Chemistry 209
The Amylenes: 2-Methyl-2-Butene
Lecture Outline

1. Purpose of the Experiment
2. Preparation of Alkenes from Alcohols
3. Elimination Reactions (Zaitsev's Rule)
4. Mechanism of Acid Catalyzed Dehydration of Alcohols
5. Test for Unsaturation
6. Procedure
7. Percent yield

Purpose

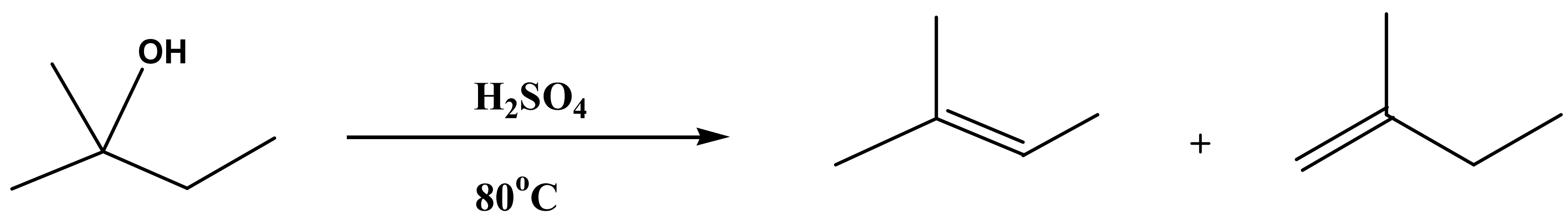
1. To review the ***synthesis*** of alkenes.
2. To ***synthesize*** an alkene (2-methyl-2-butene) by ***acid catalyzed dehydration*** of an alcohol (2-methyl-2-butanol).
3. To apply the techniques of ***extraction***, ***drying*** and ***distillation*** in the ***purification*** of the alkene.
4. To ***calculate*** the ***percent yield*** of the alkene.
5. To ***test*** the alkene for ***unsaturation***.

Theory

Amylenes is a generic name given for alkenes with general formula C_5H_{10}

2-Methyl-2-butene is prepared by the acid catalyzed dehydration of the alcohol 2-methyl-2-butanol (t-amyl alcohol)

Elimination by alcohol dehydration is readily accomplished by heating in the presence of an ***acid catalyst*** such as ***sulfuric*** or ***phosphoric***.



