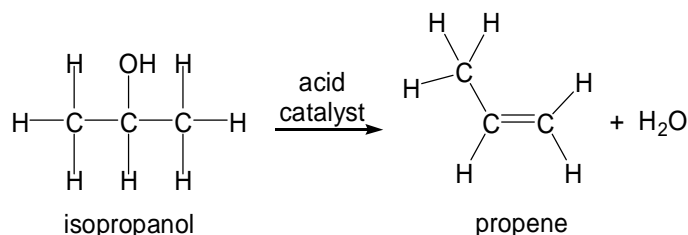


Dehydration of 2-Methyl-2-butanol

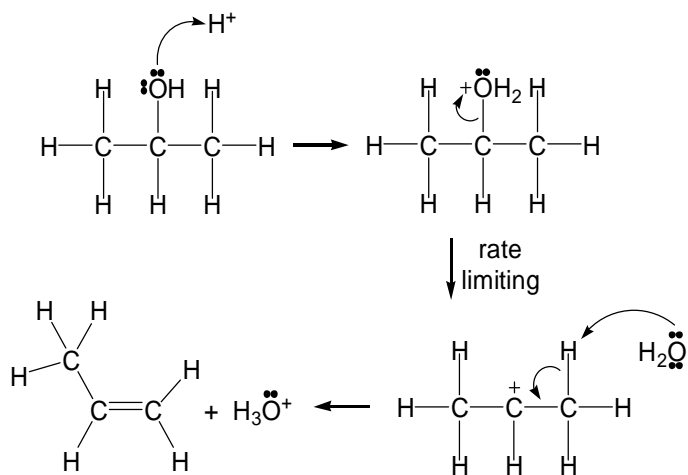
(Adapted from Fieser and Williamson, Organic Experiments, Fifth Edition, 1985)

BACKGROUND

Acid-catalyzed dehydration is common method for the conversion of alcohols to alkenes. The reaction is termed dehydration because $-OH$ and $-H$ are removed from neighboring carbon atoms and water is generated as a byproduct. A simple example is the dehydration of isopropanol to produce propene and water-



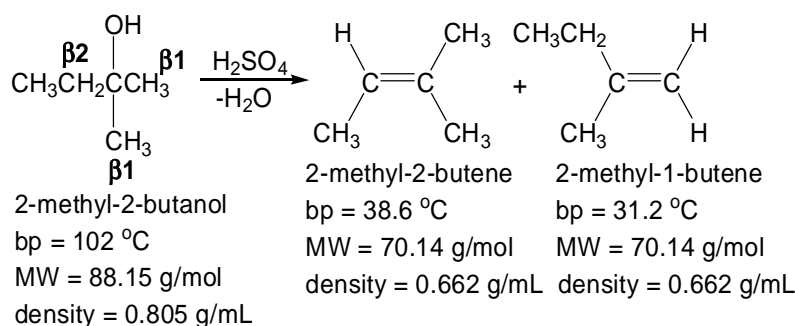
The mechanism of dehydration depends upon the type of alcohol used in the reaction. Primary alcohols dehydrate by an E2 mechanism while secondary and tertiary alcohols dehydrate by an E1 mechanism. Since OH^- is not a good leaving group (it is not a weak base), an acid is required to protonate the hydroxyl group-this converts it into a good leaving group. Commonly used acids are sulfuric acid and *para*-toluenesulfonic acid.



Note that the mechanism shows why the acid is catalytic-the H^+ used to protonate the alcohol is returned at the end of the reaction in the form of H_3O^+ . This reaction is readily reversible-alkenes can be hydrated to alcohols by using water and catalytic acid. The dehydration reaction is actually endothermic-two σ -bonds are broken; one σ -bond and one π -bond are formed. If we neglect entropy, this indicates that the starting materials are favored. Despite this problem, LeChâtelier's principle can be applied to carry out dehydration reactions in high yield. Since the alkene product is lower boiling

than the alcohol starting material, it can be boiled off and collected. Removal of a reaction product shifts the equilibrium to the product side and results in the production of additional alkene.

Dehydration of 2-methyl-2-butanol can give rise to two isomeric alkenes, depending upon which proton is removed from the tertiary carbocation intermediate. Removal of a proton from the $\beta 1$ position results in the formation of 2-methyl-1-butene, while removal of a proton from the $\beta 2$ position gives rise to 2-methyl-2-butene. This implies that formation of 2-methyl-1-butene is favored statistically (there are six hydrogen atoms that can be removed to form 2-methyl-1-butene, but only two that can be removed to form 2-methyl-2-butene). However, formation of 2-methyl-2-butene is favored on the basis of stability (it is trisubstituted). Keep these two conflicting effects in mind when you are trying to explain the relative amounts of each product formed.



