



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.

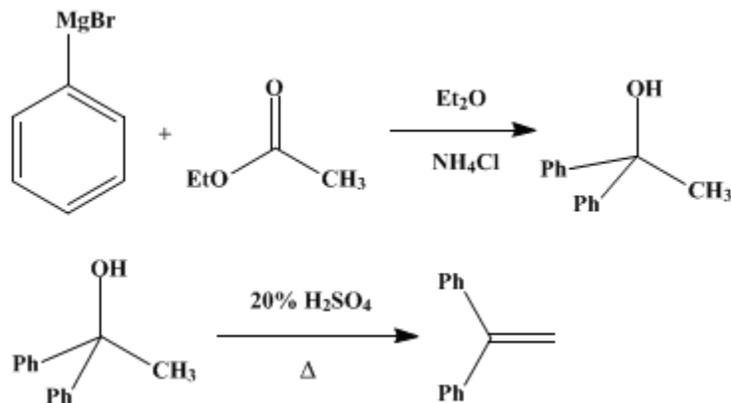
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.226 (1941); Vol. 6, p.32 (1926).

1,1-DIPHENYLETHYLENE

[Ethylene, 1,1-diphenyl-]



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1. Procedure

In a 2-l. three-necked flask, fitted with a separatory funnel, reflux condenser, and stirrer, is placed 27 g. (1.1 atoms) of **magnesium turnings**. A mixture of 30 g. of **bromobenzene** and 70 cc. of dry **ether** is run in and the flask warmed gently until the reaction becomes rapid. Stirring is then started, and the vessel is surrounded by a dish of cold water. A mixture of 151 g. of **bromobenzene** (total: 181 g., 1.15 moles) and 380 cc. of dry **ether** is run in at such a rate as to cause vigorous refluxing; when the addition is complete (one hour) the whole is stirred for ten minutes.

After the flask has been cooled by immersion in ice water, 44 g. (0.5 mole) of dry **ethyl acetate** (**Note 1**) in an equal volume of **ether** is added over a period of twelve minutes. The cooling bath is removed and stirring is continued for ten minutes. When the reaction flask has again been cooled by the ice-water bath, a previously prepared **ammonium chloride** solution (**Note 2**) is added, very slowly at first, over a period of ten minutes, during which a pasty solid separates.

The **ether** layer is decanted into a separatory funnel, and to it is added a 50-cc. **ether** extract of the pasty residue. The **ether** is removed by dropping the solution into a 500-cc. round-bottomed flask attached to a condenser and immersed in an oil bath heated to 210–215°. The flask is removed from the oil bath, cooled, and disconnected from the condenser; 100 cc. of 20 per cent **sulfuric acid** is added. The flask is fitted with a reflux condenser, and the contents are boiled for one hour. The aqueous layer is now removed, and the residual oil, without being washed, is distilled at a pressure of about 30 mm. and a bath temperature of about 210° (**Note 3**). At first a low-boiling fraction consisting of **bromobenzene** (12–14 g.) and traces of water distills, after which the **diphenylethylene** comes over as a colorless liquid, the last portions being slightly yellowish. The brownish residue contains polymerization and decomposition products. On redistillation, the pure hydrocarbon boils at 113°/2 mm. (**Note 4**). The yield is 60–66 g. (67–70 per cent of the theoretical amount based on **ethyl acetate**) (**Note 5**).

2. Notes

1. The grade of **ethyl acetate** is very important. If ordinary **ethyl acetate** is used it may be purified by washing with twice its volume of water, drying over fused **potassium carbonate**, refluxing with **phosphorus pentoxide**, filtering, and fractionating, whereupon practically all comes over at constant temperature. The addition to the Grignard reagent should be cautious at first, to avoid a vigorous reaction that frequently occurs after about 15 cc. has been added.

2. The **ammonium chloride** solution is prepared by dissolving 50 g.> of **ammonium chloride** in 150 cc.

of water at 25–30°. The literature recommends 30 per cent [sulfuric acid](#) for decomposing the magnesium compound; when this is used, the yield drops to 50–55 per cent, probably owing to the ready polymerization of the hydrocarbon in the presence of mineral acids.

3. This treatment obviates the necessity of isolating the intermediate carbinol. The carbinol, if desired, can be obtained in yields up to 75 per cent from the combined, dried, [ether](#) extracts.

4. The hydrocarbon is reported to boil at 123–5°/5 mm.; 134°/10 mm.¹; 139°/11 mm.²; 156°/25 mm.³; 164°/34 mm.³; and at 277°/760 mm.⁴

5. The yield is decreased by about 10 per cent if only an equivalent molecular quantity of [phenylmagnesium bromide](#) is used.

3. Discussion

1,1-Diphenylethylene can be prepared by the action of alcoholic [potassium hydroxide](#) on unsymmetrical [diphenylchloroethane](#);⁴ by the action of [aluminum chloride](#) on [benzene](#) and [tribromoethylene](#);⁵ and by dehydration of the carbinol which can be prepared by the action of [methylmagnesium iodide](#) on [benzophenone](#),¹²³⁶ or [phenylmagnesium bromide](#) on [acetophenone](#)⁷ or [ethyl acetate](#).⁸ The procedure described is adapted from that of Stadnikov.⁸

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 353](#)
- [Org. Syn. Coll. Vol. 3, 562](#)
- [Org. Syn. Coll. Vol. 3, 729](#)
- [Org. Syn. Coll. Vol. 3, 771](#)
- [Org. Syn. Coll. Vol. 3, 839](#)
- [Org. Syn. Coll. Vol. 5, 1124](#)
- [Org. Syn. Coll. Vol. 9, 507](#)

References and Notes

1. Lebedew, Ber. **56**, 2349 (1923);
2. Lipp, Ber. **56**, 567 (1923);
3. Klages, Ber. **35**, 2646 (1902);
4. Hepp, Ber. **7**, 1409 (1874).
5. Anschütz, Ann. **235**, 336 (1886).
6. Gilman and Crawford, J. Am. Chem. Soc. **45**, 554 (1923).
7. Tröger and Beck, J. prakt. Chem. (2) **87**, 289 (1913); Hurd and Webb, J. Am. Chem. Soc. **49**, 546 (1927).
8. Anschütz and Hilbert, Ber. **54**, 1856 (1921); Stadnikov, J. Russ. Phys. Chem. Soc. **47**, 2037, 2115 (1915) [C. A. **10**, 1355 (1916)]; Schlenck and Bergmann, Ann. **463**, 24 (1928).

Appendix

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

magnesium compound

[potassium carbonate](#) (584-08-7)

[sulfuric acid](#) (7664-93-9)

Benzene (71-43-2)

ethyl acetate (141-78-6)

ether (60-29-7)

ammonium chloride (12125-02-9)

magnesium turnings (7439-95-4)

Acetophenone (98-86-2)

aluminum chloride (3495-54-3)

potassium hydroxide (1310-58-3)

Benzophenone (119-61-9)

bromobenzene (108-86-1)

1,1-Diphenylethylene,
Ethylene, 1,1-diphenyl-,
diphenylethylene (530-48-3)

Phenylmagnesium bromide (100-58-3)

diphenylchloroethane

tribromoethylene (598-16-3)

methylmagnesium iodide (917-64-6)

phosphorus pentoxide (1314-56-3)