



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.

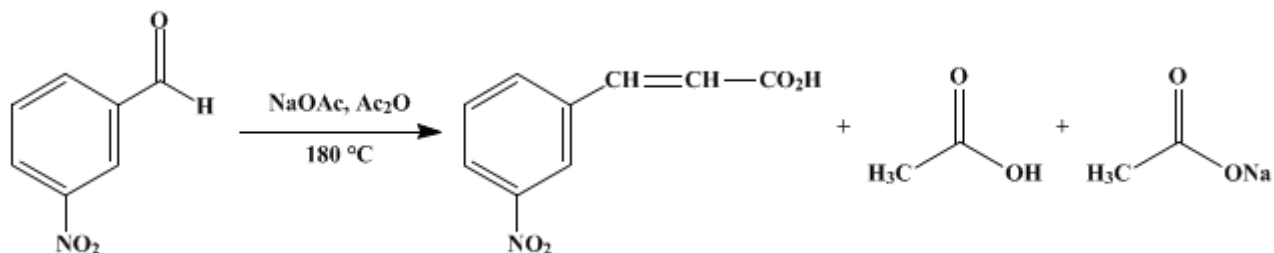
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.398 (1941); Vol. 5, p.83 (1925).*

## *m*-NITROCINNAMIC ACID

[Cinnamic acid, *m*-nitro-]



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### 1. Procedure

In a 200-cc. round-bottomed flask, fitted with a reflux condenser, are placed 50 g. (0.33 mole) of *m*-nitrobenzaldehyde (Note 1), 40 g. (0.48 mole) of freshly fused sodium acetate, and 70 g. (0.68 mole) of acetic anhydride. The contents of the flask are well mixed and the mixture heated in an oil bath held at  $180^\circ$  for about thirteen hours. After the reaction product has been allowed to cool slightly, it is poured into 200–300 cc. of water and then filtered by suction (Note 2). After the solid has been washed several times with water, it is dissolved in a solution of 20 cc. of aqueous ammonia (sp. gr. 0.9) in about 200 cc. of water. The solution of the ammonium salt, after filtering, is poured into a solution of 15 cc. of sulfuric acid (sp. gr. 1.84) in about 200 cc. of water (Note 3). The precipitated *m*-nitrocinnamic acid is filtered, redissolved in aqueous ammonia, and again precipitated by pouring the solution into dilute sulfuric acid (Note 4).

After the last precipitation, the *m*-nitrocinnamic acid is washed with a little water and then sucked as dry as possible (Note 5). The product, which still contains considerable water, is dissolved in 250–300 cc. of boiling 95 per cent alcohol from which the nitrocinnamic acid crystallizes on cooling. The yield is 47–49 g. (74–77 per cent of the theoretical amount). The product is pale yellow and melts at  $192\text{--}194^\circ$ . If a purer product is desired, it may be recrystallized from benzene or alcohol (Note 6).

### 2. Notes

1. The *m*-nitrobenzaldehyde used was the technical grade and melted at  $50\text{--}53^\circ$ .
2. In one run, the product was extracted from the reaction mixture with benzene, removed from the benzene by a sodium carbonate solution, and this solution in turn acidified to obtain the *m*-nitrocinnamic acid. Neither the product nor the yield was as satisfactory by this method.
3. If acid is added to the solution of the ammonium salt, the precipitated *m*-nitrocinnamic acid carries down a considerable quantity of ammonium salts.
4. There is always a small amount of material that is insoluble in the aqueous ammonia. This is removed by the second treatment.
5. The product is very difficult to dry. If it is removed from the filter after washing, several days are required for it to become dry. This dry product melts at about  $190\text{--}193^\circ$ .
6. The melting point of *m*-nitrocinnamic acid is given in the literature as  $195^\circ$  and  $196\text{--}197^\circ$ . Alcohol is mentioned as a good solvent for recrystallization, but experience in this work showed that benzene is also satisfactory, a white *m*-nitrocinnamic acid being obtained from this solvent.

### 3. Discussion

*m*-Nitrocinnamic acid can be prepared by the condensation of *m*-nitrobenzaldehyde with malonic acid in the presence of bases such as aniline,<sup>1</sup> ammonia,<sup>1</sup> and pyridine;<sup>2</sup> and from *m*-nitrobenzaldehyde

with sodium acetate and acetic anhydride.<sup>3</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 731

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## References and Notes

1. Knoevenagel, Ber. **31**, 2610 (1898).
2. Dutt, Quart. J. Indian Chem. Soc. **1**, 297 (1925); Kurien, Pandya, and Surange, *ibid.* **11**, 824 (1934).
3. Schiff, Ber. **11**, 1782 (1878); Tiemann and Oppermann, Ber. **13**, 2060 (1880); Reich and Koehler, Ber. **46**, 3732 (1913); Posner, J. prakt. Chem. (2) **82**, 425 (1910); Böck, Lock, and Schmidt, Monatsh. **64**, 408 (1934).

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## Appendix

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

alcohol (64-17-5)

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

Benzene (71-43-2)

acetic anhydride (108-24-7)

sodium acetate (127-09-3)

aniline (62-53-3)

sodium carbonate (497-19-8)

pyridine (110-86-1)

nitrocinnamic acid

Malonic acid (141-82-2)

m-Nitrobenzaldehyde (99-61-6)

m-Nitrocinnamic acid,  
Cinnamic acid, m-nitro- (555-68-0)