



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.

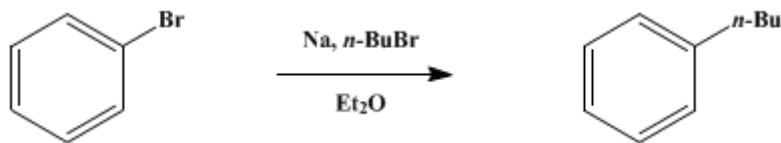
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.157 (1955); Vol. 25, p.11 (1945).

***n*-BUTYLBENZENE**

[Benzene, butyl-]



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1. Procedure

A dry, 3-l., three-necked, round-bottomed flask (Note 1) and (Note 2) is fitted with an efficient reflux condenser (Note 3) protected by a drying tube, a dropping funnel, and a thermometer which extends well into the reaction mixture (Note 4); the flask is arranged so that it can be cooled externally (Note 5). In the flask is placed 161 g. (7 gram atoms) of sodium cut into shavings 1–2 mm. in thickness (Note 6) and (Note 7); the sodium is just covered with dry ether (about 300 ml.) (Note 8). A mixture of 411 g. (321 ml., 3 moles) of *n*-butyl bromide and 471 g. (315 ml., 3 moles) of bromobenzene (Note 9) is added slowly from the dropping funnel over a period of about 2.5 hours, the temperature being kept as near 20° as possible; the mass acquires a bluish color.

After the flask and contents have been allowed to stand at room temperature for 2 days with occasional shaking, the liquid is decanted (Note 10). Three hundred milliliters of methanol is then added carefully, and the mixture is refluxed on a steam bath for 4 hours. Then 800 ml. of water is added to dissolve the salt, and the hydrocarbon layer is separated and added to the decanted liquid. The aqueous layer is extracted once with 250 ml. of ether (Note 11), and the combined hydrocarbon fraction, decanted solution, and ether extract are dried over 40 g. of calcium chloride. Most of the ether is removed on a steam bath, and the residual liquid is distilled through an electrically heated, jacketed column (Note 12). The fraction that boils at 180–182.5°/750 mm. is collected as *n*-butylbenzene (Note 13) and (Note 14); the yield is 261–281 g. (65–70%) (Note 15).

2. Notes

1. The size of the pieces of sodium, the control of temperature, and the use of an electrically heated, jacketed fractionating column are important factors in the successful preparation of the compound.
2. A copper flask and copper condenser reduce the hazard from breakage but are not essential and are less convenient with the quantities indicated.
3. Unless the reaction gets out of hand, the only function of the condenser is to prevent loss of ether. If the temperature gets above 30°, the reaction becomes violent and cannot be controlled by a single condenser.
4. A thermometer on which the scale is well above the surface of the reaction mixture is advisable; one reading from –50° to 50° is convenient.
5. The temperature range is critical. Below 15° reaction is extremely slow, but in time a vigorous reaction suddenly sets in and blows a good part of the reactants out through the condenser. Above 30° the reaction gets out of hand (Note 3).
6. This is a very tedious task. It is best accomplished by flattening the usual bars of sodium with a hammer and cutting the flattened strips with scissors. Alternatively the sodium, in 1-lb. lots, can be rolled under a heavy lawn roller (Read and Foster).
7. If the sodium is too thick, much of it fails to react, whereas sodium "sand" reacts very vigorously but gives poor yields of the desired product.
8. Larger runs require more ether. The ether may be dried over calcium chloride and used directly.
9. The *n*-butyl bromide and bromobenzene need not be redistilled.
10. Read and Foster recommend extracting the residue with benzene, using an automatic extractor.

11. Although this extract contains but 2–3 g. of hydrocarbon, its use facilitates drying later on and reduces loss through an occasional imperfect separation of layers.
12. A column such as the Whitmore-Lux or Fenske column provided with an electrically heated jacket is essential.
13. Alternatively, a crude fraction boiling at 160–185° is collected; on redistillation, the product that boils at 181–184° is collected (Read and Foster).
14. The fore-run amounts to about 45 g. The residue is largely biphenyl. Small additional amounts of product can be secured by combining these fractions from several runs and refractionating.
15. Without a heated column, the yield drops to 221 g. (54%).

3. Discussion

n-Butylbenzene has been prepared by the action of sodium (*a*) on benzyl chloride or bromide and *n*-propyl bromide without diluents,¹ or (*b*) on *n*-butyl bromide and bromobenzene without a solvent² or in benzene;³ by Clemmensen⁴ or Wolff-Kishner⁵ reduction of *n*-butyrophenone; by the action of benzylmagnesium chloride on *n*-propyl *p*-toluenesulfonate;⁶ and by the action of phenylmagnesium bromide on *n*-butyl bromide or of benzylmagnesium bromide on *n*-propyl bromide in the presence of a trace of ferric chloride.⁷ It has also been prepared from benzylsodium and *n*-propyl bromide.⁸

References and Notes

1. Radziszewski, *Ber.*, **9**, 261 (1876).
2. Read and Foster, *J. Am. Chem. Soc.*, **48**, 1606 (1926).
3. Balbiano, *Ber.*, **10**, 296 (1877); *Gazz. chim. ital.*, **7**, 343 (1877).
4. Clemmensen, *Ber.*, **46**, 1839 (1913).
5. Herr, Whitmore, and Schiessler, *J. Am. Chem. Soc.*, **67**, 2061 (1945).
6. Gilman and Beaber, *J. Am. Chem. Soc.*, **47**, 523 (1925).
7. Vavon and Mottez, *Compt. rend.*, **218**, 557 (1944).
8. Bryce-Smith and Turner, *J. Chem. Soc.*, **1950**, 1975.

Appendix

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

calcium chloride (10043-52-4)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

bromide (24959-67-9)

n-butyl bromide (109-65-9)

n-PROPYL BROMIDE (106-94-5)

sodium (13966-32-0)

benzyl chloride (100-44-7)

bromobenzene (108-86-1)

Biphenyl (92-52-4)

ferric chloride (7705-08-0)

benzylmagnesium chloride (6921-34-2)

Phenylmagnesium bromide (100-58-3)

benzylsodium

Benzene, butyl-,
n-BUTYLBENZENE (104-51-8)

benzylmagnesium bromide (1589-82-8)

n-butyrophenone (495-40-9)

n-propyl p-toluenesulfonate (599-91-7)