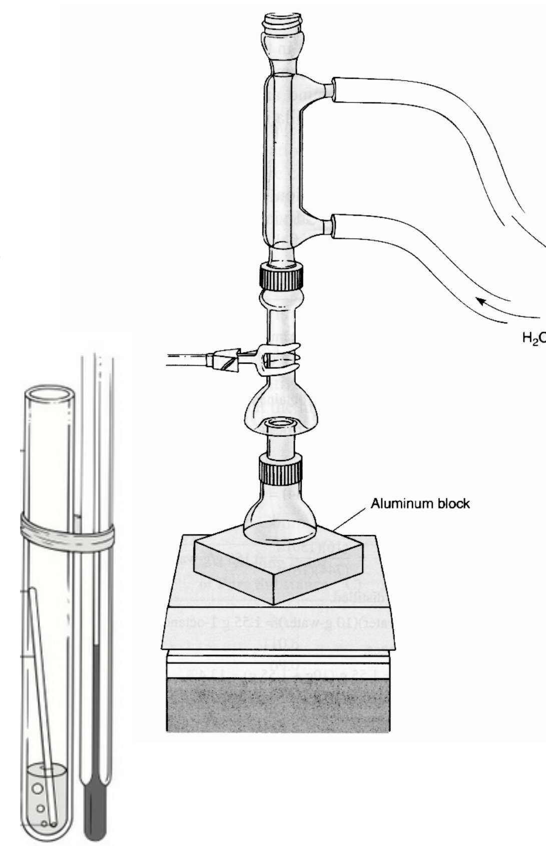
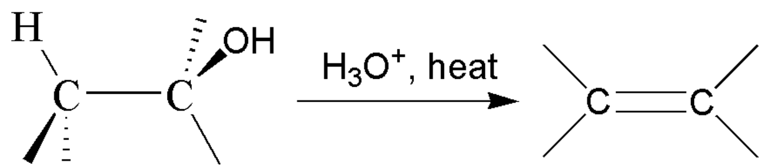
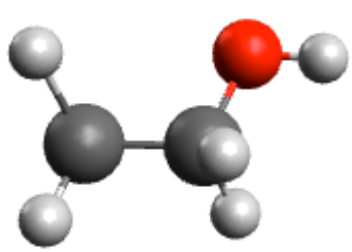
Ex24

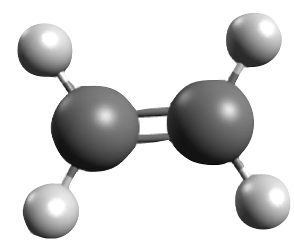
Dehydration

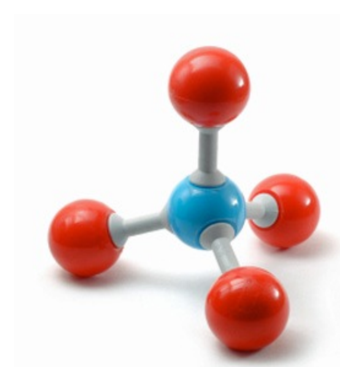
- Substances Explored
  - Olefin Properties & Structure
    - Differences in Olefins
  - Alcohol Properties & Structure
    - Differences in Alcohols
- Dehydration of an Alcohol
  - Conditions
  - Mechanism
  - Selectivity
  - Reverse Reaction
    - Hydration
- The Experiment
  - Setup
  - Reaction
  - Isolation & Drying
  - Analysis
- For Next Week











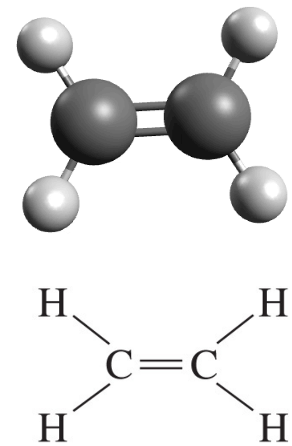
Olefins

- Hydrocarbons are molecules composed of only hydrogen and carbon.
- Carbons form four bonds.
- Alkanes are hydrocarbons that have only carbon-carbon single bonds.

- Alkenes are hydrocarbons that have one or more carbon-carbon double bonds.
  - Carbons that form double bonds are said to have a sp^2 shape.
  - The bonds connected to a sp^2 carbon have a 120˚ angle between them.

- Alkynes are hydrocarbons that have one or more carbon-carbon triple bonds.
  - Carbons that form triple bonds are said to have a sp shape.
  - The bonds connected to a sp carbon form a single line, they have a 180˚angle around the carbon.

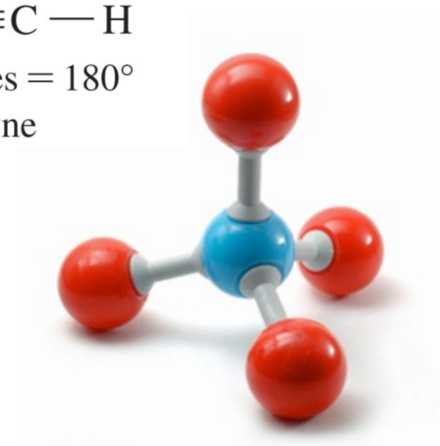
- Alkenes and alkynes are described collectively as olefins.



Bond angles = 120°
Ethene

$H-C\equiv C-H$

Bond angles = 180°
Ethyne

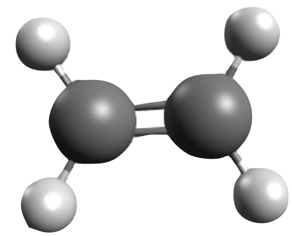


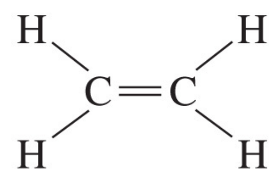
Olefin Properties

Ethene, the simplest alkene is a plant hormone, it causes fruit to ripen.

