



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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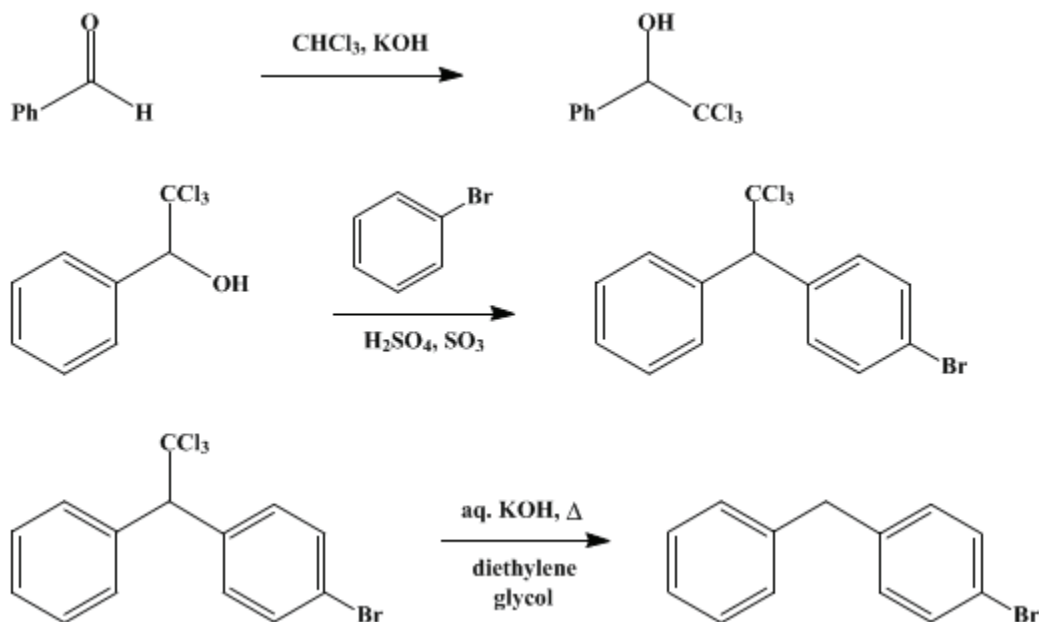
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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p-BROMODIPHENYLMETHANE

[Methane, (*p*-bromophenyl)phenyl-]



Submitted by A. B. Galun¹ and A. Kalir².
Checked by R. Breslow and H. T. Bozimo.

1. Procedure

A. *1-Phenyl-2,2,2-trichloroethanol*. In a 1-l. round-bottomed-flask fitted with a mechanical stirrer, a thermometer, and a powder funnel is placed a solution of 212 g. (2.00 moles) of freshly distilled benzaldehyde in 400 g. (270 ml., 3.35 moles) of chloroform. The mixture is cooled in an ice bath, and 123 g. of commercial powdered potassium hydroxide is added with stirring at such a rate that the temperature of the solution does not exceed 45° (1–1.5 hours). The reaction mixture is stirred and kept at 40–50° for an additional hour and then poured into a solution of 60 ml. of sulfuric acid in 3 l. of water. The resulting two-phase mixture is transferred to a separatory funnel and extracted with three 250-ml. portions of chloroform (a small amount of insoluble, black resinous material is discarded). The combined organic layers are washed with three 100-ml. portions of aqueous 10% sodium carbonate, dried over anhydrous magnesium sulfate, and filtered into a 1-l. flask. The solvent is removed under reduced pressure on a hot water bath. The residue is transferred to a 250-ml. flask and distilled under reduced pressure to give 1-phenyl-2,2,2-trichloroethanol, b.p. 155–165° (26 mm.), 90–100° (0.5 mm.) (Note 1) and (Note 2). The yield is 170–180 g. (38–40%).

B. *1-p-Bromophenyl-1-phenyl-2,2,2-trichloroethane*. In a 500-ml. round-bottomed flask fitted with a mechanical stirrer, a dropping funnel, and a thermometer are placed 136 g. (0.60 mole) of 1-phenyl-2,2,2-trichloroethanol and 120 g. (81 ml., 0.77 mole) of bromobenzene. The flask is cooled in an ice-water bath, and a mixture of 120 ml. of concentrated sulfuric acid and 50 ml. of oleum (20% SO₃) is added with stirring at such a rate that the temperature of the reaction mixture does not exceed 10° (ca. 45 minutes) (Note 3). The mixture is stirred for another 30 minutes at 10° and for 4–5 hours at room temperature. It is then poured with manual stirring onto 1 kg. of cracked ice, and the mixture is allowed to stand overnight. The precipitate (Note 4) is filtered, washed with water, and recrystallized from 300 ml. of ethanol (Note 5). The yield is 129–162 g. (59–74%), m.p. 95–96° (Note 6).

