Experiment 8
Preparation of Methylpentenes from 4-methyl-2-pentanol

Preparation

Before beginning this experiment, you should have read through the entire experiment and

1. studied "Alkenes: Reactions and Synthesis", in McMurry's *Organic Chemistry*.

2. reviewed Experiments 3 (simple distillation) and 5 (extractions).

You may also wish to read Chapter 15 of *The Organic Chem Lab Survival Manual* (Chapter 20 in 3rd ed.), particularly the section on Simple Distillation.

Objectives

The purpose of this experiment is to

1. prepare a mixture sample of methylpentenes from 4-methyl-2-pentanol using an acid catalyzed dehydration reaction, and

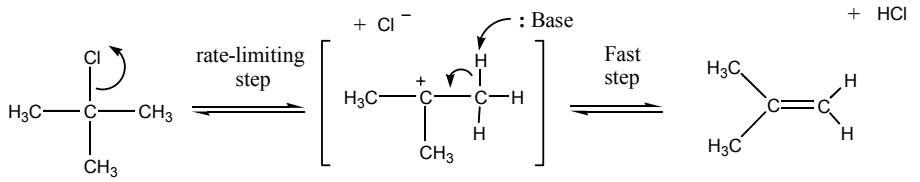
2. acquire more experience with the techniques of simple distillation and liquid-liquid separations, and the use of drying agents.

3. Learn about online control of a GC and perform GC analysis on your final product.

Optional Experiment 8 Background Information

Reactions of alcohols (R-OH) can be either: **C-O** bond reactions or **O-H** reactions. In this experiment, a C-O bond is broken, along with a neighbouring C-H bond, dehydration ($-H_2O$) of the alcohol occurs, and an alkene p bond is formed. It is important to review preparation of alkenes and reactions of alkyl halides for S_N1, E1, S_N2, E2 mechanisms.
E1 = elimination-unimolecular mechanism (analogous to the S_N1 mechanism). Two steps are involved for alkyl halides and 3 steps for alcohols.

E1 Example - Loss of HCl from a tertiary alkyl halide



(no geometric requirement because halide and hydrogen are lost in separate steps)

(Zaitsev's rule followed)

Some general characteristics of E1 reactions are:
Reactivity via the E1 mechanism is: Tertiary > Secondary > Primary
First order kinetics shown, consistent with a spontaneous dissociation process.
No deuterium isotope effect seen.
The E1 reaction has no geometric requirement because of the two separate elimination steps.

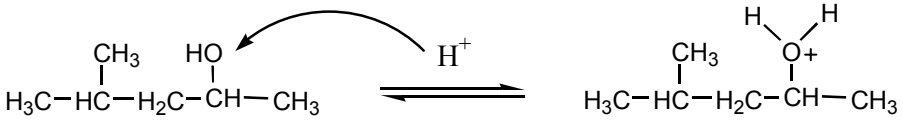
Limitations of E1 Reaction: Acid-Catalyzed Dehydrations

Competition can occur with S_N1 reaction if reaction conditions are not 'controlled' (when protic solvents, non-basic nucleophiles are used). Mixtures of products form with the E1 reaction (also S_N1). Unsymmetrical reagents and rearrangements possible (hydride and methyl shifts).This mechanism works well with only tertiary alcohols, less better with secondary (requires more harsh conditions e.g., 75% H_2SO_4, 100° C), and needs extremely harsh conditions (95% H_2SO_4, 150° C) for acid-catalyzed reaction to work with primary alcohols. (Reactivity via the E1 mechanism is: Tertiary > Secondary > Primary)

The reaction proceeds using a 3 step process: 1. protonation, 2. carbocation formation, and 3. double bond formation.

