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.

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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.

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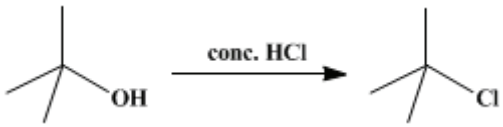
Organic Syntheses, Coll. Vol. 1, p.144 (1941); Vol. 8, p.50 (1928).

tert.-BUTYL CHLORIDE

[Propane, 2-chloro-2-methyl-]



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1. Procedure

In a 500-cc. separatory funnel are placed 74 g. (95 cc., 1 mole) of *tert.*-butyl alcohol (Note 1) and 247 cc. (3 moles) of c.p. concentrated hydrochloric acid (sp. gr. 1.19). After shaking, the layers are allowed to separate (fifteen to twenty minutes) and the upper layer is drawn off and washed first with a 5 per cent sodium bicarbonate solution, then with water until neutral to moist litmus paper (Note 2) and (Note 3). The chloride is treated with 10 g. of calcium chloride and shaken thoroughly, then transferred to a 125-cc. distilling flask. It is then distilled, using a long water condenser. The fraction boiling at 49.5–52° weighs 72–82 g. (78–88 per cent of the theoretical amount).

2. Notes

1. As it is difficult to prepare *tert.*-butyl alcohol free from water, 84 g. of the constant-boiling mixture of the alcohol and water can be used. This mixture boils at 80°, contains 88.24 per cent alcohol when the distillation is carried out at 760 mm., and can be readily obtained by distilling a sample of the dilute alcohol.
2. The chloride is very slowly hydrolyzed by cold water.
3. It is suggested that calcium chloride be added to the saturation point after the *tert.*-butyl alcohol and hydrochloric acid are mixed in order to salt out the *tert.*-butyl chloride and to concentrate the hydrochloric acid (W. W. Hartman, private communication).

3. Discussion

tert.-Butyl chloride can be prepared by passing hydrogen chloride into the alcohol kept cold in a freezing mixture;[1] by distilling a mixture of the alcohol and a large excess of concentrated hydrochloric acid;[2] and from the alcohol and thionyl chloride.[3] Procedures have also been described for the isomerization of isobutyl chloride to *tert.*-butyl chloride,[4] and for the preparation of *tert.*-butyl chloride by the catalyzed addition of hydrogen chloride to the butene fraction from cracking gases.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 524

References and Notes

1. Boedtker, Bull. soc. chim. (3) **31**, 965 (1904).
2. Norris, Am. Chem. J. **38**, 642 (1907).
3. Clark and Streight, Trans. Roy. Soc. Can. (3) **23**, Sect. 3, **77** (1929) [C. A. **24**, 586 (1930)]. This article reports a systematic study of the preparation of alkyl chlorides from the corresponding alcohols by a miscellany of methods.
4. Dow Chemical Co., U. S. pat. 1,993,719 [C. A. **29**, 2549 (1935)].

5. Rudkovskii and Trifel, Org. Chem. Ind. (U.S.S.R.) **2**, 203 (1936) [C. A. **31**, 1004 (1937)].

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

alcohol (64-17-5)

calcium chloride (10043-52-4)

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

thionyl chloride (7719-09-7)

sodium bicarbonate (144-55-8)

Propane, 2-chloro-2-methyl-,
tert.-BUTYL CHLORIDE (507-20-0)

isobutyl chloride (513-36-0)

butene (106-98-9)

tert.-butyl alcohol (75-65-0)

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