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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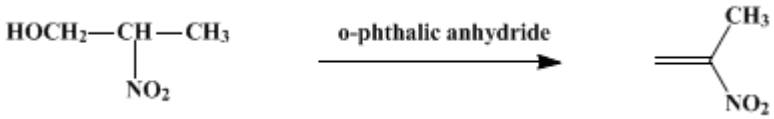
2-NITROPROPENE

[1-Propene, 2-nitro]



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Checked by D. Seebach, H. Siegel, and E. Wilka.

1. Procedure

Caution! This procedure should be carried out in a hood since 2-nitropropene is a powerful lachrymator. Nitroolefins have a tendency to undergo "fume-offs" (which can be like explosions) near the end of a distillation, particularly if air is let in on a hot distillation residue (from a vacuum distillation).

A 250 mL, one-necked, round-bottomed flask equipped with a magnetic stirring bar is charged with 96.5 g (0.65 mol) of phthalic anhydride (Note 1) and 52.5 g (0.50 mol) of 2-nitro-1-propanol (Note 2). A 10-cm vacuum-insulated Vigreux column, a stillhead fitted with a thermometer, a condenser, a 50-mL, round-bottomed receiving flask, and a water aspirator are installed in due order, and the reaction vessel is placed in an oil bath and evacuated to 110 mm (Note 3). The bath temperature is raised to 150° C and maintained for 30 min while the phthalic anhydride melts to give a homogeneous solution. The receiving flask is immersed in an ice bath, stirring is started, and the bath temperature is raised to 180° C. As the reaction mixture darkens, green-colored 2-nitropropene is gradually distilled off with water, bp 50–65°C (110 mm). The bath temperature is held at 180–185°C until the distillation ceases (ca. 1 hr). The distillate is transferred into a 50-mL separatory funnel, and the lower layer is separated from water (Note 4) and dried over anhydrous magnesium sulfate. Redistillation under reduced pressure through a 10-cm vacuum-insulated Vigreux column (Note 5) gives 25.0–31.4 g (57–72%) of 2-nitropropene, which is collected in an ice-cooled receiving flask as a transparent green liquid, bp 56–57°C (86 mm), n_D^{20} 1.4348 [lit.[2] bp 58°C (90 mm), n_D^{19} 1.4292, d^{20}1.0492] (Note 5). The distilling flask is cooled to room temperature before the vacuum is released.

2. Notes

1. Commercial phthalic anhydride, purchased from Wako Pure Chemical Industries, Ltd. (Japan) or from Fluka AG, Buchs (Switzerland), was used without purification.
2. The checkers purchased 2-nitro-1-propanol (ca. 98% purity) from EGA-Aldrich and used it without further purification. The submitters prepared this reagent from nitroethane and formalin according to the procedure of Feuer,[3] yield 70–75%, bp 79–80°C (5 mm).
3. Lower pressure may cause a loss of the product because of its volatility.
4. The layers sometimes do not separate well. In this case a small amount of magnesium sulfate should be added.
5. It is important that the bath temperature be kept as low as possible to avoid fume-off decompositions. In the checked procedure the bath temperature was never allowed to exceed 80°C. Toward the end of the distillation the pressure was reduced to ca. 60 mm to achieve complete distillation. Although pure 2-nitropropene may be stored in a freezer as a low-melting solid for several weeks, it is recommended to prepare it immediately before use since it tends to polymerize and to darken slowly on storage. 2-Nitropropene polymerizes readily in the presence of a trace of alkali.

3. Discussion

The procedure described is essentially the same as that of Buckley and Scaife.[2] The yield has been

increased from 55.5% up to 72% by using 1.3 mol eq of phthalic anhydride and by carefully controlling the pressure and cooling the receiving flask. Although 2-nitropropene has previously been prepared by pyrolysis of 2-nitro-1-propyl benzoate in 72% overall yield from 2-nitro-1-propanol,[4] the present method is preferred for its preparation since the procedure is much simpler and the product is directly obtainable from 2-nitro-1-propanol without first preparing its ester. It is also applicable to the preparation of 1-nitro-1-propene (58%),[5,6] 2-nitro-1-butene (82%),[7] and 2-nitro-2-butene (60%).[6,7] In general, aliphatic nitroolefins have the tendency to polymerize readily with alkali.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 7, 414

References and Notes

1. Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai 980, Japan.
2. Buckley, G. D.; Scaife, C. W. *J. Chem. Soc*. **1947**, 1471–1472.
3. Feuer, H.; Miller, R. *J. Org. Chem*. **1961**, *26*, 1348–1357.
4. Blomquist, A. T.; Tapp, W. J.; Johnson, J. R. *J. Am. Chem. Soc*. **1945**, *67*, 1519–1524.
5. Miyashita, M.; Kumazawa, T.; Yoshikoshi, A. *J. Chem. Soc., Chem. Commun*. **1978**, 362–363.
6. Melton, J.; McMurry, J. E. *J. Org. Chem*. **1975**, *40*, 2138–2139.
7. Miyashita, M.; Yanami, T.; Yoshikoshi, A. *J. Am. Chem. Soc*. **1976**, *98*, 4679–4681.

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

formalin (50-00-0)

phthalic anhydride (85-44-9)

magnesium sulfate (7487-88-9)

nitroethane (79-24-3)

2-Nitropropene,
1-Propene, 2-nitro (4749-28-4)

2-nitro-1-propanol (2902-96-7)

2-nitro-1-propyl benzoate

1-nitro-1-propene

2-nitro-1-butene

2-nitro-2-butene