CHE 8B Organic Chemistry:

Nucleophilic Substitution: Synthesis of 2-Chloro-2-Methylbutane

Purpose

The goal of this experiment is to prepare 2-chloro-2-methylbutane (*t*-pentyl chloride) from 2-methyl-2-butanol (*t*-pentyl alcohol). The product will be purified using distillation.

Learning Objectives

Complete the synthesis of 2-methyl-2-butanol.

Perform a distillation.

Perform an extraction.

Equipment

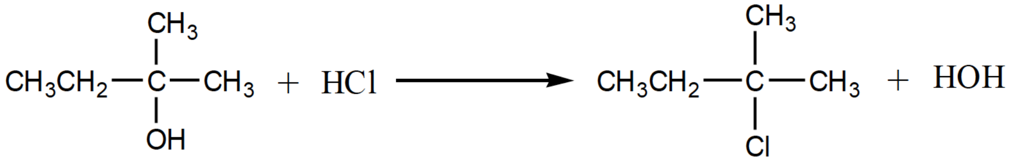
- 125 mL Erlenmeyer flask
- 125 mL Separatory funnel
- 25 mL Erlenmeyer flask
- Cork
- Disposable pipette
- 10 mL Distilling flask and distillation setup
- Hot plate and aluminum heating block
- Glass vial
- Beaker of ice

Chemicals

- 2-Methyl-2-butanol
- Conc. hydrochloric acid
- Sodium bicarbonate
- Saturated $NaHCO_3$ solution
- Anhydrous sodium sulfate

Theory and Background

In this experiment, you will prepare 2-chloro-2-methylbutane (*t*-pentyl chloride) from 2-methyl-2-butanol (*t*-pentyl alcohol) as shown in Figure 11.1 The crude 2-chloro-2-methylbutane will be washed, dried, and distilled.



$$CH_3CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_3 + HCl \longrightarrow CH_3CH_2-\overset{CH_3}{\underset{Cl}{C}}-CH_3 + HOH$$

Figure 11.1: Preparation of 2-chloro-2-methylbutane.

Physical Properties of Starting Materials and Products

Table 11.1: Physical Properties Table

Reagent/Catalyst	**Molar Mass (g/mol)**	**Boiling Point (°C)**	**Density (g/mL)**
2-methyl-2-butanol	88.15	102	0.805
2-chloro-2-methylbutane	106.6	85–86	0.866

Distillation

Distillation is the process of transferring a liquid by vaporizing it, and then condensing the vapors in a separate container. It is commonly used as a method to separate or purify liquids.

The Effect of Temperature on the Vapor Pressure of a Pure Substance

If a sealed container is partially filled with a liquid, some molecules escape from the liquid's surface into the space above it. In their random motion, some of the molecules that escape to the vapor may strike the liquid surface and stick to it. When equilibrium is established, the number of molecules leaving the liquid surface equals the number of molecules in the vapor that strike the liquid surface and stick. The molecules in the vapor also strike the walls of the container and exert a pressure, called the vapor pressure of the liquid. If the temperature of the liquid is raised, a greater number of molecules escapes to the vapor until equilibrium is once again established. The vapor pressure of a liquid increases with increasing temperature.

The variations in the pressures of ideal liquids A and B with changes in temperature are shown in Figure 11.2. The symbol P_A will be used for the pressure of pure A later on.

The boiling point of a liquid is that temperature at which the vapor pressure of the liquid is equal to the pressure of its surroundings. If the flask that contains the liquid is open to the atmosphere, the boiling point will be the temperature at which the vapor pressure of the liquid is equal to atmospheric pressure. The vapor pressure of a pure liquid rises steadily as the temperature is increased until the boiling point is reached. Thus, when the pressure of the atmosphere is 760 Torr, the boiling point of liquid A is 50 °C, and the boiling point of liquid B is 100 °C. When liquid B is under a reduced pressure of 400 Torr, its boiling point is about 75 °C. It is often advantageous to distill high boiling liquids under reduced pressure because thermal decomposition can be avoided. In the student laboratories, the pressure in a flask can be reduced by application of the water aspirator.