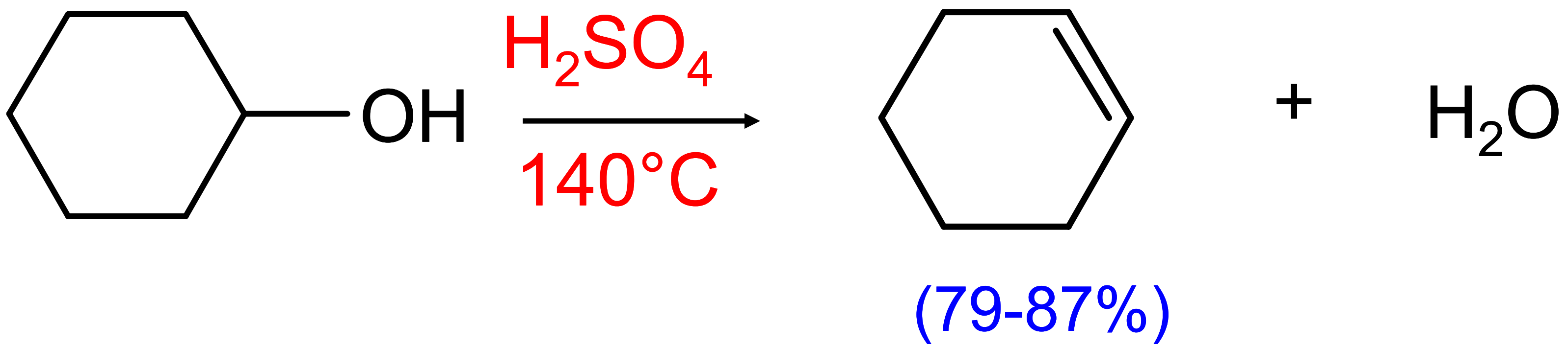
2-Methyl-2 butanol

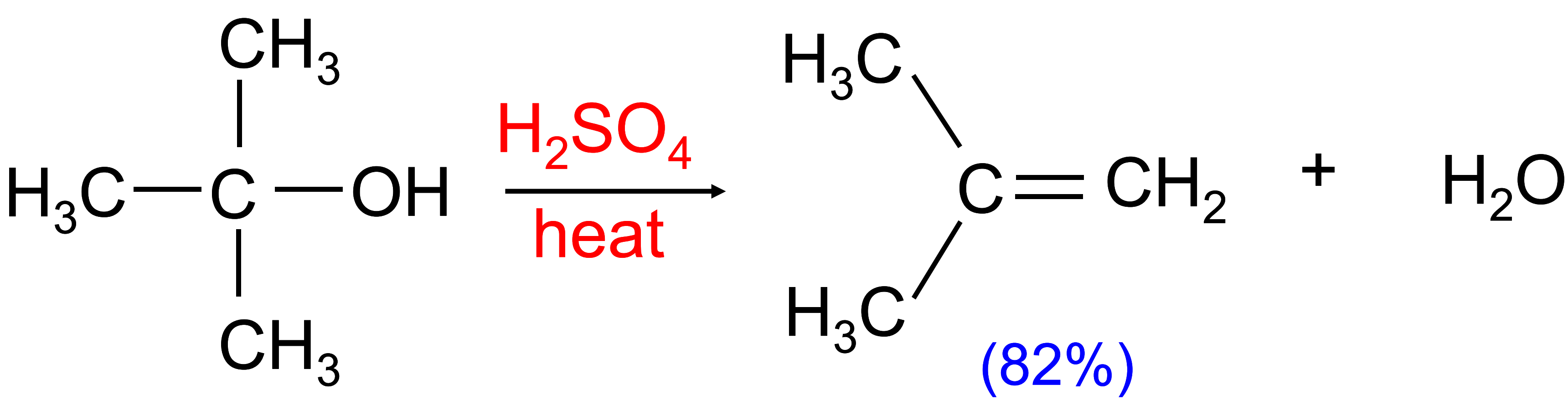
2-Methyl-2-butene *(major)*

2-Methyl-1-butene (minor)

