Organic Syntheses

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.

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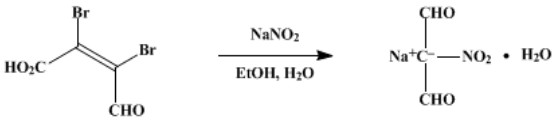
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Org. Synth.* **1952**, *32*, 95
DOI: 10.15227/orgsyn.032.0095

# SODIUM NITROMALONALDEHYDE MONOHYDRATE

## [Malonaldehyde, nitro-, sodium derivative]

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## 1. Procedure

*Caution! The sodium salt of nitromalonaldehyde is impact-sensitive and thermally unstable and should be handled as a potentially explosive material.*

*See the discussion in Org. Synth. 1973, Coll. Vol. 5, 1004 with regard to potential hazards associated with this procedure.*

In a 2-l. three-necked round-bottomed flask, equipped with a thermometer, a dropping funnel, a mechanical stirrer and a gas vent (Note 1), are placed 258 g. (3.74 moles) of sodium nitrite and 250 ml. of water. The contents of the flask are heated and stirred to dissolve the solid. A solution of 258 g. (1 mole) of mucobromic acid (p. 688) in 250 ml. of warm 95% ethanol is placed in the dropping funnel and added dropwise with constant stirring over a period of 70–80 minutes. A mildly exothermic reaction occurs; the solution in the flask becomes deep red, and gas is evolved. During the addition, the temperature is kept at 54 ± 1° by intermittent application of an ice bath to the flask (Note 2). The mixture is stirred for an additional 10 minutes at 54 ± 1°. While being stirred continuously, it is then cooled to 0–5° by application of an ice bath. The fine, yellow precipitate is collected on a previously chilled Büchner funnel.

The slightly moist cake of crude product is transferred to a 1-l. flask and heated to boiling with a mixture of 400 ml. of 95% ethanol and 100 ml. of water. The hot solution is filtered to remove a fine yellow solid, and the clear red filtrate is cooled to 0–5°. The recrystallized product is collected on a Büchner funnel and dried in air at room temperature. The yield is 57–65 g. (36–41%) of pink or tan needles of sodium nitromalonaldehyde monohydrate (Note 3).

## 2. Notes

1. The gases evolved are slightly irritating; they should be vented to a trap,[2] or the apparatus should be set up in a hood.
2. The yield is not increased and a darker, less pure product is obtained if the reaction is run at a higher temperature or for a longer time.
3. The checkers found the product to be quite pure. An almost quantitative yield of 2-amino-5-nitropyrimidine was obtained by reaction of the product with guanidine.

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## 3. Discussion

The procedure above is a modification of the method of Hill and Torrey,[3] which was also studied by Johnson[4] and others.[5,6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 1004

### References and Notes

1. Illinois Institute of Technology, Chicago, Illinois.
2. *Org. Syntheses Coll. Vol.* **2**, 4 (1943).
3. Hill and Torrey, *Am. Chem. J.*, **22**, 89 (1899).
4. Johnson, P.B. Report 31092, "Preparation of Nitro Compounds" (1941) [*U.S. Bibliog. of Scientific and Industrial Reports*, **2**, 785 (1946)].
5. Ulbricht and Price, *J. Org. Chem.*, **22**, 235 (1957).
6. Tozaki, *Repts. Sci. Research Inst. (Japan)*, **27**, 401 (1951) [*C. A.*, **47**, 2181 (1953)].

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

SODIUM NITROMALONALDEHYDE MONOHYDRATE

Malonaldehyde, nitro-, sodium derivative

sodium salt of nitromalonaldehyde

ethanol (64-17-5)

sodium nitrite (7632-00-0)

guanidine (113-00-8)

Mucobromic acid (488-11-9)

2-amino-5-nitropyrimidine (3073-77-6)