C. *p-Bromodiphenylmethane*. A 2-l. three-necked flask fitted with a distillation condenser, a thermometer, and an efficient mechanical stirrer is charged with 1.1 l. of diethylene glycol (Note 7) and

a solution of 190 g. of **potassium hydroxide** in 100 ml. of water. The mixture is stirred, and water is distilled until the internal temperature reaches 180°. The resulting solution is allowed to cool to 100° or below, and 146 g. (0.40 mole) of **1-*p*-bromophenyl-1-phenyl-2,2,2-trichloroethane** (Note 8) is added. The condenser is set for reflux, and the mixture is stirred and heated to boiling for 5 hours (Note 9). The hot solution is then poured onto 3 kg. of cracked ice, and the mixture is allowed to stand overnight. The oily layer is separated and dissolved in **ether** (any insoluble material is discarded), and the aqueous layer is extracted with 250 ml. of **ether**. The combined ethereal solution and extracts are dried over **calcium chloride** and filtered. The **ether** is removed under reduced pressure on a hot water bath. The product is distilled under reduced pressure; b.p. 120–130° (3 mm.), 155–163° (13 mm.) (Note 10), n_D^{24} 1.6028, d_4^{24} 1.342. The yield is 74–79 g. (75–80%) (Note 11).

2. Notes

1. The purpose of the distillation is to separate the product from tars. Therefore no fractionation is required, and the distillation may be carried out rapidly.
2. The carbinol, which has a tendency to supercool, may crystallize overnight; m.p. 38°.
3. Solid material is sometimes deposited on the walls of the reaction flask.
4. In some cases the organic layer separates as an oil; it is then obtained in crystalline form by trituration with 200 ml. of cold **methanol**, which dissolves the excess of **bromobenzene**.
5. Wet material may require larger amounts of **ethanol**.
6. Trituration of the crude precipitate with **methanol** gives a 90% yield of material, m.p. 90–93°.
7. Eastman Organic Chemicals white label **2,2-oxidiethanol** was used.
8. The material should be thoroughly freed of alcohol, preferably over **phosphorus pentoxide** under reduced pressure, before use. Even traces of alcohol may reduce the yield to 60%.
9. The temperature of the refluxing solution should be above 165°. Efficient stirring is essential; otherwise the precipitating **potassium carbonate** entrains much material, causing reduction of yield.
10. Good fractionation is not required.
11. Runs on a fourfold scale give the same yield.

3. Discussion

The procedure for the preparation of **1-phenyl-2,2,2-trichloroethanol** is based on the work of Bergmann, Ginsburg, and Lavie.³ **1-Phenyl-2,2,2-trichloroethanol** has also been prepared from **phenylmagnesium bromide** and **chloral**.⁴

***p*-Bromodiphenylmethane** has been reported as a product of the reduction of ***p*-bromobenzophenone** with **hydriodic acid** and red phosphorus in a sealed tube at 160°.⁵ The present method is a modification of the synthesis published by Galun, Kaluszyner, and Bergmann.⁶

4. Merits of the Preparation

In this method inexpensive, commercially available chemicals are used as starting materials. The operations are simple, the yields acceptable, and the final products are free of isomers.

This procedure is especially suited for preparing variously substituted diarylmethanes.⁶ The 1,1-diaryl-2,2,2-trichloroethanes may be converted to the corresponding benzophenones via the 1,1-diaryl-2,2-dichloroethylenes⁷ and to 1,1-diarylacetic acids.⁸

References and Notes

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4. P. Hébert, *Bull. Soc. Chim. France*, [4] **27**, 45 (1920); Z. I. Iotsich, *Zh. Russ. Fiz.-Khim. Obshch.*, **34**, 96 (1902).
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6. A. B. Galun, A. Kaluszyner, and E. D. Bergmann, *J. Org. Chem.*, **27**, 1426 (1962).
 7. O. Grummitt, A. Buck, and A. Jenkins, *J. Am. Chem. Soc.*, **67**, 155 (1945).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

red phosphorus

ethanol (64-17-5)

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

methanol (67-56-1)

ether (60-29-7)

chloroform (67-66-3)

sodium carbonate (497-19-8)

benzaldehyde (100-52-7)

potassium hydroxide (1310-58-3)

bromobenzene (108-86-1)

hydriodic acid (10034-85-2)

Phenylmagnesium bromide (100-58-3)

magnesium sulfate (7487-88-9)

chloral (75-87-6)

diethylene glycol,
2,2-oxydiethanol (111-46-6)

1-Phenyl-2,2,2-trichloroethanol (2000-43-3)

phosphorus pentoxide (1314-56-3)

p-Bromodiphenylmethane,
Methane, (p-bromophenyl)phenyl- (2116-36-1)

1-p-Bromophenyl-1-phenyl-2,2,2-trichloroethane (39211-93-3)

p-bromobenzophenone (90-90-4)

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