Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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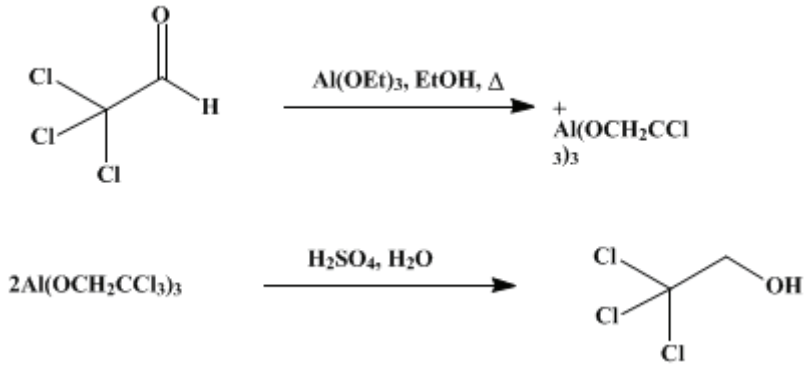
TRICHLOROETHYL ALCOHOL

[Ethanol, 2-trichloro-]



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1. Procedure

In a 2-l. three-necked flask immersed in an oil bath are placed 250 g. (1.7 moles) of anhydrous chloral, 650 cc. of anhydrous alcohol (Note 1), and 75 g. (0.46 mole) of pure aluminum ethoxide (Note 2). An efficient fractionating column (Note 3) is attached to the flask through a cork in the central neck, and through one of the side necks is passed a tube leading to the bottom of the flask for the introduction of dry nitrogen (Note 4). The remaining neck is tightly stoppered. It is used to withdraw portions of liquid for testing.

To the outlet of the column is attached a U-tube and a Peligot tube each of about 100-cc. capacity. The U-tube is immersed in a freezing mixture, and the Peligot tube is filled with saturated sodium bisulfite solution. The oil bath is then heated to 135° and a slow current of gas is admitted. The mixture boils vigorously, but the alcohol is returned by the refluxing device whereas the acetaldehyde formed by the reaction is allowed to pass through and is caught in the freezing mixture and the Peligot tube.

The end of the reaction is easily determined by removing a few drops of the reaction mixture and treating with water in a test tube. After the aluminum hydroxide settles, the clear liquid is decanted and a few drops of yellow ammonium sulfide are added to it. So long as chloral is present, even in traces, a dark brown coloration will be produced on heating to incipient boiling. If the liquid collecting in the U-tube is removed every few hours, the completion of the reaction will be readily noticed by the diminishing quantity of acetaldehyde coming over. After twenty-three or twenty-four hours of heating (over a period of two or three days) the reaction is complete. The temperature of the bath is then allowed to fall to 120° and the alcohol is distilled through an ordinary condenser which replaces the fractionating column. When the residue of aluminum trichloroethoxide is nearly dry (Note 5), the flask is removed from the oil bath and the solid is treated with 250 cc. of 20 per cent sulfuric acid and stirred thoroughly to ensure complete decomposition.

The mixture is then subjected to steam distillation until no more trichloroethyl alcohol passes over. About 4 l. of distillate is obtained (Note 6). The oil is separated from the aqueous layer, which is saturated with sodium sulfate and extracted with three 200-cc. portions of ether. The ether solution is added to the main portion of the alcohol, and the whole is dried over anhydrous sodium sulfate.

The ether is removed by distillation and the product distilled under reduced pressure (Note 7). There is obtained 215 g. (84 per cent of the theoretical amount) of trichloroethyl alcohol boiling at 94–97°/125 mm. and melting at 16–17° (Note 8). A purer compound can be obtained by refractionating under reduced pressure and pressing the crystals on a cooled porous plate. Pure trichloroethyl alcohol has a

melting point of 19° (Note 9).

2. Notes

1. The action of a small proportion of aluminum ethoxide on pure chloral or chloral diluted with benzene leads to the formation of trichloroethyl trichloroacetate in the same manner that ethyl acetate is formed from acetaldehyde by aluminum ethoxide, but the yields are small. A slightly better yield is obtained when molecular proportions are employed, but it is only in the presence of a large amount of an alcohol that good yields are obtained.

2. Aluminum ethoxide is now obtainable commercially. The submitter recommends the following method of preparation,[1] which has been checked:

In a flask fitted with a reflux condenser is placed 27 parts of aluminum filings or groats. This is treated with 276 parts of absolute alcohol, 0.1 to 0.25 part of mercuric chloride, and several crystals of iodine. After a few minutes a violent evolution of hydrogen takes place, and by heating on the water bath for several hours the ethoxide is produced in the form of a grayish powder.

Unchanged alcohol is removed by distillation from an oil bath until the residual material melts to a dark-colored liquid. It is then poured into a Claisen flask and distilled under reduced pressure, using a short air condenser and a Pyrex suction flask as a receiver. Since aluminum ethoxide tends to sublime, a glass-wool filter is inserted between the receiving flask and the vacuum line to prevent clogging. A free flame is necessary, and distillation should be rapid. While the distillate is still liquid it is poured into a Pyrex flask and allowed to cool. It forms a tough, white mass which must be preserved in a well-stoppered flask to prevent adsorption of water vapor. A yield of 90 per cent of the theoretical amount may be obtained.