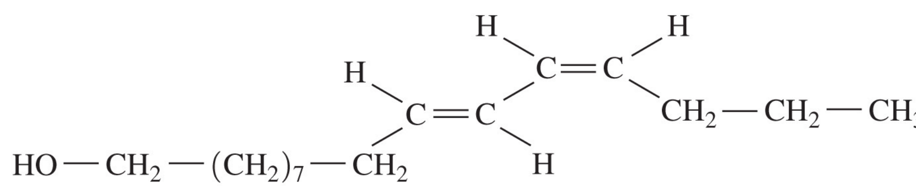
Plastic bags from the supermarket are made of poly-ethylene (many ethenes stuck together).

The longer you leave fruit in those bags, the faster that hormone will cause them to ripen.



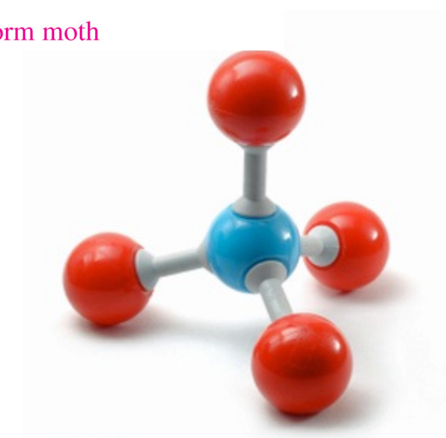


Bond angles = 120°
Ethene



Bombykol, sex attractant for the silkworm moth

Alkene structures are important in many biological structures, like the pheromone of silkworm moths.



Olefin Properties

- Burning alkynes produces *less* heat than alkanes.
  - But they also produce less gases.
- The gases produced in burning alkynes have more heat *per mole* of product
  - Those gases have a higher temperature.
- Alkynes burn hotter.
- If you want to put heat into your house, burn an alkane.
- If you want to create gases to push pistons in your car, burn an alkane.
- But if you want concentrated heat to cut metal, burn an alkyne.
  - Like ethyne (also called acetylene).

$$CH_3CH_3 + \tfrac{7}{2}\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O \qquad \Delta H^\circ = -1561\text{ kJ } (-373\text{ kcal})$$
$$-1561\text{ kJ divided by 5 moles of products} = -312\text{ kJ/mol of products } (-75\text{ kcal/mol of products})$$

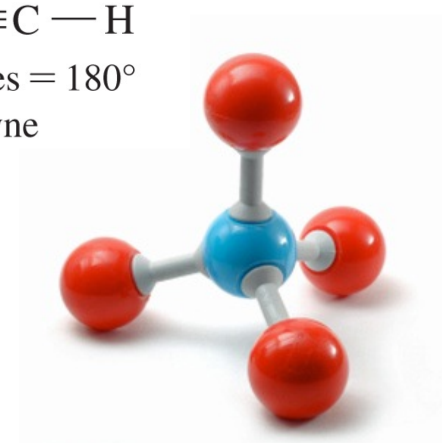
$$H_2C{=}CH_2 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O \qquad \Delta H^\circ = -1410\text{ kJ } (-337\text{ kcal})$$
$$-1410\text{ kJ divided by 4 moles of products} = -352\text{ kJ/mol of products } (-84\text{ kcal/mol of products})$$

$$HC{\equiv}CH + \tfrac{5}{2}\,O_2 \longrightarrow 2\,CO_2 + 1\,H_2O \qquad \Delta H^\circ = -1326\text{ kJ } (-317\text{ kcal})$$
$$-1326\text{ kJ divided by 3 moles of products} = -442\text{ kJ/mol of products } (-106\text{ kcal/mol of products})$$

$H{-}C{\equiv}C{-}H$

Bond angles = 180°

Ethyne

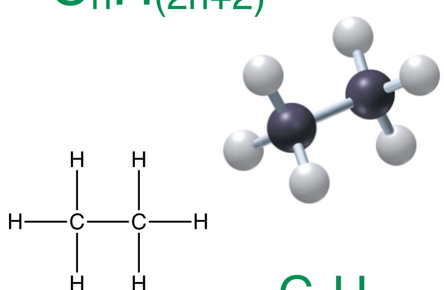


Saturated & Unsaturated

- We describe hydrocarbons are either saturated or unsaturated.
- Saturated hydrocarbons are hydrocarbons with only single carbon-carbon bonds.
  - This means they have the most hydrogens their carbon skeletons can possibly have.
  - Alkanes are saturated hydrocarbons.
- Unsaturated hydrocarbons have double and triple carbon-carbon bonds.
  - Unsaturated hydrocarbons are not saturated with hydrogen, their carbon skeletons could hold more hydrogen.
  - Alkenes & Alkynes are unsaturated hydrocarbons.
- Hydrocarbons can be monounsaturated (one unsaturation) or polyunsaturated (more than one unsaturation).
- Each unsaturation in a compound reduces the number of hydrogen atoms in the molecular formula by 2.

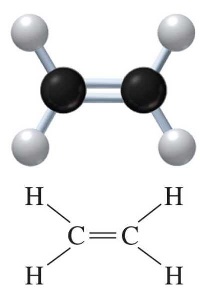
Sunflower oil is a mixture of monounsaturated and polyunsaturated hydrocarbon oils. The world's largest sunflower oil producers are Ukraine, Russia and Argentina.

