



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.

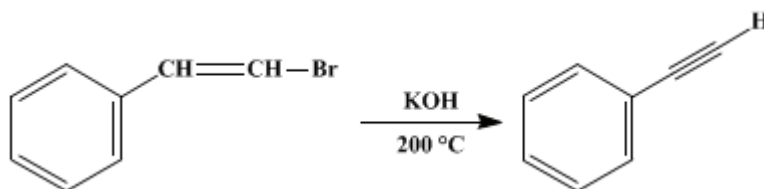
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.438 (1941); Vol. 2, p.67 (1922).

PHENYLACETYLENE

[Benzene, ethynyl-]



Submitted by John C. Hessler

Checked by J. B. Conant and G. R. Barrett.

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.

It is convenient to have such a rod or stirrer passing through a mercury seal in the stopper of the flask. 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 [phenylpropionic acid](#), and the elimination of halogen acid from either [styrene dibromide](#) or an α - or β -halostyrene. [Phenylpropionic 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:

- [Org. Syn. Coll. Vol. 4, 763](#)

References and Notes

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5. Vaughn, *J. Am. Chem. Soc.* **56**, 2064 (1934).
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7. Vaughn, Vogt, and Nieuwland, *J. Am. Chem. Soc.* **56**, 2121 (1934).
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10. Nef, *Ann.* **308**, 265 (1899); Straus, *Ann.* **342**, 220 (1905).
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12. Bodroux, *Compt. rend.* **208**, 1022 (1939).

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)

Phenylpropionic 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)