



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.

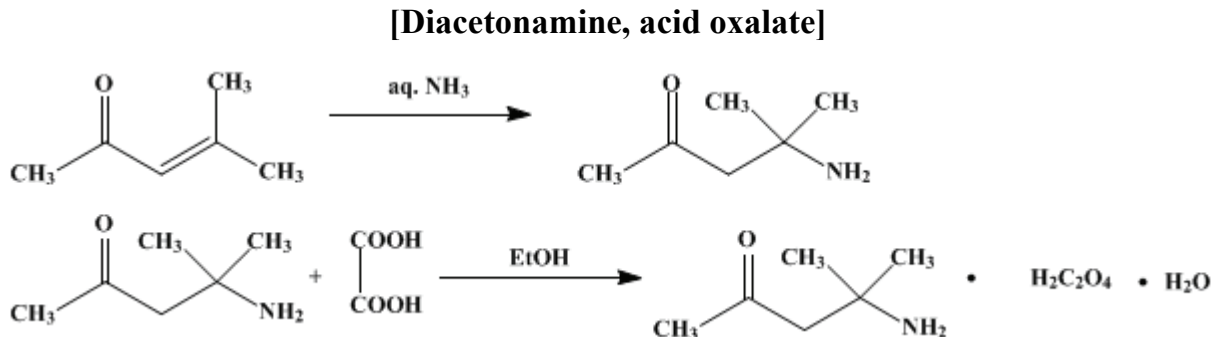
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior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

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. 1, p.196 (1941); Vol. 6, p.28 (1926).

DIACETONAMINE HYDROGEN OXALATE



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1. Procedure

A mixture of 200 g. (2 moles) of [mesityl oxide](#) (p. 345) and 280 cc. of aqueous [ammonia](#) (27 per cent) is placed in a 1-l. round-bottomed flask which is equipped with an efficient mechanical stirrer. The stirrer should be inserted through a stopper in such a way that the flask is nearly air-tight. Because of the heat generated during the reaction it is desirable to keep tap water running over the flask. After stirring for several hours ([Note 1](#)) the system becomes homogeneous. When this point is reached the stirring is discontinued, and the well-stoppered flask is allowed to stand at room temperature for three days ([Note 2](#)).

Dry air is blown through the solution to remove the excess of [ammonia](#), and the solution is then dissolved in its own volume of absolute [alcohol](#). A sample of this solution is titrated with standard [oxalic acid](#), litmus being used as an outside indicator ([Note 3](#)). The amount of [oxalic acid](#) ([Note 4](#)) necessary to form the acid salt is placed in a large evaporating dish and dissolved in 4 l. of 95 per cent [alcohol](#). The amine solution is then slowly run into the acid with constant stirring. During the addition of the last half of the amine solution, the container must be cooled in order to avoid the formation of the neutral [oxalate](#).

The resulting mixture is then heated on a steam cone or an air bath with constant stirring until the temperature of the mixture reaches 70°. The mixture is filtered, while hot, through a previously heated Büchner funnel. The filtrate is immediately placed in a large beaker or evaporating dish for the crystallization of the [diacetoneamine hydrogen oxalate](#) ([Note 5](#)). The residue is treated with boiling [alcohol](#) and filtered, the filtrate containing a small additional quantity of the [amine hydrogen oxalate](#). The mother liquor is distilled until nothing further passes over at 78° ([Note 6](#)), and the residue is allowed to stand for a day in a cool place. The crystals that separate are washed with cold absolute [alcohol](#) and dried. A total yield of 285–320 g. (63–70 per cent of the theoretical amount) of product that melts at 126–127° is obtained ([Note 7](#)).

2. Notes

1. The time required varies between three and eight hours, and the lower time limit is very materially favored when the reaction is carried out in the sunlight.
2. The period of three days seems to be the most desirable length of time to allow the reaction mixture to stand; the reaction is not complete in less time and the yields tend to become smaller if a much longer time is employed.
3. The volume of the diluted amine is usually between 800 and 860 cc. A 10-cc. portion of this may be conveniently drawn off with a pipette and usually requires from 35 to 50 cc. of 0.5 *N* [oxalic acid](#).
4. The end point to litmus occurs when the neutral salt is formed. As the acid salt is desired, twice the amount of [oxalic acid](#) calculated above is used. This is usually between 230 and 260 g.

5. If the crystals are allowed to remain in contact with the mother liquor for several hours without filtering, they become somewhat dark in color. This color may be removed by washing with hot absolute [alcohol](#).
6. The [alcohol](#) recovered in this way may be used as a solvent in subsequent runs. When about 3.5 l. of [alcohol](#) has been distilled, the residue gives a small yield (10–15 g.) of dark crystals which must be washed several times with warm absolute [alcohol](#) to remove most of the color.
7. The product is entirely free from [triacetoneamine](#), [triacetondiamine](#), and other troublesome condensation products, thus making its purification very simple. There is, however, a small quantity of [ammonium hydrogen oxalate](#) (1–1.2 per cent) mixed with this salt, but since it offers no difficulty when the product is used for synthetic purposes it is usually ignored. A small amount of ammonium salt has practically no effect on the melting point. It is possible to get pure [diacetoneamine hydrogen oxalate](#) by recrystallizing from absolute [alcohol](#).

3. Discussion

[Diacetoneamine](#) can be prepared from a mixture of commercial [acetone](#) and [calcium chloride](#) by treatment with anhydrous [ammonia](#);¹ from [acetone](#) and [ammonia](#) in the presence of a "promoter" such as [ammonium nitrate](#);² and from [mesityl oxide](#) with aqueous [ammonia](#)³ or liquid [ammonia](#).⁴

References and Notes

1. Everest, J. Chem. Soc. **115**, 588 (1919).
2. Suzuki and Horie, Bull. Inst. Phys.-Chem. Research (Tokyo) **11**, 383 (1932) [C. A. **26**, 4302 (1932)].
3. Sokoloff and Latschinoff, Ber. **7**, 1387, 1776 (1874); Haeseler, J. Am. Chem. Soc. **47**, 1195 (1925).
4. Smith and Adkins, *ibid.* **60**, 408 (1938).

Appendix

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

[ammonium salt](#)

[Diacetoneamine, acid oxalate](#)

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

[calcium chloride](#) (10043-52-4)

[ammonia](#) (7664-41-7)

[Oxalic acid](#) (144-62-7)

[acetone](#) (67-64-1)

[DIACETONAMINE HYDROGEN OXALATE](#) (53608-87-0)

[Mesityl oxide](#) (141-79-7)

oxalate

amine hydrogen oxalate

triacetoneamine

triacetondiamine

ammonium hydrogen oxalate (5972-72-5)

Diacetoneamine

ammonium nitrate