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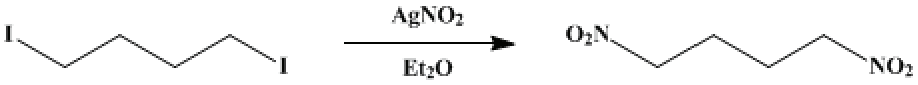
1,4-DINITROBUTANE

[Butane, 1,4-dinitro-]



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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

1. All light should be excluded. It is most convenient to run the reaction in a dark room.
2. The cooling bath should not be removed, or the temperature of the mixture will rise above room temperature.
3. 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.
4. 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.
5. The methanol solution may be treated with charcoal if a colorless product is not obtained.
6. 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.
7. 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,[2,3] 1,4-dinitrobutane,[4,5] 1,5-dinitropentane,[4,5] and 1,6-dinitrohexane[5] 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 α,α'-dinitroadiponitrile.[6]

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).

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

dipotassium α,α'-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)