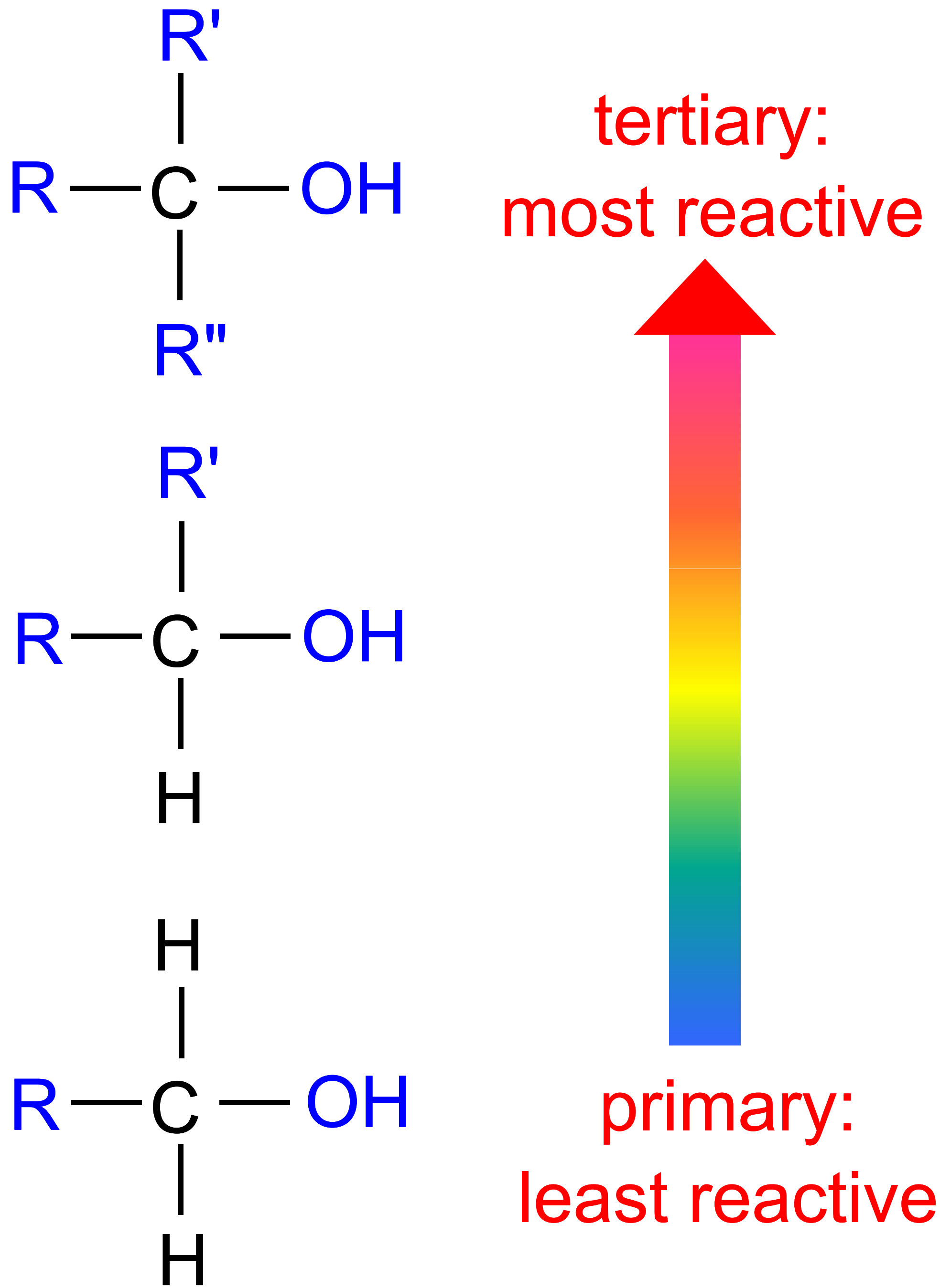
Dehydration of Alcohols

$$CH_3CH_2OH \xrightarrow[160°C]{H_2SO_4} H_2C{=}CH_2 + H_2O$$





Relative Reactivity

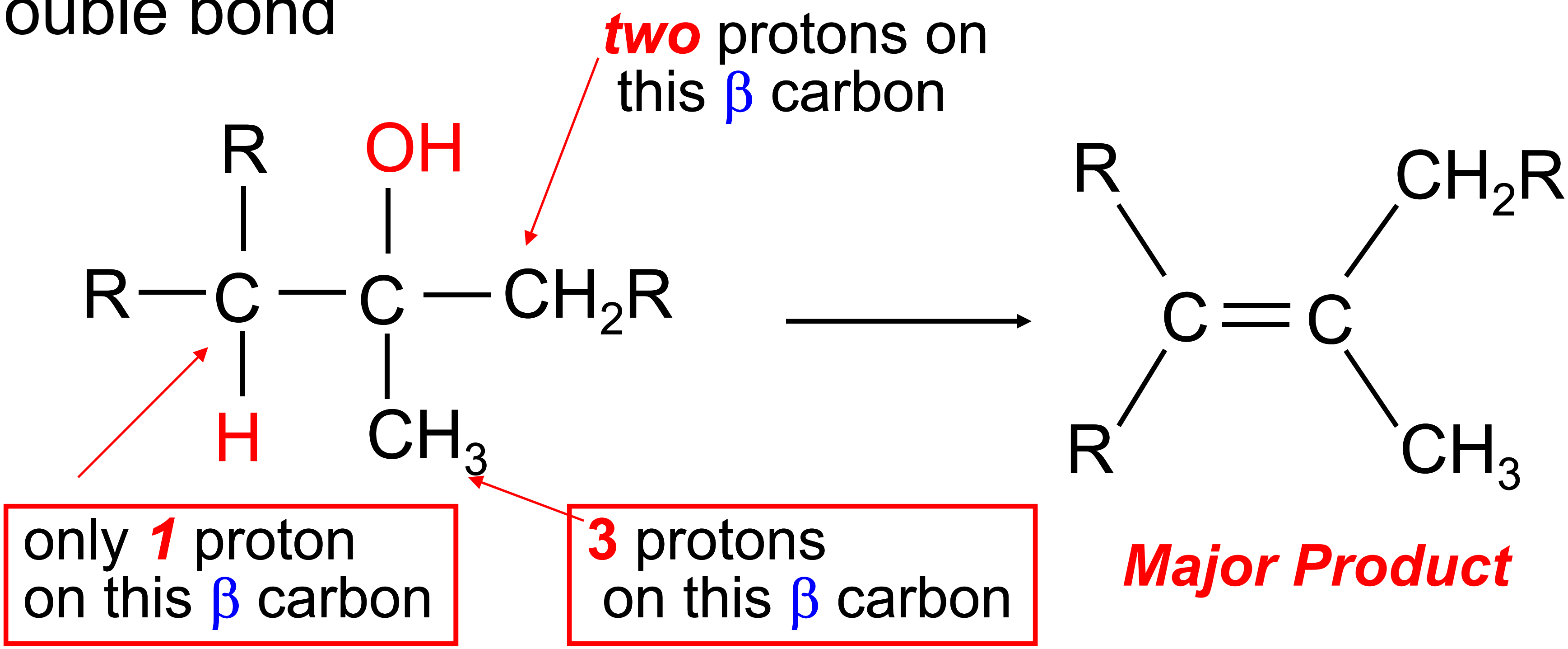


