



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.

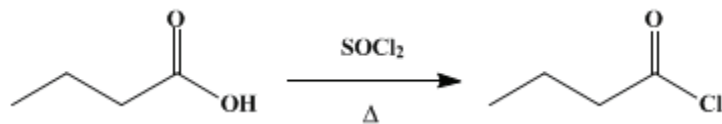
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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. 1, p.147 (1941); Vol. 9, p.32 (1929).

***n*-BUTYRYL CHLORIDE**



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1. Procedure

In a 125-cc. distilling flask, provided with a water-cooled side arm to act as reflux condenser (Note 1), is placed 56 g. (33.4 cc., 0.47 mole) of thionyl chloride (Note 2). This is heated on a water bath, and to it is added during the course of one hour 35.2 g. (0.4 mole) of *n*-butyric acid (Note 3) by means of a separatory funnel attached to the neck of the flask. The evolved gases are absorbed in water (Note 4).

When all the acid has been added, the mixture is heated for one-half hour on the water bath and then distilled directly from an oil bath into a second distilling flask. The crude acid chloride thus obtained boils between 70° and 110°; it is purified by distillation through a column and boils almost entirely at 100–101°, only a few drops of forerun being obtained. The yield is 36 g. (85 per cent of the theoretical amount) (Note 5).

2. Notes

1. If a Claisen distilling flask is used for the preparation of the acid chloride the side arm is plugged by a small cork; the short neck holds the reflux condenser, and the long neck the separatory funnel.
2. The yield is influenced by the purity of the thionyl chloride; the results reported above were obtained with a pure product which boiled over a two-degree range.
3. The presence of traces of water in the butyric acid is of no disadvantage if a correspondingly larger quantity (1 mole for 1 mole of water) of thionyl chloride is used.
4. The gas-absorption trap shown in Fig. 7 on p. 97 may be used.
5. It is reported that the major loss in this preparation is due to the formation of butyric anhydride and that, if the thionyl chloride is kept cool by means of a water bath during the addition of the acid, the formation of anhydride is suppressed with a consequent improvement in the yield of the acid chloride (R. R. Read, private communication).

3. Discussion

n-Butyryl chloride can be prepared from *n*-butyric acid with phosphorus trichloride,¹ with phosphorus pentachloride,¹ with benzotrichloride and zinc chloride,² with phthaloyl chloride,³ and with benzoyl chloride.⁴ A study has been made of the preparation of butyryl chloride using phosphorus pentachloride, phosphorus trichloride, and thionyl chloride.⁵

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 312

References and Notes

1. Burcker, Ann. chim. phys. (5) **26**, 468 (1882).
2. Rabcwicz-Zubkowski, Roczniki Chem. **9**, 523 (1929) [C. A. **24**, 61 (1930)].
3. Kyrides, J. Am. Chem. Soc. **59**, 208 (1937).
4. Brown, *ibid.* **60**, 1325 (1938).

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

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

benzoyl chloride (98-88-4)

benzotrichloride (98-07-7)

phosphorus trichloride (7719-12-2)

butyric acid,
n-butyric acid (107-92-6)

zinc chloride (7646-85-7)

butyric anhydride (106-31-0)

phthaloyl chloride (88-95-9)

Butyryl chloride,
n-BUTYRYL CHLORIDE (141-75-3)