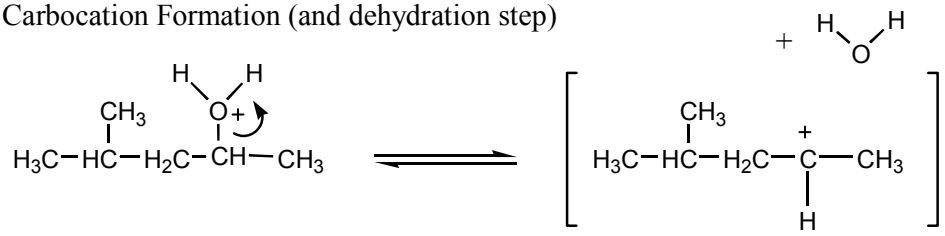
Methylpentene isomers via acid-catalyzed dehydration reaction of 4-methyl-2-pentanol in 3 steps:

1. Protonation by Acid-Catalyst

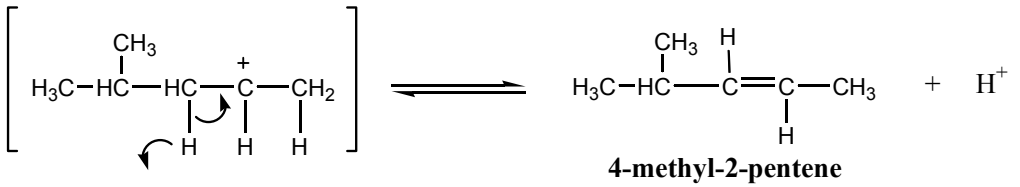


4-methyl-2-pentanol

2. Carbocation Formation (and dehydration step)

