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.

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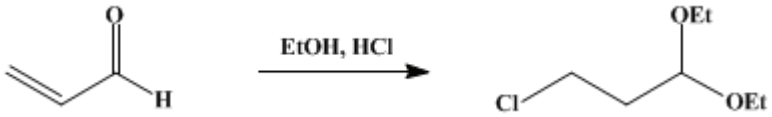
Organic Syntheses, Coll. Vol. 2, p.137 (1943); Vol. 11, p.26 (1931).

β-CHLOROPROPIONALDEHYDE ACETAL

[Propionaldehyde, β-chloro-, diethyl acetal]



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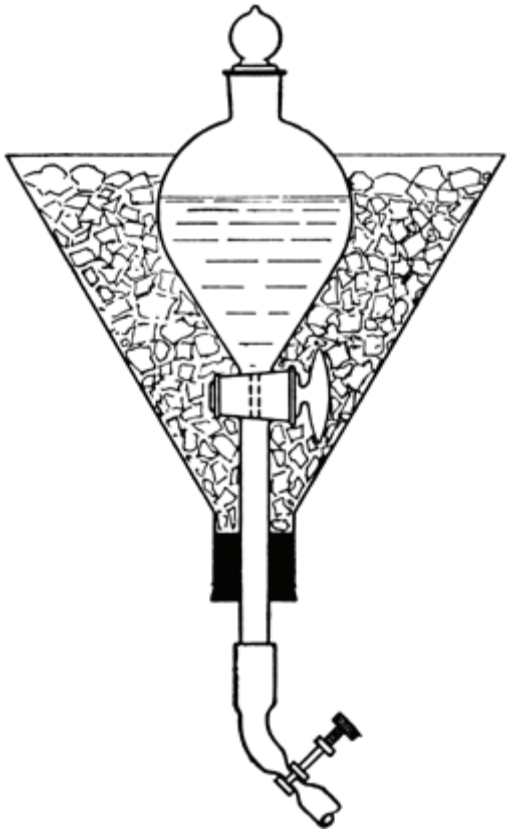
1. Procedure

In a 3-l. round-bottomed flask, fitted with a mechanical stirrer and an inlet tube, is placed 200 g. (253 cc.) of absolute alcohol (Note 1). The flask is surrounded by an ice-salt bath, and the alcohol is saturated with dry hydrogen chloride at 0°. The stem of a 200-cc. separatory funnel is fitted to a one-holed stopper inside a large short-stemmed funnel (Fig. 6). The space between the funnels is filled with finely cracked ice and water. In the separatory funnel is placed 112 g. (2 moles) of cold acrolein (Org. Syn. Coll. Vol. I, **1941**, 15) (Note 2).

Fig. 6



When the alcohol is saturated with hydrogen chloride, the generator is disconnected and the stem of the separatory funnel is connected to the inlet tube by a rubber tube provided with a screw clamp for adjusting the flow. The acrolein is added, with stirring, to the alcoholic hydrogen chloride solution at about 0°. The addition should require from one to two hours. After two layers have formed, the lower layer of acetal is separated and treated gradually with powdered sodium bicarbonate until all acid is neutralized (Note 3). The mixture is filtered. The filtrate is washed with two 50-cc. portions of ice water

and dried over 10 g. of potassium carbonate for five to ten hours (Note 4). It is then filtered and distilled under reduced pressure. The yield of product boiling at 58–62°/8 mm. is 112 g. (34 per cent of the theoretical amount).

2. Notes

1. At least 99.5 per cent alcohol should be used (Org. Syn. Coll. Vol. I, **1941**, 259).
2. If the acrolein is not kept cold, the vapors become unbearable. The stopper of the separatory funnel should be provided with a fine glass capillary.
3. All acid must be removed before washing the product with water, because dilute acid hydrolyzes the acetal very readily.
4. It is recommended that the ice water be prepared from distilled water as the impurities in some samples of tap water lead to decomposition of the acetal. (Private communication from C. F. H. Allen.)

3. Discussion

β-Chloropropionaldehyde acetal has been prepared by the action of acrolein on alcoholic hydrogen chloride alone,[1] or in the presence of calcium chloride.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 17

References and Notes

1. Alsberg, Jahresber. **1864**, 495; Wohl, Ber. **31**, 1797 (1898); Wohl and Emmerich, ibid. **33**, 2761 (1900); Brabant, Z. physiol. Chem. **86**, 208 (1913); Witzemann, J. Am. Chem. Soc. **36**, 1909 (1914); Spoehr and Young, Carnegie Inst. Washington Yearbook, **25**, 176 (1925–1926); Expt. Sta. Record, **57**, 817 (1927) [C. A. **22**, 2368 (1928)].
2. Crawford and Kenyon, J. Chem. Soc. **1927**, 399.

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

alcohol (64-17-5)

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

hydrogen chloride (7647-01-0)

Acrolein (107-02-8)

sodium bicarbonate (144-55-8)

β-chloropropionaldehyde acetal (35573-93-4)

Propionaldehyde, β-chloro-, diethyl acetal