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.

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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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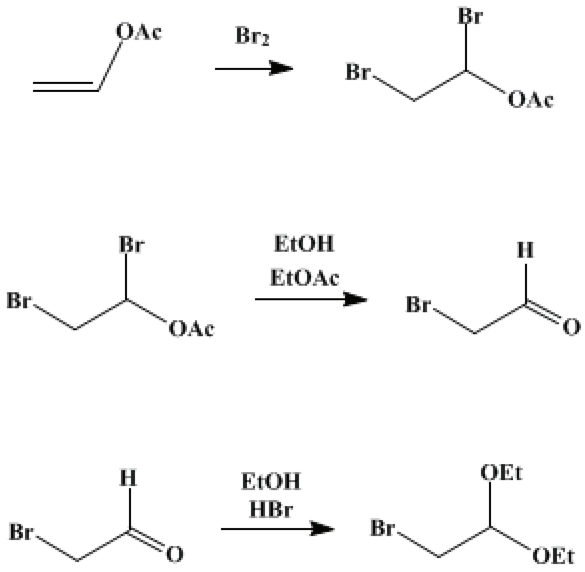
BROMOACETAL

[Acetaldehyde, bromo-, diethyl acetal]



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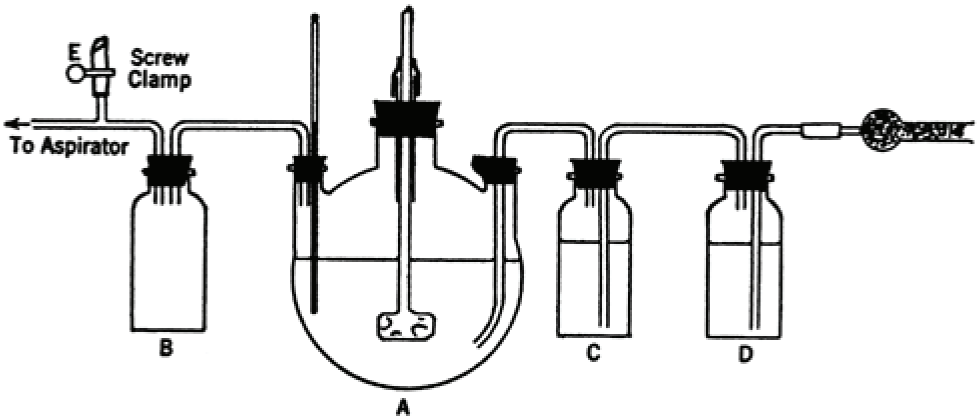
1. Procedure

An apparatus is assembled as shown in Fig. 5. The 3-l. three-necked round-bottomed flask *A* is equipped with a mechanical stirrer sealed with a well-lubricated rubber sleeve. In one neck of the flask are fitted a thermometer and a glass tube leading through a safety trap *B* to a water pump. In the other neck a 7-mm. glass tube, extending to the bottom of the flask, is attached to a 500-ml. bottle *C* in which is placed 255 ml. (5 moles) of bromine (Note 1). This bottle is connected to a 500-ml. wash bottle *D* containing 250 ml. of sulfuric acid. The inlet tube of *D* is connected to a calcium chloride tube.

Fig. 5.



A solution of 430 g. (5 moles) of vinyl acetate (Note 2) in 1.5 l. (26 moles) of absolute ethanol is placed in flask *A*. The solution is cooled to about −10° by an ice-salt mixture, and stirring is started. Gentle suction is applied at the outlet tube of *B*, and the bromine is introduced into *A* by a rapid current of air. The rate of introduction of the bromine, controlled by adjustment of the clamp *E*, should be regulated so that 8–10 hours is required to volatilize all the bromine. Stirring is stopped, and the reaction mixture is allowed to stand overnight and to come to the temperature of the room. The mixture is poured into 1.7 l. of ice water (Note 3); the lower layer of bromoacetal and ethyl acetate is separated (Note 4), washed twice with 300-ml. portions of cold water and once with 300 ml. of cold 10% sodium carbonate solution, and dried over two successive 25-g. portions of anhydrous calcium chloride for 30 minutes. The crude product weighs 990–1010 g.; it is purified by distillation under diminished pressure (water pump) through a 6-in. Widmer column or a 20-cm. Vigreux column. The first fraction consists of ethyl acetate; this is followed by the pure bromoacetal which boils at 62–63°/15 mm. (84–85°/30 mm.) and which amounts to 610–625 g. (62–64%) (Note 5).

2. Notes

1. The bromine is previously washed with 100 ml. of concentrated sulfuric acid.
2. The vinyl acetate (Eastman Kodak Company) is distilled from the added preservative; the first turbid portion containing water is discarded, and the fraction boiling at 69–71°/740 mm. is used.
3. If an emulsion forms at this point, 320 g. of hydrated sodium sulfate is added.
4. Bromoacetal is a fairly strong lachrymator and is best handled under a hood.
5. A yield of 78% of bromoacetal has been obtained by a slight modification of the procedure described above. One-half of the amounts of materials specified above were used, and, after the bromination was complete, the reaction mixture was allowed to stand for 64 hours before it was processed. The yield of bromoacetal was 380 g.[1]

3. Discussion

The procedure given above is essentially a large-scale adaptation of that of Filachione.[2] Bromoacetal has been prepared by the bromination of acetal directly,[3] or in the presence of calcium carbonate;[4] by action of sodium ethoxide on α,β-dibromodiethyl ether;[5] by bromination of paraldehyde followed by action of ethanol;[6,7] by the action of ethanol on bromoacetaldehyde;[8,9] and by bromination of acetal with N-bromosuccinimide.[10]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 60
- Org. Syn. Coll. Vol. 3, 623
- Org. Syn. Coll. Vol. 6, 448

References and Notes

1. Private communication, C. F. H. Allen.
2. Filachione, *J. Am. Chem. Soc.*, **61**, 1705 (1939).
3. Pinner, *Ber.*, **5**, 149 (1872).
4. Fischer and Landsteiner, *Ber.*, **25**, 2551 (1892).
5. Wislicenus, *Ann.*, **192**, 112 (1878).
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7. Wizinger and Al-Attar, *Helv. Chim. Acta*, **30**, 189 (1947).
8. Rotbart, *Ann. chim.*, (11) **1**, 451 (1934).
9. Shchukina, *J. Gen. Chem. U.S.S.R.*, **18**, 1653 (1948).
10. Marvell and Joncich, *J. Am. Chem. Soc.*, **73**, 973 (1951).

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

Bromoacetal

ACETAL (105-57-7)

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

ethyl acetate (141-78-6)

sodium carbonate (497-19-8)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

calcium carbonate (471-34-1)

sodium ethoxide (141-52-6)

N-bromosuccinimide (128-08-5)

Acetaldehyde, bromo-, diethyl acetal

vinyl acetate (108-05-4)

α,β-dibromodiethyl ether (2983-26-8)

bromoacetaldehyde (17157-48-1)

paraldehyde (123-53-7)