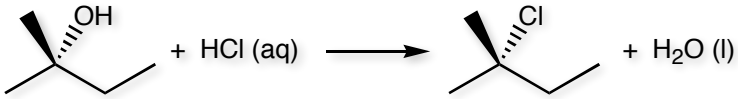
t-Pentyl Chloride Synthesis

Objective

To develop organic laboratory techniques, synthesize *t*-pentyl chloride (2-methyl-2-chlorobutane), to gain experience using Fourier Transform Infrared (FTIR) Spectroscopy to characterize the product of a reaction, and to explore the solubility of long chain alcohols in water and aqueous hydrochloric acid.

Background

As we have previously noted, alcohols are not good leaving groups. However, the addition of an acid to an alcohol can convert a bad leaving group, hydroxide, to an effective leaving group, water. Thus, the synthesis of *t*-pentyl chloride can be conveniently accomplished by the reaction of aqueous HCl with *t*-pentanol.



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Although the synthesis of *t*-pentyl chloride is straight forward, its isolation is complicated by the fact that *t*-pentyl chloride can be hydrolyzed by water. The product, therefore, is slowly converting back to the starting material while it is being isolated. To separate the product from the starting material, a fractional distillation is performed.

Because the boiling point of *t*-pentyl chloride is lower than that of *t*-pentanol, the vapor that forms over the crude product solution will contain a larger fraction of *t*-pentyl chloride as compared to the solution from which the vapor formed. As the vapor condenses in the fractionating column a new solution is formed. Since the new solution has the same composition as the vapor from which it is formed, it is enriched in *t*-pentyl chloride as compared to the crude product solution. Once again, as this newly formed solution vaporizes, it forms a vapor that is enriched in the more easily volatilized component, *t*-pentyl chloride. As this process repeats itself the concentration of *t*-pentyl chloride in the vapor becomes higher and higher as the vapor progresses up the column. Collecting the material that condenses at the appropriate temperature will yield a solution that is enriched in the desired material.

Procedure[1]

> **Warning: concentrated hydrochloride acid is corrosive and it will cause burns on contact with skin. Wear protective gloves and test your 15-mL screw cap centrifuge tube for leaks before adding concentrated HCl.**

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[1] Adapted from Pavia, Lampman, Kiz, and Engel, "Synthesis of *t*-Pentyl Chloride", *Introduction to Organic Laboratory Techniques: A Microscale Approach.* Saunders College Publishing, 1999.

Synthesis of *t*-pentyl chloride
Place 3.0 mL of *t*-pentanol (2-methyl-2-butanol) in a pre-weighed 15-mL screw cap centrifuge tube (remember to determine the exact mass of the *t*-pentanol). **Before adding hydrochloric acid to the t-pentanol, make a prediction about whether the reactants will form a homogeneous solution or not.** It is **important** that you make this prediction, whether your prediction is correct or not will not affect your grade. Add 7.5 mL of concentrated hydrochloric acid to the screw cap centrifuge tube. **Before shaking, make note of whether the reaction mixture a homogeneous solution or not.** Shake the centrifuge tube vigorously for one minute, vent and shake for three more minutes, venting occasionally. Remove the aqueous layer and set aside. Confirm the identity of the layers by adding a drop of aqueous HCl to the supposed aqueous layer. After confirming the identity of the aqueous hydrochloric acid layer, discard it.

Isolation of *t*-pentyl chloride
Working quickly to minimize hydrolysis of your product, add 2 mL of water to the organic layer isolated above. Shake briefly and remove the aqueous layer. (Confirm that you have removed the aqueous layer and discard it). Add 2 mL of an aqueous 5% sodium bicarbonate solution to the organic layer. Stir the solutions gently, and once mixed, gently shake for 1 minute. After venting the CO_2 produced by the bicarbonate, shake vigorously for 30 additional seconds. Remove the aqueous layer, and transfer the organic layer to a clean dry 15-mL centrifuge tube. Dry the organic layer with three to four microspatula-sized scoops of anhydrous sodium sulfate.

Distillation
Transfer your dried *t*-pentyl chloride to a 5-mL conical vial. Add a boiling stone to the conical vial, and place the vial in an aluminum block. Assemble a distillation apparatus, turn on the cooling water, and distill your product. In a 3-mL conical vial collect the material that boils between 80 to 84 °C. Remember to determine the mass of the isolated *t*-pentyl chloride.

Solubility Tests and the reaction of *n*-pentanol with Hydrochloric Acid

Before doing each of the following tests, make certain to make a prediction.
Use plastic disposable pipets to measure and transfer the liquids in the following section.
Solubility of t-pentanol in water:
Place 0.5 mL of t-pentanol in a small test tube and add 1.25 mL of water. Record your observations. Shake the mixture as described in the *Synthesis of t-pentyl chloride* section, and record your observations.
Solubility of n-pentanol in water:
Place 0.5 mL of t-pentanol in a small test tube and add 1.25 mL of water. Record your observations. Shake the mixture as described in the *Synthesis of t-pentyl chloride* section, and record your observations.
Solubility of *n-pentanol in aqueous concentrated hydrochloric acid*:
Place 0.5 mL of t-pentanol in a small test tube and add 1.25 mL of water. Record your observations. Shake the mixture as described in the *Synthesis of t-pentyl chloride* section, and record your observations.

IR Spectra

Obtain an IR spectrum of your products (crude and purified) and of *t*-pentanol using the Attenuated Total Reflectance FTIR Spectrometer. Make certain to have the computer label the positions of prominent peaks in the IR spectra.

Experimental Report

Do not write a formal "experimental" describing the synthesis of *t*-pentyl chloride. Instead, write a report using the directions in Section 1 and 2.

Section 1

Report the yield (actual yield, in grams and moles, and percent yield) and the boiling point (from the distillation) of your product. Obtain an IR spectrum of *t*-pentyl chloride (search the database using the IUPAC name for the compound) from the *Spectral Database for Organic Compounds (SDBS)* maintained by the *National Institute of Advanced Industrial Science and Technology (AIST),* Japan (https://sdbs.db.aist.go.jp). Compare the IR spectrum of your product to the SBDS IR spectrum of *t*-pentyl chloride. Compare the IR spectrum of your product to the IR spectrum of *t*-pentanol. Attach your IR spectra (*t*-pentyl chloride and *t*-pentanol) and the IR spectrum downloaded from the SBDS to your report. Remember to cite the SBDS in your report as described on the SBDS home page.

If you were unsuccessful at isolating *t*-pentyl chloride, determine and report the theoretical yield in grams and moles based on your starting mass, and compare the IR spectra of *t*-pentanol and *t*-pentyl chloride, which can obtained from the SBDS.

Section 2

In a table, state your predictions for the solubility of the alcohols in water and aqueous HCl and the results of your solubility experiments.

Experiment	Prediction	Result
n-pentanol in water		
n-pentanol in aqueous HCl		
t-pentanol in water		
t-pentanol in aqueous HCl		

Respond to the following questions (when responding remember to think about all the intermolecular forces between the various molecules and ions):
Methanol, ethanol, and propanol are all soluble in water. Why might the solubility of the pentanol molecules differ from the solubilities of methanol, ethanol, and propanol? How might you test this hypothesis?

Did the pentanol molecules' solubilities change when aqueous HCl was used as the solvent? Why might the solubilities of the pentanols change when HCl is present (remember to think about how molecules of HCl might interact with an alcohol)?

Why did an organic layer eventually form after shaking a mixture of t-pentanol and concentrated hydrochloric acid and why didn't one form when the mixture of *n*-pentanol was shaken? How might you test your hypotheses?