



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](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.

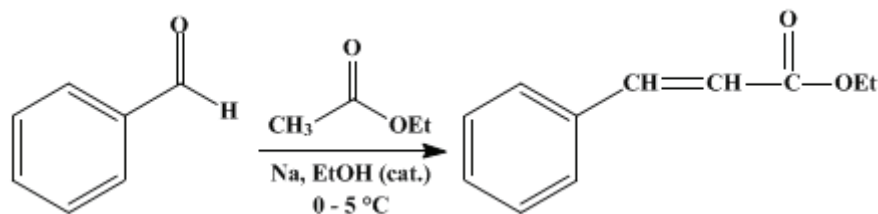
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.*

*Organic Syntheses, Coll. Vol. 1, p.252 (1941); Vol. 9, p.38 (1929).*

## ETHYL CINNAMATE



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### 1. Procedure

In a 2-l. two-necked flask fitted with a short reflux condenser and mechanical stirrer (Note 1) are placed 400 cc. of dry *xylene* (Note 2) and 29 g. (1.26 atoms) of clean *sodium* (Note 3) cut in small pieces. The flask is surrounded by an oil bath and heated until the *sodium* has melted. At this point the stirrer is started and the *sodium* is broken up into very small particles (Note 4). The oil bath is removed, but stirring is continued until the *sodium* has solidified in very fine particles. The *xylene* is then poured off, and to the *sodium* is added 460 cc. (4.7 moles) of absolute *ethyl acetate* (Note 5) containing 3–4 cc. of absolute *ethyl alcohol* (Note 6). The flask is quickly cooled to 0° and 106 g. (1 mole) of pure *benzaldehyde* (Note 7) is added slowly from a separatory funnel while the mixture is stirred. The temperature is held between 0 and 5° (Note 8). The reaction starts as soon as the *benzaldehyde* is added, as is shown by the production of a reddish substance on the particles of the *sodium*. About one and one-half to two hours are required for this addition. The stirring is continued until practically all of the *sodium* has reacted (one hour after all the aldehyde has been added).

When most of the *sodium* (Note 9) has disappeared, 90–95 cc. of glacial *acetic acid* is added and the mixture is carefully diluted with water. The ester layer is separated, the water layer is extracted with about 25–50 cc. of *ethyl acetate*, and the combined ester portions are washed with 300 cc. of 6 *N* *hydrochloric acid* and then dried with *sodium sulfate*. The *ethyl acetate* is distilled from a water bath and the remaining liquid is transferred to a Claisen flask and distilled from an oil bath under reduced pressure. A small fraction comes over below 128°/6 mm. and is discarded. The *ethyl cinnamate* (Note 10) boils at 128–133°/6 mm.; 168–173°/46 mm. The yield is 120–130 g. (68–74 per cent of the theoretical amount).

### 2. Notes

1. The stirrer must be very efficient in order to powder the *sodium* without splashing it onto the walls of the flask above the solvent.
2. The use of *sodium* powdered under *xylene* allows the reaction to be carried out much more rapidly than is the case if the *sodium* is cut into small pieces with a knife. *Toluene* may be used in place of *xylene*. The *sodium* should be as free as possible from oxide.
3. To obtain the maximum yield it is necessary to use slightly more than one equivalent of *sodium*. When exactly one equivalent is used the yield is about 60 per cent of the theoretical amount.
4. The powdered *sodium* may also be prepared by melting the *sodium* under hot *xylene* and shaking in a tightly stoppered flask wrapped in a heavy cloth.
5. The grade of *ethyl acetate* used in the preparation is very important. The absolute *ethyl acetate* (99.5 per cent) sold by the U. S. Industrial Alcohol Company is very satisfactory. If this grade is not available the ordinary ester may be purified by washing first with *sodium carbonate* solution, then with saturated *calcium chloride* solution and finally drying over anhydrous *potassium carbonate*.
6. A small amount of absolute *alcohol* is needed to start the reaction. When no alcohol is added the yields are consistently 55–60 per cent of the theoretical amount. When too much *alcohol* (10–15 cc.) is added the yields drop again.

7. Technical [benzaldehyde](#) is washed with [sodium carbonate](#) and distilled under reduced pressure with minimum atmospheric exposure before use. The material used in checking these directions boiled over a 3° range.
8. The temperature should never be allowed to go above 10° and the best yields of pure product are obtained when the temperature is kept within the limits mentioned in the procedure.
9. Usually during the reaction a certain amount of [sodium](#) is thrown on the upper part of the flask out of the reaction mixture and forms a cake. In decomposing the mixture with glacial [acetic acid](#) and water care must be taken that this [sodium](#) does not react violently and thus cause a fire.
10. During the distillation of the ester a reddish semi-solid mass sometimes appears in the flask. This mass melts down if the oil bath is heated to 220–230° and the distillation continues smoothly.

### 3. Discussion

[Ethyl cinnamate](#) can be prepared by the action of [ethyl alcohol](#) on [cinnamic acid](#) in the presence of [hydrogen chloride](#) or [sulfuric acid](#),<sup>1</sup> and by the condensation of [ethyl acetate](#) and [benzaldehyde](#) in the presence of [sodium](#).<sup>2</sup> The procedure described is a slight modification of that by Claisen.<sup>2</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 194](#)
- [Org. Syn. Coll. Vol. 2, 270](#)
- [Org. Syn. Coll. Vol. 4, 910](#)

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### References and Notes

1. Kopp, *Ann.* **95**, 318 (1855); Weger, *Ann.* **221**, 75 (1883); Brühl, *Ann.* **235**, 19 (1886); Fischer and Speier, *Ber.* **28**, 3254 (1895).
  2. Claisen, *Ber.* **23**, 977 (1890); Stoermer and Kippe, *Ber.* **38**, 3034 (1905).
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### Appendix

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

[ethyl alcohol](#),  
[alcohol](#) (64-17-5)

[calcium chloride](#) (10043-52-4)

[potassium carbonate](#) (584-08-7)

[sulfuric acid](#) (7664-93-9)

[hydrogen chloride](#),  
[hydrochloric acid](#) (7647-01-0)

[acetic acid](#) (64-19-7)

[ethyl acetate](#) (141-78-6)

[sodium carbonate](#) (497-19-8)

sodium sulfate (7757-82-6)

benzaldehyde (100-52-7)

toluene (108-88-3)

sodium (13966-32-0)

xylene (106-42-3)

Ethyl cinnamate (103-36-6)

cinnamic acid (621-82-9)