$C_nH_{(2n+2)}$



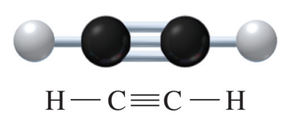
C_2H_6

$C_nH_{(2n)}$



C_2H_4

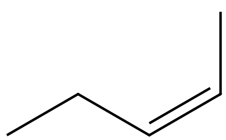
$C_nH_{(2n-2)}$



C_2H_2

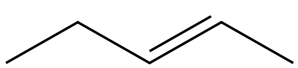
Cis-Trans Isomers

- The concept of stereo isomers can quickly take us beyond the scope of this class.
- We will confine our discussions of geometric isomers to cis trans relationships within the backbone of the hydrocarbon.
- There is more than one way to indicate the stereochemistry of a double bond.
- We will use only the cis-trans naming convention.
- Cis isomers are isomers where the two hydrogens on a double bond are on the same side.
  - Prefix the full name of the substances with "cis".

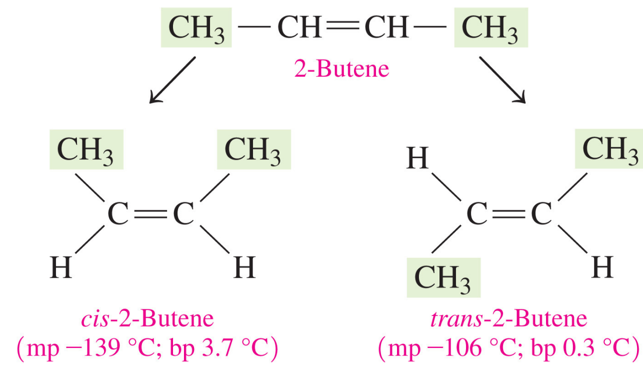


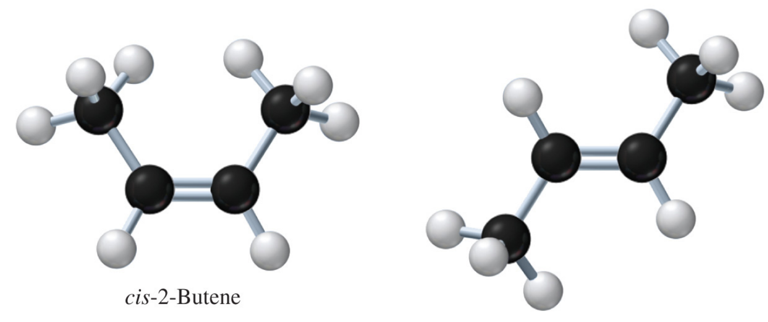
cis-2-Pentene
or *cis*-Pent-2-ene

- Trans isomers are isomers where the two hydrogens on a double bond are on opposite sides.
  - Prefix the full name of the substances with "trans".



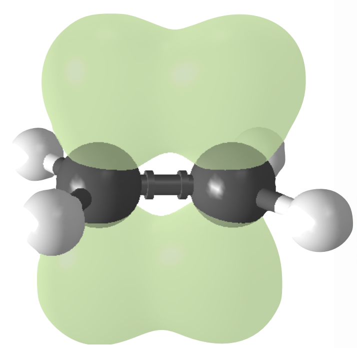
trans-2-Pentene
or *trans*-Pent-2-ene

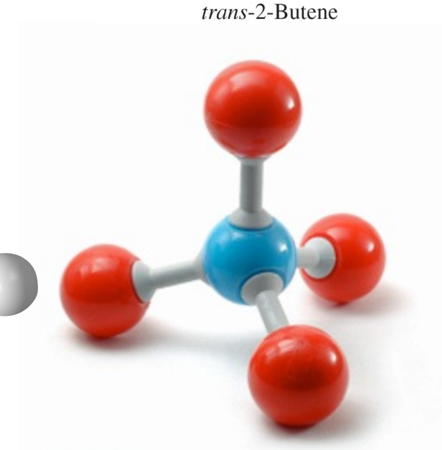




cis-2-Butene

trans-2-Butene





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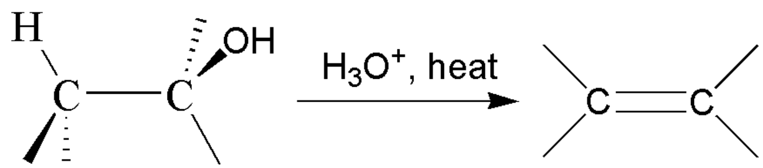
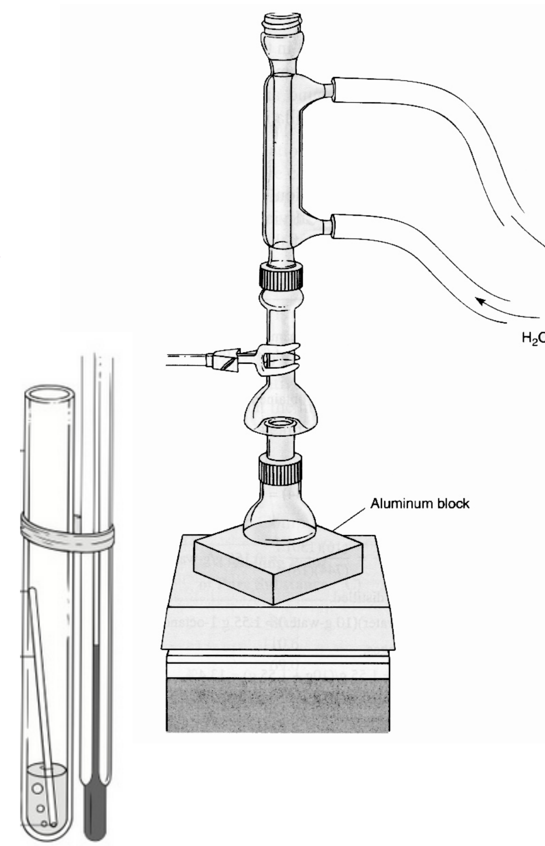
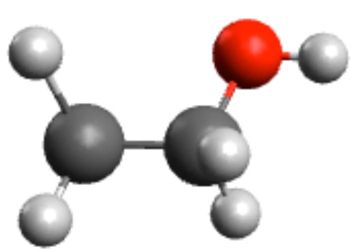
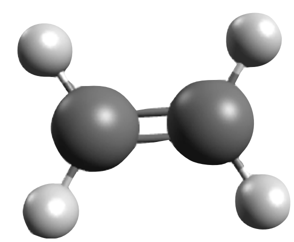
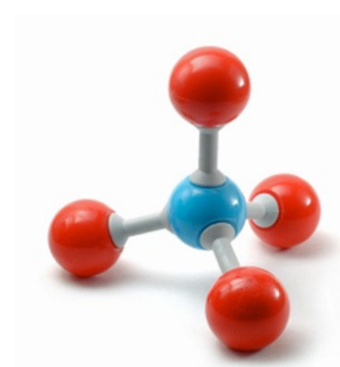




