

## EXPERIMENT 4: Alkenes – Preparations and Reactions

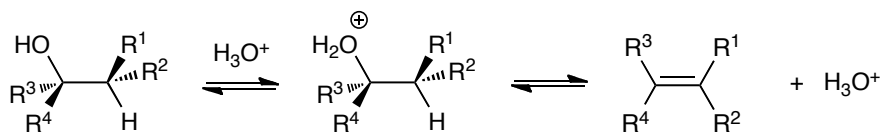
Relevant Sections in the text (Wade, 7<sup>th</sup> ed.)

- 11.10 (p. 484) Dehydration reactions of alcohols
- 8.2 (p. 324), 8.8 (p. 344), 8.14 (p. 360) Electrophilic addition to alkenes

### General Concepts

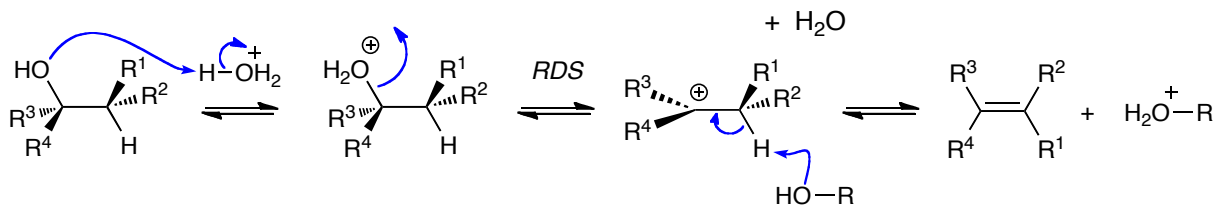
#### (i) Preparation of Alkenes

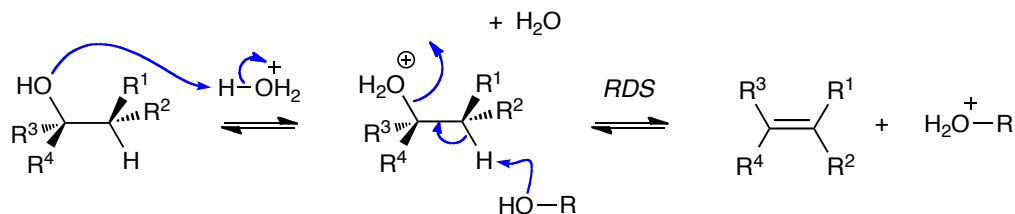
Alkenes are commonly synthesized by the dehydration of an alcohol, which is usually catalyzed by addition of a strong and high boiling mineral acid such as sulfuric or phosphoric acid. The alcohol group is protonated by the acid producing the oxonium ion, which causes the positively charged oxygen atom to further polarize the carbon-oxygen bond. Consequently, the hydroxide ion (a strong base and poor leaving group) is transformed into a water group (weak base), which is an excellent leaving group. After the water molecule and a proton are eliminated, an alkene is produced:



Two mechanisms are possible for this dehydration reaction. The loss of  $\text{H}_2\text{O}$  and  $\text{H}^+$  can occur in one step if the alcohol is primary: **E2 mechanism** (bimolecular elimination). Otherwise, if the alcohol is tertiary or has other structural features that can stabilize the corresponding carbocation, the elimination proceeds stepwise: **E1 mechanism** (unimolecular elimination). Secondary alcohols can proceed with either mechanism, depending on the conditions. It is possible to produce several different alkenes if the R groups attached to the central carbon (C-OH) have a different number of protons.