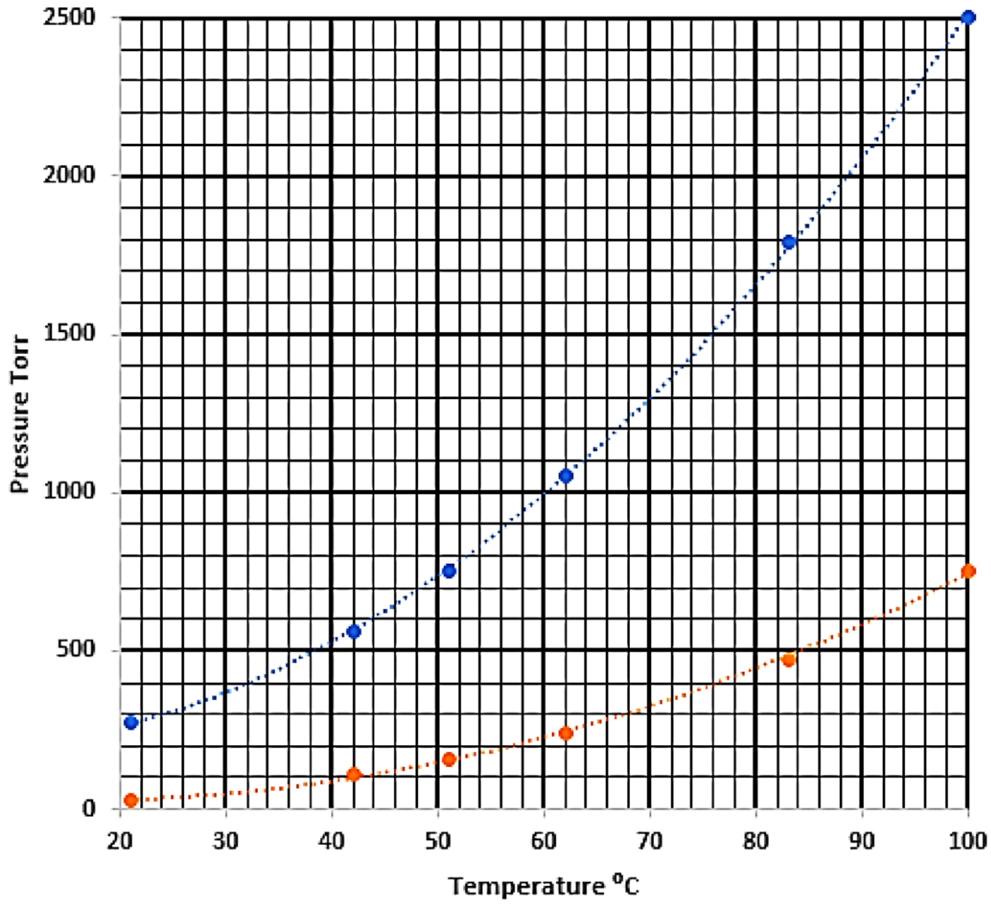


Figure 11.2: Pressures of Ideal Liquids A (blue) and B (orange) at Different Temperatures.

When a pure liquid is distilled, the temperature of the condensing vapors remains constant as long as the liquid and vapor are in equilibrium. This temperature can be determined by a thermometer suspended in the condensing vapor.

The Vapor Pressure of a Pure Substance in an Ideal Solution.

When two liquids, A and B, form an ideal solution, the boiling point of the mixture will be between T_A (the boiling point of pure A) and T_B (the boiling point of pure B).

Question: Mixtures of A and B will boil between what two temperatures? ________________________

If a mixture of two miscible liquids with different boiling points is heated to boiling, the vapor will not have the same composition as the liquid. Rather, it will be richer in the more volatile, lower boiling component. As the boiling point gradually rises, the mixture becomes richer in the less volatile, higher boiling component.

In an ideal solution which contains n_A moles of A and n_B moles of B,

- the pressure of A (P_A) above the liquid is

$$P_A = [\frac{n_A}{(n_A + n_B)}]P$$

- the pressure of B (P_B) above the liquid is

$$P_B = [\frac{n_B}{(n_A + n_B)}]$$

- P is the total pressure, the pressure of the atmosphere.
- Boiling will occur when $P_A + P_B$ is equal to the pressure of the atmosphere, P.

$$P_A + P_B = [\frac{n_A}{(n_A + n_B)}]P + [\frac{n_B}{(n_A + n_B)}$$

The Composition of the Vapor Above the Ideal Solution.

