



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](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.

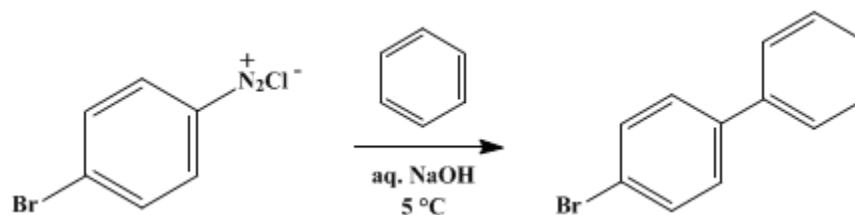
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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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## ***p*-BROMOBIPHENYL**

[Biphenyl, 4-bromo-]



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### 1. Procedure

Forty-three grams (0.25 mole) of *p*-bromoaniline (Note 1) and 20 cc. of water are warmed in a 400-cc. beaker until the bromoaniline melts, and then 50 cc. of concentrated hydrochloric acid (sp. gr. 1.19) is added with mechanical stirring. The mixture is heated and stirred until solution is practically complete (Note 2). The beaker is then set in a dish of ice water and the solution is stirred as it cools in order to precipitate the *p*-bromoaniline hydrochloride in fine crystals. A few small pieces of ice are added, and the cold (about 0–5°) suspension is diazotized with a solution of 18 g. (0.26 mole) of sodium nitrite in 36 cc. of water to an end-point with starch-iodide paper.

The diazotized solution is poured into a 1.5-l. wide-mouthed flask or bottle which is surrounded by ice water. Three hundred cubic centimeters of cold benzene is now poured into the diazonium solution, and by means of a good stirrer the two liquids are intimately mixed. The mixture, which is at the temperature of melting benzene, is now ready for the addition of alkali.

To this well-stirred mixture is added 58 cc. of 5 *N* sodium hydroxide solution over a period of one-half to three-quarters of an hour. This may be added drop by drop from a separatory funnel or in portions of a few cubic centimeters. The addition of the alkali causes the formation of a yellow precipitate which, on being stirred into the benzene, reacts with the benzene and gives *p*-bromobiphenyl. If too much of this reactive "oxide" is precipitated at one time, some of it may decompose to a dark brown product. The alkali is, therefore, added at such a rate that the amount of precipitate is at no time greater than can readily react with the benzene, and the stirring must be efficient. The temperature during the reaction is kept at about 5°; when all the alkali has been added, the mixture is allowed to warm to room temperature.

If an emulsion has formed, it may be broken by acidifying with hydrochloric acid, whereupon two clear layers are obtained. The benzene solution may be dried and then fractionated or, preferably, it may be steam distilled. In the latter case it is transferred to a 1-l. Claisen flask, the flask is set in an oil bath (Note 3), and the benzene distilled. Steam is then passed in, and after the last of the benzene is removed, the *p*-bromobiphenyl distils with the steam. The temperature of the oil bath is held at 170° in order to hasten the distillation. The product solidifies in the condenser and receiving flask. There is obtained 23–24 g. of *p*-bromobiphenyl which melts at 85–86.5°.

The crude product is usually yellow or orange in color. The color may be readily removed by dissolving the crude product in 200 cc. of hot ethyl alcohol and treating this solution with 5 g. of zinc dust and about 5 cc. of concentrated hydrochloric acid (sp. gr. 1.19). This solution is then filtered and the *p*-bromobiphenyl allowed to crystallize. This gives a white product melting at 89.5–90°. The yield is 20–21 g. (34–35 per cent of the theoretical amount).

### 2. Notes

1. The *p*-bromoaniline used was somewhat colored and melted at 62.5–63°.
2. The volume of the diazonium solution is kept as small as possible in order that the proportion of benzene to water may be as large as possible. The bromoaniline does not completely dissolve in this quantity but is entirely converted to the salt.
3. There is some tendency toward foaming during the steam distillation. To avoid this the flask should be submerged almost completely in the oil bath.

### 3. Discussion

*p*-Bromobiphenyl can be obtained along with some of the ortho derivative from the bromination of biphenyl.<sup>1</sup> However, according to Schlenk,<sup>2</sup> the product so obtained is contaminated with some *p,p'*-dibromobiphenyl which is very difficult to remove. Bamberger obtained *p*-bromobiphenyl from the action of benzene on solid *p*-bromobenzenediazoanhydride.<sup>3</sup> The procedure described has been reported in the literature.<sup>4</sup> *p*-Bromobiphenyl has also been prepared from *p*-dibromobenzene, activated magnesium, and cyclohexanol by a series of reactions which involves the formation and dehydrogenation of 1-bromo-4-cyclohexenylbenzene.<sup>5</sup>

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### References and Notes

1. Schultz, Ann. **174**, 207 (1874).
2. Schlenk, Ber. **46**, 1477 (1913).
3. Bamberger, Ber. **29**, 470 (1896).
4. Gomberg and Bachmann, J. Am. Chem. Soc. **46**, 2339 (1924).
5. v. Braun, Irmisch, and Nelles, Ber. **66**, 1478 (1933).

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### Appendix

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

*p*-bromobenzenediazoanhydride

ethyl alcohol (64-17-5)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

magnesium (7439-95-4)

Cyclohexanol (108-93-0)

sodium nitrite (7632-00-0)

zinc (7440-66-6)

Biphenyl, 4-bromo-,  
*p*-Bromobiphenyl (92-66-0)

bromoaniline

Biphenyl (92-52-4)

1-bromo-4-cyclohexenylbenzene

p-dibromobenzene (106-37-6)

p-bromoaniline (106-40-1)

p-bromoaniline hydrochloride

p,p'-dibromobiphenyl (92-86-4)