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.*
PHENYLACETYLENE

[Benzen[e, ethynyl-]

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1. Procedure

In a 500-cc. Pyrex distilling flask (Note 1) is placed 150 g. (2.7 moles) of potassium hydroxide. The mouth of the flask is provided with a one-holed stopper holding a dropping funnel; the side tube of the flask is connected with a condenser set for downward distillation.

The distilling flask is gradually heated in an oil bath until the temperature of the bath is 200°, and 100 g. (0.55 mole) of β-bromostyrene is then dropped in upon the molten potassium hydroxide (Note 2), at the rate of somewhat less than a drop a second. Since the boiling point of phenylacetylene is 142–143°, and that of bromostyrene is 218–220°, the phenylacetylene distils away from the unchanged bromostyrene.

While the bromostyrene is being dropped in (Note 3), the temperature of the oil bath is raised very gradually to 215–220° and is kept there until all the bromostyrene has been added. Finally the temperature is raised to 230° and is held there until no more distillate comes over. The distillate is colorless; it consists of two layers, the lower one being water. The upper layer is separated and dried with solid potassium hydroxide. It is then distilled. The yield of the distilled phenylacetylene, boiling at 142–144°, is 37 g. (67 per cent of the theoretical amount) (Note 4).

2. Notes

1. A single Pyrex flask can be used for only three or four runs. The flask should be emptied while still very hot. The use of steel or copper vessels in place of a glass flask seems to diminish the yield slightly.

2. The potassium hydroxide usually available contains sufficient moisture so that it will liquefy at 200°. If pure dry potassium hydroxide is used, it is necessary to add a little water so that the fusion point will be lowered to the temperature indicated.

It is suggested that equally good yields can be obtained if the eutectic of sodium hydroxide and potassium hydroxide is used, under which conditions the alkali is molten at 200° and the reaction takes place very readily.1

3. Toward the end of the reaction, a crust of potassium bromide may tend to cover the melted potassium hydroxide. The crust can be broken by shaking the distilling flask gently, or by using a glass rod inserted through a second hole in the stopper holding the dropping funnel.

An occasional turn of this stirrer breaks the crust and facilitates the operation. Mechanical stirring should not be employed, as it reduces the yield tremendously. Apparently this is because it facilitates the solution of bromostyrene in the tarry by-products and thus causes it to polymerize instead of reacting with the potassium hydroxide.

4. The yield of material can be somewhat increased by working with small lots (25 g. of β-bromostyrene).

3. Discussion
Two methods are available for preparing phenylacetylene: the elimination of carbon dioxide from phenylpropiolic acid, and the elimination of halogen acid from either styrene dibromide or an α- or β-halostyrene. Phenylpropiolic acid has been converted to phenylacetylene by means of phenol\(^2\) or aniline\(^3\) or by heating with barium hydroxide.\(^4\) Styrene dibromide has been converted to phenylacetylene by treatment with sodium in liquid ammonia,\(^5\) or sodamide,\(^6\)\(^7\) or potassium hydroxide in alcohol.\(^8\) α-Chlorostyrene and α-bromostyrene have been converted to phenylacetylene by means of sodamide.\(^7\)\(^9\) β-Chlorostyrene and β-bromostyrene have been converted to phenylacetylene by treatment with sodium ethoxide or potassium hydroxide in alcohol\(^10\) with sodium in liquid ammonia,\(^5\) with sodamide,\(^7\) with molten potassium hydroxide,\(^11\) and with the sodium derivative of aniline.\(^12\)

This preparation is referenced from:


### References and Notes

2. Holleman, Ber. 20, 3081 (1887).
4. Weger, Ann. 221, 70 (1883).
6. Bourguel, Ann. chim. (10) 3, 225, 228 (1925);
8. Glaser, Ann. 154, 155 (1870); Bruhl, Ann. 235, 13 (1886); Friedel and Balsohn, Bull. soc. chim. 35, 55 (1881); Moureu and Delange, ibid. (3) 25, 309 (1901).

### Appendix

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

- α- or β-halostyrene
- sodium derivative of aniline
  - alcohol (64-17-5)
  - ammonia (7664-41-7)
  - aniline (62-53-3)
- sodium hydroxide (1310-73-2)
- phenol (108-95-2)
- carbon dioxide (124-38-9)
potassium hydroxide (1310-58-3)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

potassium bromide (7758-02-3)

barium hydroxide (17194-00-2)

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

β-bromostyrene, bromostyrene (103-64-0)

Phenylpropiolic acid (637-44-5)

styrene dibromide (93-52-7)

α-Chlorostyrene

α-bromostyrene (98-81-7)

β-Chlorostyrene (622-25-3)

sodamide (7782-92-5)