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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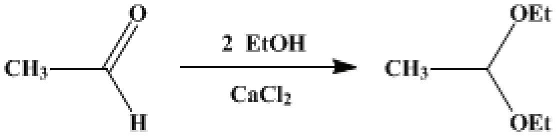
ACETAL



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1. Procedure

In a 1-gallon (4-l.) bottle are placed 1050 g. (1305 cc., 21.7 moles) of 95 per cent ethyl alcohol and 200 g. (1.8 moles) of granulated anhydrous calcium chloride (Note 1). The mixture is cooled to 8° or below by immersion in ice water, and 500 g. (620 cc., 11.4 moles) of freshly distilled acetaldehyde (b. p. 20–22°) is slowly added down the sides of the bottle so that it forms a layer on the alcoholic calcium chloride. The bottle is then tightly closed with a cork stopper and shaken vigorously for a few minutes (Note 2). It is then allowed to stand at room temperature with intermittent shaking for one to two days. The mixture divides into two layers after one to two hours; after the first twenty-four hours no appreciable change in volume of the two layers takes place.

The upper layer, which weighs 1280–1285 g., is separated and washed three times with 330 cc. portions of water. The weight has now fallen to 990–995 g. The oil is dried by standing over 25 g. of anhydrous potassium carbonate and is then fractionally distilled with the use of an efficient column at least 90 cm. long (Note 3), and the fraction which boils at 101–103.5° collected as pure acetal. In this way 700–720 g. can be obtained by one or two fractionations. The yield can be further increased by washing the low-boiling fractions and residue with small quantities of water, drying, and again fractionally distilling, so that a total of 790–815 g. is obtained (61–64 per cent of the theoretical amount). (Note 4)

2. Notes

1. It is essential that the calcium chloride should be anhydrous; if it contains water of crystallization, stratification may be long delayed and the yield be much decreased. On the other hand, no great advantage is observed by substituting absolute alcohol for the 95 per cent material.
2. On mixing the acetaldehyde and the alcoholic calcium chloride solution, a considerable rise in temperature takes place; for this reason it is necessary to chill the reagents and to close the stopper before mixing intimately, otherwise losses might occur by volatilization.
3. A fractionating column containing a condensing unit at the head[1] has been found satisfactory.
4. It is suggested that acetaldehyde be distilled directly into the mixture of alcohol and calcium chloride. The aldehyde is generated by warming paraldehyde with a little sulfuric acid. The yield of acetal thus obtained is somewhat lower than that in the procedure described (V. H. Wallingford, private communication).

3. Discussion

Acetal can be prepared by the action of acetaldehyde upon alcohol in the presence of small quantities of mineral acid,[2] or Twitchell's reagent,[3] or certain metallic salts;[4] by the action of acetylene on alcohol in the presence of sulfuric acid and mercuric salts;[5] by the action of acetaldehyde on tetraethyl silicate with hydrogen chloride as a catalyst;[6] from paraldehyde and ethyl alcohol with hydrogen chloride or *p*-toluenesulfonic acid as catalyst;[7] and from metaldehyde and ethyl alcohol in the presence of calcium chloride and a trace of hydrogen chloride.[8] The procedure described is essentially that of Adkins and Nissen.[9]

References and Notes

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

Twitchell's reagent

mercuric salts

metaldehyde

ACETAL (105-57-7)

ethyl alcohol,
alcohol (64-17-5)

calcium chloride (10043-52-4)

acetaldehyde (75-07-0)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

acetylene (74-86-2)

tetraethyl silicate (78-10-4)

hydrogen chloride (7647-01-0)

p-toluenesulfonic acid (104-15-4)

paraldehyde (123-53-7)