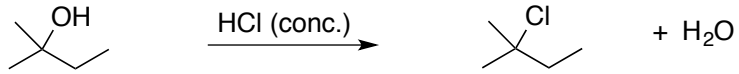
Experiment 6 (LAB PRACTICAL) – Synthesis of *t*-Pentyl Chloride

General Preparation

- Students come to lab with a pen/pencil, calculator, IR table of values, prepared notebook, and pre-lab questions. STUDENTS CANNOT USE THIS HANDOUT.
- Students will carry out the experiment individually; no help from labmates or the TA.
- The exam packet will include GC chromatograms and IR spectra.
- Make sure you know your time slot for your lab practical. The entire lab will be performed and turned in with the 1 hour, 45 minute exam period. **All experimentation must be completed within one hour** and clean-up 15 minutes after that, leaving a minimum of 30 minutes for analysis of provided spectra and chromatograms.
- It's in your best interest to read this first page carefully rather than skipping to the procedure or pre-lab questions!

Alcohols are a versatile starting material in organic synthesis. Depending on the reagent they are paired with, they can function as an acid, base, nucleophile, or electrophile. In the dehydration lab, students observed the acid-catalyzed elimination of alcohols at an elevated temperature. Elimination was the only product possible because the conjugate base of the acid ($H_2SO_4 \rightarrow HSO_4^-$) is not a nucleophile. When a haloacid such as HCl is used, however, the reaction favors the substitution route (**Figure 1**). When the alcohol is protonated by HCl, a chloride ion (Cl^-) is formed as the conjugate base. This reaction occurs under S_N1 conditions due to the tertiary alcohol. The chloride ion is the nucleophile and water is the leaving group.



***t*-Pentanol (2-methyl-2-butanol)** ***t*-Pentyl chloride (2-chloro-2-methyl-butane)**

Figure 1. Synthesis of *t*-Pentyl chloride

Since the reaction occurs at room temperature, side-products such as alkenes are not formed so the purification of alkyl halide is straightforward. The reaction "work-up," meaning separation of the target compound from solvent and by-products, involves simple washes with sodium bicarbonate and water to remove unreacted HCl. Although a mild base is used, these washes should be done relatively quickly to prevent hydrolysis of the product back to alcohol. Use of a stronger base would facilitate rapid hydrolysis.

Notebook Preparation

Students bring their own prepared notebook and pre-lab questions, just like any other lab. Make sure you know your time slot for your lab practical.

- *Purpose:* Draw the reaction scheme from **Figure 1**.
- *Reagent Table*: Make a table with amounts and physical properties of *t*-pentanol, *t*-pentyl chloride, and HCl. This includes amounts (mg or mL), mmol, MW, bp or mp, density, and a one-word hazard if applicable (irritant, corrosive, etc.).
- *Procedure:* Step-wise written procedure in your own words, including diagrams and/or flow chart.
- *Cleanup & Safety:* Copy **Table 1** into your notebook.

PROCEDURE

Students will carry out this experiment individually with little to no outside help from the TA. This is extra incentive to thoroughly prepare and speak with your instructors in advance if you have questions! There should be no surprises during the lab if you've read this handout carefully. **You can write anything you want in the lab notebook, but you cannot bring this handout!**

**Do not cross-contaminate pipets and be extra careful not to spill HCl. Keep all reagent bottles in the fume hoods. Recap reagent bottles immediately, even if someone is right behind you about to use it.

Reaction set-up: Check the provided conical vial for leaks by adding a little water, closing, and inverting. Discard the water and dry the vial with a paper towel. Use a Pasteur pipet and pluringe to carefully transfer 1.00 mL of *t*-pentanol (2-methyl-2-butanol) and 2.5 mL of concentrated HCl (37% w/w, d = 1.2 g/mL) directly into a 5-mL conical vial. Record the least count of the pluringe and determine the ILE. Cap the vial and let the mixture stand for a minute. Then carefully shake the mixture with occasional venting in the fume hood (partially unscrew the cap to vent, then close). None of the mixture should leak from the vial but do not tighten so much that you can't unscrew it later. When pressure builds, it will be harder to open.

Reaction work-up: Allow a few minutes for the two phases to completely separate. Remove the water using a pipet and save the layer containing alkyl halide. **Use the densities to determine which layer is aqueous.** Quench and wash the reaction mixture with water as follows: Add 1 mL of water, mix, allow the layers to separate, then remove the water. Add 1 mL of 5% $NaHCO_3$ solution. Carefully agitate and vent. **What gas is formed in this step?** Allow the layers to separate and remove the aqueous layer. Add 1 mL of water, mix, then remove as much water as possible on this last wash.

Analysis: Pipet the product into a tared vial. **Weigh the product** and **calculate % yield** on the report sheet. The GC and IR spectra of starting material and product will be provided with the exam packet. Be prepared to interpret these chromatograms and spectra. **Bring your own IR table** (handed out in lecture, also online). **Perform *either* the Silver Nitrate *or* Sodium Iodide chemical tests as described below, but prepare notes for both. Chemical tests are performed in the fume hood.** Raise your hand to show your completed chemical test results to your TA for credit.

Obtain four clean, dry medium test tubes and label with #1-4 using the following designations.

