A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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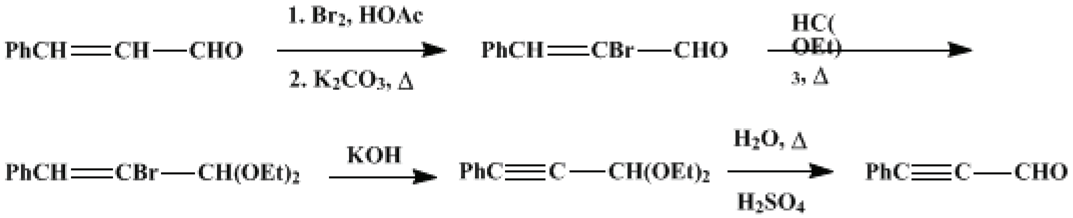
PHENYLPROPARGYL ALDEHYDE

[Propiolaldehyde, phenyl-]



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1. Procedure

A. *α-Bromocinnamic aldehyde*. A mixture of 44 g. (0.33 mole) of cinnamic aldehyde and 167 ml. of acetic acid in a 500-ml. three-necked round-bottomed flask, surrounded by a cold-water bath and fitted with a stirrer, reflux condenser, and dropping funnel, is stirred vigorously while 17.1 ml. (53.5 g., 0.33 mole) of bromine is added. This is followed by the addition of 23 g. (0.17 mole) of anhydrous potassium carbonate. When the evolution of gas has ceased, the mixture is refluxed for 30 minutes, then cooled and poured into 435 ml. of water in a 1-l. flask; a lower, reddish layer of crude α-bromoaldehyde separates. The flask is stoppered, cooled under running water, and shaken vigorously. The resulting granular solid is filtered with suction and dissolved without drying by warming with 220 ml. of 95% ethanol. After the addition of 50 ml. of water, the solution is warmed until it becomes clear and is then set aside to crystallize at room temperature and finally in a refrigerator. α-Bromocinnamic aldehyde separates as nearly colorless needles, which are filtered with suction, rinsed with 17 ml. of 80% ethanol, and air-dried. The yield of product melting at 72–73° is 52–60 g. (75–85%) (Note 1).

B. *α-Bromocinnamic aldehyde acetal*. In a 250-ml. flask are placed 45 g. (0.21 mole) of α-bromocinnamic aldehyde, 50 ml. (0.3 mole) of ethyl orthoformate, 40 ml. of absolute ethanol, and 0.5 g. of ammonium chloride. After the mixture has been refluxed for 30 minutes, it is transferred to a modified Claisen flask, and the low-boiling constituents are removed at atmospheric pressure and a bath temperature up to 150° (Note 2). The yield of acetal boiling at 146–149°/5 mm. and with n_D^{22} 1.5500 is 50–52 g. (82–86%).

C. *Phenylpropargyl aldehyde acetal.* A solution of 20.7 g. (0.25 mole) of potassium hydroxide in 200 ml. of absolute ethanol is added to 50 g. (0.18 mole) of α-bromocinnamic aldehyde acetal in a 500-ml. flask. The mixture is refluxed for 1.5 hours and poured into a 3-l. separatory funnel containing 1.5 l. of water. The oil that separates is extracted with three 170-ml. portions of chloroform, and the combined chloroform extracts are washed with three 75-ml. portions of water and then dried over 15 g. of anhydrous sodium sulfate. The chloroform is removed by distillation, and the residual oil is distilled from a modified Claisen flask. The yield of phenylpropargyl aldehyde acetal boiling at 153–156°/19 mm. is 28–31 g. (80–86%).

D. *Phenylpropargyl aldehyde.* Twenty-nine grams (0.14 mole) of the acetal is added to 140 ml. of water containing 10 ml. of concentrated sulfuric acid, and the mixture is heated on a steam bath with occasional shaking for 30 minutes. The aldehyde is then steam-distilled and extracted from the distillate with two 250-ml. portions of ether. The ethereal solution is dried over 20 g. of anhydrous sodium sulfate, the solvent is removed, and the residue is distilled from a 100-ml. modified Claisen flask. The yield of phenylpropargyl aldehyde boiling at 114–117°/17 mm. and with n_D^{25} 1.6032 is 13–15 g. (70–81%).

2. Notes

1. The same percentage yield is obtained in runs three times as large.
2. Both the reaction and the distillation can be carried out in the same flask.

3. Discussion

The procedure given for the preparation of phenylpropargyl aldehyde is a modification of Claisen's directions[1] in part due to Kalff.[2] The monobromocinnamic aldehyde was described by Zincke.[3] Other methods of possible preparative value for the aldehyde are the interaction of sodium phenylacetylene,[4,5,6,7] or the Grignard reagent from phenylacetylene with ethyl orthoformate. Sodium[5] and lithium[8] phenylacetylene react with ethyl formate to yield the aldehyde.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 801

References and Notes

1. Claisen, *Ber.*, **31**, 1020 (1898).
2. Kalff, *Rec. trav. chim.*, **46**, 594 (1927).
3. Zincke and Hagen, *Ber.*, **17**, 1815 (1884).
4. Moureu and Delange, *Compt. rend.*, **133**, 106 (1901).
5. Moureu and Delange, *Bull. soc. chim. France*, (3) **31**, 1329 (1904).
6. Brachim, *Bull. soc. chim. France*, (3) **35**, 1165 (1906).
7. Charon and Dugoujon, *Compt. rend.*, **137**, 126 (1903).
8. Nightingale and Wadsworth, *J. Am. Chem. Soc.*, **69**, 1181 (1947).

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

ACETAL (105-57-7)

ethanol (64-17-5)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ether (60-29-7)

ammonium chloride (12125-02-9)

chloroform (67-66-3)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

Ethyl orthoformate

ethyl formate (109-94-4)

cinnamic aldehyde

Phenylacetylene (536-74-3)

lithium (7439-93-2)

PHENYLPROPARGYL ALDEHYDE,
Propiolaldehyde, phenyl- (2579-22-8)

α-Bromocinnamic aldehyde,
monobromocinnamic aldehyde (5443-49-2)

α-Bromocinnamic aldehyde acetal

phenylpropargyl aldehyde acetal

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