



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.

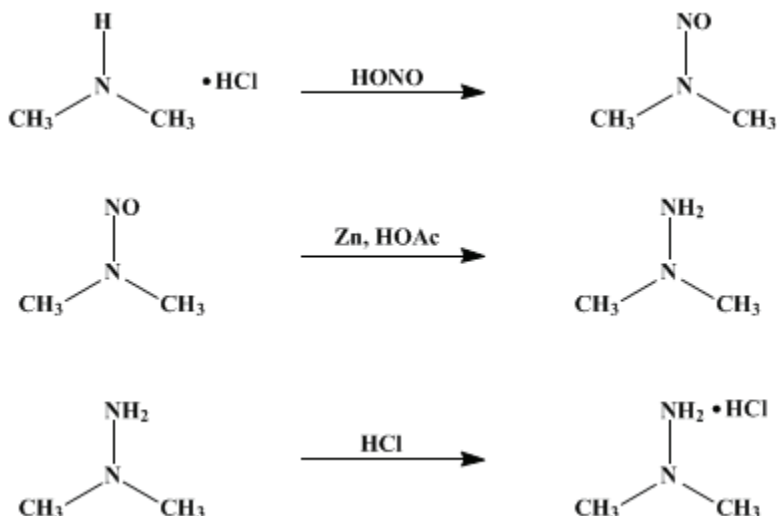
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.211 (1943); Vol. 16, p.22 (1936).*

## ***unsym.*-DIMETHYLHYDRAZINE HYDROCHLORIDE**

### **[Hydrazine, 1,1-dimethyl-, hydrochloride]**



Submitted by H. H. Hatt

Checked by W. W. Hartman and W. D. Peterson.

### **1. Procedure**

(A) *Nitrosodimethylamine*.—In a 2-l. round-bottomed flask provided with a mechanical stirrer are placed 245 g. (3 moles) of *dimethylamine hydrochloride*, 120 cc. of water, and 10 cc. of approximately 2 *N* *hydrochloric acid*. The resulting solution is stirred vigorously and maintained at 70–75° by heating on a water bath, while 235 g. (3.23 moles) of 95 per cent *sodium nitrite* suspended in 150 cc. of water is added from a dropping funnel over a period of an hour. The reaction mixture is tested frequently and maintained barely acid to litmus by further 1-cc. additions of 2 *N* *hydrochloric acid* when necessary (about 30–35 cc. of acid is required). Stirring and heating are continued for two hours after all the *sodium nitrite* has been added.

The flask is arranged for distillation, and the reaction mixture is distilled under slightly diminished pressure on a water bath until the residue is practically dry. To the residue 100 cc. of water is added, and the process of distillation to dryness is repeated. The distillates are combined and saturated with *potassium carbonate* (about 300 g. is required); the upper layer of *dimethylnitrosoamine* is removed, and the water layer is extracted with three 140-cc. portions of *ether*. The combined nitrosoamine and ethereal extracts are dried over anhydrous *potassium carbonate* and distilled through a 30-cm. fractionating column. The yield of product boiling at 149–150° /755 mm. is 195–200 g. (88–90 per cent of the theoretical amount). *Nitrosodimethylamine* is a yellow oil which darkens in bright light.

(B) *unsym.-Dimethylhydrazine Hydrochloride*.—In a 5-l. round-bottomed flask, provided with a mechanical stirrer, dropping funnel, and thermometer, are put 200 g. (2.7 moles) of *nitrosodimethylamine*, 3 l. of water, and 650 g. (10 gram atoms) of 100 per cent *zinc* dust, or an equivalent amount of lower-quality material (Note 1). While the mixture is stirred and maintained at 25–30° by immersion in a water bath, 1 l. (14 moles) of 85 per cent *acetic acid* is added from the dropping funnel over a period of two hours. Subsequently the reaction mixture is heated for one hour at 60°, allowed to cool, and the excess *zinc* dust filtered and washed with a little water. The aqueous liquors are combined and transferred to a 12-l. flask arranged for steam distillation. The flask is fitted with a dropping funnel, and the steam inlet is provided with a trap. A large filtering or distilling flask serves as the receiver, and the side tube is connected with two absorption flasks, each containing 1 : 1 *hydrochloric acid* (Note 2). The aqueous liquors are made distinctly alkaline by adding a concentrated

solution of 1 kg. of [sodium hydroxide](#) through the dropping funnel, and the mixture is then steam-distilled until a test portion of the distillate shows only a faint reduction with Fehling's solution. Usually about 5–6 l. of distillate suffices to remove the [dimethylhydrazine](#). The distillation is more rapid if a free flame is placed under the distillation flask.