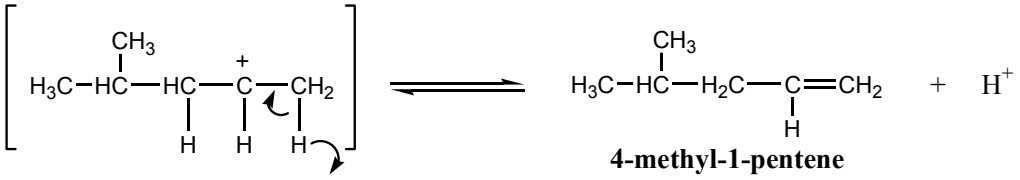


3. Double Bond Formation (with rearrangements and regeneration of catalyst)



4-methyl-2-pentene

or

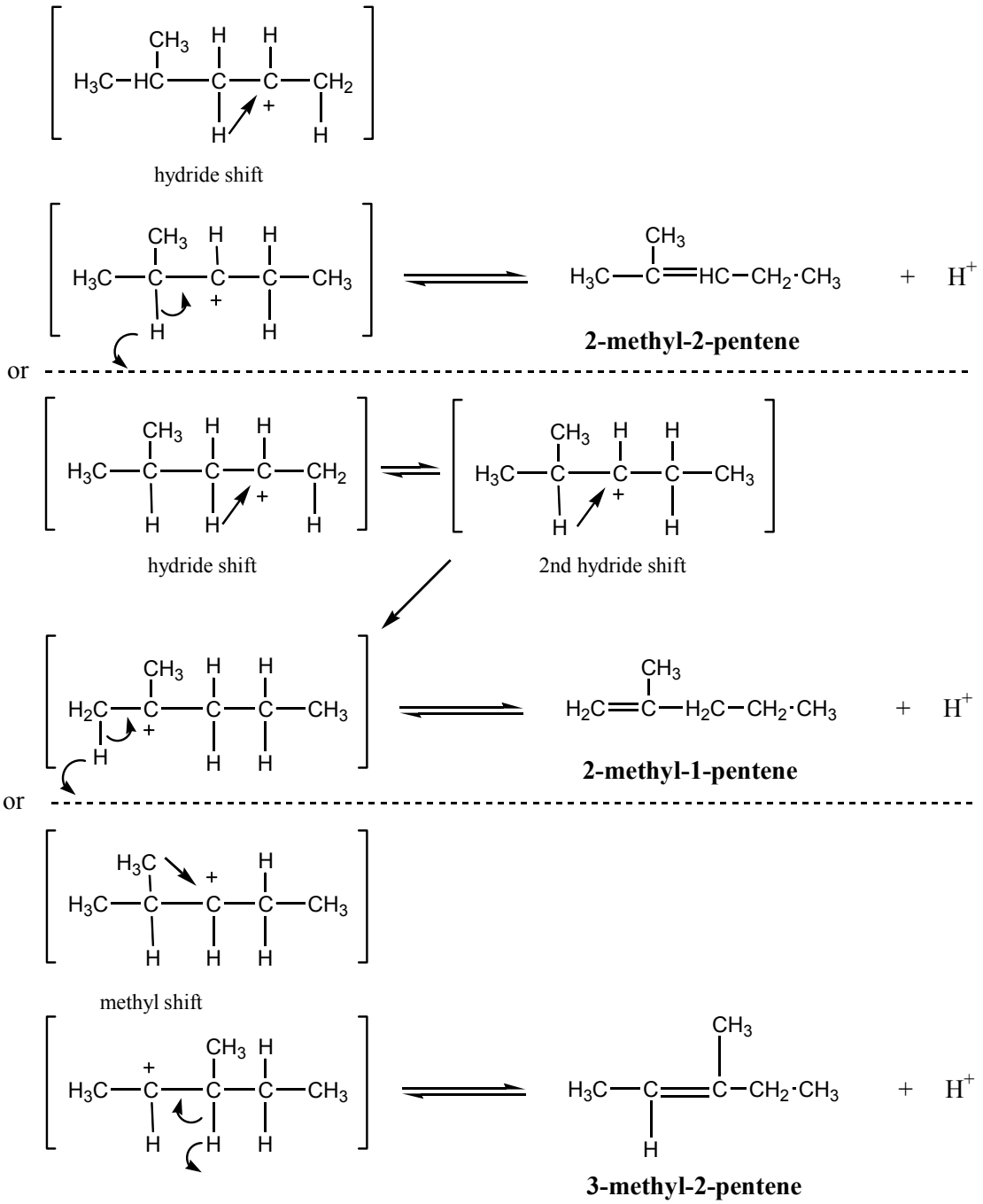


4-methyl-1-pentene

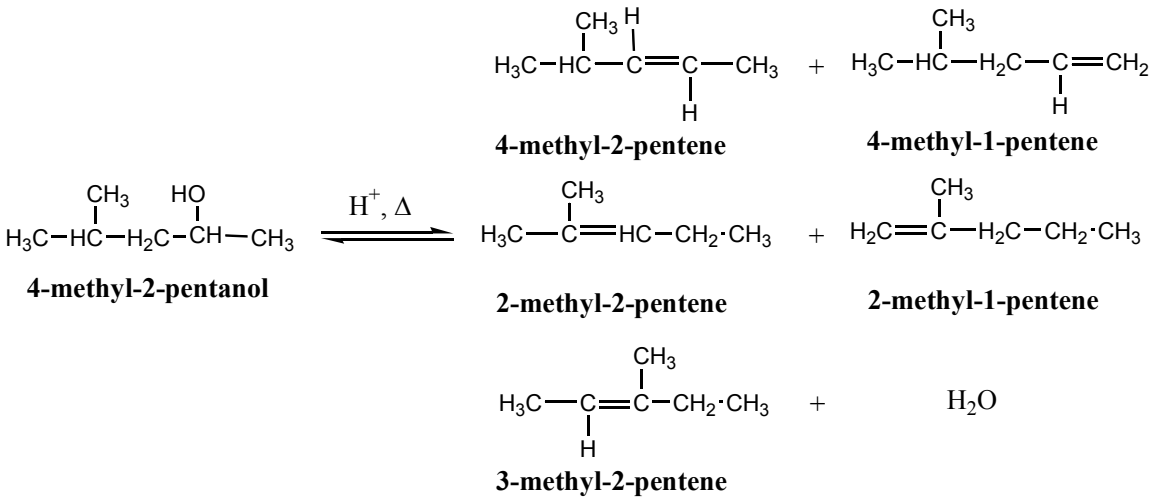
or ...

