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.

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.

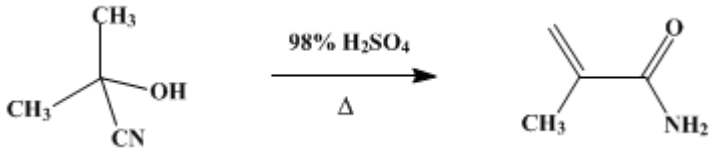
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

DOI:10.15227/orgsyn.029.0061

Organic Syntheses, Coll. Vol. 3, p.560 (1955); Vol. 29, p.61 (1949).

METHACRYLAMIDE



Submitted by Richard H. Wiley and Walter E. Waddey.
Checked by R. L. Shriner and Arne Langsjoen.

1. Procedure

In a 1-l. three-necked round-bottomed flask fitted with an efficient stirrer, a dropping funnel, and a thermometer, are placed 150 g. (82 ml., 1.5 moles) of 98% sulfuric acid (Note 1) and 1 g. of flowers of sulfur. To this is added, with rapid stirring, 85 g. (91 ml., 1 mole) of acetone cyanohydrin[1] (Note 2) over a period of 25 minutes, the temperature of the contents of the flask being kept at 75–80° by cooling in a water bath. At the end of this period, the water bath is replaced with an oil bath preheated to 160°. With continued stirring, the temperature of the reaction mixture is raised to 150° within 5 minutes and maintained at 150° for 15 minutes (Note 3). The reaction mixture is quickly cooled to room temperature by replacing the oil bath with an ice bath and is then poured into 300 ml. of cold water, and the flask is rinsed with 75 ml. of water. The diluted mixture is filtered (Note 4) through a 10-cm. Büchner funnel with the aid of suction. The filtrate is placed in a 1-l. beaker, cooled with an ice bath and 180–190 g. of anhydrous sodium carbonate sifted in with vigorous stirring (*Caution! foaming*) (Note 5). The precipitate is collected on a 20-cm. Büchner funnel and pressed and sucked as dry as possible. The crude product is dried in a vacuum desiccator over anhydrous calcium chloride for 36–48 hours (Note 6). The light cream- or tan-colored crude product weighs 300–400g.

The crude dried soild is crushed to break up lumps and is placed in a 2-l. flask and heated and stirred mechanically with 500 ml. of boiling benzene. The solution is decanted, and the extraction is repeated four times using 200-ml. portions of benzene. The combined benzene solutions are heated to boiling, treated with 2–4 g. of Norit, and filtered. On cooling, 48–52 g. of methacrylamide separates; m.p. 105–107° (Note 7). An additional 5–8 g., m.p. 103–105°, is obtained when the mother liquor is concentrated to 150 ml. and cooled. The yield of methacrylamide is 52–60 g. (61–70%) after storing in a vacuum desiccator over paraffin wax and anhydrous calcium chloride.

2. Notes

1. Acid of 98% strength may be prepared by the addition of 33.5 ml. of fuming sulfuric acid (15% SO_3) to 48 ml. of concentrated sulfuric acid of sp. gr. 1.84.
2. Acetone cyanohydrin of 98% purity may be purchased from the Rohm and Haas Company, Philadelphia, Pennsylvania.
3. This heating converts the intermediate compounds into methacrylamide sulfate. Longer periods of heating decrease the yield.
4. A small amount of dark polymeric material, which may form, is separated at this point.
5. Care is taken to crush lumps of sodium carbonate formed during the addition. The final reaction mixture should be slightly alkaline to litmus paper, and the temperature of the mixture should not rise above 25–30°.
6. The precipitated methacrylamide contains varying amounts of sodium sulfate. It is essential to obtain a dry product for the benzene extraction. The desiccator should be evacuated with an oil pump to about 5 mm. several times during 24–36 hours in order to obtain a sufficiently dry material.
7. The methacrylamide tends to retain some solvent. By placing the product in a vacuum desiccator containing paraffin wax shavings and anhydrous calcium chloride for 36–48 hours material with a melting point of 109–110° may be obtained.

3. Discussion

Methacrylamide has been prepared by the reaction of acetone cyanohydrin with concentrated sulfuric acid[2,3,4,5,6,7] and sulfuric acid with ammonium sulfate,[8] and by the hydrolysis of methacrylonitrile.[9] The method described is an adaptation of that of Crawford and McGrath.[4]

References and Notes

1. *Org. Syntheses* Coll. Vol. **2**, 7 (1943).
2. Verhulst, *Bull. soc. chim. Belg.*, **39**, 563 (1930); **40**, 475 (1931).
3. Crawford, *J. Soc. Chem. Ind.*, **64**, 231 (1945).
4. Crawford and McGrath, U. S. pat. 2,140,469 [*C. A.*, **33**, 2536 (1939)]; Brit. pat. 440,967 [*C. A.*, **30**, 4180 (1936)]
5. Crawford and Grigor, U. S. pat. 2,101,822 [*C. A.*, **32**, 952 (1938)]; Brit. pat. 456,533 [*C. A.*, **31**, 2230 (1937)].
6. I. G. Farbenind. A.-G., Fr. pat. 813,844 [*C. A.*, **32**, 953 (1938)].
7. Rohm und Haas A.-G., Fr. pat. 815,908 [*C. A.*, **32**, 1816 (1938)].
8. U. S. pat. 2,431,468 [*C. A.*, **42**, 3429 (1948)].
9. Bruylants and Castille, *Bull. sci. acad. roy. Belg.*, **13**, 767 (1928) [*C. A.*, **27**, 2366 (1928)].

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

SO_3

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

sulfur (7704-34-9)

Norit (7782-42-5)

ammonium sulfate (7783-20-2)

Acetone cyanohydrin (75-86-5)

Methacrylamide (79-39-0)

methacrylamide sulfate

methacrylonitrile (126-98-7)