3. Compare the energy diagrams for the $S_N1$ reaction in solvents with two different percentages of water. Explain any differences in the diagrams and their effect on the reaction rate.

4. Compare the expected rates of hydrolysis of $t$-cumyl chloride (2-chloro-2-phenyl propane) and $t$-phenylethyl chloride (1-chloro-1-phenylethane) in the same solvent. Explain any differences that might be expected.

**Experiment 23**

**Synthesis of $n$-Butyl Bromide and $t$-Pentyl Chloride**

*Synthesis of alkyl halides*

*Extraction*

*Simple distillation*

The synthesis of two alkyl halides from alcohols is the basis for these experiments. In the first experiment, a primary alkyl halide $n$-butyl bromide is prepared as shown in Equation 1.

$$\text{CH}_3\text{CH}_{2}\text{CH}_{2}\text{CH}_2\text{OH} + \text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{CH}_{2}\text{CH}_{2}\text{CH}_2\text{Br} + \text{NaHSO}_4 + \text{H}_2\text{O} \quad [1]$$

$n$-Butyl alcohol $n$-Butyl bromide

In the second experiment, a tertiary alkyl halide $t$-pentyl chloride ($t$-amyl chloride) is prepared as shown in Equation 2.

$$\text{CH}_3\text{CH}_{2}\text{CH}_2\text{C} = \text{CH}_3 + \text{HCl} \rightarrow \text{CH}_3\text{CH}_{2}\text{C} = \text{CH}_3 + \text{H}_2\text{O} \quad [2]$$

$t$-Pentyl alcohol $t$-Pentyl chloride

These reactions provide an interesting contrast in mechanisms. The $n$-butyl bromide synthesis proceeds by an $S_N2$ mechanism, whereas $t$-pentyl chloride is prepared by an $S_N1$ reaction.

$n$-Butyl Bromide

The primary alkyl halide $n$-butyl bromide can be prepared easily by allowing $n$-butyl alcohol to react with sodium bromide and sulfuric acid by Equation 1. The sodium bromide reacts with sulfuric acid to produce hydrobromic acid.

$$2\text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow 2\text{HBr} + \text{Na}_2\text{SO}_4$$

Excess sulfuric acid serves to shift the equilibrium and thus to speed the reaction by producing a higher concentration of hydrobromic acid. The sulfuric acid also protonates the hydroxyl group of $n$-butyl alcohol so that water is displaced. The acid also protonates the water as it is produced in the reaction and deactivates it as a nucleophile. Deactivation of water keeps the alkyl
halide from being converted back to the alcohol by nucleophilic attack of water. The reaction of the primary substrate proceeds via an $S_N2$ mechanism.

During the isolation of the $n$-butyl bromide, the crude product is washed with sulfuric acid, water, and sodium bicarbonate to remove any remaining acid or $n$-butyl alcohol.

$t$-Pentyl Chloride

The tertiary alkyl halide can be prepared by allowing $t$-pentyl alcohol to react with concentrated hydrochloric acid according to Equation 2. The reaction is accomplished simply by shaking the two reagents in a sealed conical vial. As the reaction proceeds, the insoluble alkyl halide product forms on upper phase. The reaction of the tertiary substrate occurs via an $S_N1$ mechanism.

A small amount of alkene, 2-methyl-2-butene, is produced as a by-product in this reaction. If sulfuric acid had been used as it was for $n$-butyl bromide, a much larger amount of this alkene would have been produced.

**REQUIRED READING**

Review: Techniques 1 through 7
Techniques 12, 13, and 14
SPECIAL INSTRUCTIONS

CAUTION

Take special care with concentrated sulfuric acid. It causes severe burns.

As your instructor indicates, perform either the n-butyl bromide or the t-pentyl chloride procedure or both.

SUGGESTED WASTE DISPOSAL

Dispose of all aqueous solutions produced in this experiment in the container for aqueous waste.

EXPERIMENT 23A

n-Butyl Bromide

PROCEDURE

Preparation of n-Butyl Bromide

Using an automatic pipet or a dispensing pump, place 1.4 mL of n-butyl alcohol (1-butanol, MW = 74.1) in a preweighed 10-mL round-bottom flask. Reweigh the flask to determine the exact weight of the alcohol. Add 2.4 g of sodium bromide and 2.4 mL of water. Cool the mixture in an ice bath and slowly add 2.0 mL of concentrated sulfuric acid dropwise using a Pasteur pipet. Add a magnetic stirring bar and assemble the reflux apparatus and trap shown in the figure. The trap absorbs the hydrogen bromide gas evolved during the reaction period. While stirring, heat the mixture to a gentle boil (aluminum block temperature about 145°C) for 60–75 minutes.