For the present reaction, where a trace of water does no harm, some of the ethoxide may be fused and poured into a mortar and covered with a watch glass until cool, when it can be powdered and weighed.

The submitter has found that it is possible to make a large quantity of the ethoxide by the above method with 95 per cent alcohol, but that success is more certain if the alcohol is refluxed and distilled twice over quicklime.

3. This column must be capable of separating acetaldehyde from ethyl alcohol with the greatest completeness. A very efficient type is that of Hahn,[2] in which the column is kept at a constant temperature by means of boiling methyl alcohol in a central tube, the vapors passing up an outer annular space. It is necessary that the lower part of the condenser employed be sufficiently broad (say 2 cm. in diameter) so that when in operation there will be no tendency for liquid to collect in the column.

A column involving the same principle can be made from two reflux condensers. The lower outlet of the outer jacket of the condenser connected to the flask is closed, and the jacket is filled to about two-thirds its height with methyl alcohol. A few small pieces of pumice are introduced to prevent bumping of the alcohol. The upper outlet of this jacket is joined to a second condenser to prevent loss of the methanol vapors. The inner tube of the fractionating column is filled with glass beads which are held in place by indentations made in the lower part of the tube. The outlet of this tube is connected to the U-tube immersed in the freezing mixture.

Care is essential to ensure the complete separation of aldehyde and alcohol, because any slight continual loss of solvent is multiplied into a serious loss in the long period of heating necessary. The boiling point of chloral is only twenty degrees above that of ethyl alcohol, and any loss of the latter would lead to some loss of the reagent.

4. The nitrogen is supplied from a cylinder and is dried by passing through a calcium chloride tube and a tube containing phosphorus pentoxide mixed with glass wool or beads. A tube filled with glass wool is placed between the phosphorus pentoxide tube and the flask to prevent the pentoxide from being blown into the reaction mixture if the nitrogen is turned on too rapidly.

5. The residue must not be heated too strongly as it becomes compact and some tarry material is formed which makes the action of the acid upon it very slow.

6. A small amount of trichloroaldol, $CCl_3CHOHCH_2CHO$, can be extracted from the residue of the steam distillation by means of ether.

7. The product can be distilled at ordinary pressure at a temperature of 151°, but the distillate has a brown color due to slight decomposition.

8. Even by simple refluxing of the mixture without separation of the aldehyde, a yield of 65 per cent may be obtained.[3] The reaction between the aluminum ethoxide and the chloral is in equilibrium with

that between the aluminum trichloroethoxide and the acetaldehyde. A certain amount of the acetaldehyde is removed from the reaction by condensation to ethyl acetate under the catalytic influence of aluminum ethoxide, but the change takes place only slowly in this mixture. A great deal of the aldehyde is converted into paraldehyde and acetal, but these changes are reversible.
9. The use of aluminum ethoxide in the presence of alcohol offers a means of reducing many compounds which could not be reduced in the desired manner by the more customary methods. Meerwein and his students have used the method to convert bromal into tribromoethyl alcohol and have also prepared cinnamyl alcohol and various halogenated cinnamyl and crotyl alcohols from the corresponding aldehyes.[4], [5] Excellent yields are obtained.

3. Discussion

The method given here is essentially that of Meerwein and his pupils Schmidt[5] and von Bock.[3] The theory of the reaction and applications are also discussed by Dworzak[4] and by Verley.[6] A number of patents have appeared covering this reaction, in some of which a secondary alcohol such as isopropyl alcohol[7] is used in place of ethyl alcohol. Trichloroethyl alcohol is one of the chlorination products of alcohol and is found in the high-boiling fractions in the production of chloral.[8] It was prepared by Garzarolli-Thurnlackh[9] and by Delacre[10] by the action of diethylzinc on chloral.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 48

References and Notes

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

ACETAL (105-57-7)

ethyl alcohol,
alcohol (64-17-5)

calcium chloride (10043-52-4)

acetaldehyde (75-07-0)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

ethyl acetate (141-78-6)

methyl alcohol,
methanol (67-56-1)

ether (60-29-7)

hydrogen (1333-74-0)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

aluminum filings or groats (7429-90-5)

sodium bisulfite (7631-90-5)

iodine (7553-56-2)

isopropyl alcohol (67-63-0)

mercuric chloride (7487-94-7)

ammonium sulfide

diethylzinc (557-20-0)

aluminum hydroxide

Bromal (115-17-3)

chloral (75-87-6)

ethoxide

Trichloroethyl alcohol (115-20-8)

Ethanol, 2-trichloro-

aluminum ethoxide

aluminum trichloroethoxide

trichloroethyl trichloroacetate

tribromoethyl alcohol (75-80-9)

cinnamyl alcohol (104-54-1)

phosphorus pentoxide (1314-56-3)

paraldehyde (123-53-7)