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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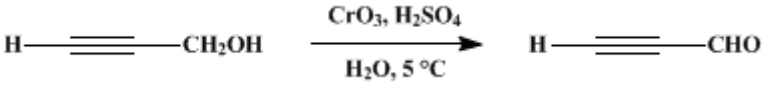
PROPIOLALDEHYDE



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1. Procedure

Caution! Propiolaldehyde is a lachrymator.

A 3-l. three-necked round-bottomed flask is fitted with a thermometer, a graduated dropping funnel (Note 1), a stirrer (Note 2), a fine capillary tube for introducing nitrogen near the bottom of the flask, and an exit tube attached through a manometer to three traps set in series. In the flask are placed 360 ml. of 33% (by volume) propargyl alcohol [112.1 g. (120 ml., 2.0 moles)] (Note 3) and a cooled solution of 135 ml. of sulfuric acid and 200 ml. of water. The flask is cooled in an ice-salt mixture. While the contents of the flask are cooling, the first trap is cooled to about −15° with acetone and Dry Ice. The last two traps in the series are cooled to −78° with acetone and Dry Ice (Note 4). The pressure in the system is reduced to 40–60 mm., nitrogen is introduced through the capillary, and the mixture is stirred vigorously. A solution of 210 g. of commercial chromium trioxide (2.1 moles) in 400 ml. of water and 135 ml. of sulfuric acid is added dropwise in the course of about 3 hours while maintaining a reaction temperature of 2–10°. After the addition of the chromium trioxide, the ice bath is removed, and the flask is permitted to warm to room temperature while the pressure is gradually lowered to 14–20 mm. to remove the last of the aldehyde. The condensates of the three traps are combined (Note 5) and dried over anhydrous magnesium sulfate. The propiolaldehyde is distilled through a 16-in. column packed with platinum gauze. The fraction distilling at 54–57° weighs 38–44 g. (35–41%), n_D^{25} 1.4050 (Note 6) and (Note 7).

2. Notes

1. The end of the dropping funnel extends about 2 in. into the flask from the opening and is drawn into a capillary. This is done to ensure the introduction of the chromic acid solution in the form of small droplets.
2. A "Trubore" stirring system with a 29/26 joint was used for stirring under vacuum.
3. Propargyl alcohol is available from the General Aniline and Film Corporation, Easton, Pennsylvania.
4. If the cooling bath for the first trap is lowered much below −15°, plugging of the trap is likely to occur. These traps are connected so that the vapor enters the larger, annular space, impinging on the cold wall before entering (and possibly plugging) the smaller inner tube.
5. The material in the first trap contains a considerable amount of water. In order to facilitate separation, the checkers saturated this mixture with sodium chloride. The upper layer, consisting of nearly pure propiolaldehyde, was combined with the contents of the second and third traps and dried over 5 g. of anhydrous magnesium sulfate. Distillation through a 12-in. vacuum-jacketed Vigreux column gave directly propiolaldehyde comparable in yield and quality with the final product described by the submitter in (Note 6).
6. Considerable water is carried into the traps, and the distillate contains 3–10% water. The last of the water can be removed by drying the distillate a second time over magnesium sulfate and redistilling. In this way there is obtained 30–37 g. (28–34%) of propiolaldehyde distilling at 55–56°, n_D^{25} 1.4032–1.4034.
7. The material should be stored in glass-stoppered bottles, since contaminants from rubber stoppers may be sufficient to catalyze decomposition. A sample of propiolaldehyde underwent no noticeable change after four months' storage in a Dry Ice chest. However, this aldehyde undergoes extremely vigorous polymerization or decomposition in the presence of alkalies. For example, propiolaldehyde

undergoes a change with almost explosive force in the presence of pyridine. Accordingly, *exceptional care should be used in the handling of propiolaldehyde.*

3. Discussion

The procedure described is that of Wille, Saffer, and Weisskopf.[2] Propiolaldehyde also has been prepared by the oxidation of propargyl alcohol using ammonium dichromate,[3] potassium dichromate,[4] or manganese dioxide in sulfuric acid.[5] In addition, it has been obtained by the electrolytic oxidation of propargyl alcohol[6] and by warming the dimethyl or diethyl acetal of propiolaldehyde with dilute sulfuric acid.[7]

References and Notes

1. Contribution No. 364 from the Chemical Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.
2. Wille, Saffer, and Weisskopf, *Ann.*, **568**, 34 (1950).
3. Quilico and Palazzo, *Proc. XI Intern. Congr. Pure and Appl. Chem.*, **2**, 253 (1947) [*C. A.*, **45**, 7107 (1951)].
4. Maemoto (to Nissin Chemical Industries Co.), Jap. pat. 6159 (1951) [*C. A.*, **47**, 9997 (1953)].
5. Copenhaver and Bigelow, *Acetylene and Carbon Monoxide Chemistry*, p. 124, Reinhold Publishing Corporation, New York, 1949.
6. Wolff, *Chem. Ber.*, **87**, 668 (1954).
7. Claisen, *Ber.*, **31**, 1022 (1898).

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

dimethyl or diethyl acetal of propiolaldehyde

sulfuric acid (7664-93-9)

sodium chloride (7647-14-5)

nitrogen (7727-37-9)

acetone (67-64-1)

pyridine (110-86-1)

chromic acid (7738-94-5)

manganese dioxide (1313-13-9)

potassium dichromate (7778-50-9)

magnesium sulfate (7487-88-9)

chromium trioxide (1333-82-0)

ammonium dichromate

Propiolaldehyde (624-67-9)

propargyl alcohol (107-19-7)