-66-6)

m-nitrobutoxybenzene,
p-nitrobutoxybenzene

p-n-hexyloxynitrobenzene