#### E1 Mechanism:



**E2 Mechanism:**

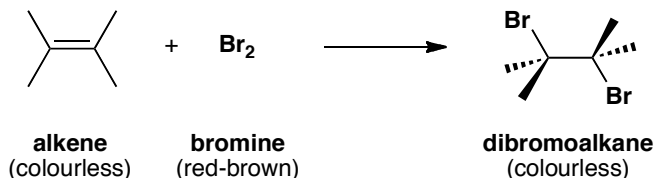
Although elimination reactions may also occur from alkyl halides, alcohols are preferred even though they tend to undergo molecular rearrangement. The ease of dehydration of an alcohol depends on the structure (tertiary > secondary > primary) and the conditions (concentration of acid and temperature). Since tertiary alcohols are most reactive, they require milder conditions (less concentrated acid, lower temperatures). The equilibrium tends to be further to the right for tertiary alcohols than for secondary or primary alcohols (see E1 mechanism).

This experiment involves continuous product removal during the course of the reaction, which is a very important experimental principle and technique. The reaction for this particular laboratory experiment will be the dehydration of 4-methyl-2-pentanol. It demonstrates the common problem of obtaining complex product mixtures, which will then be analyzed and separated by use of gas chromatography.

**(ii) Reactions of Alkenes**

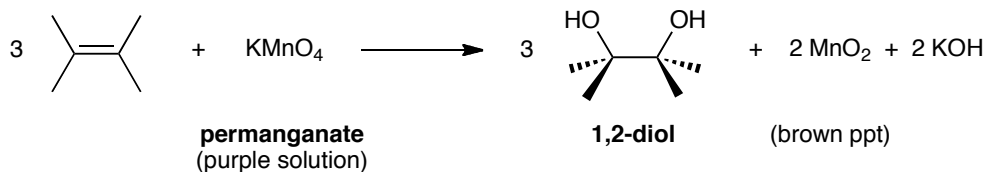
Alkenes, containing a site of unsaturation, undergo electrophilic addition reactions with several reagents such as halogens, oxidizing agents, and sulfuric, halogen, and hypohalous acids. In particular, bromine and oxidizing agents such as permanganate are widely used in qualitative tests to detect the presence of unsaturation.

Bromine reacts with alkenes, yielding a dibromoalkane (below). The distinctive colour change of bromine (dark red-brown) to dibromoalkanes as well as alkenes (colourless) demonstrates the ease and usefulness of this qualitative test. The test for unsaturation uses a dilute solution of bromine in a colourless solvent such as dichloromethane.

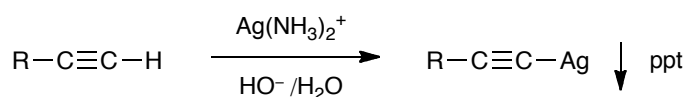


Some unsaturated compounds do not actively react with bromine unless under special conditions, so negative results should also be tested with permanganate (see next page) to confirm results.

Oxidizing agents such as permanganate also react with alkenes in a qualitative manner. The alkaline permanganate (purple) reacts with sites of unsaturation to produce 1,2-diols (see below). Also known as the Baeyer test, the permanganate ion is destroyed in the reaction and a brown precipitate ( $\text{MnO}_2$ ) is formed. While alkanes do not react with permanganate, it must be noted that other functional groups (most commonly aldehydes) also decolourize the purple ion.



Although these qualitative tests prove to be very useful, they do not allow the distinction between alkenes and alkynes. However, terminal alkynes (i.e., 1-alkynes) undergo a reaction in the presence of silver ions, whereas other alkynes and alkenes do not. Terminal alkynes form salts (acetylides) due to their weakly acidic hydrogen:



### (iii) Gas Chromatography

Gas chromatography is a versatile and widely used method for the examination of volatile mixtures by distributing each component in the mixture between a gas phase and either a liquid or solid phase. The method can be used to follow the course of a reaction both qualitatively and quantitatively, to separate and isolate components of a mixture, to examine purity, and to assist in the identification of compounds.