Extraction

Remove the heat source and allow the apparatus to cool until you can disconnect the round-bottom flask without burning your fingers.

NOTE: Do not let the reaction mixture cool to room temperature. Complete the operations in this paragraph as quickly as possible. Otherwise, salts may precipitate, making this procedure more difficult to perform.

The n-butyl bromide layer should be on top. If the reaction is not yet complete, the remaining n-butyl alcohol will sometimes form a second organic layer on top of the n-butyl bromide layer. Treat both organic layers as if they were one. Remove and discard as much of the aqueous (bottom) layer as possible using a Pasteur pipet, but do not remove any of the organic layer (or layers). Ignore the salts during this separation. If they are drawn into the pipet, treat them as part of the aqueous layer. Transfer the remaining liquid to a 5-mL conical vial. Remove and discard any aqueous layer remaining in the conical vial.
The organic and aqueous layers should separate as described in the following instructions. However, to make sure that you do not discard the wrong layer, it would be a good idea to add a drop of water to any aqueous layer you plan to discard. If a drop of water dissolves in the liquid, you can be confident that it is an aqueous layer.

Add 2 mL of 9M H₂SO₄ to the conical vial. Cap the vial and shake it gently, venting occasionally. Allow the layers to separate. Because any remaining n-butyl alcohol is extracted by the H₂SO₄ solution, there should now be only one organic layer. The organic layer should be the top layer. Remove and discard the aqueous (bottom) layer.

Add 2 mL of water to the vial. Cap the vial and shake it gently, venting occasionally. Allow the layers to separate. This time, the organic layer should be the bottom layer. The bottom layer may form into a globule (ball) instead of separating cleanly. Use a microspatula to prod the ball gently into the bottom of the vial. Using a Pasteur pipet, transfer the bottom layer (or globule) to a clean 5-mL conical vial. Add 2 mL of saturated aqueous sodium bicarbonate solution, a little at a time, while stirring. Cap the vial and shake it vigorously for 1 minute, venting frequently to relieve any pressure that is produced. Allow the layers to separate and then carefully transfer the lower alkyl halide layer to a dry 3-mL conical vial using a dry Pasteur pipet. Dry the liquid over granular anhydrous sodium sulfate (Technique 12, Section 12.9, page 680).

**Apparatus for Experiment 23A, n-butyl bromide.**
Distillation
When the solution is dry, transfer it to a clean, dry, 3-mL vial using a Pasteur pipet and distill it (aluminum block about 140°C) using a clean, dry Hickman still (Figure 14.5, p. 708). Each time the Hickman head becomes full, transfer the distillate to a preweighed conical vial using a Pasteur pipet.

When the distillation is complete (one or two drops remaining), weigh the vial, calculate the percentage yield, and determine a microscale boiling point (Technique 13, Section 13.2, p. 695). Determine the infrared spectrum of the product using salt plates (Technique 25, Section 25.2, p. 834). Submit the remainder of your sample in a properly labeled vial, along with the infrared spectrum, when you submit your report to the instructor.

23B EXPERIMENT 23B
n-Butyl Bromide
(Semimicroscale Procedure)

PROCEDURE
Follow the procedure given in Experiment 23A, except double the amounts of all reagents. Use a 25-mL round-bottom flask rather than a 10-mL round-bottom flask for running the reaction. For the separation and extraction procedures, use a screw-cap centrifuge tube in place of a 5-mL conical vial. Distill the crude n-butyl bromide using an apparatus similar to the semimicroscale apparatus for a simple distillation (see Figure 14.10). Make the following changes: Use a 5-mL conical vial as the distilling flask and collect the distillate in a preweighed 3-mL conical vial rather than a graduated cylinder. The bulb of the thermometer must be placed below the side arm or it will not read the temperature correctly. All the glassware must be dry. Use a boiling stone or magnetic spin vane to prevent bumping. Collect the material that boils between 85 and 102°C.

Infrared spectrum of n-butyl bromide (neat).
PROCEDURE

NOTE: In the following procedures, it may be difficult to see the interfaces between layers because the refractive index of the product will be similar to the refractive indices of the extraction solvents.

