



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.

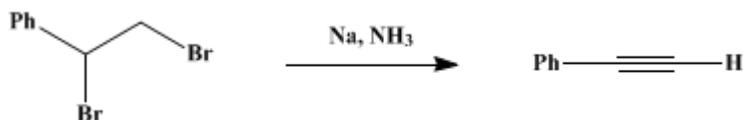
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.763 (1963); Vol. 30, p.72 (1950).

PHENYLACETYLENE

[Benzene, ethynyl-]



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1. Procedure

Avoid contact with styrene dibromide, which is a skin irritant. This preparation should be conducted in a hood to avoid exposure to ammonia.

A 5-l. three-necked flask is equipped with a high-speed, motor-driven stirrer passing through a bushing in the center neck (Note 1). The side necks are equipped with rubber stoppers each carrying a short length of 8-mm. glass tubing, bent at right angles. A 10–12 in. length of stout, flexible iron wire is passed through one of these pieces of tubing. Two liters of liquid ammonia (Note 2) and 2 g. of ferric nitrate hydrate are placed in the flask. One hundred grams of sodium (4.35 g. atoms) is cut into rectangular pieces about 3 by $\frac{3}{4}$ by $\frac{3}{4}$ in. in size. One of the pieces of sodium is hooked onto the lower end of the iron wire and lowered into the liquid ammonia. Stirring is not necessary during this part of the reaction, but it is advisable. When the lump of sodium has reacted, the solution turns from blue to gray, and the remaining pieces of sodium are added in the same manner. The addition requires about 45 minutes (Note 3).

The stopper carrying the iron wire is removed, 2 g. of anil is added, and then 528 g. (2 moles) of finely powdered, dry styrene dibromide is added gradually with vigorous stirring. The addition requires about 1 hour (Note 4). Stirring is continued for 2 hours (Note 5) after the addition has been completed, after which 600 ml. of concentrated ammonium hydroxide is added, followed by 1 l. of distilled water, and the mixture is allowed to stand until the frost on the outside of the flask is entirely melted.

The aqueous solution is then steam-distilled from the same flask (Note 6) until no more oil passes over. This usually requires about 6 hours, and 1.5–2 l. of distillate is collected. The phenylacetylene in the distillate is separated and washed several times with distilled water to remove ammonia (Note 7). The washed material is dried over anhydrous magnesium sulfate and distilled through an efficient column (Note 8) under reduced pressure. Almost the entire product distils at 73–74°/80 mm. The yield is 93–106 g. (45–52%); n_D^{20} 1.5465–1.5484.

2. Notes

1. A suitable stirrer has been described earlier.²
2. Additional liquid ammonia should be added from time to time. Liquid ammonia can be handled satisfactorily in fairly large amounts in an open flask, as the frost that quickly forms on the outside of the flask slows down evaporation.
3. This is an excellent method for making sodium amide for many purposes. If the sodium amide is to be used in another solvent, the solvent should be added to the liquid ammonia after the sodium amide is prepared; the ammonia is allowed to evaporate, and the last traces of ammonia are expelled by heating the flask on a steam bath.
4. The styrene dibromide must not be added too rapidly, or the heat of reaction may cause rapid boiling of the ammonia and possible loss of part of the mixture.
5. In one run an increase of this stirring period to 2.8 hours resulted in an 11% increase in yield.

6. Because the large amount of ammonia that comes over may entrain considerable phenylacetylene, a very efficient cooling system³ is essential.
7. If acid is used to remove the ammonia, the product is likely to be dark colored.
8. The checkers used an 18-in. column packed with Berl saddles.

3. Discussion

Phenylacetylene has been prepared by treatment of β -bromostyrene with potassium hydroxide⁴ and with sodium amide in liquid ammonia;⁵ from styrene dibromide by treatment with sodium amide in liquid ammonia⁶ or potassium hydroxide in methanol;⁷ and by the reduction of phenylchloroacetylene.⁸

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 128
- Org. Syn. Coll. Vol. 4, 387
- Org. Syn. Coll. Vol. 4, 404
- Org. Syn. Coll. Vol. 4, 755
- Org. Syn. Coll. Vol. 4, 801

References and Notes

1. University of Notre Dame, Notre Dame, Indiana.
2. *Org. Syntheses Coll. Vol. 1*, 34 (1941).
3. *Org. Syntheses Coll. Vol. 2*, 89 (1943).
4. *Org. Syntheses Coll. Vol. 1*, 438 (1941).
5. Vaughn, Vogt, and Nieuwland, *J. Am. Chem. Soc.*, **56**, 2120 (1934).
6. Campbell and O'Connor, *J. Am. Chem. Soc.*, **61**, 2898 (1939).
7. Fiesselmann and Sasse, *Chem. Ber.*, **89**, 1775 (1956).
8. Viehe, Franchimont, and Valange, *Chem. Ber.*, **92**, 3064 (1959).

Appendix

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

ammonia (7664-41-7)

methanol (67-56-1)

iron wire (7439-89-6)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

ammonium hydroxide (1336-21-6)

Phenylacetylene,
Benzene, ethynyl- (536-74-3)

β -bromostyrene (103-64-0)

styrene dibromide (93-52-7)

magnesium sulfate (7487-88-9)

sodium amide (7782-92-5)

ferric nitrate hydrate

phenylchloroacetylene (1483-82-5)