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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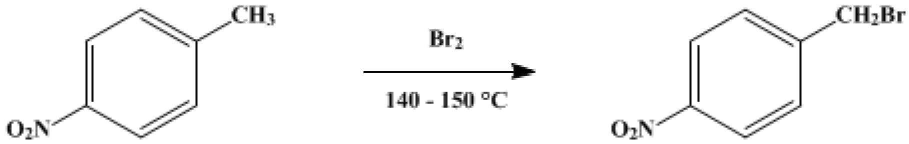
p-NITROBENZYL BROMIDE

[Toluene, α-bromo-*p*-nitro-]



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1. Procedure

In a 1-l. three-necked flask is placed 300 g. (2.2 moles) of technical *p*-nitrotoluene (m.p. 51–52°). The flask is fitted with a liquid-sealed stirrer, reflux condenser, and a separatory funnel arranged so that the stem reaches nearly to the bottom of the flask. The condenser is attached to a gas trap. The flask is heated in an oil bath at 145–150° (Note 1), and 368 g. (118 cc., 2.3 moles) of bromine is added dropwise over a period of two hours (Note 2).

After all the bromine has been added, the heating and stirring are continued for ten minutes. While still liquid, the contents of the flask (Note 3) are poured into a 5-l. round-bottomed flask containing 4 l. of hot ligroin (b.p. 90–100°), and 15 g. of Norite is added. The material is brought into solution by heating on an electric hot plate, and, after boiling for ten minutes, the solution is filtered rapidly with suction (Note 4). After cooling to 20°, the crystals are filtered with suction, pressed thoroughly, and washed with two 50-cc. portions of cold ligroin. The crude product, m.p. 94–97°, weighs 280–315 g. (59–66 per cent of the theoretical amount) and is sufficiently pure for some purposes.

For purification, this material is dissolved in 3–3.5 l. of hot ligroin, boiled with 10–15 g. of decolorizing carbon, and filtered with suction (Note 4). After cooling in an ice bath the crystals are collected on a Büchner funnel, pressed, and washed with two 25-cc. portions of cold ligroin. The pale yellow product melts at 97.5–99° and weighs 250–280 g. (53–59 per cent of the theoretical amount) (Note 5) and (Note 6).

2. Notes

1. The temperature should be kept within the limits mentioned to obtain the best results.
2. The bromine should be added within two hours even though a small amount may be lost through the condenser.
3. *p*-Nitrobenzyl bromide and its solution should be handled with caution. If the substance comes in contact with the skin, bathing the affected parts in alcohol will give relief.
4. The inverted filtration method of Bost and Constable (p. 610) is particularly advantageous for filtering hot solutions of nitrobenzyl bromide, since it reduces the fire hazard and the manipulation of the lachrymatory solutions. To avoid clogging, a tube of 8- to 10-mm. bore must be used for connecting the filtering flasks. About 3.5 l. of ligroin may be recovered from the mother liquors.
5. *p*-Nitrobenzyl bromide has been used as a reagent for the identification of many acids[1] and phenols[2] by conversion into their *p*-nitrobenzyl esters and ethers.
6. It is reported that the bromination procedure described by Brewster[3] is simpler and more convenient than that given above if tungsten lamps are employed as a source of artificial light. The light from two 300-watt tungsten lamps is satisfactory for the bromination of 300 g. of *p*-nitrotoluene. The yield of *p*-nitrobenzyl bromide is 60–70 per cent of the theoretical amount. (Leonard Weisler and Donald Pearlman, private communication.)

3. Discussion

p-Nitrobenzyl bromide has usually been prepared by brominating *p*-nitrotoluene.[1], [3] It has also been prepared by treating *p*-nitrobenzyl alcohol with hydrobromic acid,[4] and by nitrating benzyl bromide.[5]

References and Notes

1. Reid, J. Am. Chem. Soc. **39**, 126 (1917); Lyons and Reid, ibid. **39**, 1728 (1917).
2. Reid, ibid. **39**, 304 (1917); Lyman and Reid, ibid. **42**, 615 (1920).
3. Brewster, ibid. **40**, 406 (1918).
4. Norris, Watt, and Thomas, ibid. **38**, 1077 (1916).
5. Moureu and Brown, Bull. soc. chim. (4) **29**, 1008 (1921).

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

ligroin

phenols

p-nitrobenzyl esters and ethers

HYDROBROMIC ACID (10035-10-6)

bromine (7726-95-6)

Norite,
carbon (7782-42-5)

nitrobenzyl bromide

benzyl bromide (100-39-0)

p-Nitrobenzyl alcohol (619-73-8)

p-Nitrobenzyl bromide,
Toluene, α-bromo-p-nitro- (100-11-8)

p-nitrotoluene (99-99-0)