Organic Syntheses

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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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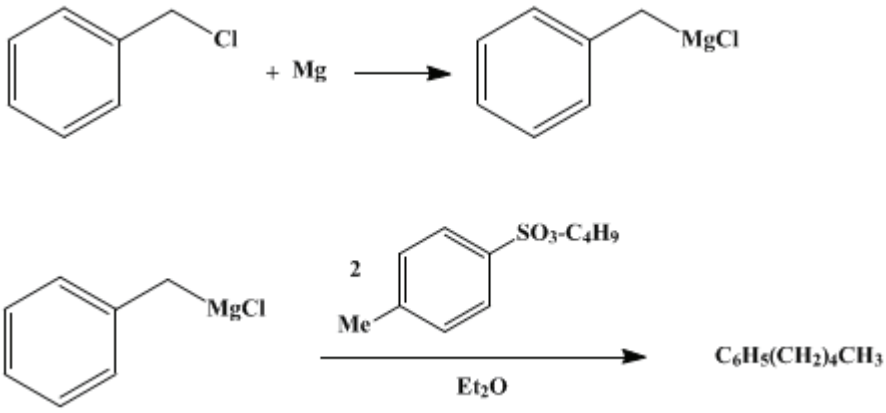
Organic Syntheses, Coll. Vol. 2, p.47 (1943); Vol. 10, p.4 (1930).

n-AMYLBENZENE

[Benzene, amyl-]



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Checked by C. S. Marvel and S. S. Rossander.

1. Procedure

One mole of benzylmagnesium chloride is prepared in a 2-l. three-necked, round-bottomed flask from 24.3 g. (1 gram atom) of magnesium turnings, 126.5 g. (115 cc., 1 mole) of benzyl chloride, and 500 cc. of anhydrous ether, according to the directions given in Org. Syn. Coll. Vol. I, **1941**, 471.

The solution of benzylmagnesium chloride is cooled with running water, and 456 g. (2 moles) of *n*-butyl *p*-toluenesulfonate (Note 1) dissolved in about twice its volume of anhydrous ether is then added slowly with stirring through the separatory funnel at such a rate that the ether just boils. The time required for the addition is about two hours. A white solid soon forms and the mixture assumes the consistency of a thick cream. Stirring is continued, without cooling, for about two hours, and the mixture is hydrolyzed by pouring onto crushed ice to which is then added about 125 cc. of concentrated hydrochloric acid (Note 2).

The ether layer is separated and combined with a 200-cc. ether extract of the aqueous layer. The combined ether solution is washed once with about 100 cc. of water and then dried by shaking for a few minutes with about 10 g. of anhydrous potassium carbonate. After filtration, the ether is distilled on a water bath. When practically all the ether has been removed, about 5 g. of sodium, freshly cut and in thin slices, is added and the mixture is boiled for about two hours (Note 3). The solution is decanted and then distilled, using an efficient fractionating column. The fraction boiling at 190–210° is collected. This on redistillation yields 74–88 g. (50–59 per cent of the theoretical amount) of *n*-amylbenzene boiling at 198–202° (Note 4).

2. Notes

1. Directions for the preparation of *n*-butyl *p*-toluenesulfonate are given in Org. Syn. Coll. Vol. I, **1941**, 145, and in Org. Syn. **20**, 51.
2. The hydrolysis is preferably carried out in a 5-l. Erlenmeyer flask. The magnesium *p*-toluenesulfonate is sparingly soluble in hydrochloric acid, and complete solution is brought about by the subsequent addition of about 2 l. of water.
3. Refluxing with sodium helps to remove the small amount of benzyl alcohol formed by the atmospheric oxidation of benzylmagnesium chloride.
4. The major part of the *n*-amylbenzene distils at 199–201°. A careful fractionation of the distillate that comes over around 75° yields 24 g. (26 per cent of the theoretical amount) of *n*-butyl chloride boiling at

76–80°.

3. Discussion

n-Amylbenzene has been prepared by the action of sodium on a mixture of benzyl and butyl bromides;[1] by the reaction between benzyl sodium and butyl chloride;[2] by the reduction of *n*-valerophenone with formic acid over copper at 300°,[3] or with zinc and hydrochloric acid;[4] by the action of sodium ethoxide on the hydrazone[5] and the semicarbazone[6] of *n*-valerophenone; and by the procedure described, which is an adaptation of the directions of Gilman and Heck[7] and Rossander and Marvel.[8]

References and Notes

1. Schramm, Ann. **218**, 388 (1883).
2. Morton and Fallwell, Jr., J. Am. Chem. Soc. **60**, 1429 (1938).
3. Mailhe and de Godon, Bull. soc. chim. (4) **21**, 62 (1917).
4. Stenzl and Fichter, Helv. Chim. Acta **17**, 677 (1934).
5. Schmidt, Hopp, and Schoeller, Ber. **72**, 1893 (1939).
6. Ziegler, Dersch, and Wollthan, Ann. **511**, 38 (1934).
7. Gilman and Heck, J. Am. Chem. Soc. **50**, 2223 (1928).
8. Rossander and Marvel, ibid. **50**, 1491 (1928).

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

benzyl and butyl bromides

hydrazone

semicarbazone

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

ether (60-29-7)

magnesium turnings (7439-95-4)

formic acid (64-18-6)

copper (7440-50-8)

zinc (7440-66-6)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

benzyl chloride (100-44-7)

Benzyl alcohol (100-51-6)

Butyl chloride,
n-BUTYL CHLORIDE (109-69-3)

benzylmagnesium chloride (6921-34-2)

Benzene, amyl-,
n-AMYLBENZENE (538-68-1)

benzyl sodium

n-valerophenone (1009-14-9)

n-BUTYL p-TOLUENESULFONATE (778-28-9)

magnesium p-toluenesulfonate