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.

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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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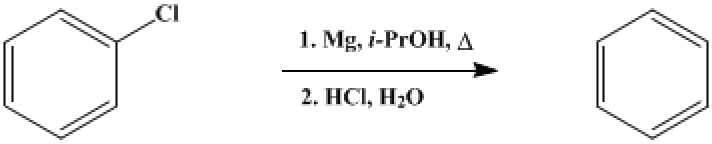
REDUCTION OF ORGANIC HALIDES. CHLOROBENZENE TO BENZENE



Submitted by D. Bryce-Smith and B. J. Wakefield[1].
Checked by William G. Dauben and Louis E. Friedrich.

1. Procedure

To a 250-ml. round-bottomed flask fitted with a glass-blade stirrer, a pressure-equalizing dropping funnel, a thermometer and a reflux condenser equipped with a nitrogen bubbler (Note 1) are added 6.0 g. (0.25 mole) of magnesium powder (Note 2) 50 ml. of decahydronaphthalene (Note 3), and a crystal of iodine. The flask is swept with nitrogen, and a nitrogen atmosphere is maintained throughout the reaction. The mixture is heated to reflux without stirring, and from the dropping funnel there is added slowly one-fifth of a solution of 11.3 g. (0.1 mole) of chlorobenzene (Note 4) and 9.0 g. (0.15 mole) of dry 2-propanol. Reaction is almost immediately apparent in the region of the iodine crystal, and as the reaction becomes progressively more vigorous (*ca.* 15 minutes) the stirrer is started and the external heating is reduced (Note 5). The remainder of the chlorobenzene solution is added over a 30-minute period; this rate of addition causes the mixture to reflux gently without external heating. An additional 25 ml. of decahydronaphthalene is added to facilitate the stirring, and the mixture is heated under reflux for one additional hour.

To the cooled mixture 6*N* hydrochloric acid is added dropwise with stirring, until no solid remains. The organic layer is separated, washed four times with 30-ml. portions of water (Note 6), dried over powdered calcium chloride (Note 7), and distilled through a 1 × 15 cm. column packed with Fenske helices (Note 8). The yield of benzene is 5.5–6.5 g. (70–83%), b.p. 80–82°, n^{20}D 1.5007. The fraction boiling at 82–180° contains no unreacted chlorobenzene (Note 9), (Note 10), (Note 11).

2. Notes

1. To minimize loss of volatile products such as benzene, it is advisable to employ a dry ice condenser on top of the conventional condenser.
2. Magnesium powder (Grade 4) from Magnesium Elektron, Inc., 610 Fifth Avenue, New York 20, New York, or from Magnesium Elektron Ltd., Manchester, England, was employed within six months of the date of its grinding by the manufacturer. The use of older or coarser material may lead to lengthened induction periods, particularly when chlorides are used.
3. Freshly distilled decahydronaphthalene was used. With the more easily reduced halides, and where the boiling point of the neutral reduction product was close to that of decahydronapthalene, an excess of 2-propanol was used as the reaction medium. Other hydrocarbons and secondary or tertiary alcohols may be employed for convenience in particular reductions. Diethyl ether and tetrahydrofuran were not found to be generally suitable media.
4. The checkers found it necessary to distil the chlorobenzene just before use.
5. When there is no sustained reaction after 10 minutes, initiation can often be accomplished by the addition of another crystal of iodine (no stirring) and/or a small amount of an easily reduced halide such as 1-bromobutane.
6. These washings remove the bulk of the 2-propanol.
7. This drying also removes the last traces of 2-propanol.
8. The checkers used a Nester-Faust 44-cm. spinning-band column.
9. This procedure has been used to effect the following reductions at *ca.* 150°: bromobenzene to benzene (89%), iodobenzene to benzene (95%), 1-chlorobutane to *n*-butane (95%), 2-chloro-2-

methylbutane to 2-methylbutane (32%), and isopropyl chloroacetate to isopropyl acetate (63%).

10. The following reductions have been carried out at 80° with the use of an excess of 2-propanol as the reaction medium (see (Note 3)): carbon tetrachloride to methane (47%), 1-bromonaphthalene to naphthalene (90%), β-bromostyrene to styrene (72%), *p*-bromoaniline to aniline (61%), *p*-bromophenol to phenol (66%), and monochloroacetone to acetone (30%).