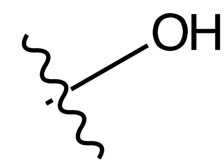


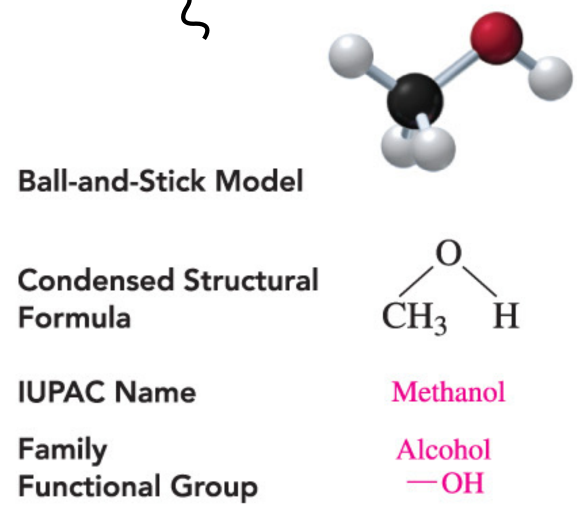


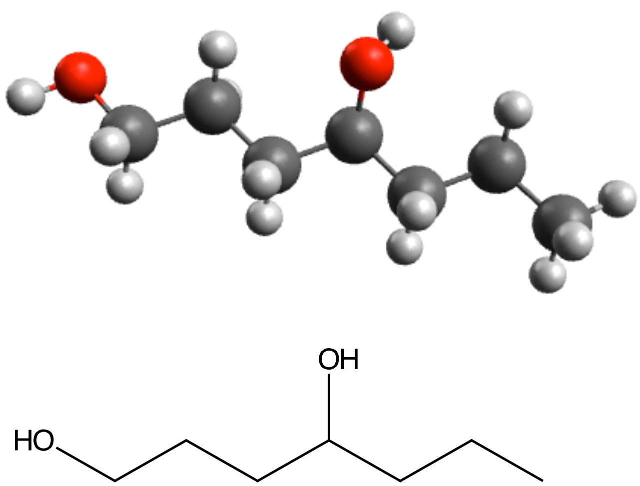


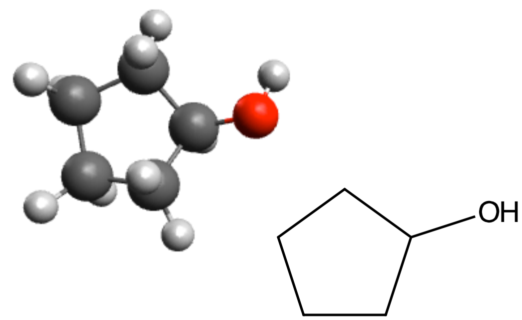
Alcohols

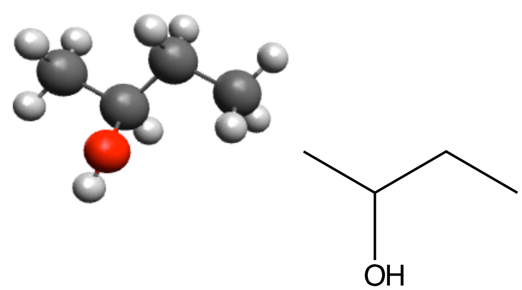
- Any compound which has a hydroxy group attached to it's backbone is a member of the class of compounds known as alcohols.
- The presence of the hydroxy functional group changes the chemical and physical properties of the substance.

