



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.

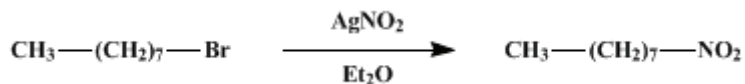
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1-NITROOCTANE

[Octane, 1-nitro-]



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Checked by John C. Sheehan and M. Gertrude Howell.

1. Procedure

1-Bromoöctane (96.5 g., 0.5 mole) (Note 1) is added dropwise during 2 hours to a stirred suspension of silver nitrite (116 g., 0.75 mole) (Note 2) in 150 ml. of dry ether (Mallinckrodt anhydrous), contained in a 500-ml. three-necked round-bottomed flask equipped with dropping funnel, reflux condenser, and a sealed Hershberg-type stirrer (Trubore) and immersed in a 1-gal. Dewar flask filled with ice and water (Note 3). The mixture is stirred for 24 hours in an ice bath. The bath is removed, and stirring is continued at room temperature (26–28°) until the supernatant liquor gives a negative test for halides (approximately 40 hours, (Note 4) and (Note 5).

The silver salts are removed by filtration, slurried with two 100-ml. portions of dry ether, and the ether washings are added to the ethereal solution of reaction products (Note 6). The combined ethereal solutions are distilled at atmospheric pressure through a 2 × 45 cm. column packed with 4-mm. Pyrex helices (Note 7). The residue remaining after removal of the ether is fractionated under reduced pressure. The yellow liquid distilling at 37°/3 mm. has n_D^{20} 1.4127–1.4129 and weighs 11.3 g. (14%); this is 1-octyl nitrite. It is followed by an interfraction of b.p. 38–70°/3 mm., n_D^{20} 1.4133–1.4320, yield 6.83 g., which contains some nitrite, some 1-octanol, and a little 1-nitroöctane. Finally, pure, colorless 1-nitroöctane distils at 66°/2 mm., n_D^{20} 1.4321–1.4323, yield 59.6–63.6 g. (75–80%) (Note 8) and (Note 9).

2. Notes

- 1-Bromoöctane b.p. 50–51°/0.8 mm., n_D^{20} 1.4526, was employed.
- Silver nitrite can be prepared as follows: silver nitrate (169.9 g., 1 mole) dissolved in 500 ml. of distilled water is added in small portions, with vigorous shaking, to a solution of 76 g. (1.1 mole) of sodium nitrite, dissolved in 250 ml. of distilled water contained in a 1-l. Erlenmeyer flask. (These operations are best carried out under a yellow safelight or, in any case, with minimum exposure to light.) Then the mixture is allowed to stand in the dark for 1 hour. The yellow precipitate is collected by filtration with suction, suspended in 250 ml. of distilled water, and again filtered. The washing is repeated twice, and the product is collected by filtration and dried to constant weight in a vacuum desiccator over potassium hydroxide pellets; yield 134 g. (87%). The silver nitrite drying process can be facilitated by washing the material with methanol.
- It is preferable to carry out the entire reaction in a dark room equipped with a yellow safelight. The reaction mixture should be protected from moisture by means of drying tubes.
- The stirrer is stopped, and the precipitate is allowed to settle. Unchanged alkyl halide is detected in the supernatant liquor by the Beilstein test (copper wire spiral) or by adding a few drops of the ethereal solution to alcoholic silver nitrate.
- According to the submitters, with primary straight-chain bromides the time needed to reach a negative test for halide is 24 hours at 0° followed by 48 ± 12 hours at room temperature. When primary straight-chain iodides are employed, the reaction time is shorter: 24 hours at ice temperature followed by 36 ± 12 hours at room temperature.
- It is more difficult to remove an alcohol from the corresponding nitroalkane than it is to separate the nitrite ester and the nitroalkane. Minimal exposure to a moist atmosphere is, therefore, desirable since anhydrous ether is hygroscopic and nitrite esters hydrolyze readily, especially if a little acid is present.

7. A column of high efficiency is undesirable because of the thermal instability of the nitrite, and a column of lesser efficiency cannot accomplish a complete separation of the products. The column used by the submitters was equipped with a total condensate, partial take-off head with small holdup.

8. 1-Nitroöctane is completely soluble in aqueous alkali. It is converted to a crystalline colorless sodium salt on shaking with 20% aqueous sodium hydroxide, and this salt dissolves completely on adding enough water to make the solution 10% aqueous base. That the nitro compound is free from nitrate is shown by the absence of the infrared absorption bands at 6.15, 7.85 and 11.6 μ characteristic of nitrate esters.

9. A recent study² has shown that this is a general reaction for primary straight-chain bromides and iodides; in contrast, primary chlorides fail to react. Primary bromides and iodides having branched chains also give excellent yields of nitro compounds, especially if the branching is not on the carbon *alpha* to the one holding the halogen (Table I).

TABLE I YIELDS OF NITRO
COMPOUNDS

Halide	RNO ₂ , %	Halide	RNO ₂ , %
<i>n</i> -Butyl Br	73	<i>n</i> -Octyl I	83
<i>n</i> -Butyl I	74	Isoamyl Br	72
<i>n</i> -Hexyl Br	76	Isoamyl I	78
<i>n</i> -Hexyl I	78	Isobutyl Br	18
<i>n</i> -Heptyl Br	79	Isobutyl I	59
<i>n</i> -Heptyl I	82	Neopentyl I	0
<i>n</i> -Octyl Br	80		

The reaction of silver nitrite with secondary halides gives yields of nitroparaffins in the vicinity of 15%, while with tertiary halides the yields are even lower (0–5%). There is no question that the reaction of silver nitrite with alkyl halides is useful only for the synthesis of primary nitroparaffins.

3. Discussion

The present procedure is based on a published paper.² 1-Nitroöctane has been prepared from 1-iodoöctane and silver nitrite,³ from octane by boiling with nitric acid,^{4,5} from 1-nitroöctylene by catalytic hydrogenation,⁶ from *n*-octaldehyde oxime and peroxytrifluoroacetic acid in acetonitrile,⁷ and from 1-bromoöctane and sodium nitrite in dimethyl sulfoxide or dimethylformamide.⁸ 1-Nitroöctane also has been obtained from *n*-octyl *p*-toluenesulfonate and sodium nitrite in 17% yield.⁹

References and Notes

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(Registry Number)

n-Butyl Br

n-Octyl I

n-Butyl I

Isoamyl Br

n-Hexyl Br

Isoamyl I

n-Hexyl I

Isobutyl Br

n-Heptyl Br

Isobutyl I

n-Heptyl I

Neopentyl I

n-Octyl Br

n-octaldehyde oxime

[methanol \(67-56-1\)](#)

[ether \(60-29-7\)](#)

[acetonitrile \(75-05-8\)](#)

[sodium hydroxide \(1310-73-2\)](#)

[nitric acid \(7697-37-2\)](#)

[silver nitrate \(7761-88-8\)](#)

[1-Bromooctane \(111-83-1\)](#)

[sodium nitrite \(7632-00-0\)](#)

[nitrite \(14797-65-0\)](#)

[potassium hydroxide pellets \(1310-58-3\)](#)

[nitro \(10102-44-0\)](#)

silver nitrite (7783-99-5)

1-Octanol (111-87-5)

1-iodooctane (629-27-6)

dimethylformamide (68-12-2)

octane (111-65-9)

dimethyl sulfoxide (67-68-5)

Octane, 1-nitro-,
1-Nitrooctane (629-37-8)

1-octyl nitrite

1-nitrooctylene

peroxytrifluoroacetic acid

n-octyl p-toluenesulfonate (3386-35-4)