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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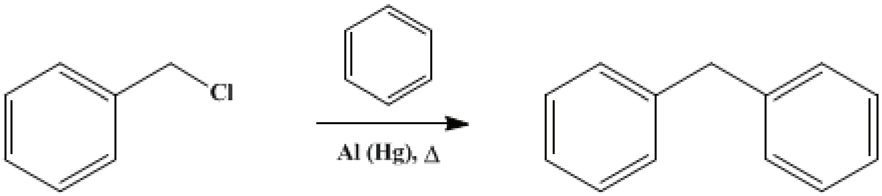
DIPHENYLMETHANE

[Methane, diphenyl-]



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1. Procedure

In a 5-l. flask, provided with a reflux condenser and an S-tube attached to a dropping funnel, are placed 2 kg. (2.3 l., 25.6 moles) of benzene, which has been dried by distilling until the distillate comes over clear, and 10 g. of amalgamated aluminum turnings (Note 1). The benzene is heated to boiling on a steam bath, the steam is turned off, and 500 g. (3.96 moles) of benzyl chloride is added at such a rate as to cause the solution to boil (Note 2). The hydrogen chloride is absorbed in water or allowed to pass out-of-doors. When all the benzyl chloride has been added (one hour), the mixture is warmed for ten to fifteen minutes, or until the evolution of hydrogen chloride ceases. When cool, the benzene solution of diphenylmethane is decanted from the small amount of tarry material (Note 3) and washed with 5 per cent sodium hydroxide solution and then with water. After a partial drying with calcium chloride, the benzene is distilled from a steam bath and the residue fractionated under diminished pressure. The fore-run is collected up to 125°/10 mm., the main product at 125–130°/10 mm., and an after-run up to 150°/10 mm. (Note 4). Redistillation of the fore-run and after-run yields a small amount of material which is added to the main fraction. The latter is chilled and a small amount of oil is decanted from the crystals. The yield of material melting at 24–25° is 330–350 g. (49.5–52.5 per cent of the theoretical amount).

2. Notes

1. Amalgamated aluminum is prepared as follows: Aluminum turnings, freed from any oil by washing with ether, are stirred with a 5 per cent mercuric chloride solution for a few minutes and then washed quickly with water followed by methyl alcohol. The amalgamated aluminum is used at once.
2. At times the reaction is slow in starting. Not more than 50–60 g. of benzyl chloride is added at first, and the mixture is heated until the evolution of hydrochloric acid indicates that the reaction is under way. If too much benzyl chloride is present when the reaction starts, the contents of the flask may boil over.
3. Succeeding batches may be started in the same flask containing the aluminum turnings and the trace of tarry material without the addition of further catalyst; these batches do not show an induction period.
4. The material in the residue and high-boiling fraction may be partially converted into diphenylmethane by heating with one-third its weight of aluminum chloride and five times its weight of benzene.

3. Discussion

Diphenylmethane can be prepared from benzene and benzyl chloride with aluminum chloride,[1] hydrogen fluoride,[2] beryllium chloride,[3] the double salt of aluminum and sodium chlorides,[4] zinc dust,[5] zinc chloride,[6] or aluminum amalgam[7] as a condensing agent. The procedure described above is a slight modification of the last method.

Benzene and benzyl alcohol furnish diphenylmethane on treatment with boron fluoride,[8] hydrogen fluoride,[9] or beryllium chloride.[3] Diphenylmethane has also been prepared from benzene, methylene chloride, and aluminum chloride,[10] and from benzene, formaldehyde, ethanol, and concentrated sulfuric acid.[11] The reduction of benzophenone to diphenylmethane has been effected by hydriodic acid and phosphorus,[12] sodium and alcohol,[13] and fusion with zinc chloride and sodium chloride.[14] The condensation of benzylmagnesium chloride and benzene to diphenylmethane can be brought about by small amounts of magnesium and water.[15]

References and Notes

1. Friedel and Balsohn, Bull. soc. chim. (2) **33**, 337 (1880).
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10. Friedel and Crafts, Bull. soc. chim. (2) **41**, 324 (1884); Schwarz, Ber. **14**, 1526 (1881).
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12. Graebe, Ber. **7**, 1624 (1874).
13. Klages and Allendorff, ibid. **31**, 999 (1898).
14. Clar, ibid. **72**, 1645 (1939).
15. Kharasch, Goldberg, and Mayo, J. Am. Chem. Soc. **60**, 2004 (1938).

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

amalgamated aluminum turnings

Amalgamated aluminum

double salt of aluminum and sodium chlorides

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methyl alcohol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

formaldehyde (50-00-0)

magnesium (7439-95-4)

sodium chloride (7647-14-5)

PHOSPHORUS (7723-14-0)

aluminum,
Aluminum turnings (7429-90-5)

hydrogen fluoride (7664-39-3)

aluminum chloride (3495-54-3)

Benzophenone (119-61-9)

zinc (7440-66-6)

sodium (13966-32-0)

Diphenylmethane,
Methane, diphenyl- (101-81-5)

benzyl chloride (100-44-7)

Benzyl alcohol (100-51-6)

zinc chloride (7646-85-7)

hydriodic acid (10034-85-2)

mercuric chloride (7487-94-7)

benzylmagnesium chloride (6921-34-2)

methylene chloride (75-09-2)

beryllium chloride (7787-47-5)

boron fluoride (7637-07-2)