The mole fractions of A and B in the vapor are different from their mole fractions in the liquid. According to the Ideal Gas Law, the number of moles of a gas is proportional to its pressure. The pressure of A in the vapor, P_A, is proportional to the number of moles of A in the vapor. The pressure of B in the vapor, P_B, is proportional to the number of moles of B in the vapor. The vapor is always enriched in the component which, as a pure liquid, has the higher vapor pressure. A glance at the chart on the previous page shows that a liquid with a higher P is also the lower boiling component. It is possible in some cases to completely remove the lower boiling liquid from the mixture.

Questions: At 82 °C, a mixture containing 2.1 moles of A and 7.9 moles of B will boil at 760 Torr.

1. Using values from Figure 11.2 determine the pressures of pure A, of pure B at 82 °C.

2. Determine the vapor pressures of A and of B from the liquid mixture at 82 °C.

3. Determine the mole fraction of A in the vapor.

4. Determine the mole fraction of B in the vapor.

5. Compare your values from questions (3) and (4) with the mole fractions of A and B in the liquid mixture. Is the vapor enriched in A or B?

Fractional Distillation

During distillation of an A-B mixture, even the first drop of distillate obtained was not pure A, but rather a mixture containing mainly A, but some B. If these first fractions were to be combined and redistilled, the first vapor to be condensed would be richer in A. Repetition of this process (vaporization, condensation, and revaporization) could gradually lead to isolation of pure A from the A-B mixture. Similar redistillation of the higher-boiling fractions could lead to isolation of pure B in the final fractions. The repeated redistillation is a laborious process.

The fractionating column is a device used to increase the efficiency of the distillation process. The column consists of a vertical tube packed with some inert material such glass beads, or some other device (indentations in the walls of the column) to increase the surface upon which the vapors may condense. As the hot vapors rise through the column, they condense and flow back down the column. As the condensate hits the lower, hotter portions of the column, it is revaporized and the more volatile components proceed up the column once again. If the column is efficient, this process is repeated many times in the column, and the distillate will consist of the lower-boiling component of the mixture in nearly pure form. The head temperature is the boiling point of the lower boiling component. The higher boiling component will condense back to the pot and will distill at its boiling point when all of the lower boiling component has been collected.

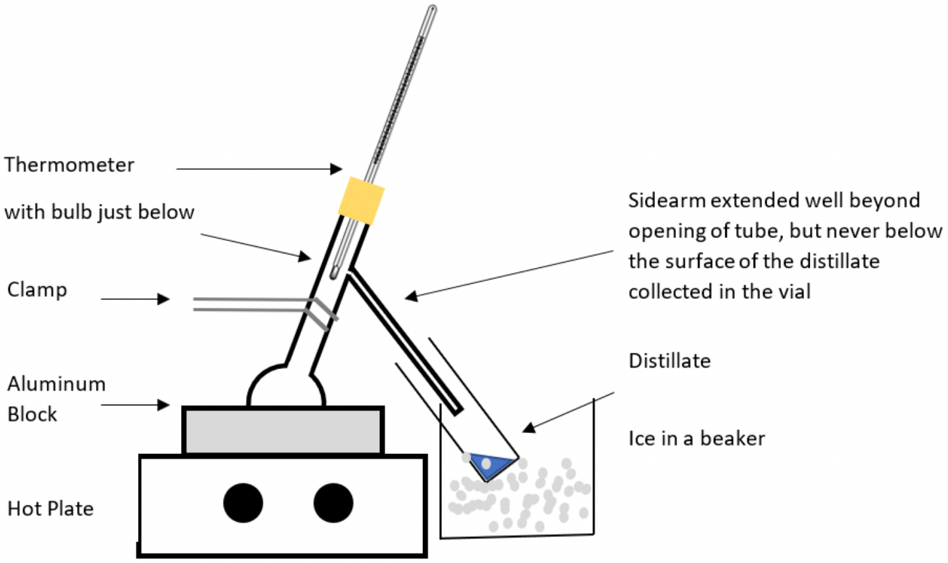


Figure 11.3: Distillation setup

Extraction

See Experiment VIII for detail.

