



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.

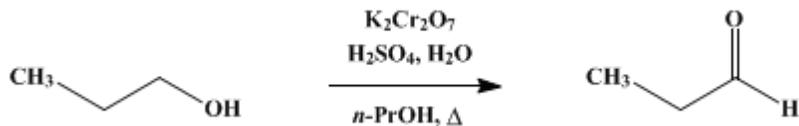
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

Organic Syntheses, Coll. Vol. 2, p.541 (1943); Vol. 12, p.64 (1932).

PROPIONALDEHYDE



Submitted by Charles D. Hurd and R. N. Meinert.

Checked by W. L. McEwen and W. H. Carothers.

1. Procedure

One hundred grams (125 cc., 1.7 moles) of *n*-propyl alcohol, b.p. 96–96.6°, is placed in a 2-l. three-necked, round-bottomed flask fitted with a mercury-sealed stirrer (Note 1), a dropping funnel, and a 60-cm. bulb condenser (Note 2) set at an angle of 45°. Water at 60° is kept circulating through this condenser. A condenser set for downward distillation is connected to the top of the first condenser. Cold water circulates through the second condenser. By means of an adapter, the lower end of the second condenser is fitted to a receiver which is cooled with ice water.

The alcohol in the flask is heated to boiling, stirred, and a mixture of 164 g. (0.56 mole) of potassium dichromate, 120 cc. of concentrated sulfuric acid (2.2 moles), and 1 l. of water is added through the dropping funnel. The addition takes about thirty minutes, and during this time the contents of the flask are kept vigorously boiling. After all the oxidizing mixture has been added, the contents of the flask are boiled for fifteen minutes to distil the last of the aldehyde. The propionaldehyde which collects in the receiver is dried with 5 g. of anhydrous sodium sulfate and fractionally distilled. The yield of propionaldehyde boiling at 48–55°, and having a refractive index of 1.364 (Note 3), is 44–47 g. (45–49 per cent of the calculated amount).

2. Notes

1. The yield of propionaldehyde depends largely upon the efficiency of the stirrer.
2. The purpose of the first condenser is to condense and return to the flask any propyl alcohol which escapes.
3. The recorded value for the index of refraction (N_D^{20}) is 1.3636.

3. Discussion

Propionaldehyde has been prepared by passing propyl alcohol over finely powdered reduced copper;¹ by passing a mixture of propyl alcohol and air over a hot platinum spiral² or a silver catalyst containing a small amount of samarium oxide;³ by passing a mixture of steam and propylene oxide over silica gel at 300°;⁴ by adding propyl alcohol to a dichromate oxidizing mixture⁵ or adding a dichromate oxidizing mixture to propyl alcohol;⁶ by heating propylene glycol to 500°;⁷ by heating a mixture of calcium formate and calcium propionate;⁸ by the action of ethylmagnesium iodide on amyl formate;⁹ by catalytic hydrogenation of acrolein;¹⁰ by electrolysis of calcium chloride or dilute sulfuric acid solutions of propyl alcohol;¹¹ by passing vapors of propyl alcohol over cadmium oxide at 325°;¹² by passing vapors of propionic acid and formic acid over titanium oxide at 250–300°;¹³ by oxidizing propyl alcohol with a stream of air in the presence of copper bronze, nitrobenzene, and quinoline;¹⁴ and by treating ethyl orthoformate with ethylmagnesium bromide.¹⁵

References and Notes

1. Sabatier and Senderens, *Compt. rend.* **136**, 923 (1903).
2. Trillat, *Bull. soc. chim.* (3) **29**, 38 (1903).
3. Day and Eisner, *J. Phys. Chem.* **36**, 1912 (1932).

4. I. G. Farbenind. A.-G., Ger. pat. 618,972 [C. A. **30**, 1066 (1936)].
 5. Lieben and Zeisel, Monatsh. **4**, 14 (1883); Lagerev, J. Gen. Chem. (U.S.S.R.) **5**, 515 (1935) [C. A. **29**, 6887 (1935)].
 6. Hurd, Meinert, and Spence, J. Am. Chem. Soc. **52**, 1140 (1930).
 7. Nef, Ann. **335**, 203 (1904).
 8. Linneman, *ibid.* **161**, 21 (1872).
 9. Bayer and Company, Ger. pat. 157,573 [Frđl. **8**, 156 (1905–07)].
 10. Sabatier and Senderens, Ann. chim. phys. (8) **4**, 398 (1905); (8) **16**, 72 (1909); Skita, Ber. **45**, 3316 (1912).
 11. Reitlinger, Z. Elektrochem. **20**, 261 (1914); Feyer, *ibid.* **25**, 142 (1919).
 12. Sabatier and Mailhe, Ann. chim. phys. (8) **20**, 303 (1910).
 13. Sabatier and Mailhe, Compt. rend. **154**, 563 (1912).
 14. Rosenmund and Zetzsche, Ber. **54**, 2034 (1921).
 15. Wood and Comley, J. Soc. Chem. Ind. **42**, 431T (1923).
-

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

silica gel

copper bronze

platinum spiral

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

Acrolein (107-02-8)

propionic acid (79-09-4)

sodium sulfate (7757-82-6)

formic acid (64-18-6)

Propionaldehyde (123-38-6)

propylene oxide (75-56-9)

copper (7440-50-8)

Nitrobenzene (98-95-3)

propyl alcohol,
n-propyl alcohol (71-23-8)

Ethyl orthoformate

Quinoline (91-22-5)

potassium dichromate (7778-50-9)

ethylmagnesium bromide (925-90-6)

propylene glycol (57-55-6)

silver (7440-22-4)

calcium formate (544-17-2)

samarium oxide (12060-58-1)

calcium propionate (4075-81-4)

ethylmagnesium iodide

amyl formate (638-49-3)

cadmium oxide

titanium oxide