Other methylpentene isomers via hydride (:H-) or methyl shifts:

4. Double Bond Formation (with hydride shift rearrangements and regeneration of catalyst)



Exp. 8 Overall Acid Catalyzed Dehydration Reaction of 4-methyl-2-pentanol



Methylpentene Isomers

About Assembling Distillation Glassware and Using Heating Mantles

- Inspect all glassware for star-cracks (especially the distillation round bottom flask).
- Do not use a heating mantle with a damaged electrical cord.

About The Use of Brine and Drying Agents

- Organic solvents that are wet (have been in previous contact with aqueous solutions) need to be dried before they are distilled. The is achieved by the addition of a solution of saturated sodium chloride (sat. NaCl (aq)). The brine helps to draw the bulk of the water from the organic solvent, while also limiting the amount of organic solvent that can dissolve in the brine (i.e., organic solvents are less soluble in brine than in water).
- Once the organic solvent has been pre-dried with brine, the final trace water can be bound by the addition of a suitable drying agent. The drying agent then can be removed by gravity filtration or decantation. Be careful. The over addition of a drying agent can significantly reduce your yield.

Chemicals, Equipment, Utilities Required

All equipment used for the reaction must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
4-methyl-2-pentanol (purified), conc. sulfuric acid, distilled water, ice, 10% sodium hydroxide, brine, anhydrous calcium chloride, wash acetone, vacuum (glass joint) grease	-graduated cylinders -heating mantle, lab jack, retort stands, utility clamps -distillation apparatus (distillation flask, three way connector, thermometer adapter, condenser, vacuum adapter, receiving flask, boiling stones) -125 mL separatory funnel -hazardous waste disposal containers (in fume hood) -Varian Gas Chromatograph	-115V electrical, -cold water supply

Optional Procedure for Methylpentenes Synthesis

You must complete at least steps 1-9 before stopping.

A. Reagent and Equipment Preparation

1. Use graduated cylinders to measure out 0.40 mol of concentrated sulphuric acid (conc. H_2SO_4 = 18M, using L = mol/M, L = 0.4 mol/18M = 0.022L or 22 mL) and add it to 20 mL distilled water in a 100mL round bottom flask. Mix well and allow to cool back to room temperature.
   Caution: conc. sulfuric acid is very corrosive. Wear gloves, protect your eyes and work with it in the fume hood. Pipette carefully.

2. Slowly add 0.15 mole of 4-methyl-2-pentanol (commercially supplied) all the while gently swirling the mixture in the 100mL round bottom flask.

3. Add a few boiling stones, and then attach the 100-mL round bottom flask to a simple distillation apparatus (see *The Organic Chem Lab Survival Manual*, pp. 103-109; pp.189-194 in 3rd ed.), making sure that the thermometer has been positioned correctly (see Experiment 3). For the receiving/collecting vessel, use a 125-mL separatory funnel.

B. Dehydration Reaction

4. Start the cooling water circulating through the condenser, and begin to slowly heat the reaction mixture using a heating mantle (setting ~3-4), collecting all the distillate up to 75° C.

C. Quenching the Reaction

5. When the distillate temperature exceeds 75° C, stop the distillation by lowering the lab jack and removing the heating mantle. Proceed immediately to the next step.

D. Reaction Workup/Product Recovery

6. Wash the organic layer in the separatory funnel with 10 mL of 10% NaOH. Remove and discard the wash/aqueous layer.

7. Wash the organic layer in the separatory funnel with 10 mL of distilled water. Remove and discard the wash/aqueous layer.

8. Wash the organic layer in the separatory funnel with 10 mL of brine (=saturated sodium chloride). Remove and discard the wash/aqueous layer.