The product(s) of the reaction will be analyzed to determine if one alkene is formed, or if a mixture is produced. You will analyze your reaction mixture by IR, ^{13}C NMR, DEPT-135 NMR, and gas chromatography (GC). Refer to the table below for relevant IR absorption bands.

In principle, gas chromatography is similar to the column chromatography experiment you conducted earlier in the semester. However, in gas chromatography, the mobile phase is helium gas rather than a liquid such as hexanes. The sample travels through a long narrow tube called a column. Lower boiling components of the mixture reach the end of the column (“elute”) prior to higher boiling components. When a compound elutes from the column, a detector sends a signal to a computer or chart recorder that produces a graph called a chromatogram. Each compound produces a peak on the chromatogram. The areas under the peaks are proportional to the amounts of each compound in the mixture.

Selected IR C-H Absorption Bands for Alkenes

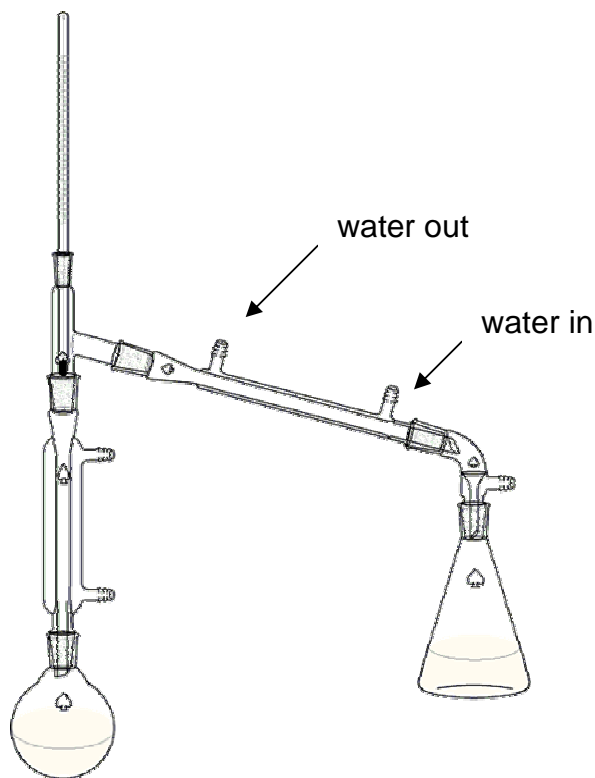
Double bond out-of-plane bending	cm^{-1}
RCH=CH ₂	910 - 920 AND 990 - 1000
<i>cis</i> -RCH=CHR	675 - 730 (variable)
<i>trans</i> -RCH=CHR	965 - 975
R ₂ C=CH ₂	880 - 900
R ₂ C=CHR	790-840

SETTING UP THE REACTION MIXTURE

Get a large beaker (500 mL or larger) and add about 200 mL of ice. Then add cold H₂O to increase the volume to about 300 mL. This will serve as an ice bath. Next, get a 100 mL 19/22 neck round bottom flask from your “foam kit”. Add 20 mL of distilled water to the round-bottomed flask, then cool the flask on the ice bath for 5 minutes. Next, carefully pour in 10 mL of concentrated sulfuric acid to the water while maintaining contact between the flask and the round-bottomed flask. Pour slowly and carefully. (You may want to wear gloves as you do this). Continue to cool the acid/water mixture on the ice bath for another 5 minutes. As you continue to swirl the mixture, carefully pour 20 mL of 2-methyl-2-butanol into the flask (while maintaining contact with the ice bath).

DISTILLING THE PRODUCT

While one partner is preparing the solution described above, the other partner should set up a fractional distillation apparatus as shown below. Hoses will be connected to the horizontal condenser so that water from the tap flows in the lower end and out the upper end. The fractionating column will be the one in your kits that is packed with copper mesh. Because the distillate is very volatile, the liquid that comes out the other end needs to be collected in Erlenmeyer flask that is cooled on an ice bath. Before proceeding with the distillation, check with your instructor to make sure your apparatus is assembled correctly.



A fractional distillation apparatus-sketch this diagram in your notebook

To make the reaction proceed and simultaneously distill the volatile product to separate it from the aqueous sulfuric acid, heat the round-bottomed flask with a powermite. You should set the regulator to about 20 initially, with further power adjustments as needed later. Heat the flask until distillation is complete. Monitor the thermometer during the distillation. In order to prevent unreacted alcohol from distilling with your product, do not allow the temperature to exceed 45 °C. You will know the distillation is finished when the temperature reading on the thermometer drops and the dripping of the liquid out of the condenser stops. (Ask your instructor if you are done).