Elimination reactions produce more than one alkene, however only ***one*** predominates in accordance with Zaitsev's rule.

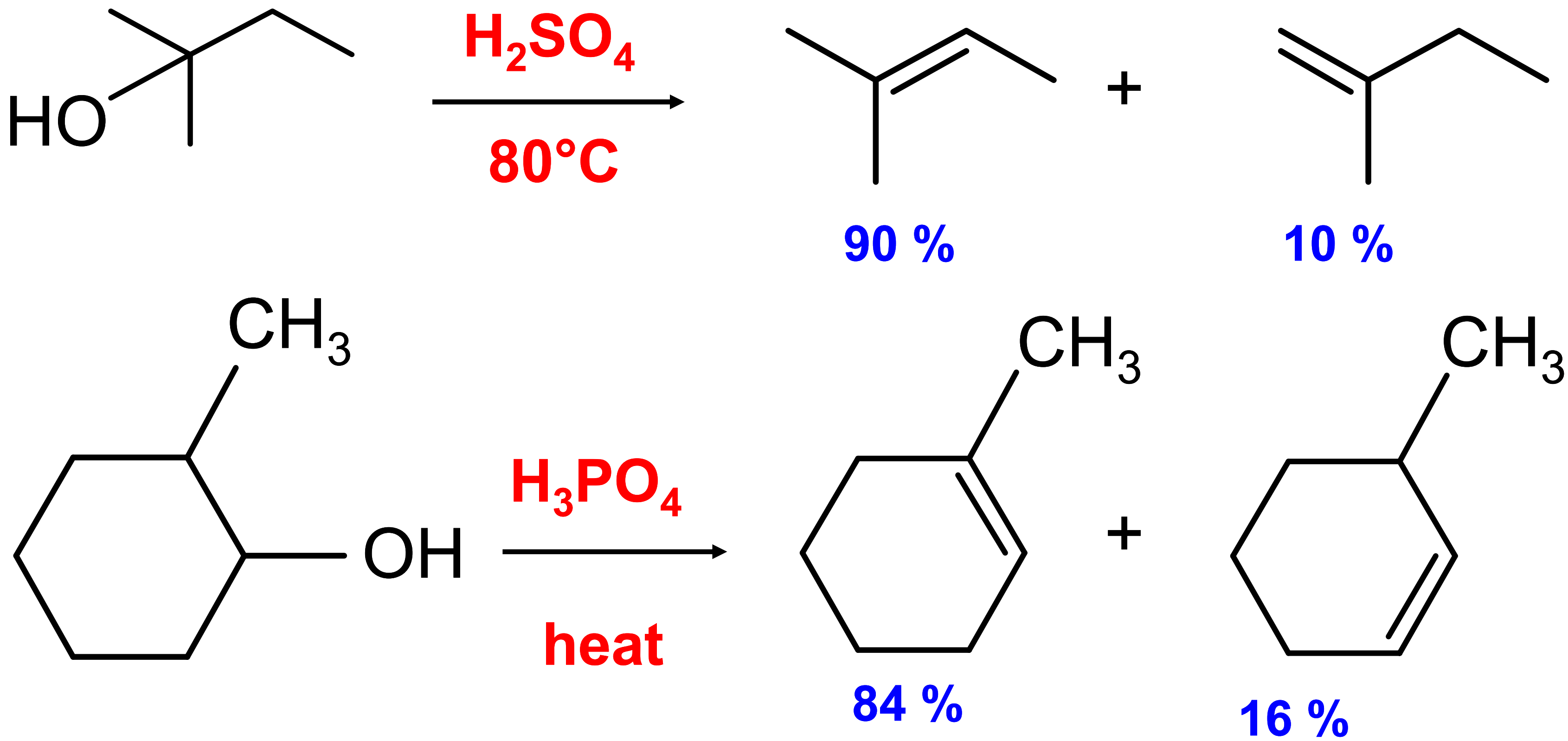
Zaitsev's rule: When two or more alkenes are capable of being formed by an elimination reaction, the one with the ***more*** highly ***substituted*** double bond (the ***more stable*** alkene) is the ***major*** product

