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.

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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.

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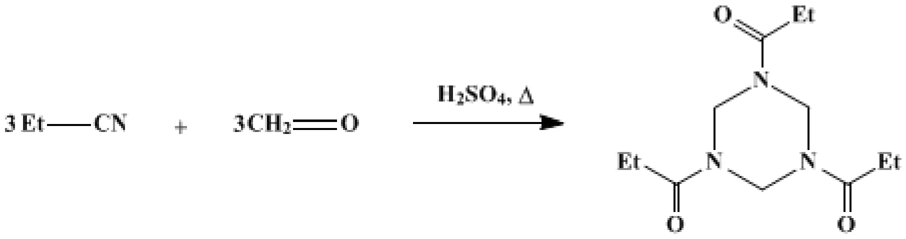
HEXAHYDRO-1,3,5-TRIPROPIONYL-*s*-TRIAZINE

[*s*-Triazine, hexahydro-1,3,5-tripropionyl]



Submitted by W. O. Teeters and M. A. Gradsten[1].
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1. Procedure

In a 3-l. three-necked flask equipped with a mechanical stirrer, a dropping funnel, a reflux condenser, and a thermometer are placed 110 g. (138 ml., 2 moles) of propionitrile (Note 1) and 8 g. (4.35 ml.) of concentrated sulfuric acid (sp. gr. 1.84). To the stirred mixture, which is heated to 90°, is added gradually a solution of 60 g. of trioxane (equivalent to 2 moles of formaldehyde) in 110 g. (138 ml., 2 moles) of propionitrile. During the addition the temperature of the reaction mixture is kept between 95° and 105° (Note 2). When the addition is complete (30 to 60 minutes) (Note 3) the reaction mixture is heated under reflux for an additional 3 hours, the internal temperature being kept at approximately 105°. The mixture is then allowed to cool to room temperature; during the cooling period the product crystallizes. The light-brown crystals are collected by filtration with suction on a Büchner funnel (Note 4). The solid (160 to 170 g.) is washed three times with 100-ml. portions of ether and air-dried. The crude yellow product (130 to 135 g., melting point between 164° and 170°) is recrystallized from 160 ml. of 90% ethanol. The product is collected on a Büchner funnel, washed on the funnel with 100 ml. of ether, and air-dried. In this way 105 to 115 g. (62 to 68%) of white crystals of hexahydro-1,3,5-tripropionyl-*s*-triazine melting at 170–172° is obtained (Note 5). Recrystallization from 95% ethanol (2.4 ml. per g.) results in 91% recovery of an analytically pure product, m.p. 173.2–174.1° (cor.).

2. Notes

1. A practical grade of propionitrile obtained from the Eastman Kodak Company was used.
2. During the addition external heating may be discontinued and the internal temperature regulated by the rate of addition.
3. The reaction mixture turns from light yellow to a reddish brown color during the addition.
4. An appreciable amount of propionitrile (100 to 110 g.) can be recovered from the filtrate. If subsequent batches of hexahydro-1,3,5-tripropionyl-*s*-triazine are being prepared the filtrate can be added to the next charge without isolating the propionitrile. To counteract the accumulation of impurities, activated carbon may be used in the recrystallization of the reaction product.
5. Another 35 to 50 g. of a less pure product (m.p. 160–165°) may be isolated by concentrating the mother liquor.

3. Discussion

A hexahydro-1,3,5-triacyl-*s*-triazine was first prepared by Duden and Scharff[2] from ammonium chloride, formalin, and benzoyl chloride or from hexamethylenetetramine and benzoyl chloride. Procedures similar to the one described[3,4] also have been used for the preparation of hexahydro-1,3,5-triacetyl-, tri(β-chloropropionyl)-, triacrylyl-, trimethacrylyl-, and tribenzoyl-*s*-triazine. Several of these compounds also have been prepared by Wegler and Ballauf[5] from the corresponding nitriles and paraformaldehyde in the presence of acetic anhydride and sulfuric acid.

References and Notes

1. Sun Chemical Corp., New York, New York.
2. Duden and Scharff, *Ann.*, **288**, 247 (1895).
3. Gradsten and Pollock, *J. Am. Chem. Soc.*, **70**, 3079 (1948).
4. Emmons, Rolewicz, Cannon, and Ross, *J. Am. Chem. Soc.*, **74**, 5524 (1952).
5. Wegler and Ballauf, *Chem. Ber.*, **81**, 527 (1948).

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

hexahydro-1,3,5-triacyl-s-triazine

hexahydro-1,3,5-triacetyl-, tri(β-chloropropionyl)-,

triacrylyl-, trimethacrylyl-, and tribenzoyl-s-triazine

ethanol (64-17-5)

sulfuric acid (7664-93-9)

ether (60-29-7)

acetic anhydride (108-24-7)

ammonium chloride (12125-02-9)

formaldehyde, formalin (50-00-0)

carbon (7782-42-5)

benzoyl chloride (98-88-4)

hexamethylenetetramine (100-97-0)

propionitrile (107-12-0)

trioxane

Hexahydro-1,3,5-tripropionyl-s-triazine,
s-Triazine, hexahydro-1,3,5-tripropionyl (30805-19-7)

paraformaldehyde (30525-89-4)