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.

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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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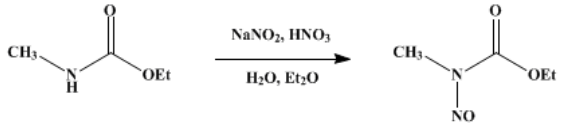
NITROSOMETHYLURETHANE

[Carbamic acid, methylnitroso-, ethyl ester]



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1. Procedure

Caution! See the discussion in Org. Synth. 1973, Coll. Vol. 5, 842 with regard to potential hazards associated with the title compound.

To 206 g. (2 moles) of ethyl N-methylcarbamate (p. 278) and 600 cc. of ordinary ethyl ether in a 5-l. flask is added, along with 200 g. of ice, 650 g. (9 moles) of 96 per cent sodium nitrite (Note 1) dissolved in 1 l. of cold water. The flask is provided with a stopper carrying a thermometer, a tube to lead off evolved nitric oxide, and a separatory funnel with an extension tube reaching to the bottom of the flask. A solution of 1.2 kg. (6.7 moles) of cold 35 per cent nitric acid, prepared by pouring 600 g. (426 cc.) of concentrated acid onto 600 g. of ice, is then cautiously added through the funnel in the course of one and one-half hours. The flask is given an occasional swirl to ensure some mixing, but most of the stirring is done by the evolved gases. Ice is added as required to keep the temperature below 15°. The ether layer first becomes pale red and gradually changes to a blue-green. As soon as the color has changed to green, the ether layer is separated (Note 2), washed twice with cold water, and then with cold potassium carbonate solution until carbon dioxide is no longer evolved. The solution is dried with solid potassium carbonate, and the ether is distilled from a water bath using a 1-l. flask with a 30-cm. column arranged for vacuum distillation. The vacuum is applied as soon as most of the ether has been removed, and the flask is heated gently so that the temperature of the liquid does not exceed 45–50° (Note 3) until the pressure has been reduced below 20 mm. The yield of nitrosomethylurethane boiling at 59–61/10 mm. is 200 g. (76 per cent of the theoretical amount). The density is 1.133 at 20°.

2. Notes

1. A large excess of sodium nitrite is required to give a satisfactory yield. This may be due to reaction according to the following equations: Nitric oxide (NO) is lost during the reaction. It is not thought advisable to use this by passing in oxygen because of the danger of an explosion, or by passing in air because of the loss of material by evaporation.
2. Nitrosomethylurethane irritates the skin.
3. According to the literature, nitrosomethylurethane explodes when attempts are made to distil it at normal pressure.

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3. Discussion

Nitrosomethylurethane has been prepared by treating ethyl methylcarbamate with sodium nitrite and sulfuric acid,[1] and by passing the gases generated from arsenious oxide and nitric acid into an ethereal solution of ethyl methylcarbamate.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 119
- Org. Syn. Coll. Vol. 4, 780
- Org. Syn. Coll. Vol. 5, 842

References and Notes

1. Klobbie, Rec. trav. chim. **9**, 139 (1890).
2. v. Pechmann, Ber. **28**, 856 (1895); Schmidt, ibid. **36**, 2477 (1903); Brühl, ibid. **36**, 3635 (1903).

Appendix

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

arsenious oxide

Nitric oxide (NO)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

ether,
ethyl ether (60-29-7)

nitric acid (7697-37-2)

oxygen (7782-44-7)

sodium nitrite (7632-00-0)

carbon dioxide (124-38-9)

nitric oxide

Nitrosomethylurethane

Ethyl N-methylcarbamate,
ethyl methylcarbamate (105-40-8)

Carbamic acid, methylnitroso-, ethyl ester (615-53-2)