



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.

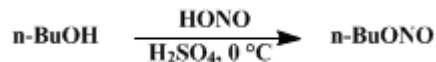
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

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.*

*Organic Syntheses, Coll. Vol. 2, p.108 (1943); Vol. 16, p.7 (1936).*

## ***n*-BUTYL NITRITE**



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### 1. Procedure

In a 3-l. three-necked, round-bottomed flask, fitted with a mechanical stirrer (Note 1), a separatory funnel extending to the bottom of the flask, and a thermometer, are placed 380 g. (5.5 moles) of c.p. sodium nitrite and 1.5 l. of water. The flask is surrounded by an ice-salt mixture, and the solution is stirred until the temperature falls to 0°. A mixture of 100 cc. of water, 136 cc. (250 g., 2.5 moles) of concentrated sulfuric acid (sp. gr. 1.84) (Note 2), and 457 cc. (370 g., 5 moles) of commercial *n*-butyl alcohol is cooled to 0° and by means of the separatory funnel is introduced slowly beneath the surface of the nitrite solution, with stirring. The alcohol solution is added slowly enough so that practically no gas is evolved, and the temperature is kept at ±1°. This usually requires from one and one-half to two hours.

The resulting mixture is allowed to stand in the ice-salt bath until it separates into layers, and the liquid layers are decanted from the sodium sulfate into a separatory funnel (Note 3). The lower aqueous layer is removed and the butyl nitrite layer washed twice with 50-cc. portions of a solution containing 2 g. of sodium bicarbonate and 25 g. of sodium chloride in 100 cc. of water. After drying over 20 g. of anhydrous sodium sulfate, the yield of practically pure butyl nitrite amounts to 420–440 g. (81–85 per cent of the theoretical amount) (Note 4) and (Note 5). If desired, the product may be distilled under reduced pressure when 98 per cent distils at 24–27°/43 mm. (Note 6). Butyl nitrite boils at 75° under atmospheric pressure, with some decomposition.

### 2. Notes

1. A stirrer capable of keeping solid material in motion and driven by a strong motor should be used because of the precipitation of large amounts of sodium sulfate towards the end of the reaction.
2. The concentration of sulfuric acid which is used keeps the butyl alcohol in solution but does not dissolve butyl nitrite.
3. If more butyl nitrite separates from the sodium sulfate after the first decantation, a second decantation is made. Care must be exercised in handling butyl nitrite; inhalation of the vapor may cause severe headache and heart excitation.
4. The same procedure is quite satisfactory for runs of one-tenth this size. In small runs mechanical stirring is unnecessary since gentle rotation of the flask by hand gives good mixing.
5. Isoamyl nitrite may be made in the same manner and with approximately the same yields.
6. Butyl nitrite decomposes slowly on standing and should be kept in a cool place and used within a few days or, at most, a few weeks after it is prepared. A sample which stood for five months during a warm summer seemed to contain only 20–25 per cent of the original nitrite. The products of decomposition consist of oxides of nitrogen, water, butyl alcohol, and polymerization products of butyraldehyde.

### 3. Discussion

Butyl nitrite has always been prepared by the action of nitrous acid on butyl alcohol.<sup>1</sup> The method described<sup>2</sup> is a modification of that of Wallach and Otto<sup>3</sup> for ethyl nitrite.

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 2*, 363
- *Org. Syn. Coll. Vol. 3*, 191

- [Org. Syn. Coll. Vol. 5, 623](#)
- [Org. Syn. Coll. Vol. 6, 840](#)

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## References and Notes

1. Bertoni, *Gazz. chim. ital.* **18**, 434 (1888); Adams and Kamm, *J. Am. Chem. Soc.* **40**, 1285 (1918).
  2. Noyes, *ibid.* **55**, 3888 (1933).
  3. Wallach and Otto, *Ann.* **253**, 251 (1889).
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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

oxides of nitrogen

[sulfuric acid \(7664-93-9\)](#)

[sodium bicarbonate \(144-55-8\)](#)

[sodium chloride \(7647-14-5\)](#)

[sodium sulfate \(7757-82-6\)](#)

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

[nitrous acid \(7782-77-6\)](#)

[butyl alcohol,  
n-butyl alcohol \(71-36-3\)](#)

[butyraldehyde \(123-72-8\)](#)

[Butyl nitrite,  
n-butyl nitrite \(544-16-1\)](#)

[ethyl nitrite \(109-95-5\)](#)

[Isoamyl nitrite \(110-46-3\)](#)