9. Add 2 to 3 g of anhydrous calcium chloride to the crude methylpentenes in the Erlenmeyer flask. Place a cork in the mouth of the flask, and swirl the contents occasionally as the crude methylpentenes dries over a period of 10 to 15 minutes. The crude methylpentenes should be 'clear' when all the water has been removed. While you are waiting, clean your condenser and prepare to carry out another simple distillation (use dry equipment).

E. Product Purification and Analysis

10. Gravity filter or decant the dry crude methylpentenes into a clean, dry 50-mL round bottom flask, and add a few boiling stones. Connect the flask to the simple distillation apparatus using a tared 25 mL round bottom flask in an ice bath as the receiving flask.

11. Distil the crude methylpentenes, collecting the fraction that boils over a range of 25-75^{o} C (corr.). Record the actual boiling point range and barometric pressure.

F. Product Analysis

12. Determine the mass of purified methylpentenes obtained and calculate your percentage yield. Optional: Perform Online Gas Chromatography on the sample (see procedure below).

13. Transfer the sample to a suitably labelled screw cap vial and submit it to your instructor. Save this sample as it is needed for use in Experiment 6.

Gas Chromatography Procedure and Analysis

14. Using a clean Pasteur pipette, place a small amount of sample (<1mL) into the special auto-sampler GC vial provided by the instructor. Receive the 'vial code' and write the code number for your product here:_____. You will use this code when you access the GC online, to perform your analysis.

15. Run a ___ μL sample of the product mixture on the gas chromatograph and calculate the relative % concentration of each compound in the product mixture using the areas for each peak.

16. Compare your results to the following reference values, arranged in order of ascending retention times:

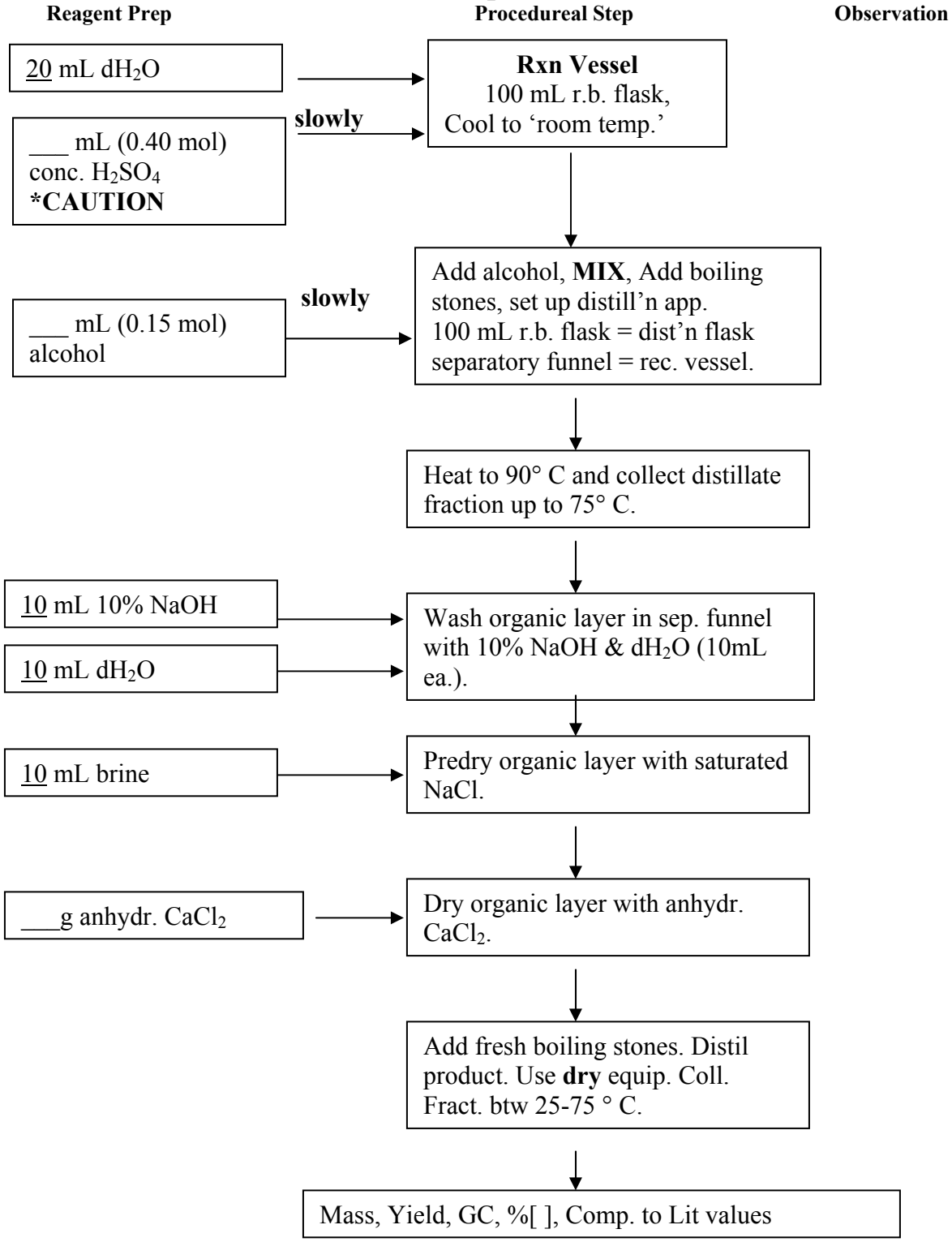
Name of Compound	**Literature Area %**
4-methyl-1-pentene	5.2
cis and *trans*-4-methyl-2-pentene	69.4
2-methyl-1-pentene	3.8
2-methyl-2-pentene	19.7
cis and *trans*-3-methyl-2-pentene	1.9

