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.

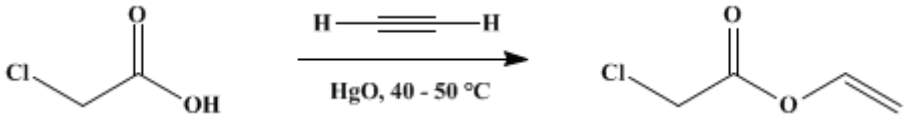
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.028.0094

Organic Syntheses, Coll. Vol. 3, p.853 (1955); Vol. 28, p.94 (1948).

VINYL CHLOROACETATE

[Acetic acid, chloro-, vinyl ester]



Submitted by Richard H. Wiley
Checked by Maynette Vernsten and Homer Adkins.

1. Procedure

Vinyl chloroacetate is lachrymatory.

A 1-l. three-necked flask is equipped with an efficient stirrer, a thermometer, a gas inlet tube 10 mm. in diameter, and a reflux condenser. The bulb of the thermometer and the lower end of the gas inlet tube are sufficiently close to the bottom of the flask to be covered by the reactants (Note 1). The upper end of the condenser is attached to a small gas-washing bottle containing enough water so that the rate of passage of the exit gases may be noted. The flask is charged with 200 g. (2.12 moles) of monochloroacetic acid, 0.2 g. of hydroquinone, and 20 g. of yellow mercuric oxide (Note 2). A slow stream of acetylene is passed through a spiral trap cooled in Dry Ice-acetone mixture, a mercury safety valve, an empty wash bottle, a sulfuric acid wash bottle, a soda-lime tower, and then into the reaction flask through the gas inlet tube. The stirrer is started, and the contents of the flask are heated gently with steam until the chloroacetic acid just melts (Note 3). The temperature of the reaction mixture is lowered to 40–50° after 30 minutes or as soon as the melting point of the mixture permits the lower temperature to be attained without solidification. An ice bath is used for cooling the mixture when necessary (Note 4). The stirrer is operated fast enough to throw the contents of the flask vigorously against the walls, in order to obtain the most rapid absorption. The absorption of acetylene, very rapid at first, becomes very slow after about 3 hours, and the introduction of the gas is discontinued (Note 5).

The contents of the flask are decanted and filtered or centrifuged to remove as much as possible of the finely divided mercury salt (Note 6). The filtrate is distilled from a Claisen flask, and 117–135 g. of material boiling at 45–55°/20 mm. is collected (Note 7). The distillate is fractionated, and 107–125 g. (42–49%) of vinyl chloroacetate, b.p. 37–38°/16 mm., n_D^{25} 1.4422, is collected (Note 8) and (Note 9).

2. Notes

1. The apparatus is similar to that previously shown[1] except that one of the inlet tubes, T_1 or T_2, is replaced by a thermometer and the stirrer is equipped with a short sleeve which is connected to the shaft by a rubber tube moistened with glycerol.
2. Merck or Mallinckrodt Reagent grade or Baker C.P. monochloroacetic acid was used without further purification. Distillation of the acid did not improve the yield. Baker or Mallinckrodt yellow mercuric oxide, C.P., was used. The hydroquinone may be added at this point or before the distillation.
3. The submitter suggested that the mixture be heated to 50–55°. The melting point of the chloroacetic acid used by the checkers required that the temperature at the beginning of the reaction be somewhat above 60°. The chief difficulty in carrying out the reaction is due to solidification of chloroacetic acid in the inlet tube if the temperature of the reaction mixture is allowed to fall to the point where the mixture begins to crystallize. If the inlet tube becomes plugged, the pressure in the system will be relieved by the mercury safety valve. The safety valve may consist of a small bottle containing a layer of mercury and carrying a stopper fitted with two glass tubes; one of the tubes, extending just below the stopper, is connected to the acetylene line, and the other, which extends *just* beneath the surface of the mercury, is open to the air.

4. Higher temperatures are said to facilitate the formation of the ethylidene compound. Similar yields have been obtained, however, when the temperature was maintained at 50–55° during the entire reaction period.
5. Addition of more mercuric oxide at this time or after 1½ hours' operation does not affect the rate of absorption or increase the yield. If less than 20 g. of mercuric oxide is used the yield is poorer; for example, an experiment with 10 g. of mercuric oxide resulted in a 37% yield of crude ester.
6. It is difficult to remove the finely divided mercury salt completely by decantation or filtration. All the suspended salt can be removed by centrifuging, but dissolved salt remains and separates from the solution on distillation. The suspended salt does not interfere if the product is distilled rapidly. Long-continued heating of the crude product, such as would be required in a careful fractionation, has resulted in a vigorous decomposition of the mixture.
7. Hydroquinone should be added to the crude ester immediately to stabilize it against polymerization. If it is to be kept for any length of time before refractionation it should be stored in a cold chest.
8. The submitter observed a somewhat higher boiling point (41–42°/15 mm.) and did not report the refractive index of the product. Both the submitter and checkers used a column 20 cm. in length, 12 mm. in diameter, packed with glass helices, and equipped with a partial take-off head. If the fractionation is carefully conducted, the product is sufficiently pure for most polymerization work. The compound should be stabilized with hydroquinone and stored in a cold chest if it is not to be used immediately.
9. According to the submitter the crude ester may also be purified as follows: The centrifuged reaction mixture is placed in a 1-l. separatory funnel with 500 ml. of ether and washed with 200-ml. portions of a 5% sodium carbonate solution until the unchanged acid is removed. Difficulty with emulsions is sometimes encountered at this point. The ether layer is dried with anhydrous sodium sulfate, and the ether is evaporated on a water bath. The residue is fractionated as above.

3. Discussion

Vinyl chloroacetate has been prepared from acetylene and chloroacetic acid in the vapor phase at 250° with a zinc-cadmium catalyst,[2] and in the liquid phase with a mercury salt catalyst.[3] The procedure described is an adaptation of that employed by Klatte,[4] by Skirrow and Morrison,[5] and by others.[6]

References and Notes

1. *Org. Syntheses* Coll. Vol. **2**, 363 (1943).
2. Hermann, Deutsch, and Baum, U. S. pat. 1,822,525 [*C. A.*, **25**, 5900 (1931)].
3. Ger. pat. 271,381 [*Frdl.*, **11**, 54 (1912–1914)].
4. U. S. pat. 1,084,581 [*C. A.*, **8**, 991 (1914)].
5. U. S. pat. 1,710,197 [*C. A.*, **23**, 2724 (1929)].
6. The preparation of vinyl esters has been reviewed by Ellis, *The Chemistry of Synthetic Resins*, Vol. II, p. 1017, Reinhold Publishing Corporation, New York, 1935.

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

mercury salt

Dry Ice

acetylene (74-86-2)

ether (60-29-7)

glycerol (56-81-5)

hydroquinone (123-31-9)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

mercury (7439-97-6)

mercuric oxide (21908-53-2)

chloroacetic acid,
monochloroacetic acid (79-11-8)

acetone (67-64-1)

zinc (7440-66-6)

cadmium (7440-43-9)

Vinyl chloroacetate,
Acetic acid, chloro-, vinyl ester (2549-51-1)