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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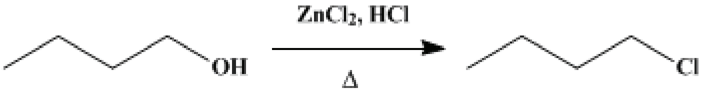
n-BUTYL CHLORIDE

[Butane, 1-chloro-]



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1. Procedure

In a 3-l. round-bottomed, short-necked flask, 1363 g. (10 moles) of anhydrous zinc chloride is dissolved in 864 cc. (10 moles) of concentrated hydrochloric acid, the flask being cooled to prevent loss of hydrogen chloride (Note 1). To this solution is added 371 g. (5 moles) of *n*-butyl alcohol. The flask is attached to a vertical, water-cooled reflux condenser (Note 2), the top of which carries a thermometer and a goose-neck tube connected with an efficient downward condenser. To the end of the downward condenser is attached a 1-l. Florence flask which is connected to a 250-cc. Erlenmeyer flask by a bent tube. A tube from the second receiving vessel is connected with a gas-absorption trap (Note 3) or to a funnel inverted over 800 cc. of 10 per cent sodium hydroxide solution in a 1-l. beaker. Rubber stoppers are used throughout. Both the receiving vessels are cooled in a large ice-salt bath.

The flask is heated by an oil bath to 150° (bath temperature), at which temperature the solution starts to boil and butyl chloride begins to distil. After a few moments, it is necessary to control the temperature in the reflux condenser at 75–80° by a very slow stream of water. The temperature of the oil bath is gradually raised to 155°, and one hour from the time of initial boiling practically all the butyl chloride has distilled. If necessary, however, heating at 155° may be continued for ten to fifteen minutes longer and the temperature of the bath then raised to 160–165°, the reflux temperature not being allowed to get above 80°. The distillate is washed with 100 cc. of cold water, 50 cc. of cold concentrated sulfuric acid (in four portions), 10 cc. of water, and finally with 25 cc. of 10 per cent sodium carbonate solution. It is dried over 10 g. of calcium chloride and distilled (Note 4) and (Note 5). The fraction boiling from 75.5° to 77.5° weighs 352–361 g. (76–78 per cent of the theoretical amount). (Note 6).

2. Notes

1. The sticks of zinc chloride are crushed before being mixed with the acid, and then the mixture is agitated with frequent cooling under the water tap. After the initial heat of solution is over (about five minutes), and there is no further tendency for the mixture to heat up, the flask is closed with a rubber stopper which is wired on and the solution process completed by thirty minutes of mechanical shaking. If a few grams of zinc chloride remain, they will dissolve soon after the beginning of the reaction.
2. A five-bulb Allihn condenser provides sufficient refluxing to insure separation of the butyl chloride and the alcohol. When the reflux temperature reaches 75°, a very slow stream of water is necessary to keep it within the desired range.
3. The gas-absorption trap described on p. 97 may be used.
4. Distillation of the crude product was carried out through a Carborundum-filled column about 1 in. in diameter and 18 in. long. The forerun and residue were both small but may be reduced still further by mixing, drying, and redistilling.
5. The zinc chloride may be recovered for future runs by removing the reflux condenser and connecting the reaction flask directly to the downward condenser and absorber. The oil bath is gradually raised to 250–260° and held at that temperature until the zinc chloride begins to crystallize. Much time is saved in dissolving the zinc chloride in the hydrochloric acid for the next run if it is stirred while cooling. Seven runs have been made with the same zinc chloride; the same or better yields being obtained each time regardless of the fact that the zinc chloride changes to a light brown color.
6. This method may be used to prepare other alkyl chlorides. The temperatures for *n*-propyl and *sec.*-

butyl chlorides are, respectively, as follows: bath, 125–130° and 138–140°; reflux, 45–50° and 65–69°. Yields: 65–70 per cent and 85–88 per cent of the theoretical amounts.

3. Discussion

n-Butyl chloride can be prepared by the interaction of *n*-butyl alcohol and hydrochloric acid or hydrogen chloride either with[1] or without a catalyst;[2] and from *n*-butyl alcohol with phosphorus pentachloride[3] or thionyl chloride.[3] The method described above is based on a recently published study.[4]

References and Notes

1. Ricard, Allenet and Co., Fr. pat. 545,290; Brit. pat. 191,002 [Chem. Zentr. II, 907 (1923)]; Norris and Taylor, J. Am. Chem. Soc. **46**, 756 (1924); Clark and Streight, Trans. Roy. Soc. Can. (3) **23**, Sect. 3, 77 (1929) [C. A. **24**, 586 (1930)]. Alexander Wacker, Ges. für elektrochemische Ind. G. M. B. H., Fr. pat. 687,855 [C. A. **25**, 709 (1931)], for the preparation of alkyl halides by passing a mixture of alcohol and halogen acid over or through phosphoric acids at a temperature of about 200°; E. I. du Pont de Nemours & Co., Fr. pat. 692,790 [C. A. **25**, 1537 (1931)].
2. Lieben and Rossi, Ann. **158**, 160 (1871); Karvonen, Acad. Sci. Fennicæ. **5***A*, 1 (1914) [C. A. **14**, 2176 (1920)]; Alexander Wacker Ges. für Elektrochem. Ind., Ger. pat. 462,993 [C. A. **22**, 4133 (1928)]; Norris and Taylor, J. Am. Chem. Soc. **46**, 756 (1924); Guyer, Bieler, and Hardmier, Helv. Chim. Acta **20**, 1462 (1937).
3. Clark and Streight, Trans. Roy. Soc. Can. (3) **23**, Sect. 3, 77 (1929) [C. A. **24**, 586 (1930)]. This article is a systematic study of the preparation of alkyl chlorides from the corresponding alcohols by a miscellany of methods.
4. Whaley and Copenhaver, J. Am. Chem. Soc. **60**, 2497 (1938).

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

alcohol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

sodium carbonate (497-19-8)

n-butyl alcohol (71-36-3)

Butane, 1-chloro-,

Butyl chloride,
n-BUTYL CHLORIDE (109-69-3)

zinc chloride (7646-85-7)

sec.-butyl chloride (78-86-4)

n-propyl chloride (540-54-5)