School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Organic Chemistry (MSE 211)

Synthesis and Purification of *tert*-Butyl Chloride

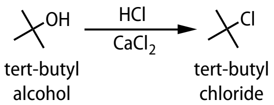
1. Introduction

The conversion of alcohols into alkyl halides is a fundamental transformation in organic synthesis, as the resulting halides serve as versatile intermediates for numerous subsequent reactions. The method chosen for this conversion depends strongly on the structure of the alcohol. Often, the hydroxyl group can be replaced by the halide through a nucleophilic substitution reaction under acidic conditions.

See also: *Chapter 4.3* of the class.
Reading Recommendation: *Clayden*, Chapter 15

2. General Principle of the Synthesis

The conversion of *tert*-butyl alcohol into *tert*-butyl chloride proceeds via an acid-promoted nucleophilic substitution. Under these conditions, the hydroxyl group is activated and replaced by chloride. The product is significantly less polar than the starting alcohol, allowing their separation by liquid-liquid extraction. Because *tert*-butyl chloride is also highly volatile, it can be further purified by simple distillation at atmospheric pressure.



3. Required Equipment

- two 250 mL separating funnels
- a 250 mL and a 100 mL graduated cylinder
- DrySin© with heating plate and magnetic stirrer
- a 100 mL and two 250 mL round bottom flasks
- Liebig's condenser
- thermometer (0 – 100 °C)
- Büchner funnel
- Spatula

4. Experimental Procedure

tert-Butyl alcohol (32 mL) and concentrated hydrochloric acid (35 %) (85 mL) are mixed in a 250 mL separating funnel. 5 g of calcium chloride is added to the mixture. The reaction mixture is vigorously shaken for at least 30 minutes, with venting the funnel every ~30 seconds to release pressure. After shaking, the resulting two layers are separated. The aqueous layer is discarded and the organic layer is transferred to another 250 mL separating funnel. The organic layer is then washed once with 25 mL of 5 % K_2CO_3 aqueous solution and three times with 25 mL of distilled water. The liquid product is then dried over magnesium sulfate and filtered.

5. Purification

The crude product is purified by distillation at atmospheric pressure (boiling point: ~51 °C).

6. Control of the Purity

6.1 Mass Spectrometry

Compare the mass spectra of the starting *tert*-butyl alcohol and the product *tert*-butyl chloride. In case you see two signals, comment on this.

6.2 ^{1}H-NMR Spectroscopy

Analyse the ^{1}H-NMR spectrum of the starting and the target compound dissolved in $CDCl_3$ and compare them.

7. End of the Manipulation

1/ *tert*-butyl chloride is weighed in a sample vial labelled with compound name, student name, and date. Then it is trashed as halogenated organic solvent waste.

2/ All starting materials are put back into the retention trays.

3/ The glassware is cleaned, dried, and put back in place:

- Remaining traces of organic chemical compounds are removed by rinsing the flask with a minimum of solvent (for example acetone), which is subsequently disposed as non-halogenated organic solvent waste in case of the starting compound and as halogen containing organic solvent waste in case of the product.
- Being free of any chemical contamination, the dirty glassware is washed with a conventional detergent and rinsed thoroughly. It is then rinsed with deionized water to avoid the presence of limestone. It is possible to dry the glassware with acetone.
- All the glassware used is placed back into its original location. Any defective part is signaled to the assistant.

4/ The fume hood is tidied up. All electrical appliances are unplugged. Ventilation and lighting of the hood are switched off.

5/ The sink is cleaned.

6/ All waste contaminated with chemicals (absorbent paper, etc.) is collected in specific recovery cans, according to the indications of the assistants.

Be sure you have also completed the prelab protocol with the relevant safety information (**BEFORE** the lab course).

Learning Objective: **Liquid-Liquid Extraction**

The different solubility of a compound in different solvents is utilized for the isolation of pure products, for the separation of mixtures, as well as for the separation of impurities, and provides an indispensable method for the work-up of a reaction mixture. The distribution of a dissolved compound in two non-miscible solvents is the basis for solvent extraction.
In equilibrium, the distribution of a compound (A) between two non-miscible solvents (1 and 2), often water and an organic solvent, is described by Nernst's distribution law:

$$\frac{c(A)_{sol.1}}{c(A)_{sol.2}} = D$$

with $c(A)_{sol.1}$ as the concentration of (A) in solvent 1, $c(A)_{sol.2}$ as the concentration of (A) in solvent 2, and D as distribution coefficient. The ratio of $c(A)_{sol.1}$ and $c(A)_{sol.2}$ is constant at equilibrium and independent of the amount of (A). Thus, a compound can be more completely transferred from solvent 1 into solvent 2, the lower its solubility in 1 and the higher its solubility in 2.
In case of small D, repeated extractions with small solvent volumes give a much better separation than a single extraction with large solvent amounts. A single extraction is therefore often not sufficient. The exchange of the compound occurs at the phase interface. A large interface accelerates the establishment of the distribution equilibrium. In practice, a large and continuously revolving interface is achieved by shaking of the two phases within a separating funnel for several minutes. A

8. To be Addressed in the Protocol

1.) Give a detailed reaction mechanism including the elementary steps. Comment on the potential side reaction and show its mechanism.

2.) What is the role of $CaCl_2$ in this synthesis?

3.) Which compounds are separated during the extraction and the washing step?

4.) What would be the main product and would the mechanism be the same if the starting compound was isobutyl alcohol (2-methylpropan-1-ol)?