



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.

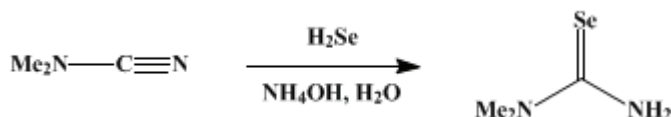
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.359 (1963); Vol. 36, p.23 (1956).

N,N-DIMETHYLSELENOUREA

[Urea, 1,1-dimethyl-2-seleno-]



Submitted by Frank Bennett and Ralph Zingaro¹.

Checked by C. F. H. Allen and K. C. Kennard.

1. Procedure

Caution! Hydrogen selenide is very toxic. This preparation should be carried out in a well-ventilated hood. The operator should wear rubber gloves. The apparatus should be screened from bright light.

A mixture of 37 g. (0.5 mole) of [dimethylcyanamide](#) (Note 1), 75 ml. of concentrated [ammonium hydroxide](#), and 25 ml. of water is placed in a 250-ml. round-bottomed three-necked flask fitted with a stirrer, thermometer, and glass delivery tube (Note 2). The solution is stirred slowly, while [hydrogen selenide](#) (Note 3) is slowly bubbled in, maintaining the temperature at 20–30° by occasional external cooling. At the end of the reaction (4–5 hours) when there is no more gas evolution from the generator (4–5 hours), the flask and contents are cooled to 5–10° and stirred vigorously for one-half hour. The solid is then collected on a 9-cm. Büchner funnel and washed with 250 ml. of ice-cold 95% [ethanol](#). The crude, gray product weighs 65–73 g. (81–91%).

For purification, it is dissolved in 9–9.5 l. of boiling [benzene](#) (Note 4). The solution is filtered rapidly, using a 32-cm. folded filter in an 8-in. short-stem glass funnel. The recovery is 59–70 g. The fine, white crystals, which melt at 169–170° (Note 5), are stored in a brown glass bottle under [nitrogen](#) (Note 6), (Note 7), (Note 8).

2. Notes

1. The practical grade, b.p. 162–164°, obtained from the Eastman Kodak Company, was used.
2. A tube 8 mm. in diameter is used. A sintered-glass gas addition tube is quickly clogged by [selenium](#).
3. [Hydrogen selenide](#) is generated from [iron](#) or [aluminum selenide](#) and a mineral acid. In a 2-l. three-necked, flask, fitted with sealed stirrer, reflux condenser, and dropping funnel are placed 135 g. (1 mole) of powdered [iron selenide](#) (Note 9) and 350 ml. of water. The generator is heated on a steam cone, while 350 ml. of concentrated [hydrochloric acid](#) is admitted slowly with stirring, so that the [hydrogen selenide](#) is evolved at a steady rate. (The generation of gas is regulated both by the rate of heating and the rate of addition of acid, so that the gas is absorbed almost entirely; it is led from the top of the condenser to the delivery tube.) The amount of selenide used is sufficient. The residual liquid in the generator is left open to the air overnight in a hood. Then sufficient 50% [sodium hydroxide](#) solution is added to make it basic, and the whole is flushed down the sink, using a large amount of water.
4. Recrystallization from [benzene](#) affords a product that has superior storage qualities. A liter dissolves 5–6 g. at the boiling point.
5. The melting point is unchanged by further recrystallization.
6. The product turns pink, and eventually gray, if exposed to air for an extended period. It should be stored under [nitrogen](#).²
7. The submitters indicate that [N,N-diethylselenourea](#) may be prepared similarly, using [diethylcyanamide](#). In this case, a solution of 50 ml. each of concentrated aqueous [ammonium hydroxide](#) and [ethanol](#) is used as a solvent. The reaction is carried out at 60°, the solvent being replenished as needed by a solution containing 80 ml. of [ethanol](#) and 20 ml. of concentrated [ammonium hydroxide](#).

The yield of crude material is 65–80%. Recrystallization from [benzene](#) gives a white product, m.p. 117–118°.

8. The procedure gives a commensurate yield when carried out on twice the scale.

9. [Iron selenide](#) can be obtained from the Canadian Copper Refiners Ltd., Montreal, Quebec.

3. Discussion

The procedure used is that of Zingaro, Bennett, and Hammar.²

References and Notes

1. Camera Works Division, Eastman Kodak Company, Rochester 17, New York.
 2. Zingaro, Bennett, and Hammar, *J. Org. Chem.*, **18**, 292 (1953).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

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

[hydrochloric acid](#) (7647-01-0)

[Benzene](#) (71-43-2)

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

[iron](#) (7439-89-6)

[nitrogen](#) (7727-37-9)

[ammonium hydroxide](#) (1336-21-6)

[selenium](#)

[hydrogen selenide](#) (7782-49-2)

[N,N-Dimethylselenourea,
Urea, 1,1-dimethyl-2-seleno-](#) (5117-16-8)

[dimethylcyanamide](#) (1467-79-4)

[aluminum selenide](#) (1302-82-5)

[iron selenide](#)

[N,N-diethylselenourea](#) (15909-81-6)

[diethylcyanamide](#) (617-83-4)

