



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.

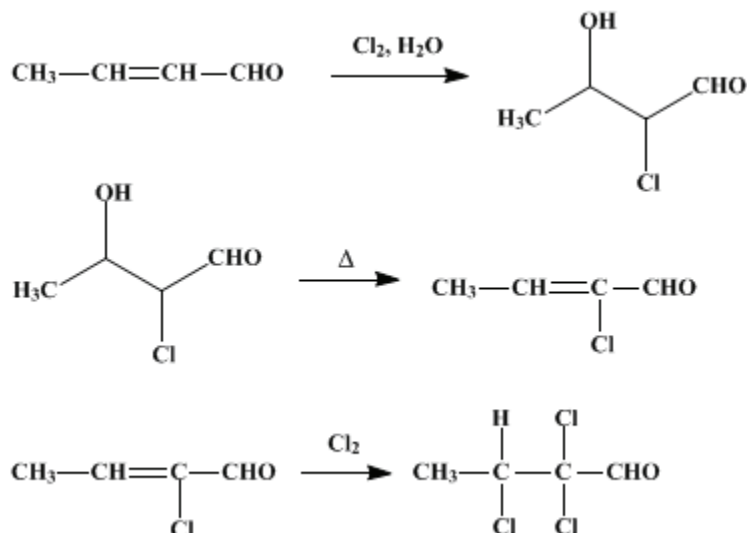
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.130 (1963); Vol. 33, p.15 (1953).

BUTYRCHLORAL

[Butyraldehyde, 2,2,3-trichloro-]



Submitted by Gus A. Ropp, W. E. Craig, and Vernon Raaen¹.
 Checked by T. L. Cairns and H. N. Cripps.

1. Procedure

Crotonaldehyde (Note 1) (70 g., 1 mole) and 300 ml. of water are stirred with a glass-enclosed bar magnet while chlorine gas is passed in from a cylinder. The reaction vessel, equipped with a water-cooled reflux condenser, is cooled in an ice bath to maintain the temperature at about 10°, and the introduction of chlorine is continued for about 2 hours until the temperature does not rise rapidly when the bath is removed. At this point, the total weight increase is 70–80 g. and the upper oil layer has been converted entirely to a lower layer of viscous white oil. The reaction mixture is heated for 30 minutes at reflux temperature with slow stirring to dehydrate the chlorohydrin. The light-brown oil layer is extracted with chloroform, and the extract (Note 2) is washed twice with water and dried thoroughly over anhydrous magnesium sulfate in the refrigerator. The dry solution is filtered into a thoroughly dried flask (Note 3) equipped with a thermometer, a reflux condenser, and a bubbler tube for the introduction of dry chlorine. Over a period of 2.5 hours, chlorine, passed first through a drying tube filled with Drierite, is introduced. The temperature in the reaction mixture is kept at 0° to 10° by an ice bath, and chlorination is continued until the weight increase indicates that 1 mole of chlorine has been added. The reaction mixture is stirred for 1 hour longer in the ice bath. Then dry carbon dioxide (or nitrogen) is bubbled through the solution at room temperature to remove excess chlorine. The reaction vessel is fitted to a dry 20-mm. by 12-in. Vigreux column wrapped with glass-wool insulation and equipped with a vacuum-jacketed, total take-off-type still head and a water-cooled condenser. The receiver is a dry tared flask with side arm leading to a manometer and, through a Drierite-filled U-tube, to a water pump. Dry carbon dioxide is passed through the still pot during the distillation. The chloroform is distilled (Note 4) at atmospheric pressure. The pressure is then decreased, and the pale yellow butyrchloral is distilled. The yield is 91–93 g. (52–53%); b.p. 57–60°/23 mm.; $n_D^{25} = 1.4712$ –1.4740. The oil has a persistent and characteristic but not unpleasant odor (Note 5).

2. Notes

- Best yields were obtained from Eastman's best grade crotonaldehyde which had been distilled immediately before use.
- When this extract is dried and distilled, a high yield of α -chlorocrotonaldehyde, b.p. 147–148°, is

obtained. This aldehyde is a powerful lachrymator.

3. Care is necessary to ensure absolute dryness of all glassware in which butyrchloral is contained since the aldehyde quickly forms a solid, insoluble hydrate.

4. If only a moderately pure sample of butyrchloral is needed as a reaction intermediate, the concentrate remaining after evaporation of the [chloroform](#) may be used.

5. For best yields, the entire series of reactions should be completed within 1 or 2 days. Distillation at higher pressures tends to cause some decomposition. Analysis of the product showed % Cl, 60.40, 60.64 (calculated % Cl, 60.63).

3. Discussion

Butyrchloral has been prepared by chlorination of [acetaldehyde](#)² and [paraldehyde](#).³ Butyrchloral hydrate has been prepared by treatment of [\$\alpha,\beta\$ -dichlorobutyraldehyde](#) with [chlorine](#) and water.⁴ Butyrchloral has also been prepared⁵ by treatment of [crotonaldehyde](#) with [hydrogen chloride](#) followed by chlorination. Brown and Plump have used a procedure similar to the one described here.⁴

References and Notes

1. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
2. Kraemer and Pinner, *Ber.*, **3**, 383 (1870).
3. Reicheneder and Zobelein, Ger. pat. 814,594 [*C. A.*, **52**, 1204 (1958)].
4. Brown and Plump (to Pennsylvania Salt Manufacturing Company), U. S. pat. 2,351,000 (1944) [Brit. pat. 576,435 (1946)].
5. High (to Udylyte Corporation), U. S. pat. 2,280,290 (1942).

Appendix

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

Butyrchloral

Crotonaldehyde

Butyrchloral hydrate

[acetaldehyde](#) (75-07-0)

[hydrogen chloride](#) (7647-01-0)

[chloroform](#) (67-66-3)

[nitrogen](#) (7727-37-9)

[carbon dioxide](#) (124-38-9)

[chlorine](#) (7782-50-5)

[magnesium sulfate](#) (7487-88-9)

[crotonaldehyde](#) (123-73-9)

Butyraldehyde, 2,2,3-trichloro- (76-36-8)

α -chlorocrotonaldehyde (53175-28-3)

α,β -dichlorobutyraldehyde

paraldehyde (123-53-7)