Extraction is a common technique used to transfer a desired organic product, selectively, from one solvent into another. Usually extraction is accomplished by shaking a solution or suspension with another solvent which is immiscible with the first one. On standing, the solvents form two layers which can be separated from each other. The separatory funnel is most commonly used device for this purpose. With the stopcock closed, the mixture is poured into the separatory funnel through the ground glass opening. *The plastic stopper is replaced and, with the index finger of one hand over the stopper, the funnel is picked up, tilted onto its side, and gently swirled once or twice. With the stem pointed up and away from anybody, the stopcock is opened slowly. Any pressure will be released by this action. Pressure buildup is especially great if a low boiling solvent is used, or if gas is generated in the extraction process. After the initial pressure has been released, the stopcock is closed, and the procedure repeated from * two or three more times.

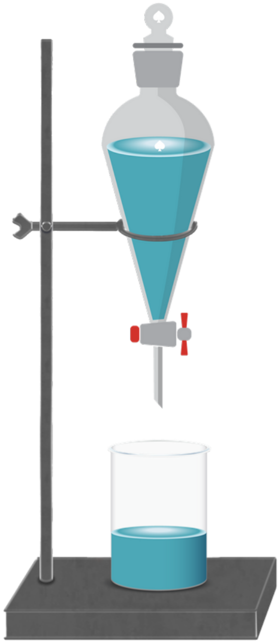


Figure 11.4: Separatory funnel setup

The funnel is replaced in the separatory funnel rack and the stopper removed. Allow the mixture to sit for a few minutes, then drain the lower layer through the stem into a flask or beaker. The interface should be watched carefully, and the stopcock closed just as the upper layer enters the stopcock bore. If the original solvent, M, is the upper layer, it is left in the separatory funnel to be re-extracted by portions of fresh solvent, S. Otherwise, the upper layer is poured out through the stopper and the lower layer returned to the funnel for re-extraction with fresh solvent.

The positions of the layers depend on the relative densities of the solutions. Relative densities are:

$$CH_2Cl_2, CHCl_3 > H_2O > \text{hydrocarbons, ethyl ether}$$

If in doubt, place a drop of a layer into a few ml of water in a test tube and shake. The aqueous layer will be miscible.

General Principles of Extraction

The efficiency of a single extraction procedure is based on the solubility C, (usually in grams of compound/100 ml of a saturated solution) in each of the two solvents used. The ratio of solubilities of a compound in two solvents is referred to as the distribution coefficient K_P.

$$K_P = \frac{C_\text{S}}{C_\text{M}} \qquad \text{(Equation 11.1)}$$

where C_S is the solubility of the compound in solvent S and C_M is the solubility of the compound in solvent M.

The larger the value of K_P, the more efficient each extraction will be.

Not all of the compounds can be extracted from one solvent to the other in a single extraction. Usually two or more extractions are required to extract a compound in good yield. For example, if you have 1.00 g of compound in 100 mL of solution in M and you want to extract the compound into a total of 100 mL of solvent S, we can calculate the efficiency of a single vs. multiple extractions.

If $K_P = 5$, a single extraction using 100 mL of each solvent and 1.00 g of compound would still leave x g in solvent M.

Solving the problem,

$$K_P = 5 = \frac{[(1-x)\text{ g/100 mL S}}{x\text{ g/100 mL M}} \qquad \text{(Equation 11.2)}$$

Thus, $x = 0.17$ g

$$\frac{(0.17 \times 100)}{1.00\text{ mL}} = 17\%\text{ of the compound is still in solvent M} \qquad \text{(Equation 11.3)}$$

Alternatively, if two extractions are made using 100 mL of M with two 50 mL portions of S, the first extraction would leave y grams of compound in solvent M.

