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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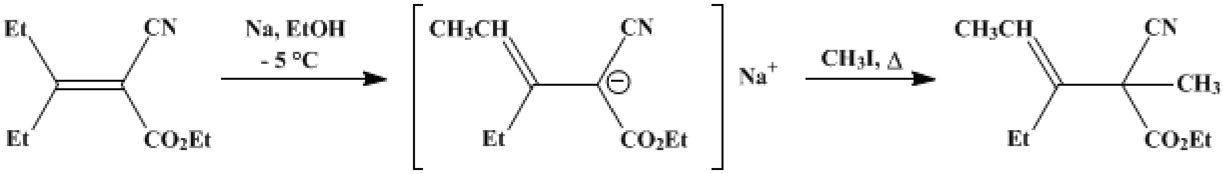
*Organic Syntheses, Coll. Vol. 3, p.397 (1955); Vol. 25, p.44 (1945).*

# ETHYL (1-ETHYLPROPENYL)METHYLCYANOACETATE

## [3-Pentenoic acid, 2-cyano-3-ethyl-2-methyl-, ethyl ester]



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## 1. Procedure

A solution of sodium ethoxide is prepared from 9.2 g. (0.40 mole) of freshly cut sodium and 400 ml. of absolute ethanol (Note 1) in a 1-l. three-necked flask fitted with a dropping funnel, a thermometer, a mercury-sealed stirrer, and a condenser protected by a drying tube (Note 2). To the stirred solution, which is kept at −5° (conveniently by partially immersing the flask in a Dry Ice bath), 72.4 g. (0.40 mole) of ethyl (1-ethylpropylidene) cyanoacetate (p. 399) is added dropwise from the funnel during 8–10 minutes. After the mixture has been stirred for an additional 20 minutes at −5°, 62.5 g. (0.44 mole) of methyl iodide is added from the dropping funnel as rapidly as possible. The flask is heated immediately with a strong flame which is withdrawn just as the solution reaches the boiling point. The alkylation is vigorous, but the flask is not cooled unless loss of material through the reflux condenser appears imminent (Note 3). After the spontaneous reaction has subsided, the solution is refluxed until a piece of red litmus paper dipped into the liquid and subsequently moistened shows a neutral reaction (15–30 minutes).

The solution is cooled and diluted with 1 l. of water, and the ester layer is separated. The aqueous layer is extracted with four 50-ml. portions of benzene, and the combined ester and benzene extracts are washed with two 25-ml. portions of water and then distilled from a 500-ml. modified Claisen flask. The fraction (above 75 g.) which is collected at 95–118°/10 mm. is shaken mechanically for 4 hours with 100 ml. of 20% sodium bisulfite solution (Note 4). The ester layer is separated, the aqueous layer is extracted with three 25-ml. portions of benzene, and the combined ester and benzene extracts are washed with 25 ml. of water. The product remaining after removal of the benzene is distilled under reduced pressure from a 250-ml. modified Claisen flask or through a Widmer column. The yield of ester boiling at 112–113°/8 mm. is 63.5–68 g. (81–87%).

## 2. Notes

1. Commercial absolute ethanol is dried with sodium and ethyl phthalate[1] and redistilled. The checkers obtained a considerably lower yield in a run employing ethanol dried over magnesium methoxide.
2. The various pieces of apparatus are dried in an oven and assembled rapidly in order to exclude moisture.
3. Excessive cleavage (alcoholysis) of the product is avoided by carrying out the alkylation rapidly. This procedure minimizes the time during which the product is in contact with sodium ethoxide.
4. This treatment removes ethyl (1-ethylpropylidene) cyanoacetate as a water-soluble sodium bisulfite addition product (p. 399).

## 3. Discussion

The above procedure illustrates a general method for preparing homologous ethyl (dialkylvinyl) alkylcyanoacetates by the alkylation of ethyl alkylidenecyanoacetates.[2]

## References and Notes

1. *Org. Syntheses* Coll. Vol. **2**, 155 (1943).
2. Cope and Hancock, *J. Am. Chem. Soc.*, **60**, 2903 (1938).

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

ethanol (64-17-5)

Benzene (71-43-2)

sodium bisulfite (7631-90-5)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

Methyl iodide (74-88-4)

magnesium methoxide

ethyl phthalate

ETHYL (1-ETHYLPROPENYL)METHYLCYANOACETATE,
3-Pentenoic acid, 2-cyano-3-ethyl-2-methyl-, ethyl ester (53608-83-6)

ethyl (1-ethylpropylidene) cyanoacetate (868-04-2)