



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](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.

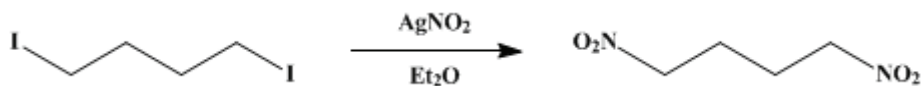
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 4, p.368 (1963); Vol. 34, p.37 (1954).*

## 1,4-DINITROBUTANE

[Butane, 1,4-dinitro-]



Submitted by Henry Feuer and Gerd Leston<sup>1</sup>.  
Checked by John C. Sheehan and J. Iannicelli.

### 1. Procedure

The reaction is carried out in 1-l. three-necked round-bottomed flask fitted with a ball-sealed mechanical stirrer, a reflux condenser, and a dropping funnel. The openings of the condenser and dropping funnel are protected from moisture by drying tubes. In the flask, which is protected from light (Note 1), are placed 170 g. (1.1 moles) of *silver nitrite* and 300 ml. of absolute *ether*. The *silver nitrite* is suspended by vigorous stirring, and the mixture is cooled to 0° by an ice bath. Then 155 g. (0.5 mole) of *1,4-diiodobutane* (p.321) is added dropwise over a period of 3 hours. The temperature is maintained at 0° for an additional 2 hours, and then the reaction mixture is allowed to come slowly to room temperature (25°) by permitting the ice in the cooling bath to melt (Note 2). Twenty-four hours after the addition of the *diiodobutane* has been completed, the solution is tested for unreacted iodide (Note 3). If the test is negative, the mixture is filtered and the *silver iodide* washed with a total of 200 ml. of *benzene* (Note 4). The ethereal solution and the *benzene* washings are combined, and the solvents are distilled on a steam bath, the pressure being reduced (water aspirator) toward the end of the distillation.

In a 500-ml. three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a thermometer is placed 200 ml. of concentrated *sulfuric acid*. The flask is immersed in an ice-salt bath, and the acid is cooled to 0–5°. The crude *dinitrobutane* is added dropwise with vigorous stirring at such a rate that the temperature does not exceed 8°. Stirring is continued for an additional 10 minutes after completion of the addition. The solution is poured cautiously onto 1 kg. of crushed ice with manual stirring. The ice is allowed to melt, and the product is separated by suction filtration, washed with water, and air-dried. Recrystallization from *methanol* at –70°, using a Dry Ice-methylene chloride cooling bath, yields 30–34 g. (41–46%) of *1,4-dinitrobutane*, m.p. 33–34° (Note 5), (Note 6), (Note 7), and (Note 8).

### 2. Notes

- All light should be excluded. It is most convenient to run the reaction in a dark room.
- The cooling bath should not be removed, or the temperature of the mixture will rise above room temperature.
- The Beilstein test is carried out in the following manner: A copper wire is cleaned in the flame of Bunsen burner and allowed to cool. The stirring is stopped, and the wire is inserted carefully into the clear ether solution so as not to touch the *silver iodide* at the opening and at the bottom of the flask. The wire is withdrawn and held in the reducing part of the flame. A green color constitutes a positive test, and stirring is resumed until the test is negative.
- An alternative method of purification is to wash the *silver iodide* with 250 ml. of *methanol* instead of *benzene*. The *ether* is evaporated, and the residue is combined with the *methanol* solution. The product is crystallized at –70°. Recrystallization of this crude product from *methanol* at –70° gives the same yields as the other method of purification.
- The *methanol* solution may be treated with *charcoal* if a colorless product is not obtained.
- Starting with 169 g. of *1,6-diiodohexane* (p.323), *1,6-dinitrohexane* may similarly be obtained in 46–48% yield, m.p. 36.5–37.5°. The alternative procedure of isolation described in Note 4 may also be used.
- 1,3-Dinitropropane* may be prepared in a similar manner starting with 148 g. of *1,3-diiodopropane*

(supplied by the Eastman Kodak Company and by the Eastern Chemical Corporation). However, the dinitro compound is a liquid and has to be purified in the following manner: The crude 1,3-dinitropropane is extracted from the aqueous acid layer with four 150-ml. portions of benzene. The benzene is removed by distillation at atmospheric pressure, and the residue is distilled from a 50-ml. Claisen flask, b.p. 108–110°/1 mm.,  $n_D^{20}$  1.465. The yield is 24–25 g. (36–37%). It is colorless during the distillation but rapidly turns yellow on storage. If the aqueous layer is extracted continuously with benzene or ether for 24 hours an additional 3 g. of product may be obtained.

8. 1,5-Dinitropentane may be prepared in a similar manner starting with 162 g. of 1,5-diiodopentane prepared from tetrahydropyran according to the directions for 1,4-diiodobutane (p.321). The dinitro compound is a liquid and is obtained by extracting the aqueous acid layer with three 125-ml. portions of benzene. The benzene is removed by distillation at atmospheric pressure, and the residue is distilled from a 50-ml. Claisen flask. The fraction, b.p. 134°/1.2 mm., amounts to 36.6 g. (45% yield),  $n_D^{20}$  1.461. The distillate is colorless but rapidly turns yellow.

### 3. Discussion

1,3-Dinitropropane,<sup>2,3</sup> 1,4-dinitrobutane,<sup>4,5</sup> 1,5-dinitropentane,<sup>4,5</sup> and 1,6-dinitrohexane<sup>5</sup> have been prepared by the method described here, which is that of Victor Meyer. 1,4-Dinitrobutane also has been obtained by the hydrolysis of dipotassium  $\alpha,\alpha'$ -dinitroadiponitrile.<sup>6</sup>

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### References and Notes

1. Purdue University, Lafayette, Indiana.
  2. Keppler and Meyer, *Ber.*, **25**, 1710 (1892).
  3. Kispersky, Hass, and Holcomb, *J. Am. Chem. Soc.*, **71**, 516 (1949).
  4. von Braun and Sobecki, *Ber.*, **44**, 2528 (1911).
  5. McElroy, Ph.D. Thesis, Purdue University, 1943.
  6. Feuer and Savides, *J. Am. Chem. Soc.*, **81**, 5826 (1959).
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### Appendix

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

dipotassium  $\alpha,\alpha'$ -dinitroadiponitrile

sulfuric acid (7664-93-9)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

charcoal (7782-42-5)

1,3-diiodopropane (627-31-6)

Tetrahydropyran (142-68-7)

silver nitrite (7783-99-5)

1,6-Diiodohexane (629-09-4)

1,4-Diiodobutane (628-21-7)

1,4-Dinitrobutane,  
Butane, 1,4-dinitro- (4286-49-1)

diiodobutane

silver iodide (7783-96-2)

dinitrobutane

1,6-dinitrohexane

1,3-Dinitropropane (6125-21-9)

1,5-Dinitropentane (6848-84-6)

1,5-diiodopentane (628-77-3)