



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.

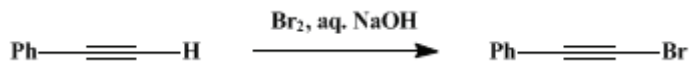
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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PHENYLBROMOETHYNE

[Benzene, bromoethynyl]



Submitted by Sidney I. Miller, Gene R. Ziegler, and R. Wieleseck¹.

Checked by William E. Parham and James N. Wemple.

1. Procedure

To a 2-l. bottle equipped with a rubber stopper and immersed in a mixture of ice and water (slush) there is added a cold (about 0°) solution containing 300 g. (7.5 moles) of sodium hydroxide (Note 1) and 800 ml. of water. The mixture is swirled or stirred while 160 g. (2 moles) of bromine is added. Phenylacetylene (84 g., 0.82 mole) (Note 2) is then added to the yellow solution, and the resulting mixture is stoppered and shaken. The rubber stopper is wired down, the bottle is covered with opaque cloth or paper, and the bottle is then placed in a mechanical shaker for 60 hours at room temperature (Note 3).

The crude oil is then separated from the aqueous phase, dried with calcium chloride (Note 4), and fractionated (Note 5) at reduced pressure under nitrogen (Caution! (Note 6)). The distillation receiver should be cooled in an ice-salt or dry ice-acetone mixture. After a small fore-run of phenylacetylene, there is obtained 109–124 g. (73–83% yield) of water-white phenylbromoethyne, b.p. 40–41° (0.1 mm.) n_D^{25} 1.6075 (Note 7).

2. Notes

1. Practical grade sodium hydroxide and bromine were used.
2. Commercially available phenylacetylene can be used. The checkers used material as obtained from Columbia Organic Chemicals co., Inc.
3. Vigorous shaking is essential. For this reaction rate = $k[\text{C}_6\text{H}_5\text{C}\equiv\text{CH}][\text{OBr}^-][\text{OH}^-]$ with $k = 7 \text{ M}^{-2} \text{ sec.}^{-1}$ at 25°.² Since the solubility of phenylacetylene at 25° is $5.1 \times 10^{-3} \text{ M}$ in water ($2.0 \times 10^{-3} \text{ M}$ in 2M sodium chloride), efficient mixing of the reagents is of paramount importance.² An ordinary motor-drive stirrer proved to be inadequate. Phenylbromoethyne gradually darkens when exposed to light or air. The product is best stored under nitrogen in a refrigerator and should be distilled within a few days of its preparation.
4. The checkers observed that the calcium chloride absorbs appreciable quantities of product. The crude oil was dissolved in peroxide-free ether (about 300 ml.) prior to drying with calcium chloride, or the calcium chloride was extracted with several 50-ml. portions of dry ether after use. The ethereal extracts were concentrated under nitrogen and added to the product before distillation.
5. The checkers distilled the product from a flask equipped with a Claisen head but no column.
6. No air should be allowed to come in contact with the hot pot liquid during the distillation, for an exothermic reaction may occur; at best this may fill the apparatus with tarry material and the room with noxious fumes; at worst, pressure built up may destroy all or part of the apparatus. As a precaution, this distillation should be carried out behind a safety shield.
7. The checkers observed that the refractive index of a sample stored for 5 days in the refrigerator in a stoppered tube wrapped in aluminum foil and cloth changed from n_D^{25} 1.6074 to n_D^{25} 1.6082.

3. Discussion

Phenylbromoethyne has been prepared by base-catalyzed dehydrobromination of 1,1- or 1,2-dibromostyrene;³ by the thermal decomposition of silver 1,2-dibromocinnamate;³ from phenylethynylmagnesium Grignard reagent and bromine;^{4,5} cyanogen bromide,⁶ or benzenesulfonic anhydride;⁷ from phenylethynylsodium and cyanogen bromide⁵ or *p*-toluenesulfonylbromide⁸; from

phenylethynylsilver and bromine in pyridine;⁹ and from phenylethynyllithium and N-bromoimides.¹⁰ The present method is a modification of one in which the hypobromite-phenylacetylene mixture is warmed for 1.5 hours in the presence of an emulsifying agent, 1% potassium stearate¹¹ or soap,¹² to give 88% yield of product.

4. Merits of the Preparation

The hypohalite route to 1-chloro-, 1-bromo-, or 1-iodoalkynes is both general and convenient. The purity of the reagents does not appear to be critical.

References and Notes

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

peroxide-free ether

1,1- or 1,2-dibromostyrene

calcium chloride (10043-52-4)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

bromine (7726-95-6)

nitrogen (7727-37-9)

aluminum (7429-90-5)

pyridine (110-86-1)

Phenylacetylene (536-74-3)

Cyanogen bromide (506-68-3)

Phenylbromoethyne,
Benzene, bromoethynyl (932-87-6)

silver 1,2-dibromocinnamate

phenylethynylmagnesium

benzenesulfonic anhydride (512-35-6)

phenylethynylsodium

phenylethynylsilver

phenylethynyllithium (4440-01-1)

potassium stearate

p-toluenesulfonylbromide