Ref: Nienhouse, E.J., 1969. A Unique Laboratory-Lecture in Organic Chemistry, *Journal of Chemical Education* **46**(11), pp.765-766.

Gas Chromotography Tutorial and Procedure

Please follow the "Instructions for AU Student Access to the http://www.remotelab.ca website".

CHEM350 Exp. 8 Reaction Flowchart



Safety

4-methyl-2-pentanol is flammable and irritating to the skin and eyes, and is harmful if inhaled or ingested. Flash point = 41° C.

Methylpentenes is flammable (Flash point = ~ –20° C) and irritating to the skin and eyes, and is harmful if inhaled or ingested.

Concentrated sulfuric acid burns the skin and eyes, and causes serious internal injury if swallowed. Wear gloves and eye protection.

10% Sodium hydroxide is corrosive and will cause burns to the skin and eyes, and causes serious internal injury if swallowed. Wear gloves and eye protection.

Saturated sodium chloride (brine) does not normally constitute a safety hazard, but you should treat all chemicals with respect.

Calcium chloride (anhydrous) is an irratant and is hygroscopic. Wash away any dust with lots of water.

Additional information about the potential hazards in handling these chemicals may be obtained from the *Material Safety Data Sheets* that are available in the laboratory.

Waste Disposal

4-methyl-2-pentanol residues should be placed in the bottle labelled "Organic Wastes: Non-halogenated."

The **aqueous layer from the separation** may be washed down the sink with plenty of water.

The **methylpentenes residue** from the final distillation should be placed in the bottle labelled "Organic Wastes: Non-halogenated."

Write-up

This experiment should be written-up using the standard format for preparative experiments (see the "Reports" section of this *Laboratory Manual*.)

Remember to photocopy you lab report before mailing it to your tutor for marking.

Questions

Answers to be submitted with report.

1. What is the purpose of adding 10% sodium hydroxide solution to the distillate in step 6 of the procedure? If necessary use reaction equation(s) to fully explain your answer.

2. Would infrared spectroscopy analysis be useful in identifying the methypentenes product? Briefly explain your answer.