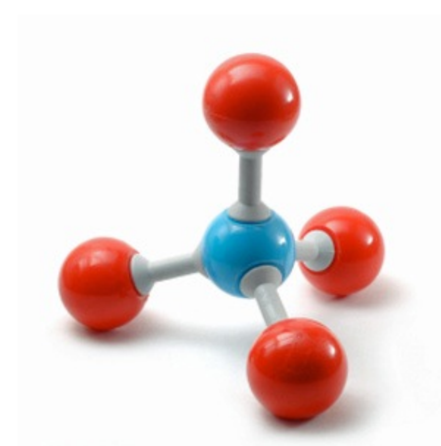






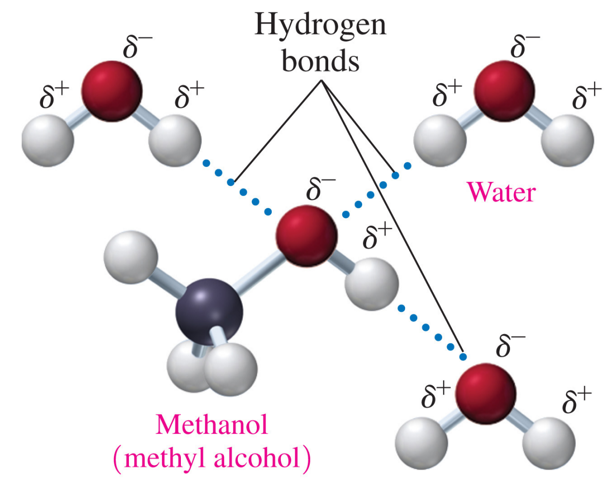


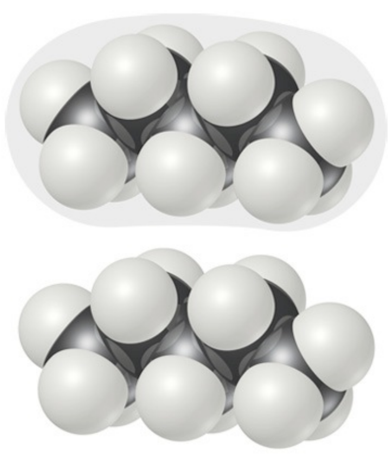


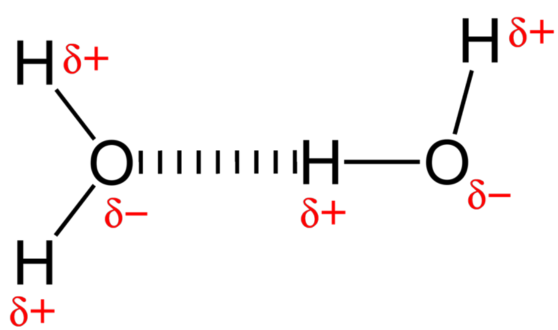


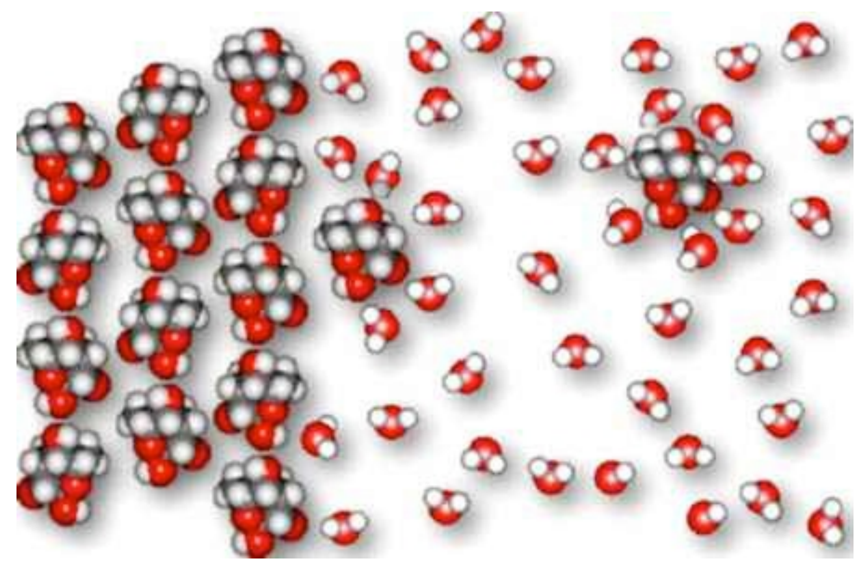
Properties of Alcohols

- Most hydrocarbons are not soluble in water.
- Hydrocarbons stick to each other primarily with non-polar London dispersion forces.
- Water molecules stick to each other primarily with hydrogen bonds.
- Nothing is gained by breaking those intermolecular binding forces to mix water and hydrocarbons.
- Because of the hydroxy functional group alcohols can take part in both kinds of intermolecular forces.
- Many alcohols are soluble in water.