11. Certain halides, notably fluorides, are comparatively inert under these reaction conditions. In such cases the *entrainment method* can be used, and reduction can be accomplished in the presence of a reactive halide such as 1-bromonaphthalene or 1-bromobutane. Also with certain halides, such as chlorocyclohexane, the tendency for dehydrohalogenation is diminished by the use of such entraining agents.

A typical example is the following reduction of chlorocyclohexane to cyclohexane. The general procedure is employed using 8.0 g. (0.33 mole) of magnesium powder in decahydronaphthalene (50 ml. + 20 ml.) and a solution of 6.0 g. (0.05 mole) of chlorocyclohexane, 10.4 g. (0.05 mole) of 1-bromonaphthalene, and 18 g. (0.3 mole) of 2-propanol. The product fraction, b.p. 78–80°, is a mixture of 3.5 g. (83%) of cyclohexane and 0.4 g. (10%) of cyclohexene. The olefin is removed by treatment with concentrated sulfuric acid in the usual manner.

Under the foregoing conditions, fluorocyclohexane gives cyclohexane (33%), and benzotrifluoride gives toluene (10%); fluorobenzene is inert.

3. Discussion

The present procedures are based on those briefly described by the submitters in conjunction with E. T. Blues,[2] and are based on the observation that magnesium does not, under normal conditions, readily react with secondary and tertiary alcohols in the absence of a halogen or an organic halide; little or no hydrogen is evolved during the reduction. Magnesium reacts readily with primary alcohols, evolving hydrogen, and the system is much less active in the reduction of organic halides. 2-Propanol is recommended as a general-purpose alcoholic component, but other secondary and tertiary alcohols can also be employed.

4. Merits of the Preparation

Reduction with magnesium and 2-propanol provides a simple and effective procedure for the reduction of alkyl and aryl chlorides, bromides, and iodides; with an entraining agent some alkyl fluorides are attacked. Groups such as amino, phenolic hydroxyl, ester carbonyl, and ethylenic linkages have not interfered. Nitro compounds must be absent as they inhibit the reaction with magnesium. Many carbonyl compounds, for example, *p*-bromobenzophenone, undergo much simultaneous reduction of the carbonyl groups, but acetone was obtained in fair yield from chloroacetone.

References and Notes

1. Department of Chemistry, The University, Reading, England.
2. D. Bryce-Smith, B. J. Wakefield, and E. T. Blues, *Proc. Chem. Soc.*, 219 (1963).

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

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

diethyl ether (60-29-7)

aniline (62-53-3)

hydrogen (1333-74-0)

magnesium,
magnesium powder (7439-95-4)

phenol (108-95-2)

Cyclohexene (110-83-8)

1-bromobutane (109-65-9)

carbon tetrachloride (56-23-5)

nitrogen (7727-37-9)

cyclohexane (110-82-7)

iodine (7553-56-2)

acetone (67-64-1)

methane (7782-42-5)

chlorobenzene (108-90-7)

toluene (108-88-3)

2-propanol (67-63-0)

bromobenzene (108-86-1)

1-bromonaphthalene (90-11-9)

Naphthalene (91-20-3)

1-chlorobutane (109-69-3)

chlorocyclohexane (542-18-7)

Iodobenzene (591-50-4)

styrene (100-42-5)

β-bromostyrene (103-64-0)

chloroacetone,
monochloroacetone (78-95-5)

Fluorobenzene (462-06-6)

n-butane (106-97-8)

2-methylbutane (78-78-4)

Tetrahydrofuran (109-99-9)

2-chloro-2-methylbutane (594-36-5)

isopropyl chloroacetate (105-48-6)

isopropyl acetate (108-21-4)

fluorocyclohexane (372-46-3)

benzotrifluoride (98-08-8)

decahydronaphthalene,
decahydronapthalene (91-17-8)

p-bromoaniline (106-40-1)

p-Bromophenol (106-41-2)

p-bromobenzophenone (90-90-4)