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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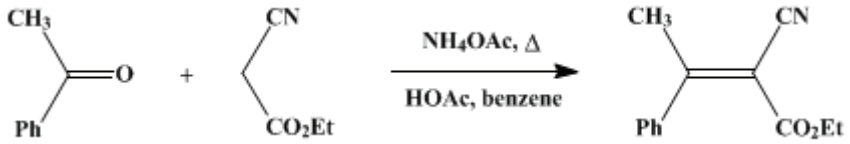
ETHYL (1-PHENYLETHYLIDENE)CYANOACETATE

[Cinnamic acid, α-cyano-β-methyl-, ethyl ester]



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1. Procedure

In a 1-l. three-necked round-bottomed flask fitted with a Hershberg stirrer and a constant water separator (Note 1) surmounted by a reflux condenser are placed 120 g. (1 mole) of acetophenone, 113 g. (1 mole) of ethyl cyanoacetate (Note 2), 15.4 g. (0.2 mole) of ammonium acetate, 48.0 g. (0.8 mole) of glacial acetic acid, and 200 ml. of benzene. The reaction mixture is stirred and heated under reflux for 9 hours during which time 28–33 ml. of lower layer is collected in the water separator (Note 3). To the cooled reaction mixture is added 100 ml. of benzene, and the whole is extracted with three 100-ml. portions of water. The combined aqueous layers are extracted with 30 ml. of benzene, which is then added to the organic layer from the previous extraction. Anhydrous magnesium sulfate (15 g.) is added, and, after swirling occasionally for 10 minutes, the mixture is filtered by suction and the magnesium sulfate washed with two 25-ml. portions of benzene. The benzene is removed by distillation at reduced pressure and the residual oil distilled rapidly through a 15-cm. column. The yield of ester is 113–125 g. (52–58%), b.p. 135–160° (0.35 mm.) (Note 4).

2. Notes

1. A typical water separator has been described by Cope et al.[2]
2. Eastman Kodak white label grade acetophenone and ethyl cyanoacetate are used without further purification. The checkers used Matheson, Coleman, and Bell acetophenone and ethyl cyanoacetate without further purification.
3. The checkers used ammonium acetate which was slightly moist; consequently 33.5–34.5 ml. of lower layer was collected.
4. The checkers report the refractive index of the product to be $n_D^{25.1}$ 1.5468–1.5469.

3. Discussion

The above procedure is essentially that described by Cope et al.[2] Ethyl (1-phenylethylidene) cyanoacetate has been prepared also by condensing acetophenone with ethyl cyanoacetate in the presence of zinc chloride and aniline,[3] and other catalysts.[4] Additional aralkylidenecyano esters have been prepared by the present procedure.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 662

References and Notes

1. University of Wisconsin, Madison, Wisconsin.
2. Cope, Hofmann, Wyckoff, and Hardenbergh, *J. Am. Chem. Soc.*, **63**, 3452 (1941).
3. Scheiber and Meisel, *Ber.*, **48**, 238 (1915).

4. Cragoe, Robb, and Sprague, *J. Org. Chem.*, **15**, 381 (1950).
5. McElvain and Clemens, *J. Am. Chem. Soc.*, **80**, 3915 (1958).

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

acetic acid (64-19-7)

Benzene (71-43-2)

ammonium acetate (631-61-8)

aniline (62-53-3)

Acetophenone (98-86-2)

zinc chloride (7646-85-7)

Ethyl cyanoacetate (105-56-6)

magnesium sulfate (7487-88-9)

ETHYL (1-PHENYLETHYLIDENE)CYANOACETATE,
Cinnamic acid, α-cyano-β-methyl-, ethyl ester