The aqueous distillate is treated with 650 cc. of concentrated [hydrochloric acid](#) and concentrated on a steam bath, under reduced pressure, until the residual liquor becomes a syrupy mass ([Note 3](#)). This is desiccated further by adding 150 cc. of absolute [ethyl alcohol](#) and evaporating under reduced pressure. Two or three such treatments with alcohol dry the crystalline material sufficiently so that it no longer sticks to the sides of the flask. The crude product is dried in a vacuum desiccator over [calcium chloride](#). The pale yellow, dry, crystalline solid weighs 200–215 g. (77–83 per cent of the theoretical amount). The dried product may be purified by dissolving it in an equal weight of boiling absolute [ethyl alcohol](#) and then chilling in an ice bath. The yield of pure white crystals melting at 81–82° is 180–190 g. (69–73 per cent of the theoretical amount) ([Note 4](#)).

## 2. Notes

1. The approximate strength of the [zinc](#) dust should be known in order to ensure complete reduction.
2. If this step is carried out under a hood, the absorption flasks are unnecessary. During the first minutes of the subsequent steam distillation, volatile nitrogen bases, consisting chiefly of [ammonia](#) and [methylamine](#), are driven over.
3. A concentrated aqueous solution of the free hydrazine may be obtained from the syrupy residue by allowing it to drop onto a large excess of solid [sodium hydroxide](#) and distilling until the temperature reaches 100°. To obtain the anhydrous base, the concentrated aqueous solution is redistilled after standing over [potassium hydroxide](#), the base is collected over [barium oxide](#) and after several days' standing is distilled again. The free hydrazine boils at 62–65° /765 mm.; it is extremely hygroscopic and attacks cork and rubber.
4. The product is the monohydrochloride of the base.

## 3. Discussion

The preparation of unsymmetrical dimethylhydrazine by reduction of [nitrosodimethylamine](#) was described by Fischer<sup>1</sup> and by Renouf.<sup>2</sup> Methylation of [hydrazine](#),<sup>3</sup> reduction of [nitrodimehylamine](#),<sup>4</sup> and the action of aminopersulfuric acid on [dimethylamine](#)<sup>5</sup> also furnish unsymmetrical dimethylhydrazine.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 12](#)

---

## References and Notes

1. Fischer, Ber. **8**, 1587 (1875).
2. Renouf, *ibid.* **13**, 2170 (1880).
3. Harries and Haga, *ibid.* **31**, 56 (1898).
4. Franchimont, Rec. trav. chim. **3**, 427 (1884); Backer, *ibid.* **31**, 150 (1912).
5. Sommer and Schulz, Ger. pat. 338,609 [Frdl. **13**, 203 (1916–21)].

---

## Appendix

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

aminopersulfuric acid

unsym.-Dimethylhydrazine Hydrochloride

unsymmetrical dimethylhydrazine

ethyl alcohol (64-17-5)

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ammonia (7664-41-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

barium oxide

sodium nitrite (7632-00-0)

potassium hydroxide (1310-58-3)

zinc (7440-66-6)

dimethylamine (124-40-3)

nitrodimehylamine (4164-28-7)

hydrazine (302-01-2)

dimethylamine hydrochloride (506-59-2)

methylamine (74-89-5)

dimethylhydrazine (57-14-7)

Hydrazine, 1,1-dimethyl-, hydrochloride (593-82-8)

Nitrosodimethylamine,  
dimethylnitrosoamine (62-75-9)