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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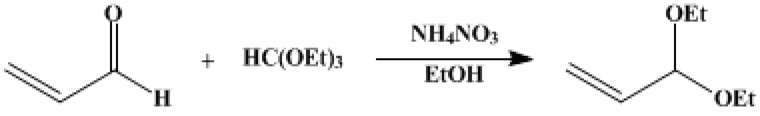
Organic Syntheses, Coll. Vol. 4, p.21 (1963); Vol. 32, p.5 (1952).

ACROLEIN ACETAL

[Acrolein diethyl acetal]



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1. Procedure

A warm solution of 3 g. of ammonium nitrate in 50 ml. of anhydrous ethanol is added to a mixture of 44 g. (52.4 ml., 0.79 mole) of acrolein and 144 g. (160 ml., 0.97 mole) of ethyl orthoformate, and the mixture is allowed to react at room temperature for 6–8 hours (Note 1). The light-red solution is filtered, 4 g. of sodium carbonate is added, and the reaction mixture is distilled from the sodium carbonate through a good column (Note 2). The fraction boiling at 120–125° is acrolein acetal and weighs 73–81 g. (72–80%); n_D^{25} 1.398–1.407 (Note 3).

2. Notes

1. Refluxing causes the formation of some resinous material. The solution remains warm for about 1.5 hours after mixing.
2. The column described by Pingert[2] is suggested.
3. This reaction appears to be of general application; crotonaldehyde diethyl acetal is formed in 68% yield; b.p. 145–147°; n_D^{25} 1.409. (In this preparation the amount of ethyl orthoformate used is reduced to exactly one equivalent since it distils at 142–143°. For this particular acetal, it is preferable to use ethyl orthosilicate according to Helferich.[3]) Tiglylaldehyde diethyl acetal is formed in 79% yield; b.p. 158–160°; n_D^{25} 1.419.

3. Discussion

These have been reviewed previously.[2,4] The procedure described above is an adaptation of a method reported in a German patent.[5] It has been claimed that the reaction of acrolein with ethanol in the presence of hydrochloric acid[2] produces a mixture of substances from which no acrolein acetal can be isolated.[6] More recently it has been reported[7] that acrolein acetal is formed in 62% yield from acrolein and ethanol in the presence of *p*-toluenesulfonic acid.

References and Notes

1. Eastman Kodak Company, Rochester, New York.
2. *Org. Syntheses*, **25**, 1 (1945).
3. Helferich, Ger. pat. 404,256 (1924) [*Frdl.*, **14**, 228 (1921–1925)].
4. *Org. Syntheses Coll. Vol.* **2**, 17 (1943).
5. Schmidt, Ger. pat. 553,177 (1932) [*Frdl.*, **19**, 229 (1932)].
6. Hall and Stern, *Chem. & Ind. (London)*, **1950**, 775.
7. Weisblat, Magerlein, Myers, Hanze, Fairburn, and Rolfson, *J. Am. Chem. Soc.*, **75**, 5893 (1953).

Appendix

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

Acrolein (107-02-8)

sodium carbonate (497-19-8)

ammonium nitrate

Ethyl orthoformate

Acrolein acetal

Acrolein diethyl acetal (3054-95-3)

crotonaldehyde diethyl acetal

ethyl orthosilicate

Tiglylaldehyde diethyl acetal (51786-74-4)

p-toluenesulfonic acid (104-15-4)