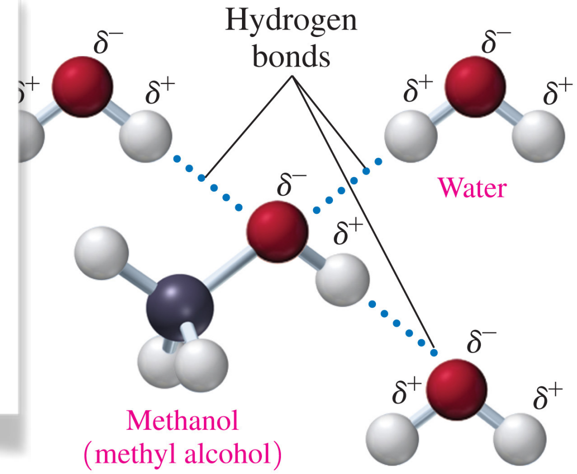




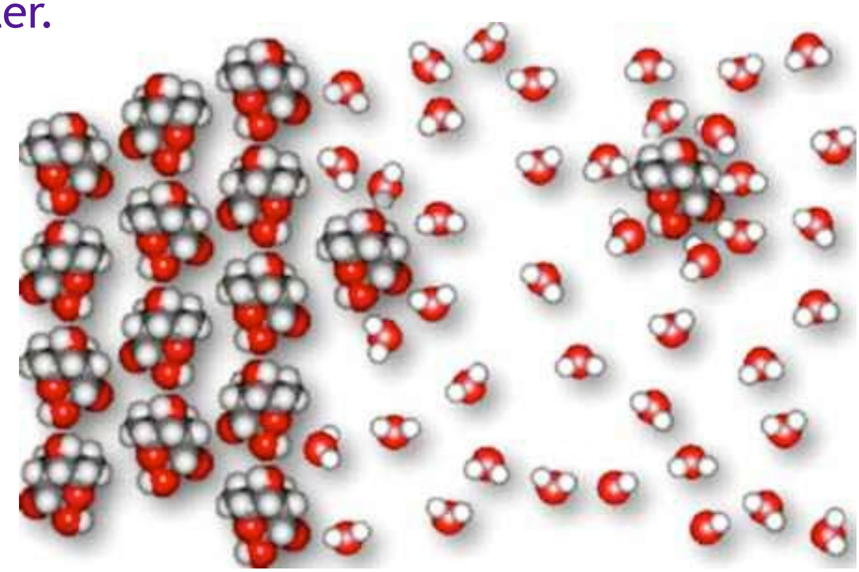


Properties of Alcohols

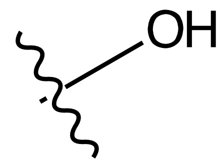
Compound	Condensed Structural Formula	Number of Carbon Atoms	Solubility in Water
Methanol	$CH_3—OH$	1	Soluble
Ethanol	$CH_3—CH_2—OH$	2	Soluble
1-Propanol	$CH_3—CH_2—CH_2—OH$	3	Soluble
1-Butanol	$CH_3—CH_2—CH_2—CH_2—OH$	4	Slightly soluble
1-Pentanol	$CH_3—CH_2—CH_2—CH_2—CH_2—OH$	5	Insoluble

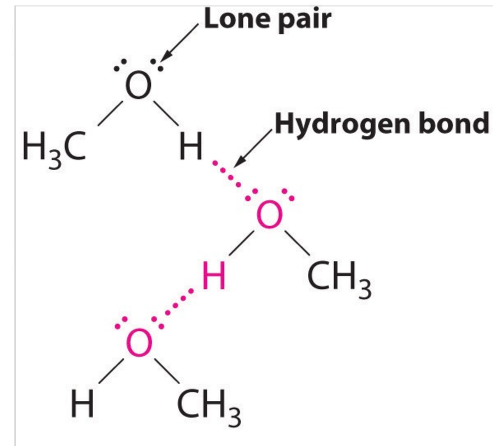


- Because of the hydroxy functional group alcohols can take part in both kinds of intermolecular forces.
- Many alcohols are soluble in water.
- Alcohols with 1-3 carbons are infinitely soluble in water.
- Simple alcohols with more than 5 carbons are insoluble in water.
- Without water around, alcohols can hydrogen bond each other, increasing their intermolecular forces.
- Hydrogen bonding in alcohols increases the alcohols boiling point and melting point.



Properties of Alcohols





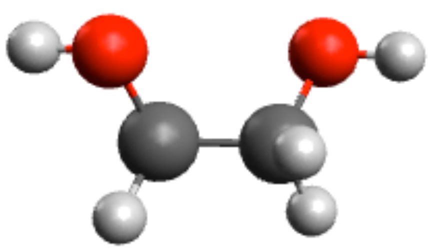
- The hydroxyl functional group changes many physical properties.
  - Solubility increases.
  - Boiling point increases.
  - Melting point increases.
- We'll see later that alcohols can undergo some chemical reactions *only* because they have the hydroxyl functional group.
- The hydroxyl functional group changes many chemical properties.
- This small group of atoms, fundamentally and predictably changes the function of the substances we call alcohols.

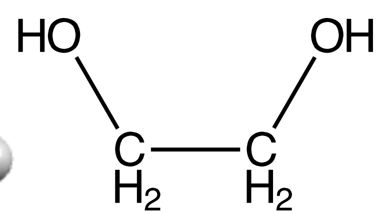
Compound	IUPAC Name	Melting Point (°C)	Boiling Point (°C)	Solubility in H_2O at 23°C
CH_3OH	Methanol	-97.8	65.0	Infinite
CH_3Cl	Chloromethane	-97.7	-24.2	0.74 g/100 mL
CH_4	Methane	-182.5	-161.7	3.5 mL (gas)/ 100 mL
CH_3CH_2OH	Ethanol	-114.7	78.5	Infinite
CH_3CH_2Cl	Chloroethane	-136.4	12.3	0.447 g/100 mL
CH_3CH_3	Ethane	-183.3	-88.6	4.7 mL (gas)/ 100 mL
$CH_3CH_2CH_2OH$	1-Propanol	-126.5	97.4	Infinite
$CH_3CH_2CH_3$	Propane	-187.7	-42.1	6.5 mL (gas)/ 100 mL
$CH_3CH_2CH_2CH_2OH$	1-Butanol	-89.5	117.3	8.0 g/100 mL
$CH_3(CH_2)_4OH$	1-Pentanol	-79	138	2.2 g/100 mL

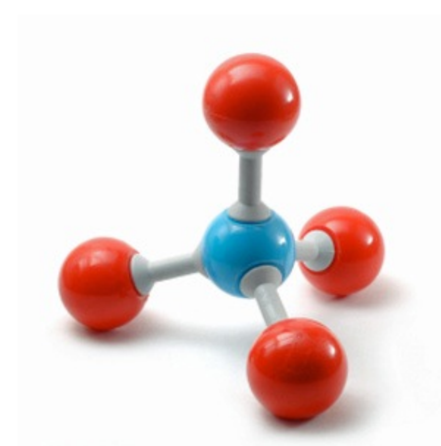
Applying the Properties of Alcohols

- We take advantage of two properties of alcohols to change the freezing point of water mixtures in our cold weather cars.
  - That alcohols have freezing points between that of pure hydrocarbons and water.
  - That alcohols have solubility in water.