PRODUCT PURIFICATION

Place a clean 125 mL separatory funnel on a ring stand. If the ring is too large, place a cork ring over the iron ring to reduce the diameter. Make sure the stopcock is closed. Transfer the distillate to the separatory funnel, add 5 mL of 10% aqueous NaOH, shake (make sure the lid is ON) the mixture then allow the layers to separate. Drain out the bottom aqueous layer. Repeat once. Drain out the organic product and dry with anhydrous sodium sulfate (Na_2SO_4) to remove all traces of water. Separate the dried organic layer from the drying agent by pouring the mixture through a funnel fitted with fluted filter paper, collecting the liquid into a clean, dry, pre-tared 50 mL Erlenmeyer flask. Weigh the liquid collected and calculate a percent yield.

PRODUCT ANALYSIS

1. Place about 1 mL of your distillate into a clean vial and submit this sample for GC analysis. You will use the GC data to determine the relative amounts of the compounds obtained.
2. Obtain an IR spectrum of your compound.
3. Place about 200 μL of your compound into an NMR tube, then add about 500 μL of CDCl_3 . Your instructor will obtain ^{13}C and DEPT-135 NMR spectra for you.

POST LAB QUESTIONS.

1. Calculate the percent yield of product(s) produced. Base this calculation on the mass of product collected after extraction.
2. What is the percentage of each alkene present in your product? Refer to your GC data for this calculation.
3. What does your IR spectrum indicate regarding the products produced from your reaction? Are the peak intensities you observe consistent with the GC data?
4. Assign the peaks in the ^{13}C and DEPT-135 NMR spectra to the carbon atoms in your product(s).

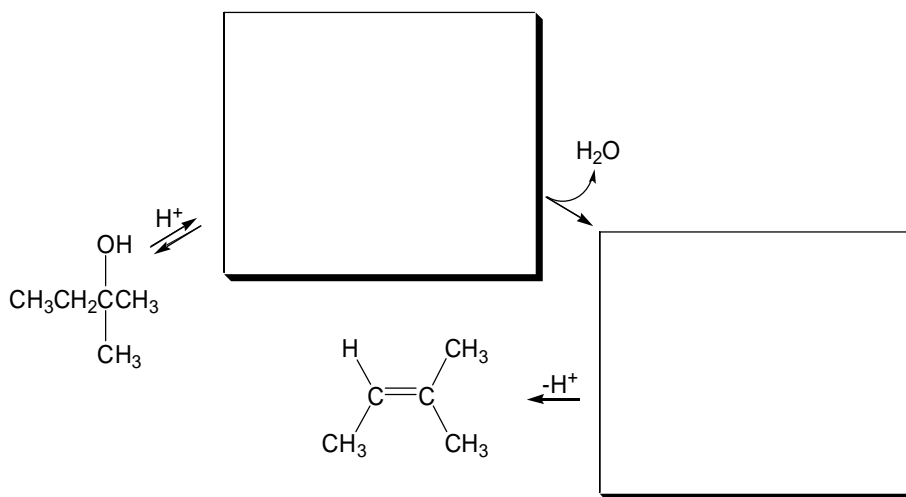
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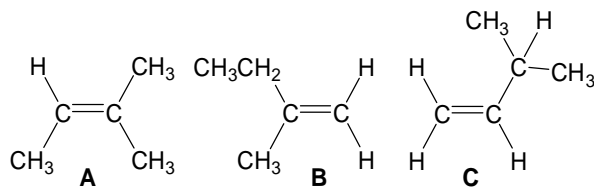
Lab Partner _____

PRELAB QUESTIONS

1. Fill in the missing intermediates in the mechanism for the dehydration of 2-methyl-2-butanol to form 2-methyl-2-butene. You do not need to add curved arrows.



2. Which of the following alkenes (A-C) is most stable? Which is least stable? Which do you expect to be the major product of this reaction?



3. List the predicted IR absorption bands for C-H out-of-plane bending for the alkenes shown in question 2.

A:

B:

C:

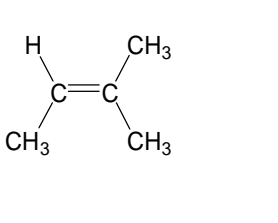
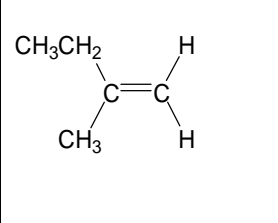
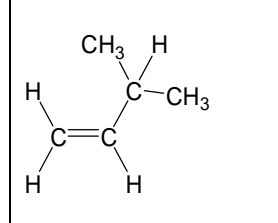
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4. Calculate the theoretical yield for the reaction. Copy your answer into your lab notebook. Show your work. Attach an additional sheet if necessary.

5. Complete the table below with the anticipated ^{13}C and DEPT-135 NMR data for each of the alkenes. I

						
Number of ^{13}C NMR signals between 0 and 50 ppm						
Number of ^{13}C NMR signals between 100 and 150 ppm						
Number of DEPT-135 NMR signals between 0 and 50 ppm	up	down	up	down	up	down
Number of DEPT-135 NMR signals between 100 and 150 ppm						