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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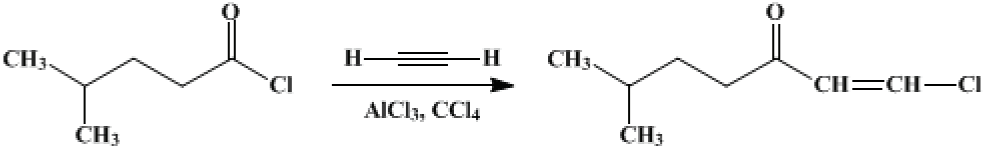
β-CHLOROVINYL ISOAMYL KETONE

[1-Hepten-3-one, 1-chloro-6-methyl-]



Submitted by Charles C. Price and Joseph A. Pappalardo[1].
Checked by R. S. Schreiber, Wm. Bradley Reid, Jr., and R. W. Jackson.

1. Procedure

Caution! This preparation should be carried out in a good hood.

A 1-l. three-necked flask fitted with a mercury-sealed stirrer, a gas inlet tube, and a gas outlet tube protected by a calcium chloride drying tower (Note 1) is surrounded by an ice-water bath. The system is flushed slowly with acetylene for 3 minutes (Note 2). Carbon tetrachloride (260 g.) (Note 3) is poured into the flask, and acetylene is bubbled through at a saturation rate for 3 minutes. Aluminum chloride (98 g., 0.74 mole) (Note 4) is added, and acetylene is bubbled continuously through the mixture with stirring for 5 minutes.

The gas inlet tube is replaced by a dropping funnel protected by a calcium chloride drying tube. Isocaproyl chloride (84.7 g., 0.63 mole) (Note 5) is added to the reaction mixture with stirring over a period of 20 minutes. The dropping funnel is replaced by the gas inlet tube (inlet tube wiped with a dry towel), and, with stirring, acetylene is bubbled just below the surface of the mixture at a rate noticeably above the saturation rate. After 15 minutes to 1 hour the rate of absorption of acetylene suddenly becomes very rapid, and the acetylene is passed through as rapidly as it is absorbed (Note 6). The introduction of acetylene is continued for 30 minutes after the rapid absorption (which lasts 1–2 hours) has subsided.

The reaction mixture is poured with stirring onto a mixture of 700 g. of crushed ice and 300 ml. of a saturated solution of sodium chloride. The organic layer is separated, and the aqueous layer is extracted with three 100-ml. portions of ether. To the combined organic layers is added 2 g. of hydroquinone, and the mixture is dried over calcium chloride (Note 7).

The liquid is decanted from the solid, and the solid is washed with 50 ml. of carbon tetrachloride. The carbon tetrachloride layers are combined and 2 g. of hydroquinone is added. The solution is then distilled from a Claisen flask at such a pressure as to maintain a distillation temperature of about 30°. When most of the solvent has been removed it is discarded, and the residue is distilled as rapidly as possible until the temperature reaches about 90° at 5 mm. Redistillation from a Claisen flask with a short Vigreux side arm gives a colorless liquid; yield 55–65 g. (54–64%) (Note 8); b.p. 96–98°/20 mm.; n_D^{25} 1.4619 (Note 9).

2. Notes

1. A rubber tube with an eye-dropper is attached to the tower. The tip of the eye-dropper is immersed in mineral oil to indicate the absorption of acetylene.
2. The reaction is carried out in a well-ventilated hood to remove excess acetylene. All subsequent operations are also carried out in the hood because the product of the reaction has an objectionable odor. The acetylene used is passed through a train consisting of an empty 300-ml. bottle, a 300-ml. bottle containing 150 ml. of concentrated sulfuric acid (through which acetylene passes by means of a gas dispersion tube), a pressure-release valve, and another empty 300-ml. bottle.

3. Carbon tetrachloride (C.P. grade) decanted from calcium chloride was used.
4. Baker and Adamson Company powdered aluminum chloride was used.
5. Eastman Kodak Company white label grade isocaproyl chloride was redistilled, and the middle 80% portion was used.
6. To keep the temperature in the immediate vicinity of the flask from rising, the ice bath should be stirred occasionally.
7. The combined organic layers should be allowed to stand in a separatory funnel about 30 minutes before drying because some additional water separates on standing.
8. The checkers consistently obtained yields of 75–76%.
9. This preparation works equally well for the isobutyl and isohexyl homologs. For β-chlorovinyl methyl ketone, which is both a lachrymator and a vesicant, the initial rapid rate of absorption of acetylene begins only after 3–9 hours.

3. Discussion

Carpmael,[2] Yakubovich and Merkulova,[3] and Price and Pappalardo[4] have used this general reaction to make β-chlorovinyl ketones from a variety of acid chlorides, employing various solvents and acidic catalysts. Bayer and Nelles[5] made β-chlorovinyl ketones by the reaction of an acid chloride and vinyl chloride.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 558

References and Notes

1. University of Notre Dame, Notre Dame, Indiana.
2. Carpmael, Brit. pat. 461,080 [*C. A.*, **31**, 4676 (1937)].
3. Yakubovich and Merkulova, *J. Gen. Chem. U.S.S.R.*, **16**, 55 (1946) [*C. A.*, **41**, 91 (1947)].
4. Price and Pappalardo, *J. Am. Chem. Soc.*, **72**, 2613 (1950).
5. Bayer and Nelles, U. S. pat. 2,137,664 [*C. A.*, **33**, 1758 (1939)].

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

calcium chloride (10043-52-4)

acetylene (74-86-2)

ether (60-29-7)

hydroquinone (123-31-9)

sodium chloride (7647-14-5)

carbon tetrachloride (56-23-5)

aluminum chloride (3495-54-3)

β-Chlorovinyl isoamyl ketone,
1-Hepten-3-one, 1-chloro-6-methyl- (18378-90-0)

Isocaproyl chloride (38136-29-7)

β-chlorovinyl methyl ketone

vinyl chloride (9002-86-2)