- This allows us to “tune” to the freezing point of water mixtures by adding in the alcohol 1,2 ethane diol (also known as ethylene glycol or “antifreeze.”

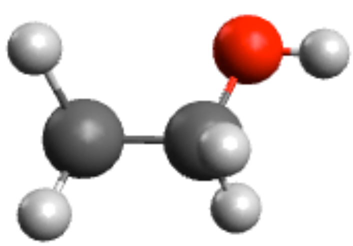


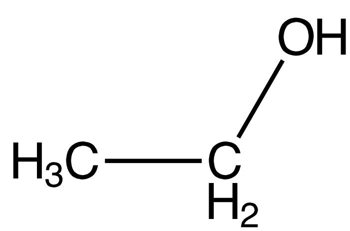


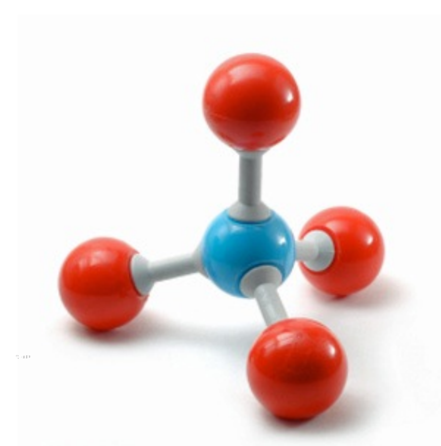


Applying the Properties of Alcohols

- Biological systems can get fooled by the structure of small alcohols.
- They can try absorb and use them like water.
  - But they don’t quite work.
- This toxicity makes alcohols good disinfectants.

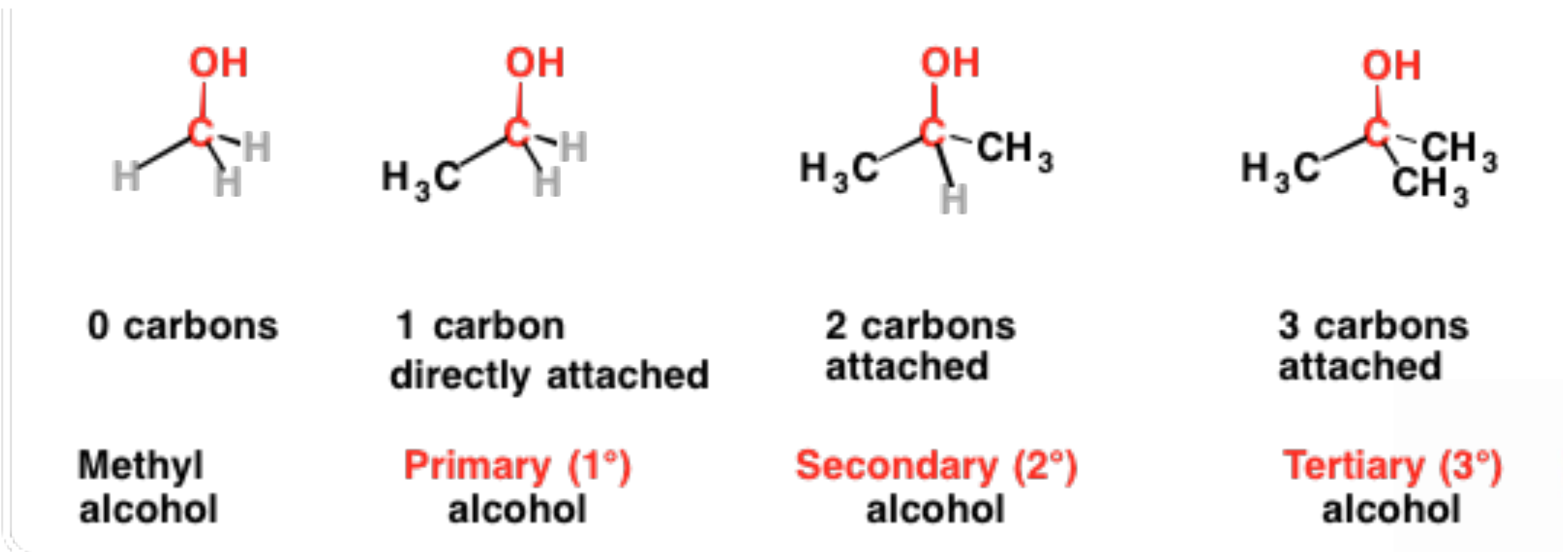


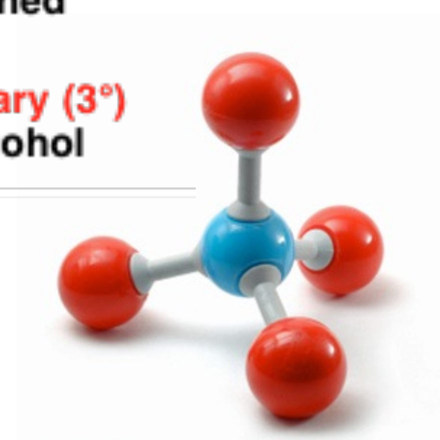




Alcohols

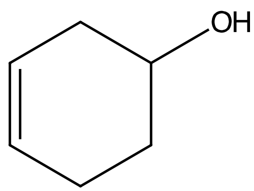
- Not all alcohols have the same properties.
- Alcohols (like halocarbons) are grouped into classes based on how many carbons are attached to the carbon bonded to the OH.
  - Beyond methyl alcohol (a unique case) all alcohols can be classified as: primary (1˚), secondary (2˚) or tertiary (3˚)



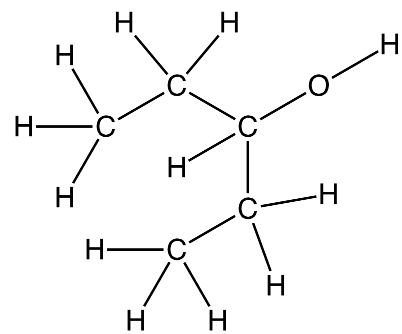


Subclasses of Alcohols

- Classify Each Alcohol as primary (1˚), secondary (2˚), or tertiary (3˚).



