



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.

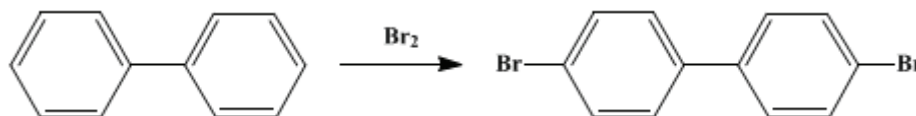
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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4,4'-DIBROMOBIPHENYL

[Biphenyl, 4,4'-dibromo-]



Submitted by Robert E. Buckles and Norris G. Wheeler¹.

Checked by R. S. Schreiber, Wm. Bradley Reid, Jr., and Robert W. Jackson.

1. Procedure

In a 15-cm. evaporating dish is placed 15.4 g. (0.10 mole) of finely powdered biphenyl (Note 1). The dish is set on a porcelain rack in a 30-cm. desiccator with a 10-cm. evaporating dish under the rack containing 39 g. (12 ml., 0.24 mole) of bromine. The desiccator is closed, but a very small opening is provided for the escape of hydrogen bromide (Note 2). The biphenyl is left in contact with the bromine vapor for 8 hours (or overnight). The orange solid is then removed from the desiccator and allowed to stand in the air under a hood for at least 4 hours (Note 3). At this point, the product weighs about 30 g. and has a melting point in the neighborhood of 152°. The crude 4,4'-dibromobiphenyl is dissolved in 75 ml. of benzene, filtered, and cooled to 15°. The resulting crystals are filtered, giving a yield of 23.4–24.0 g. (75–77%) of 4,4'-dibromobiphenyl, m.p. 162–163° (Note 4).

2. Notes

1. The checkers used Eastman Kodak Company white label grade of biphenyl.
2. If a vacuum desiccator is used, the stopcock can be opened slightly to allow for the escape of hydrogen bromide.
3. The standing period allows hydrogen bromide and bromine to escape from the crystals.
4. 4,4'-Dibromobibenzyl can be prepared in the same manner. Eighteen grams (0.10 mole) of finely divided bibenzyl is left in contact with the vapor from 39 g. (12 ml., 0.24 mole) of bromine for 24 hours. The desiccator is put under an opaque cover to keep out light, which causes the formation of α,α' -dibromobibenzyl. The somewhat sticky reaction product is allowed to stand overnight. The crude product is dissolved in 300 ml. of isopropyl alcohol, filtered, and cooled. A yield of 15.0–17.0 g. (44–50%) of 4,4'-dibromobibenzyl, m.p. 113–114°, is obtained.

3. Discussion

This method is a modification of that of Buckles, Hausman, and Wheeler.² 4,4'-Dibromobiphenyl has also been prepared by the bromination of biphenyl in water,³ carbon disulfide,⁴ and glacial acetic acid;⁵ by the bromination of a mixture of biphenylsulfonic acids in dilute sulfuric acid;⁶ by the action of sodium carbonate⁷ or ethanol⁸ on the perbromide obtained from the reaction of diazotized benzidine with bromine water; and by passing *p*-dibromobenzene vapor through a red-hot tube.⁹

4,4'-Dibromobibenzyl has been prepared by the bromination of bibenzyl in water;¹⁰ by the reaction of *p*-bromobenzyl bromide with zinc dust in water;¹¹ and by the reaction of bromobenzene with ethylene oxide in the presence of anhydrous aluminum chloride.¹²

References and Notes

1. State University of Iowa, Iowa City, Iowa.
2. Buckles, Hausman, and Wheeler, *J. Am. Chem. Soc.*, **72**, 2494 (1950).
3. Fittig, *Ann.*, **132**, 204 (1864).

4. Carnelley and Thomson, *J. Chem. Soc.*, **47**, 586 (1885).
 5. Scholl and Neovius, *Ber.*, **44**, 1087 (1911).
 6. Datta and Bhoumik, *J. Am. Chem. Soc.*, **43**, 306 (1921).
 7. Griess, *J. Chem. Soc.*, **20**, 91 (1867).
 8. Loh and Turner, *J. Chem. Soc.*, **1955**, 1274.
 9. Meyer and Hofmann, *Monatsh.*, **38**, 141 (1917).
 10. Stelling and Fittig, *Ann.*, **137**, 267 (1866).
 11. Errera, *Gazz. chim. ital.*, **18**, 236 (1888).
 12. Smith and Natelson, *J. Am. Chem. Soc.*, **53**, 3476 (1931).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

bromine water

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

hydrogen bromide (10035-10-6)

sodium carbonate (497-19-8)

bromine (7726-95-6)

aluminum chloride (3495-54-3)

zinc (7440-66-6)

isopropyl alcohol (67-63-0)

bromobenzene (108-86-1)

carbon disulfide (75-15-0)

Biphenyl (92-52-4)

Ethylene oxide (75-21-8)

benzidine (92-87-5)

α,α' -dibromobibenzyl (5789-30-0)

bibenzyl (103-29-7)

p-dibromobenzene (106-37-6)

4,4'-DIBROMOBIPHENYL,
Biphenyl, 4,4'-dibromo- (92-86-4)

p-bromobenzyl bromide (589-15-1)

4,4'-Dibromobibenzyl (19829-56-2)