The Zaitsev Rule

When elimination can occur in more than one direction, the principal alkene is the one formed by loss of H from the β carbon having the fewest hydrogens. This will lead to the formation of the more substituted double bond



Regioselectivity



A reaction that can proceed in more than one direction, but in which one direction predominates, is said to be ***regioselective.***

Mechanism of Acid Catalyzed Dehydration **E1**

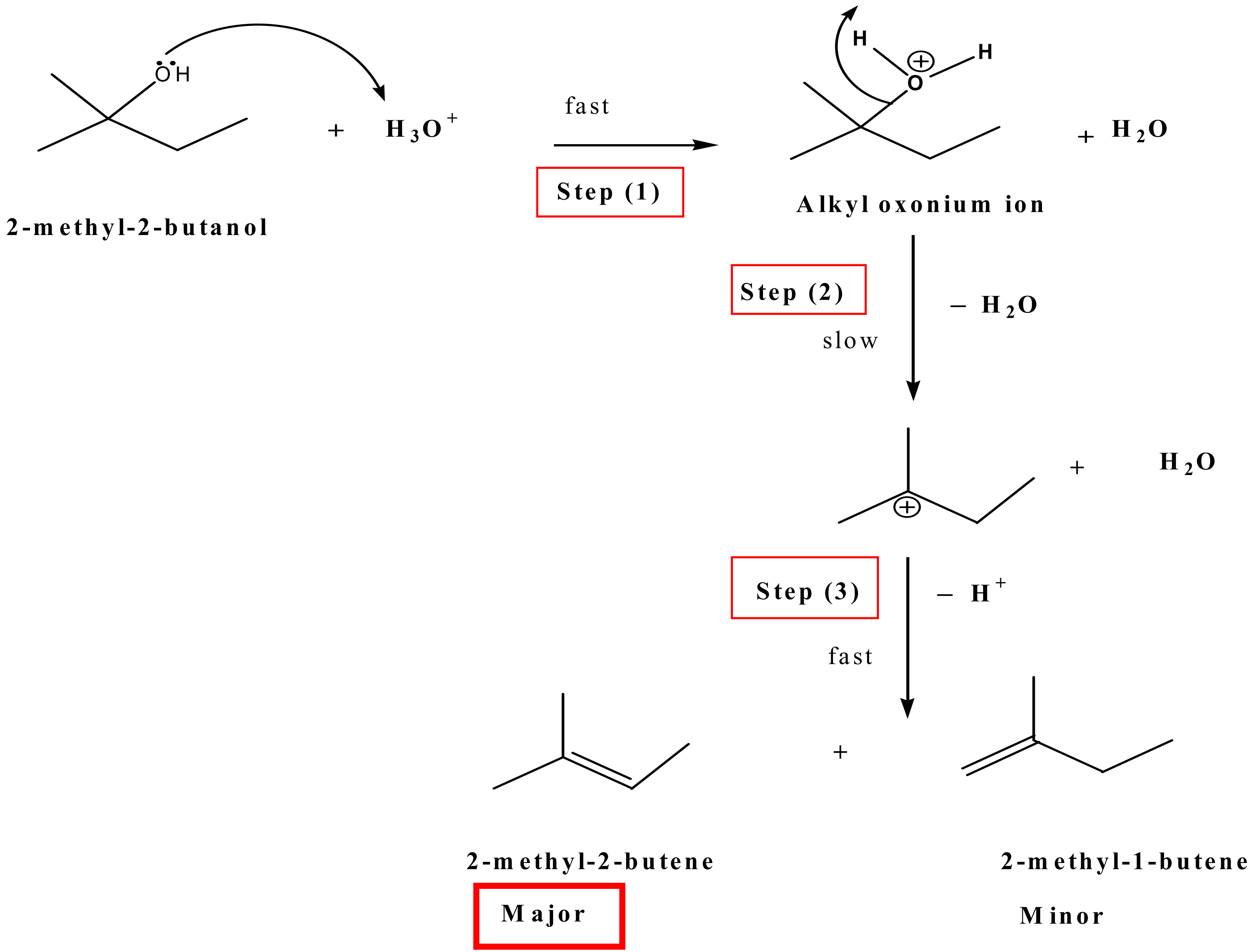
1st step in the mechanism is the ***protonation*** of the alcohol by the acid to form the alkyloxonium ion.

2nd step is the dissociation of the alkyloxonium ion by loss of water to form a tertiary ***carbocation***, the rate determining step.

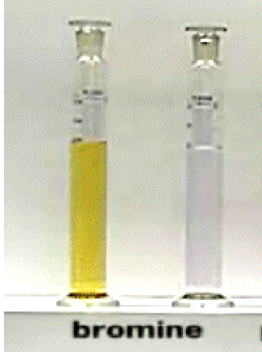
3rd step is the deprotonation of the carbocation to give a mixture of alkenes.

Relative ease of dehydration of alcohols:

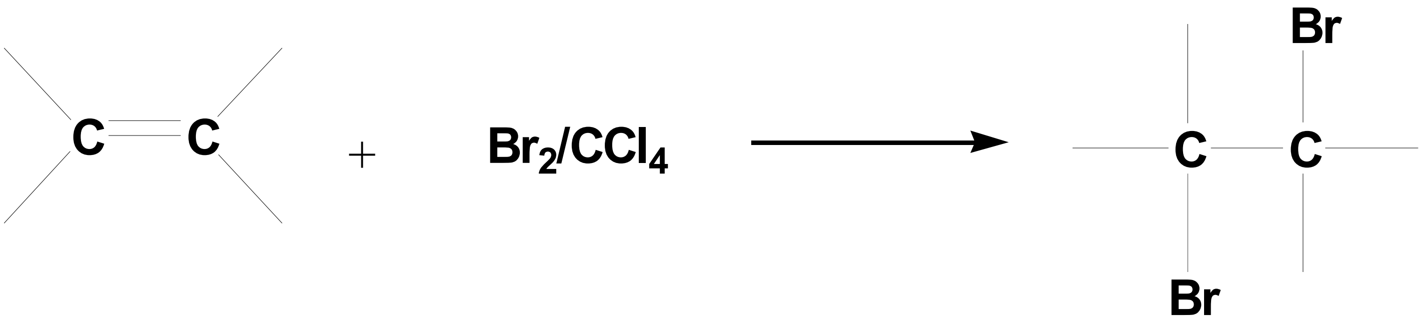
$3^o > 2^o > 1^o$


OH
H_3O^+
fast
Step (1)
H
H
O
H_2O
2-methyl-2-butanol
Alkyl oxonium ion
Step (2)
$- H_2O$
slow
H_2O
Step (3)
$- H^+$
fast
2-methyl-2-butene
2-methyl-1-butene
Major
Minor