$$K_P = 5 = \frac{(1-y)\text{ g/50 mL S}}{y\text{ g/100 mL M}} \qquad \text{(Equation 11.4)}$$

$$= \frac{(2-2y)}{y}; y = 0.28\text{ g} \qquad \text{(Equation 11.5)}$$

The second extraction with 50 ml of fresh S leaves y' grams of compound in solvent M:

$$K_P = 5 = \frac{[(0.28 - y')\ \mathrm{g/50\ mL\ S}}{y'\ \mathrm{g/100\ mL\ M}} \qquad \text{(Equation 11.6)}$$

$$= \frac{0.56 - 2y'}{y'} \qquad \text{(Equation 11.7)}$$

So, $y' = 0.08$ g.

$$\frac{(0.08 \times 100)}{1.00\ \mathrm{mL}} = 8\% \text{ of the compound is still in solvent M} \qquad \text{(Equation 11.8)}$$

Conclusion: Multiple extractions with smaller portions of a solvent are more effective than a single extraction with a large volume of solvent.

Procedure

Safety Precautions

Safety goggles are required.

Concentrated HCl is a strong acid with irritating fumes. It is highly toxic and corrosive.

2-Methyl-2-butanol (*t*-pentyl alcohol) is a flammable liquid and is toxic.

2-Chloro-2-methylbutane is a flammable liquid and an irritant.

You will be given a sample of about 6.2 g of 2-methyl-2-butanol.

1. Determine the weight of your sample by the difference in the weights of the sample in the vial and the empty vial after you have transferred the 2-methyl-2-butanol into a 125 mL Erlenmeyer flask.

2. Add 15 mL conc. hydrochloric acid, cover the top of the flask with parafilm, and thoroughly mix the two layers by swirling the mixture occasionally for about 10 minutes.

3. Transfer the mixture to the 125 mL separatory funnel, allow the layers to separate, and remove the aqueous layer. (*Which is the aqueous layer? Hint: The 2-chloro-2-methylbutane has a density of 0.866 g/mL)*. The aqueous layer is composed of the hydrochloric acid waste to be poured into the appropriate bottle. Subsequent aqueous washes should be discarded into the sink, if neutralized. Add sodium bicarbonate, if needed.

4. Wash with 5 mL ice water, allow the layers to separate, then remove the aqueous layer.

5. Repeat the washing procedure with 5 mL ice-cooled sat. $NaHCO_3$ followed with 5 mL ice water.

6. Transfer the organic material to a 25 mL Erlenmeyer flask, add a spatula tip of anhydrous sodium sulfate (Na_2SO_4). Shake and repeat until the newly added salt no longer clumps together.

7. Stopper the container with a cork. Leave it to dry for at least 15–20 minutes.

8. While the product is drying, set up the apparatus for distillation (Figure 11.3).

9. Transfer the product with a disposable pipette to a 10 mL distilling flask. Adjust the thermometer and distill, using the hot plate and aluminum heating block.

10. Collect the product in a tared glass vial nestled in a beaker of ice.

11. Monitor and report the head temperature on the Report Sheet.

12. Obtain the mass of the distilled product.

13. Determine the yield, percent yield, and turn in the labeled vial to your TA.

14. Clean distilling flask and separatory funnel with soap and water, rinse the flask and side-arm with acetone, and return them with cork(s) to the community area.

Name: ______________________________

Section: __________ Date: __________

Report Sheet:

Nucleophilic Substitution: Synthesis of 2-Chloro-2-Methylbutane

Compound Data

1. Complete Report Table 11.1.

Report Table 11.1: Compound Data

Compound	**Molar Mass (g/mol)**	**Boiling Point (°C)**	**Mass (g)**	**Moles**
2-methyl-2-butanol				
2-chloro-2-methylbutane				

2. Product distilled at: ____________________ °C

3. Yield of purified product: ____________________ g

4. Percent Yield of product: ____________________%

5. TA Signature: ____________________________

Questions

1. Write out the mechanism for the reaction of 2-methyl-2-butanol with concentrated hydrochloric acid.

2. What kind of mechanism is this? ______________________________

   This sort of mechanism is generally accompanied by a ______________________________ mechanism which will give an alkene side product.

3. Write out the mechanism of the formation of the alkene side product.

4. Why do we not see any alkene side product in our product?

5. Write out the mechanism of the reaction of the alkene side product with concentrated hydrochloric acid.

6. What kind of mechanism is this? ____________________