



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.

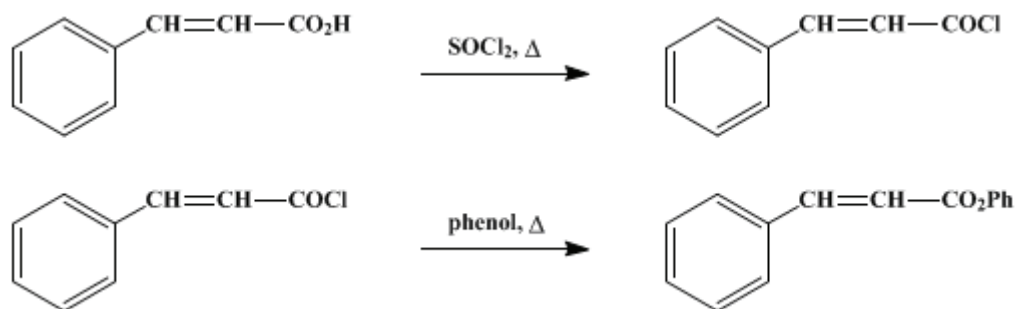
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.714 (1955); Vol. 20, p.77 (1940).

PHENYL CINNAMATE

[Cinnamic acid, phenyl ester]



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1. Procedure

A mixture of 148 g. (1 mole) of [cinnamic acid](#) and 119 g. (1 mole) of [thionyl chloride](#) ([Note 1](#)) is placed in a 500-ml. Claisen flask. The side arms are stoppered, and the flask is fitted with a reflux condenser. The apparatus is mounted at an angle so that the condensate will not run into the side arm. To the top of the condenser is attached an exit tube, for evolved [hydrogen chloride](#) and [sulfur dioxide](#), leading to a gas-absorption trap. The mixture is heated on a steam bath, cautiously at first, until no further evolution of [hydrogen chloride](#) is noted (45–60 minutes), and then allowed to cool, and 94 g. (1 mole) of [phenol](#) ([Note 2](#)) is added. The mixture is again heated on the steam bath until the evolution of [hydrogen chloride](#) has ceased (about 1 hour). It is then placed on a sand bath and brought just to the reflux temperature in order to complete the reaction and remove the [hydrogen chloride](#) more completely ([Note 3](#)).

The reaction mixture is cooled and distilled under reduced pressure ([Note 4](#)). The fraction boiling at 190–210° at 15 mm. is collected. The distillate solidifies to a pale yellow solid melting at 64° to 69° and weighing 186–200 g. (83–89%). It is purified by grinding in a mortar to a powder and washing with 500 ml. of cold 2% [sodium bicarbonate](#) solution. The residue is recrystallized from 300 ml. of 95% [ethanol](#). The recovery is 141–168 g. (63–75%) of pure white crystals melting at 75–76°.

2. Notes

1. The [thionyl chloride](#) should be redistilled before use. The material used in this preparation boiled at 75.0–75.5°.
2. The [phenol](#) used was Mallinckrodt's analytical reagent grade.
3. A sand-bath temperature of about 350° will effect refluxing. Prolonged heating on the sand bath causes considerable loss of product due to decomposition and polymerization and to the conversion of the acid to [stilbene](#) by the loss of [carbon dioxide](#).
4. In carrying out the vacuum distillation, it is well not to include the manometer in the system until the unchanged [phenol](#) and most of the [hydrogen chloride](#) have been removed. Bumping during the distillation may be minimized by holding the burner in the hand and directing the free flame at the surface of the boiling liquid. If the vapors are superheated too much, the boiling-point range may be 190–220° at 15 mm.

3. Discussion

[Phenyl cinnamate](#) and other phenolic esters have been prepared by heating the acid and [phenol](#) in the presence of [phosphorus oxychloride](#),¹ and by heating the acid anhydride and [phenol](#) together in the presence of a dehydrating agent such as fused [zinc chloride](#) or anhydrous [sodium acetate](#).² [Phenyl](#)

cinnamate has also been prepared by the careful distillation of [phenyl fumarate](#).³

References and Notes

1. Nencki, *Compt. rend.*, **108**, 254 (1889).
 2. Franchimont, *Ber.*, **12**, 2059 (1879); Liebermann, *Ber.*, **21**, 1172 (1888).
 3. Anschütz, *Ber.*, **18**, 1945 (1885).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[ethanol](#) (64-17-5)

[hydrogen chloride](#) (7647-01-0)

[sodium acetate](#) (127-09-3)

[thionyl chloride](#) (7719-09-7)

[sodium bicarbonate](#) (144-55-8)

[phenol](#) (108-95-2)

[sulfur dioxide](#) (7446-09-5)

[carbon dioxide](#) (124-38-9)

[Phosphorus Oxychloride](#) (21295-50-1)

[zinc chloride](#) (7646-85-7)

[cinnamic acid](#) (621-82-9)

[stilbene](#)

[Phenyl cinnamate,
Cinnamic acid, phenyl ester](#) (2757-04-2)

[phenyl fumarate](#)