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.

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.

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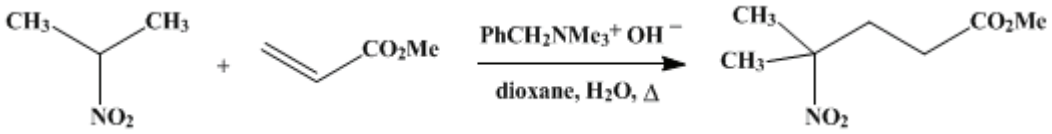
Organic Syntheses, Coll. Vol. 4, p.652 (1963); Vol. 32, p.86 (1952).

METHYL γ-METHYL-γ-NITROVALERATE

[Valeric acid, 4-methyl-, 4-nitro-, methyl ester]



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Checked by N. J. Leonard and B. L. Ryder.

1. Procedure

A 500-ml. three-necked flask is fitted with a stirrer, a dropping funnel, and a thermometer placed so that the bulb is near the bottom of the flask. In the flask are placed 89 g. (1 mole) of 2-nitropropane (Note 1), 50 ml. of dioxane, and 10 ml. of a 40% aqueous solution of benzyltrimethylammonium hydroxide (Triton B) (Note 2), and the contents of the flask are warmed to 70°. Eighty-six grams (1 mole) of redistilled methyl acrylate (Note 3) is added, with stirring, during 15 minutes. The temperature rises to about 100° during the addition and then drops to about 85°. The mixture is stirred and heated on a steam bath for 4 hours. After cooling, the contents of the flask are acidified with dilute hydrochloric acid and extracted with ether. The ether layer is washed twice with water, then with approximately 50 ml. of 0.1% sodium bicarbonate solution, and finally again with water. After the ethereal solution has been dried over anhydrous sodium sulfate, the drying agent is separated, the solvent is removed by distillation, and the product is distilled through a short fractionating column. A nearly colorless oil is obtained in a yield of 140–151 g. (80–86%); b.p. 79°/1 mm.; n_D^{20} 1.4408.

2. Notes

1. 2-Nitropropane from Commercial Solvents Corporation, Terre Haute, Indiana, was redistilled before use.
2. Available from Commercial Solvents Corporation or Rohm and Haas Company, Philadelphia, Pennsylvania.
3. Although the submitter knows of no case of an explosion with this type of nitro compound, it is recommended that adequate safety shields be employed during both the reaction and the distillation.

3. Discussion

Methyl γ-methyl-γ-nitrovalerate has been prepared by the Michael-type condensation of 2-nitropropane with methyl acrylate in the presence of a quaternary ammonium hydroxide[2] or triethylamine.[3]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 357
- Org. Syn. Coll. Vol. 5, 445

References and Notes

1. The Upjohn Company, Kalamazoo, Michigan.
2. Bruson, U. S. pat. 2,342,119 and 2,390,918 [*C. A.*, **38**, 4619 (1944)].
3. Kloetzel, *J. Am. Chem. Soc.*, **70**, 3571 (1948).

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

benzyltrimethylammonium hydroxide (Triton B)

quaternary ammonium hydroxide

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium bicarbonate (144-55-8)

sodium sulfate (7757-82-6)

methyl acrylate (96-33-3)

dioxane (123-91-1)

triethylamine (121-44-8)

Methyl γ-methyl-γ-nitrovalerate,
Valeric acid, 4-methyl-, 4-nitro-, methyl ester (16507-02-1)

2-nitropropane (79-46-9)