The compound mixture is passed through a heated column (glass capillary tubing) as a vapour, surrounded by an inert carrier gas. The column is coated with a stationary phase that varies in type and structure depending on the type of separation required. The separation process is readily understood in qualitative terms and is conceptually similar to other chromatography you have used (TLC, column chromatography). Consider a two-component mixture entering the column. Each component will be partitioned between the gas phase and the stationary liquid phase depending on the volatility of the component and its affinity for the stationary phase. Since each component will have a different distribution between the two phases, the most volatile/least soluble in the stationary phase will be sent through the column more rapidly than the other, where separation is achieved.

**PART A: DEHYDRATION OF 4-METHYL-2-PENTANOL**

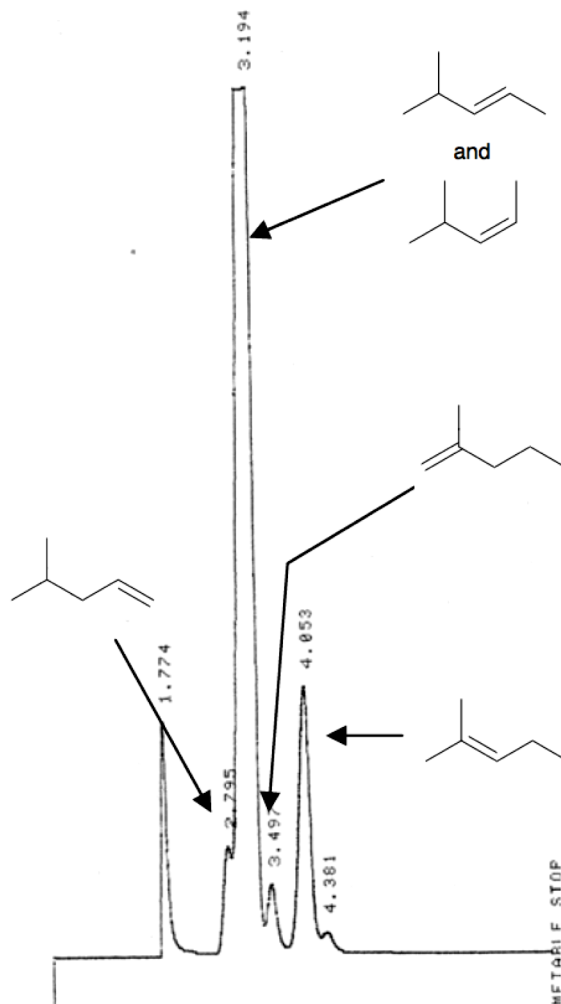
**\*HAZARDS\*:** Always work in the fumehood. Toluene, acetone, hexanes, ethanol, 1-propanol, and 2-propanol are volatile and flammable. 9 M sulfuric acid is corrosive. The alkenes you are working with have a *very unpleasant odor*; when transporting these compounds to/from your fumehood, ensure your flask/test tube is **CORKED**.

**\*Note\*:** During the distillation procedures described below, you should start Part C. Laboratory work requires multi-tasking!

- Transfer 20.0 g of 4-methyl-2-pentanol to a 100 mL round-bottomed flask, in addition to 10 mL of 9 M sulfuric acid. Thoroughly mix the solution by swirling it.
- Add two boiling chips, and assemble the flask for fractional distillation. The receiving flask should be immersed in an ice-water bath (*Important! Your product is volatile*).
- Heat the reaction flask using a hot-plate and heating mantle (do not heat too high). A heating mantle may be necessary – consult the TAs. Collect all distillates, but keeping the *head temperature* below 90 °C. If the reaction mixture is not sufficiently heated, the head temperature will remain below 80 °C for most of the period of reaction. When about 10 mL of liquid remains in the reaction flask, discontinue heating.
- Transfer the organic distillate to a small separatory funnel and add 5-10 mL of 3 M aqueous sodium hydroxide solution. Shake the funnel while being cautious to *vent* the funnel frequently. *Why is the distillate washed with a base?*
- Allow the layers to separate and remove the aqueous layer. Transfer the organic layer to a dry 50 mL Erlenmeyer flask and dry over a 10 minute period with anhydrous sodium sulfate.
- Decant the dried organic mixture into a *dry* 50 mL distilling flask. Add boiling stones and distil the mixture through a pre-dried simple distillation apparatus. Collect the fraction boiling between 53 and 69 °C in a *tared and dry* 25 mL receiving flask that is cooled in ice.
- Calculate the total yield of alkenes obtained.

