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.

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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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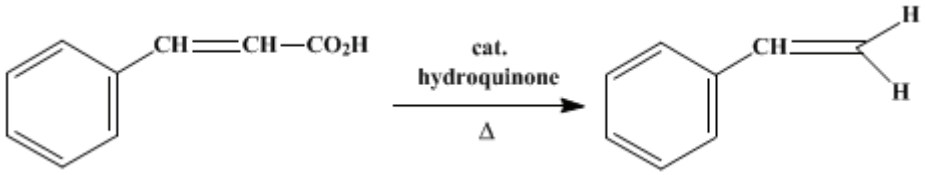
PHENYLETHYLENE

[Styrene]



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1. Procedure

In a 500-cc. flask, fitted with a 24-cm. fractionating column (Note 1) and (Note 2) attached to a water-jacketed condenser, are placed 148 g. (1 mole) of dry powdered cinnamic acid, 2 g. of hydroquinone, and several small pieces of clay plate. One-half gram of hydroquinone is also placed in the flask in which the distillate is to be collected (Note 3). The acid is rapidly heated over a wire gauze with a free flame until phenylethylene begins to distil, the heating being regulated so that the temperature of the vapors at the head of the column never exceeds 130°, and mainly remains below 120° (Note 4) and (Note 2). The cinnamic acid refluxes, but very little should escape and collect in the condenser. The decomposition is complete in three and one-half to five hours, when no more phenylethylene distils and the temperature at the head of the column rises rapidly.

The distillate consists of a straw-colored oil and a little water; a dark tarry residue (50–60 g.) remains in the reaction flask. About 100 cc. of water is added to the distillate, and the aqueous mixture is distilled. The phenylethylene is easily volatile with steam and separates in the distillate as a colorless oil. The oil (45–48 g.) is separated, dried with a small amount of calcium chloride, and carefully distilled under reduced pressure, the condenser and receiver being cooled to 0–5° by means of iced (or very cold) water. The phenylethylene is collected at 44–46°/40 mm. or 60–63°/60 mm. (Note 5). The yield is 40–42 g. (38–41 per cent of the theoretical amount) (Note 6).

2. Notes

1. The column consists of a glass tube of 13–14 mm. internal diameter, 24 cm. long from lower end to the side arm, which has an internal diameter of 7 mm. It is important that these dimensions be observed in order to avoid polymerization of the product. It has been found in checking that better results are obtained by making indentations in the tube at frequent intervals and at different angles; these tend to reduce the number of cinnamic acid particles which are carried over with the vapor. A column of the Vigreux type would no doubt also be suitable.
2. If the fractionating column does not have the exact dimensions designated in (Note 1) the temperature of the vapors at the head of the column will vary from those given. However, no difficulty will arise in obtaining the yield of product indicated if the general directions for heating the cinnamic acid, so as to avoid the carrying of the cinnamic acid into the distillate, are followed.
3. An anti-oxidant such as catechol or hydroquinone is used to prevent polymerization. Hydroquinone should be added in the ratio of one part per thousand unless the phenylethylene is to be used immediately.[1]
4. If the temperature of the escaping vapor rises above 130°, appreciable amounts of cinnamic acid pass into the condenser and the yield falls materially.
5. Phenylethylene should not be distilled under atmospheric pressure since the temperature (146°) required for the distillation causes a considerable loss by polymerization. The decomposition of cinnamic acid cannot be effected by distillation under diminished pressure, since the acid under these conditions distils below the temperature required for decomposition (approximately 300°).
6. On increasing the scale of the preparation, the yield is somewhat higher.

3. Discussion

Phenylethylene can be prepared by the addition of hydrobromic or hydriodic acid to cinnamic acid and subsequent treatment with alkali;[2] from methylphenylcarbinol by distillation of the benzoic ester or by the action of phosphoric acid;[3] by distilling β-phenylethyl phenylacetate;[4] by pyrogenic decomposition of ethylbenzene[5] or β-phenylethyl chloride;[6] from phenyl-α,β-dibromoethane and magnesium;[7] and by heating β-phenylethyl alcohol with potassium hydroxide.[8] The procedure described is that of Böeseken and Bastet.[9] The method of Sabetay[8] has been reported[10] to be superior to that described above.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 494

References and Notes

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

hydrobromic or hydriodic acid

benzoic ester

calcium chloride (10043-52-4)

hydroquinone (123-31-9)

magnesium (7439-95-4)

potassium hydroxide (1310-58-3)

phosphoric acid (7664-38-2)

Catechol (120-80-9)

ethylbenzene (100-41-4)

cinnamic acid (621-82-9)

β-phenylethyl chloride (622-24-2)

styrene,
Phenylethylene (100-42-5)

phenyl-α,β-dibromoethane (93-52-7)

methylphenylcarbinol (98-85-1)

β-phenylethyl phenylacetate (102-20-5)

β-phenylethyl alcohol (60-12-8)