Organic
Syntheses

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.

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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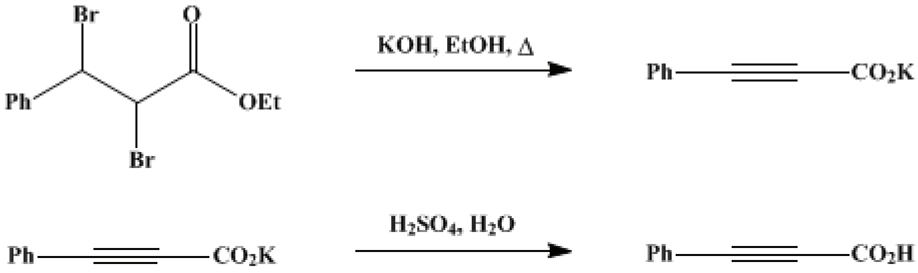
PHENYLPROPIOLIC ACID

[Propiolic acid, phenyl-]



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1. Procedure

A solution of potassium hydroxide is prepared by dissolving 252.5 g. (4.5 moles) of potassium hydroxide (Note 1) in 1.2 l. of 95 per cent alcohol contained in a 3-l. round-bottomed flask provided with a reflux condenser and heated on a steam bath. To the alkaline solution, cooled to 40–50°, is added 336 g. (1 mole) of crude ethyl α,β-dibromo-β-phenylpropionate (p. 270). When the initial reaction has subsided, the contents of the flask are refluxed for five hours on the steam bath.

The reaction mixture is cooled, and the salts which separate are filtered by suction. The filtrate is treated with concentrated hydrochloric acid until neutral to litmus (Note 2), and the salts which precipitate are separated by filtration. The filtrate is then distilled until the vapor reaches 95°. The residue and the precipitated salts, previously separated by filtration, are combined, dissolved in 800 cc. of water, and chilled by the addition of cracked ice to make a volume of 1.8 l. (Note 3). The cooled solution is immersed in an ice-water bath and stirred mechanically while a 20 per cent sulfuric acid solution is added until the solution is strongly acid to litmus. After stirring for twenty minutes the phenylpropiolic acid is filtered by suction and washed with four 30-cc. portions of a 2 per cent sulfuric acid solution.

The acid thus obtained as a light brown, granular product is dissolved in 1 l. of 5 per cent sodium carbonate solution, treated with 20 g. of Norite, and heated on a steam bath for thirty minutes with occasional stirring. The mixture is then filtered and cooled externally, and about 200 g. of cracked ice is added. The solution is stirred mechanically while a 20 per cent solution of sulfuric acid is added slowly. The precipitated acid is filtered by suction, washed first with 50 cc. of a 2 per cent sulfuric acid solution and then with a little water, and air-dried. The yield of acid melting between 115° and 125° is 112–118 g. (77–81 per cent of the theoretical amount).

One hundred grams of the crude acid can be purified by crystallization from 200–300 cc. of carbon tetrachloride, yielding 70 g. of phenylpropiolic acid melting at 135–136°.

2. Notes

1. The best yields are obtained when a 50 per cent excess of potassium hydroxide is used. The concentration of alkali has little or no effect on the yield.
2. The alcohol is best distilled from neutral rather than from alkaline solution.
3. In order to prevent decarboxylation, the temperature should be kept as low as possible. If this precaution is not observed, the yield is lowered and the product is less pure.

3. Discussion

The procedure described is essentially that of Perkin.[1] Phenylpropiolic acid can also be prepared from ether solutions of β-bromostyrene[2] and β-chlorostyrene[3] with sodium and carbon dioxide; from β-bromostyrene and butyllithium in ether;[4] by the action of alcoholic alkali on α-bromocinnamic acid,[2] β-bromocinnamic acid,[5] or ethyl α-bromocinnamate;[6] and by the action of carbon dioxide on sodium phenylacetylide.[2], [7]

The preparation of phenylpropiolic acid by the action of alkali on α,β-dibromocinnamic acid, a more direct synthesis than that involving the ester, has not been much used because of the difficulty of preparing the dibromo acid. It has been reported, however, that α,β-dibromocinnamic acid can be prepared easily and in a 95 per cent yield by the addition of bromine to cinnamic acid in boiling carbon tetrachloride, and that the crude product can be used for the preparation of phenylpropiolic acid.[8] A simplified procedure for the preparation of small amounts of phenylpropiolic acid from α,β-dibromocinnamic acid is described in the same article.

References and Notes

1. Perkin, J. Chem. Soc. **45**, 172 (1884); Liebermann and Sachse, Ber. **24**, 4113 (1891).
2. Glaser, Ann. **154**, 140, 162 (1870).
3. Erlenmeyer, Ber. **16**, 152 (1883).
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5. Barisch, J. prakt. Chem. (2) **20**, 180 (1879).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

alcohol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium carbonate (497-19-8)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

carbon dioxide (124-38-9)

Norite (7782-42-5)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

cinnamic acid (621-82-9)

β-bromostyrene (103-64-0)

Phenylpropiolic acid,
Propiolic acid, phenyl- (637-44-5)

β-Chlorostyrene (622-25-3)

α-bromocinnamic acid

Ethyl α,β-dibromo-β-phenylpropionate (5464-70-0)

butyllithium (109-72-8)

β-bromocinnamic acid

ethyl α-bromocinnamate

sodium phenylacetylide

α,β-dibromocinnamic acid