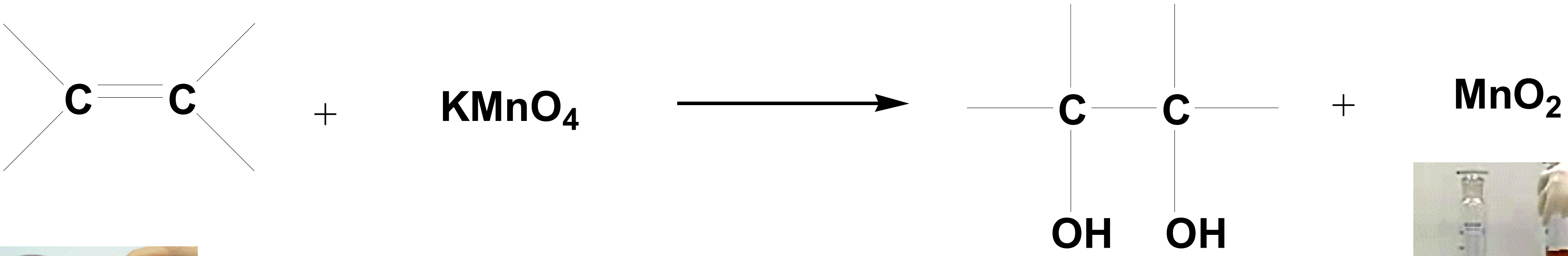
Test for Unsaturation



1. Reaction with Br_2/CCl_4



2. Reaction with aqueous $KMnO_4$ (Baeyer’s test)



Procedure

1. **Synthesis of the alkene.**

- Prepare a 1:2 sulfuric acid- water mixture (Add acid to water) in a 100 mL r.b. flask
- Add 14 mL (0.125 mol) of t-amyl alcohol with swirling and cooling
- Distil the mixture over a ***steam*** bath (~25 min)
- Collect the alkene in a 125 mL erlenmeyer flask fitted with a cotton plug and placed in an ***ice bath***.
- ***Clean*** and ***dry*** the distillation setup for use later in the final purification distillation.

2. Purification of the crude alkene.

The crude alkene contains: ***water***, ***traces of acid*** and ***ether*** (a by product of the reaction)

- Transfer the cooled alkene into a ***separatory*** funnel
- Add 5 mL of 10% dilute **NaOH** (to ***remove*** the acid)

  - observe ***two*** layers

  - remove the aqueous layer (lower)

  - pour the upper organic layer through the mouth of the funnel into a small, clean , **dry** Erlenmeyer flask.

- Add anhydrous $CaCl_2$ (0.5 g) , cover and allow the flask to stand with occasional shaking and cooling until the alkene is **dry** (***absence of turbidity)***

$$CaCl_2 + 2H_2O \rightarrow CaCl_2 \cdot 2H_2O$$

- Decant into a dry 50 mL r.b. flask
- Distil and collect the fraction boiling between **37°C-43°C**. (b.p. = 38.5°C)
- Weigh the product

3. Test for unsaturation

Pour few mL of the alkene into two test tubes

- Add to the first a few drops of Br_2/CCl_4solution
- Add to the second a few drops of $KMnO_4$ solution

Record you **observations**

4. Calculate percent yield

$$\%\ \text{yield} = \frac{\textbf{Actual yield}}{\textbf{Theoretical yield}} \times 100$$

Theoretical yield is calculated from the stoichiometry of the reaction and the number of moles used, in this experiment the mole ratio is **1:1**

⇨ Theoretical yield of ***alkene***

= # of moles x molar mass