Preparation of \( t \)-Pentyl Chloride

Using an automatic pipet or a dispensing pump, place \( 1.0 \) mL of \( t \)-pentyl alcohol (2-methyl-2-butanol, MW = 88.2) in a preweighed 5-mL conical vial. Reweight the vial to determine the exact weight of alcohol delivered.

NOTE: Before shaking the conical vial vigorously in the next step, be sure that the capped vial does not leak. If it does leak, use a Pasteur pipet to mix the two layers. Draw up as much liquid as possible into the Pasteur pipet and then expel the liquid rapidly back into the conical vial. Continue this mixing for 3–4 minutes.

Add \( 2.5 \) mL of concentrated hydrochloric acid, cap the vial, and shake it vigorously for 1 minute. After shaking the vial, loosen the cap and vent the vial. Recap the vial and shake it for 3 minutes more, venting occasionally. Allow the mixture to stand in the vial until the layer of alkyl halide product separates. The \( t \)-pentyl chloride \((d = 0.865 \) g/mL) should be the top layer, but be sure to verify this carefully by observation as you add a few drops of hydrochloric acid.

With a Pasteur pipet, separate the layers by placing the tip of the pipet squarely into the bottom of the vial and removing the lower (aqueous) layer. Discard the aqueous layer. (Are you sure which one it is?)

Extraction

Carry out the operations in this paragraph as rapidly as possible because the \( t \)-pentyl chloride is unstable in water and aqueous bicarbonate solution. It is easily hydrolyzed back to the alcohol. Be sure everything you need is at hand. In each of the following steps, the organic layer should be on top; however, you should add a few drops of water to make sure. Wash the organic layer by adding \( 1 \) mL of water to the conical vial. Shake the mixtures for a few seconds and then allow the layers to re-form. Once again, separate the layers using a Pasteur pipet and discard the aqueous layer after making certain that you saved the proper layer. Add a \( 1 \)-mL portion of 5% aqueous sodium bicarbonate to the organic layer. Gently mix the two phases in the vial with a stirring rod until they are thoroughly mixed. Now cap the vial and shake it gently for 1 minute, venting occasionally. After this, vigorously shake the vial for another 30 seconds, venting occasionally. Discard the aqueous layer and transfer the organic layer to a dry conical vial with a dry Pasteur pipet.

Dry the crude \( t \)-pentyl chloride over granular anhydrous sodium sulfate (Technique 12, Section 12.9, page 680).
Distillation

When the solution is dry (it should be clear), carefully separate the alkyl halide from the drying agent with a Pasteur pipet and transfer it to a clean, dry 3-mL conical vial. Add a microporous boiling stone and distill the crude 1-pentyl chloride (Fig. 14.5, p. 708 or, if possible, Figure 14.7B, p. 710).

Using a Pasteur pipet, transfer the product to a dry, preweighed conical vial, weigh it, and calculate the percentage yield. Determine a boiling point for the product using a microscale boiling point determination (Technique 13, Section 13.2, p. 695). Determine the infrared spectrum of the alkyl halide using salt plates (Technique 25, Section 25.2, p. 834). Submit the remainder of your sample in a properly labeled vial, along with the infrared spectrum, when you submit your report to the instructor.

EXPERIMENT 23D

t-Pentyl Chloride
(Semimicroscale Procedure)

PROCEDURE

Follow the procedure as written in Experiment 23C, except double the amounts of all reagents. Use a 15-mL screw-cap centrifuge tube instead of a 5-mL conical vial for running the reaction and performing the extractions. Distill the crude 1-pentyl chloride using an apparatus similar to the semimicroscale apparatus for a simple distillation (see Figure 14.10). Make the following changes: Use a 5-mL
conical vial as the distilling flask and collect the distillate in a preweighed 3-mL conical vial rather than a graduated cylinder. The bulb of the thermometer must be placed below the side arm or it will not read the temperature correctly. All the glassware must be dry. Use a boiling stone or magnetic spin vane to prevent bumping. Collect the material that boils between 80 and 84°C.