1. *t*-Pentanol (starting material)
2. *t*-Pentyl Chloride (product)
3. Bromobenzene
4. Butylbromide

Silver Nitrate Test: Add 0.5 mL of 0.1 M silver nitrate in ethanol to each test tube and one drop of compounds 1-4 to the appropriate test tube. Gently agitate (tap) the test tubes and patiently wait 5 minutes to observe precipitation. If no solid forms, bring the solutions to a boil in the community water bath in the fume hood set to around 80 °C. Wait another 5 minutes to see if precipitation occurs. Record your observations. The formation of a precipitate is a positive test for alkyl halides.

Sodium Iodide Test: Add 0.5 mL of the provided sodium iodide solution (15% w/v in acetone) to each test tube followed by one drop of compounds 1-4 to the appropriate tube and gently agitate. If no precipitate is observed after 3 minutes, transfer the test tubes to a water bath set to about 50 °C and heat for 5 minutes. Record your observations. The formation of a precipitate is a positive test for alkyl halides.

<table>
<tr><th colspan="2">Table 1. Clean-up & Safety</th></tr>
<tr><td rowspan="2">Liquid waste: For all the liquids, including product, after you're sure you're done with them!
*Rinse the test tubes with a small amount of ethanol into the liquid waste before washing in the sink.</td><td>Concentrated HCl is very corrosive. It will burn through your clothes and/or skin. Take only what you need and keep the bottle in the reagent hood.</td></tr>
<tr><td>t-Pentyl alcohol, butylbromide, bromobenzene, and acetone are flammable.</td></tr>
<tr><td>Solid waste: pipets</td><td></td></tr>
<tr><td colspan="2">Points will be deducted from your exam if you leave a mess (glassware, spills, etc.) – TA's will keep track of your area. If a mess is left in a community area (fume hoods, benchtops, etc.), points will be deducted from everyone's exam in that section.</td></tr>
</table>

Pre-lab Questions- *Bring your typed responses to the exam, just like any other lab, except this time you'll staple it to the back of the exam when you're done.*

1. Provide one complete sentence to state the specific type of reaction mechanism performed in this lab. Draw the full arrow-pushing mechanism for the reaction of *t*-pentanol with HCl.

2. What is/are the by-product(s) of the reaction?

3. Calculate the moles of both starting materials (*t*-pentyl alcohol and HCl) and indicate the limiting reagent in this 1:1 reaction. Calculate the theoretical yield of product in mmol and mg. Show your work.

4. Why is the product washed with sodium bicarbonate? Show the chemical equation for the reaction of sodium bicarbonate with HCl.

5. Explain why sodium bicarbonate is used instead of NaOH.

6. Show the chemical equation for the substitution reaction of *t*-pentyl chloride with sodium iodide.

In-lab Questions - *These questions will appear on the exam report sheet!*

1. Calculate the percent yield. Show your work. Use the theoretical yield from the pre-lab question (no need to re-calculate).

2. Report the ILE for each measuring device used for the reaction (numbers & units) as well as the percent intrinsic error. How did these sources of intrinsic error affect your result (reported yield)?

3. Report and discuss the silver nitrate or sodium iodide test results. Was the reaction successful?

4. Interpret the IR spectra of the starting material and product in table format (IR's and table provided on the exam). Which band(s) of the IR spectra are used to determine if the conversion of alcohol to alkyl halide was successful?

5. Interpret the GC's of starting material and product. Calculate retention times and integration to determine percent composition of products. Report your results in table format (GC's and table provided on the exam).

Adapted from Palleros, D. "Synthesis of n-Butyl Bromide and 2-Chloro-2-Methylbutane" in *Experimental Organic Chemistry*. Wiley: New York, **2000**, p. 280 - 291.

****The exam packet will include the grading rubric below.**

Exp 6 – Synthesis of *t*-Pentyl Chloride Name _____
Due at the end of the assigned 1 hr, 45 min lab period

Section Day _____ Time _____ TA Name _____

SECTION	INSTRUCTOR COMMENTS	POINTS ASSIGNED
RESULTS Data reported and in-lab questions addressed on the exam report sheet.		/ **100**
NOTEBOOK PAGES Stapled to the back of the exam. Proper format: reaction scheme, chemical info table, experimental procedure, waste and clean-up procedure.		/ **75**
INTRODUCTION Original responses to pre-lab questions stapled to the back of the exam after the notebook pages.		/ **75**
LAB TECHNIQUE Includes neatness as well as observation of lab technique.		**/ 50**
	LAB EXAM TOTAL	**/ 300**

LAB TECHNIQUE
The following will be the basis for your lab technique grade; not provided in the exam packet.

Safety & Clean up
- Wear lab coat, goggles, & gloves during the entire experiment.
- Take off gloves while washing glassware.
- Bench tops and isles should be free of clutter (non-lab-related belongings, ex. Cell phones)
- All glassware thoroughly washed and put away in drawer in an organized manner
- Student work space is clean – wipe down counters, drawer closed & left **unlocked**
- Community work spaces clean – fume hoods, side counter-tops – all students responsible!

Technique
- Proper use of pluringe, pipets, and conical vial
- Fume hood usage – work 6 inches into hood, no heads in the hood, no kneeling on the ground
- Proper waste procedures followed
- Careful not to spill chemicals or break glassware

General
- Proficiency - apparent preparation and understanding of the procedure
- All glassware labeled with contents and student name
- Ten points deducted if you re-start the experiment for any reason.