



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.

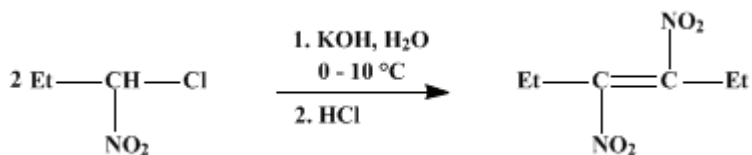
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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3,4-DINITRO-3-HEXENE

[3-Hexene, 3,4-dinitro-]



Submitted by D. E. Bisgrove, J. F. Brown, Jr., and L. B. Clapp¹.

Checked by John C. Sheehan, Richard L. Wasson, and Herbert O. House.

1. Procedure

This procedure involves the possibility of an explosion and therefore must be conducted with caution.

In a 1-l. three-necked flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel, and cooled externally with an ice-salt bath, is placed a solution of 118 g. (1.8 moles) of U.S.P. 85% potassium hydroxide (Note 1) in 300 ml. of water. The temperature of the solution is maintained between 0° and 10° (with the addition of ice to the flask if necessary) while 247 g. (205 ml., 2.0 moles) of 1-chloro-1-nitropropane (Note 2) is added from a dropping funnel over a 20-minute period. The cooling bath is removed, and concentrated hydrochloric acid is added dropwise (Note 1) until the momentary green coloration produced by the addition of each drop of acid spreads rapidly throughout the solution (near a pH of 9). The temperature of the solution rises to about 70° with the separation of a deep-green oily layer. Stirring is continued until the reaction mixture reaches room temperature (about 3 hours).

After the green oil has been separated, it is washed with 75 ml. of a warm (Caution! (Note 3)) 20% solution of potassium hydroxide in water to remove, as its potassium salt, the 1,1-dinitropropane formed as a by-product. The remaining 100–110 g. of oil is diluted with 90 ml. of 95% ethanol, and the green solution is cooled in an ice-salt bath to –5° to –10°. The crystalline product is collected on a cold (Note 4) 5.5-cm. Büchner funnel and washed with two 5-ml. portions of ice-cold alcohol. The yield is 50 g. of impure crystals.

Distillation of the alcoholic filtrate (Caution! (Note 5)) under reduced pressure and in an atmosphere of nitrogen permits the isolation of an additional 8–10 g. of 3,4-dinitro-3-hexene. The blue oil boiling below 75°/20 mm. is discarded. To the undistilled residue is added 25 ml. of 95% ethanol, the resulting solution is cooled in an ice-salt bath, and the crystals are collected on a cold Büchner funnel and washed with 5 ml. of ice-cold alcohol. The combined crops of crystals are recrystallized from 80 ml. of 95% ethanol. The pure 3,4-dinitro-3-hexene separates as light-yellow needles, m.p. 31–32°, weight 50–55 g. (29–32%) (Note 6).

2. Notes

1. Although slightly less than an equivalent amount of potassium hydroxide is used, the last of the 1-chloro-1-nitropropane dissolves slowly, and the pH drops sufficiently to allow rapid reaction only after a variable (usually about 3 hours) period of standing. The reaction may also be started by heating one spot on the container with a jet of steam, but it is more convenient and reliable to initiate reaction by cautious addition of acid in the manner described.

2. The 1-chloro-1-nitropropane used was the commercial grade obtained from Commercial Solvents Corporation. The yield was unchanged when a distilled sample, b.p. 143°, was used.

3. The temperature of the potassium hydroxide solution should not be above 35° when used. The

submitters report the isolation of 15–20 g. (9–12%) of potassium 1-nitropropylnitronate from the cooled extract. The checkers, having been advised that *this product is a hazardous explosive*, discarded the warm alkaline extract. If 1,1-dinitropropane is not desired (its preparation has been described²), it is recommended that it be extracted as its more soluble sodium salt by washing the green oil with sodium hydroxide solution rather than potassium hydroxide solution.

4. It is necessary to keep the Büchner funnel cold since the crystals melt near room temperature. An external cooling jacket for the funnel can be fabricated from a metal can by cutting a hole in the bottom of the can of such size that it fits high enough on a rubber stopper to allow a tight fit between the rubber stopper and the suction flask. The cooling jacket is filled with crushed Dry Ice. The checkers employed a 60-mm. sintered glass funnel surrounded by a 400-ml. beaker, in the bottom of which was a hole large enough to accommodate a No.3 rubber stopper surrounding the stem of the funnel.

5. *Distillation behind safety glass in a nitrogen atmosphere appears advisable in view of the nature of polynitro compounds* although the submitters have not had an explosion in the preparation of 3,4-dinitro-3-hexene.

6. 2,3-Dinitro-2-butene may be prepared from 1-chloro-1-nitroethane by the same procedure, in 30% yield. The compound melts at 28–28.5° and has a boiling point of 135°/11 mm. Commercially available 1-chloro-1-nitroethane contains about 10% 1,1-dichloro-1-nitroethane and 2-chloro-2-nitropropane which cannot be separated by distillation, but these impurities do not interfere with the preparation. *Distillation of 2,3-dinitro-2-butene behind safety glass in a nitrogen atmosphere is advisable.* The submitters, in preparing this compound, have had one explosion over a period of ten years.

3. Discussion

The action of a sodium bicarbonate solution or a 10% sodium hydroxide solution on 1-chloro-1-nitropropane will produce 3,4-dinitro-3-hexene. The procedure described here is a modification of that described by Nygaard and Noland.³

References and Notes

1. Brown University, Providence, Rhode Island. This work was supported in part by Office of Ordnance Research Contract DA-19-020-ORD-592 at Brown University.
2. ter Meer, *Ann.*, **181**, 1 (1876); Belew, Grabel, and Clapp, *J. Am. Chem. Soc.*, **77**, 1110 (1955).
3. Nygaard and Noland (to Socony-Vacuum Oil Company), U. S. pat. 2,396,282 [*C. A.*, **40**, 3126 (1946)].

Appendix

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

potassium 1-nitropropylnitronate

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

nitrogen (7727-37-9)

potassium hydroxide (1310-58-3)

3,4-Dinitro-3-hexene,
3-Hexene, 3,4-dinitro- (53684-54-1)

1-chloro-1-nitropropane (600-25-9)

1,1-dinitropropane (601-76-3)

2,3-Dinitro-2-butene (24335-44-2)

1-chloro-1-nitroethane (598-92-5)

2-chloro-2-nitropropane (594-71-8)

1,1-dichloro-1-nitroethane (594-72-9)