#### EXPERIMENT 23E

**t-Pentyl Chloride**  
(Macroscopic Procedure)

**PROCEDURE**

**Preparation of t-Pentyl Chloride**

In a 125-mL separatory funnel, place 10.0 mL of tert-pentyl alcohol (2-methyl-2-butanol, MW = 88.2, d = 0.805 g/mL) and 25 mL of concentrated hydrochloric acid (d = 1.18 g/mL). Do not stopper the funnel. Gently swirl the mixture in the separatory funnel for about 1 minute. After this period of swirling, stopper the separatory funnel and carefully invert it. Without shaking the separatory funnel, immediately open the stopcock to release the pressure. Close the stopcock, shake the funnel several times, and again release the pressure through the stopcock (Technique 12, Section 12.7, p. 677). Shake the funnel for 2–3 minutes, with occasional venting. Allow the mixture to stand in the separatory funnel until the two layers have completely separated. The tert-pentyl chloride (d = 0.865 g/mL) should be the top layer, but be sure to verify this by adding a few drops of water. The water should dissolve in the lower (aqueous) layer. Drain and discard the lower layer.

**Extraction**

The operations in this paragraph should be done as rapidly as possible because the tert-pentyl chloride is unstable in water and sodium bicarbonate solution. It is easily hydrolyzed back to the alcohol. In each of the following steps, the organic layer should be on top; however, you should add a few drops of water to make sure. Wash (swirl and shake) the organic layer with 10 mL of water. Separate the layers and discard the aqueous phase after making certain that the proper layer has been saved. Add a 10-mL portion of 5% aqueous sodium bicarbonate to the separatory funnel. Gently swirl the funnel (unstoppered) until the contents are thoroughly mixed. Stopper the funnel and carefully invert it. Release the excess pressure through the stopcock. Gently shake the separatory funnel, with frequent release of pressure. After this, vigorously shake the funnel, again with release of pressure, for about 1 minute. Allow the layers to separate and drain the lower aqueous layer. Wash (swirl and shake) the organic layer with one 10-mL portion of water and again drain the lower aqueous layer. Transfer the organic layer to a small, dry Erlenmeyer flask by pouring it from the top of the separatory funnel.
Dry the crude tert-pentyl chloride over 1.0 g of anhydrous calcium chloride until it is clear (Technique 12, Section 12.9, p. 680). Swirl the alkyl halide with the drying agent to aid the drying.

**Distillation**

Transfer the clear liquid to a dry 25-mL round-bottom flask using a Pasteur pipet. Add a boiling stone and distill the crude tert-pentyl chloride in a dry apparatus (Technique 14, Section 14.4, Figure 14.11, p. 714). Collect the pure tert-pentyl chloride in a receiver cooled in ice. Collect the material that boils between 78°C and 84°C. Weigh the product, calculate the percentage yield, and determine the boiling point (Technique 13, Section 13.2, pp. 695–699). Determine the infrared spectrum of the product using salt plates (Technique 25, Section 25.2, p. 834). Submit the remainder of your sample in a properly labeled vial, along with the infrared spectrum, when you submit your report to the instructor.

**QUESTIONS**

**n-Butyl Bromide**

1. What are the formulas of the salts that precipitate when the reaction mixture is cooled?
2. Why does the alkyl halide layer switch from the top layer to the bottom layer at the point where water is used to extract the organic layer?
3. An ether and an alkene are formed as by-products in this reaction. Draw the structures of these by-products and give mechanisms for their formation.
4. Aqueous sodium bicarbonate was used to wash the crude n-butyl bromide.
   (a) What was the purpose of this wash? Give equations.
   (b) Why would it be undesirable to wash the crude halide with aqueous sodium hydroxide?
5. Look up the density of n-butyl chloride (1-chlorobutane). Assume that this alkyl halide was prepared instead of the bromide. Decide whether the alkyl chloride would appear as the upper or the lower phase at each stage of the separation procedure: after the reflux, after the addition of water, and after the addition of sodium bicarbonate.
6. Why must the alkyl halide product be dried carefully with anhydrous sodium sulfate before the distillation? (*Hint: See Technique 15, Section 15.7.*)

**t-Pentyl Chloride**

1. Aqueous sodium bicarbonate was used to wash the crude t-pentyl chloride.
   (a) What was the purpose of this wash? Give equations.
   (b) Why would it be undesirable to wash the crude halide with aqueous sodium hydroxide?
2. Some 2-methyl-2-butene may be produced in the reaction as a by-product. Give a mechanism for its production.
3. How is unreacted t-pentyl alcohol removed in this experiment? Look up the solubility of the alcohol and the alkyl halide in water.
4. Why must the alkyl halide product be dried carefully with anhydrous sodium sulfate before the distillation? (*Hint: See Technique 15, Section 15.7.*)