**PART B: ANALYSIS**

- Analyze your product by GC. The potential products of the reaction and their boiling points are 4-methyl-1-pentene (53.9 °C), *Z*-4-methyl-2-pentene (56.4 °C), *E*-4-methyl-2-pentene (58.6 °C), 2-methyl-1-pentene (61 °C), and 2-methyl-2-pentene (67.3 °C). This is the order in which they should leave the column.
- An example of a GC trace is shown at right. The various peaks are assigned as follows: solvent front (1.774 min), 4-methyl-1-pentene (2.795 min), *Z*- and *E*-4-methyl-2-pentene (3.194 min), 2-methyl-1-pentene (3.497 min), 2-methyl-2-pentene (4.053 min), and 4.381 min is unassigned. Determine the approximate percentage composition of your own product mixture from the area of the peaks. Note that the absolute retention times vary slightly depending on column length, type, and flow rates of the carrier gas, but the order will remain the same.
- Obtain an infrared spectrum of your product (run neat). Assign peaks and interpret the spectrum in terms of the product mixture. Also assign the IR spectra provided for you of the starting material (4-methyl-2-pentanol).
- Prepare a sample of your product for  $^1\text{H}$  NMR analysis.
- You will be provided with NMR spectra of the authentic products.



***Be sure to show the mechanism that leads to the various products.***

**PART C: QUALITATIVE TESTS**

**\*HAZARDS\*:** Bromine is highly toxic and can cause severe burns; do not breathe the vapors – work in the fumehood. Avoid skin contact. If you accidentally have a spill, wash immediately with large amounts of water. In case of a bromine burn, rinse the area with lots of water and then flush with a 10% sodium sulfite solution. All samples being tested are flammable organic liquids.

**\*NOTE\*:** *Neatly* tabulate all observations and results. Discuss in your report.

- Conduct each test with the following:
- |                |               |            |
|----------------|---------------|------------|
| - your product | - cyclohexane | - 1-hexyne |
| - cyclohexene  | - benzene     |            |

**(i) Bromine Test**

- Dissolve about one drop of the sample in 2 mL of carbon tetrachloride in a small test tube.
- Slowly* add a 5% solution of bromine ( $\text{Br}_2$ ) in carbon tetrachloride *DROPWISE*. Note your observations. Continue the addition until the bromine color just persists (to a maximum of 10 drops). Note the number of drops of bromine solution required.

**(ii) Permanganate (Baeyer) Test**

- Dissolve about one drop of the sample in 2 mL of acetone in a small test tube. • Slowly add the purple 2% aqueous potassium permanganate ( $\text{KMnO}_4$ ) solution, *DROPWISE* and shake after each addition. Note any color changes and precipitate formation. Continue the addition until the permanganate color persists (to a maximum of 10 drops). Note the number of drops of potassium permanganate solution required.

**(iii) Terminal Alkyne Test**

**\*HAZARDS\*:**  $\text{AgNO}_3$  deposits a harmful silver metal and should be used cautiously!!

- Prepare a silver ammonia complex by adding 5 mL of 0.1 M silver nitrate ( $\text{AgNO}_3$ ) solution to ammonium hydroxide solution *DROPWISE*. Brown silver oxide forms first, but add *just enough* ammonium hydroxide to dissolve the silver oxide.
- Dilute the solution by adding 3 mL of water.
- Add 3 mL of the diluted silver ammonia complex solution to about 0.1 mL of sample. Note any observations.