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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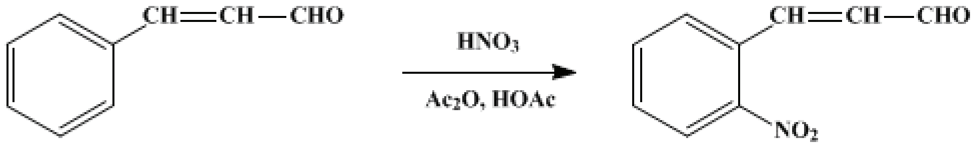
o-NITROCINNAMALDEHYDE

[Cinnamaldehyde, *o*-nitro-]



Submitted by Robert E. Buckles and M. Peter Bellis[1].
Checked by Richard T. Arnold and James D. Groves.

1. Procedure

A 1-l. three-necked round-bottomed flask, fitted with a dropping funnel and a mechanical stirrer, is cooled in an ice-salt mixture. To the flask are added 55.5 g. (50 ml., 0.42 mole) of freshly distilled cinnamaldehyde (Note 1) and 225 ml. of acetic anhydride. When the temperature of the solution has reached 0–5° a solution of 18 ml. of concentrated nitric acid (sp. gr. 1.42) in 50 ml. of glacial acetic acid is added slowly through the dropping funnel while the mixture is stirred. The time of addition is 3–4 hours, during which the temperature is kept below 5°. After the addition is complete, the mixture is allowed to warm slowly to room temperature. The reaction flask is then dismantled and stoppered, and the reaction mixture is allowed to stand 2 days.

At the end of this time, hydrochloric acid (20%) is added cautiously to the cooled solution until a precipitate begins to appear (Note 2). The addition of acid is then stopped, and the solution is allowed to cool in an ice bath or refrigerator until precipitation of the solid is completed. The light-yellow needles are collected on a Büchner funnel and dried in air. About 24 g. of *o*-nitrocinnamaldehyde, m.p. 125–127°, is obtained (Note 3). Additional product can be isolated by cautiously adding water to the mother liquor until precipitation is observed and then cooling the resultant mixture for several hours in an ice bath. Recrystallization from 95% ethanol gives 5–10 g. of *o*-nitrocinnamaldehyde, m.p. 126–127°. The total yield is 27–34 g. (36–46%).

2. Notes

1. As with other aromatic aldehydes, cinnamaldehyde is readily oxidized by air to its corresponding carboxylic acid. The latter must be separated just before the use of the aldehyde.
2. A good deal of heat is evolved when the hydrochloric acid is added to the reaction mixture, owing to the hydrolysis of acetic anhydride. The reaction mixture will become excessively hot unless it is cooled in an ice bath.
3. The product obtained is pure enough for most purposes. Recrystallization from 95% ethanol yields a nearly white product, m.p. 126–127.5°.

3. Discussion

o-Nitrocinnamaldehyde has been prepared by the condensation of *o*-nitrobenzaldehyde with acetaldehyde.[2,3] The direct nitration of cinnamaldehyde with potassium nitrate in sulfuric acid yields *o*-nitrocinnamaldehyde along with *p*-nitrocinnamaldehyde.[3] *o*-Nitrocinnamaldehyde has been obtained in 85% yield by the nitration of cinnamaldehyde diacetate.[4] The nitration of cinnamaldehyde in acetic anhydride yields *o*-nitrocinnamaldehyde as the only product,[5] and the procedure is the basis for the method given above.

References and Notes

1. State University of Iowa, Iowa City, Iowa.
2. Baeyer and Drewsen, *Ber.*, **16**, 2205 (1883).
3. Diehl and Ein horn, *Ber.*, **18**, 2335 (1885).
4. Davey and Gwilt, *J. Chem. Soc.*, **1955**, 1384.
5. Mills and Evans, *J. Chem. Soc.*, **117**, 1035 (1920).

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

ethanol (64-17-5)

acetaldehyde (75-07-0)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

acetic anhydride (108-24-7)

nitric acid (7697-37-2)

cinnamaldehyde

potassium nitrate (7757-79-1)

o-Nitrobenzaldehyde (552-89-6)

cinnamaldehyde diacetate

o-Nitrocinnamaldehyde,
Cinnamaldehyde, o-nitro- (1466-88-2)

p-nitrocinnamaldehyde