



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.

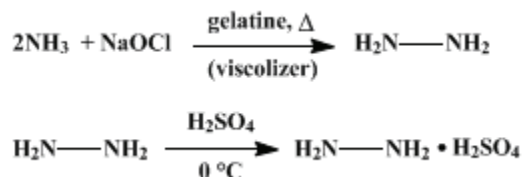
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior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

Organic Syntheses, Coll. Vol. 1, p.309 (1941); Vol. 2, p.37 (1922).

HYDRAZINE SULFATE



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1. Procedure

A normal solution of [sodium hypochlorite](#) is prepared as follows: in a 5-l. round-bottomed flask are placed 1800 g. of [sodium hydroxide](#) solution [300 g. (7.5 moles) of [sodium hydroxide](#) to 1500 g. of water] and 1500 g. of ice. [Chlorine](#) gas is then passed into the solution until it has gained in weight approximately 213 g. (3 moles). During this addition, the solution must be kept thoroughly cooled with ice, in order that chlorates will not be formed ([Note 1](#)). After all the [chlorine](#) has been passed in, it is necessary to be certain that the mixture is slightly alkaline, since any free [chlorine](#) in the solution prevents the formation of [hydrazine](#).

In a 36-cm. evaporating dish are placed 1350 g. (1.5 l., 23 moles) of c.p. aqueous [ammonia](#) (sp. gr. 0.90), 900 cc. of distilled water ([Note 2](#)), 375 cc. of 10 per cent gelatine solution ([Note 3](#)), and 1200 cc. of the normal [sodium hypochlorite](#) solution prepared as above. This mixture is heated as rapidly as possible and boiled down until one-third of the original volume is left. This solution is then cooled thoroughly with ice and filtered with suction, first through two layers of toweling and then through one thickness of ordinary filter paper over cloth, in order to remove finely divided solid impurities. The solution is then placed in a precipitating jar, and cooled thoroughly (0°) with ice and salt; 10 cc. of concentrated [sulfuric acid](#) for each 100 cc. of solution is gradually added with constant stirring ([Note 4](#)). A precipitate of [hydrazine sulfate](#) ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{SO}_4$) forms. The mixture is allowed to stand in the cold for a few hours in order to complete the precipitation, and is then filtered by suction in the usual way and the precipitate washed with cold [alcohol](#). The yield varies from 53 g. to 58 g. per 1.5 l. of aqueous [ammonia](#) (34–37 per cent of the theoretical amount). The product is perfectly white and crystalline, and satisfactory for almost any purpose. If a very pure product is desired, it must be recrystallized from water. For every 21 g. of crude product, 100 g. of boiling water is used. If the crude [hydrazine](#) is brown, it is advisable to use a little animal charcoal. After the mixture has been filtered and cooled to 0° , 19 g. of pure white crystals are obtained ([Note 5](#)).

2. Notes

1. In the preparation of the [sodium hypochlorite](#) solution it is quite necessary that the mixture be kept cold and be alkaline to litmus paper at the end of the reaction, if good yields of [hydrazine](#) are to be obtained.
2. Since [iron](#) is an anti-catalyzer, it is necessary to use distilled water throughout the process.
3. As a viscolizer, a substance such as starch, [glycerol](#), glue, or gelatine may be used; the last, however, gives by far the most satisfactory results.
4. In order to obtain a pure white [hydrazine sulfate](#) as the first precipitate, it is necessary to cool the [hydrazine](#) solution thoroughly and filter it twice before the [sulfuric acid](#) is added. Moreover, the [sulfuric acid](#) must be added slowly and with stirring. If these conditions are not followed, material containing brown particles results.
5. The mother liquor obtained from the crystallized [hydrazine sulfate](#) contains a small amount of [hydrazine](#). If 200 g. of [copper sulfate](#) is dissolved in water and added to 10 l. of the filtrates from the above processes, a light-blue crystalline precipitate of the double salt of copper sulfate and [hydrazine sulfate](#) will be formed after ten hours. This salt, when suspended in ten times its weight of distilled

water and treated with [hydrogen sulfide](#), decomposes into [copper sulfide](#) and [hydrazine sulfate](#). After the [copper sulfide](#) has been filtered off, the solution is concentrated until the [hydrazine sulfate](#) crystallizes. The yield of product is small, so that it is hardly advisable to undertake this recovery in the laboratory.

It is possible for one person, simultaneously evaporating six dishes of the [hydrazine](#) mixture, to turn out from 20 to 25 runs in nine hours. The time for the evaporation of a solution, such as is mentioned in the experimental part, with a four-flame Bunsen burner, is two to three hours; if the evaporation is carried out more slowly than this, the yield of product is distinctly diminished.

3. Discussion

Hydrazine salts can be prepared by the action of hypochlorites on [ammonia](#)¹ or [urea](#);² by the reduction of nitrates or nitrites with [zinc](#) in neutral solution;³ and by the action of [ammonia](#) on [dichlorourea](#).⁴

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 450](#)
- [Org. Syn. Coll. Vol. 2, 85](#)
- [Org. Syn. Coll. Vol. 2, 208](#)
- [Org. Syn. Coll. Vol. 2, 228](#)
- [Org. Syn. Coll. Vol. 2, 395](#)
- [Org. Syn. Coll. Vol. 2, 496](#)
- [Org. Syn. Coll. Vol. 3, 73](#)
- [Org. Syn. Coll. Vol. 3, 656](#)
- [Org. Syn. Coll. Vol. 4, 74](#)
- [Org. Syn. Coll. Vol. 4, 351](#)

References and Notes

1. Raschig, Ger. pat. 192, 783 [Chem. Zentr. I, 427 (1908)]; Chem. Ztg. **31**, 926 (1907), Ger. pat. 198,307 [Chem. Zentr. I, 1957 (1908)]; Brit. pat. 22,957 [C. A. **2**, 1999 (1908)]; U. S. pat. 910,858 [C. A. **3**, 1065 (1909)]; Fr. pat. 382,357 [C. A. **3**, 2358 (1909)]; Ber. **40**, 4587 (1907); "Laboratory Manual of Inorganic Preparations," A. B. Lamb, Harvard University, Cambridge, Mass.; Magidson and Frenkel, Trans. Sci. Chem. Pharm. Inst. (Moscow) **6**, 25 (1923) [C. A. **22**, 3881 (1928)].
2. Schestakov, J. Russ. Phys. Chem. Soc. **37**, 1 (1905) [Chem. Zentr. I, 1227 (1905)]; Ger. pat. 164,755 [Frld. **8**, 53 (1905-07)]; Fr. pat. 329,430 [J. Soc. Chem. Ind. **22**, 1063 (1903)].
3. Wohl, Brit. pat. 11,216 [J. Soc. Chem. Ind. **14**, 595 (1895)].
4. Chattaway, J. Chem. Soc. **95**, 235 (1909); Chem. News **98**, 166 (1908).

Appendix

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

double salt of copper sulfate

Hydrazine salts

[alcohol](#) (64-17-5)

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

sodium hydroxide (1310-73-2)

glycerol (56-81-5)

iron (7439-89-6)

hydrogen sulfide (7783-06-4)

copper sulfate (7758-98-7)

chlorine (7782-50-5)

zinc (7440-66-6)

urea (57-13-6)

Hydrazine sulfate (10034-93-2)

sodium hypochlorite (7681-52-9)

hydrazine (302-01-2)

copper sulfide

dichlorourea