Secondary (2˚)



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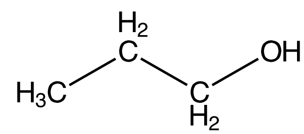
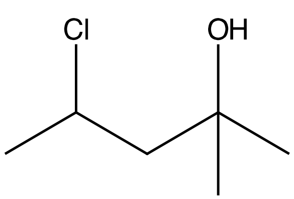
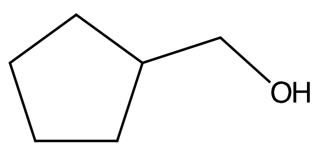


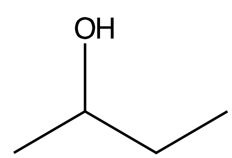
Primary (1˚)



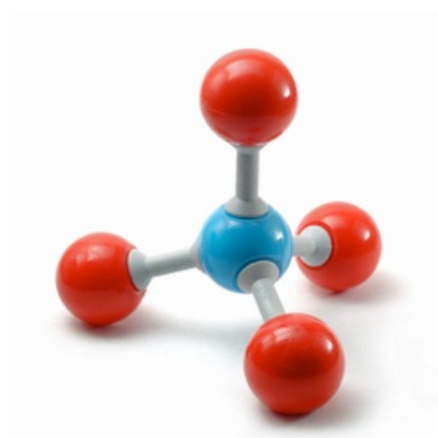
Tertiary (3˚)



Primary (1˚)



Secondary (2˚)



Ex24

Dehydration

- Substances Explored
  - Olefin Properties & Structure
    - Differences in Olefins
  - Alcohol Properties & Structure
    - Differences in Alcohols
- Dehydration of an Alcohol
  - Conditions
  - Mechanism
  - Selectivity
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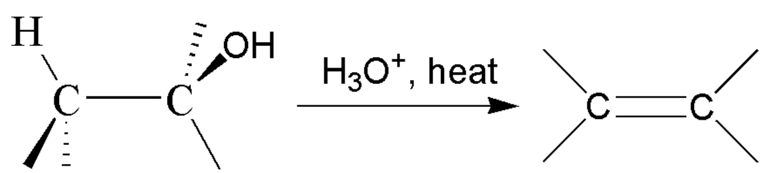
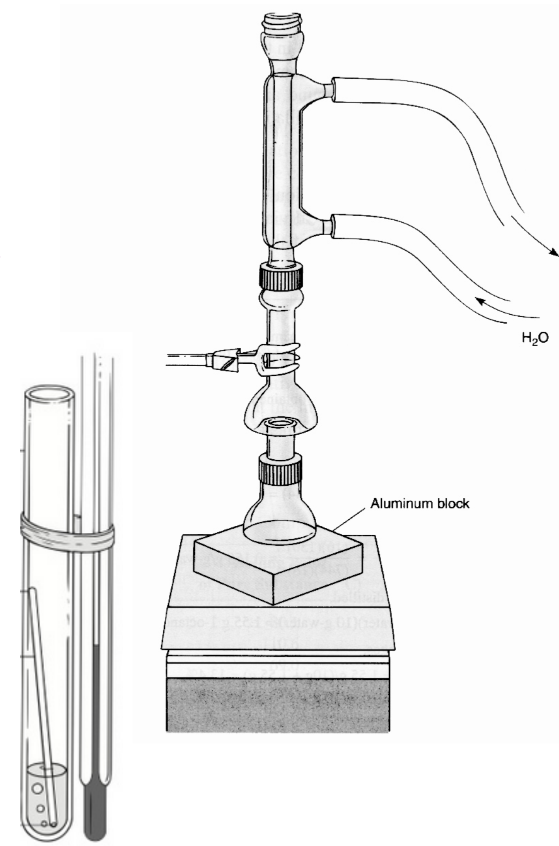
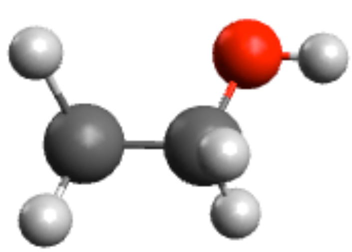
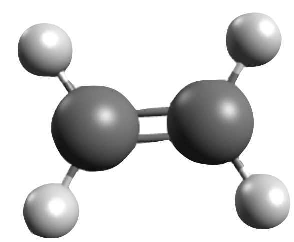
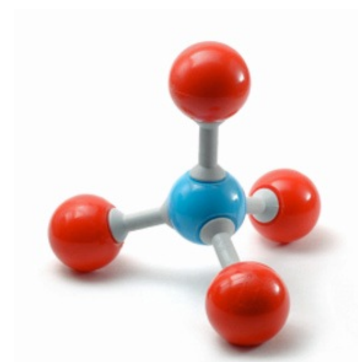
- For Next Week





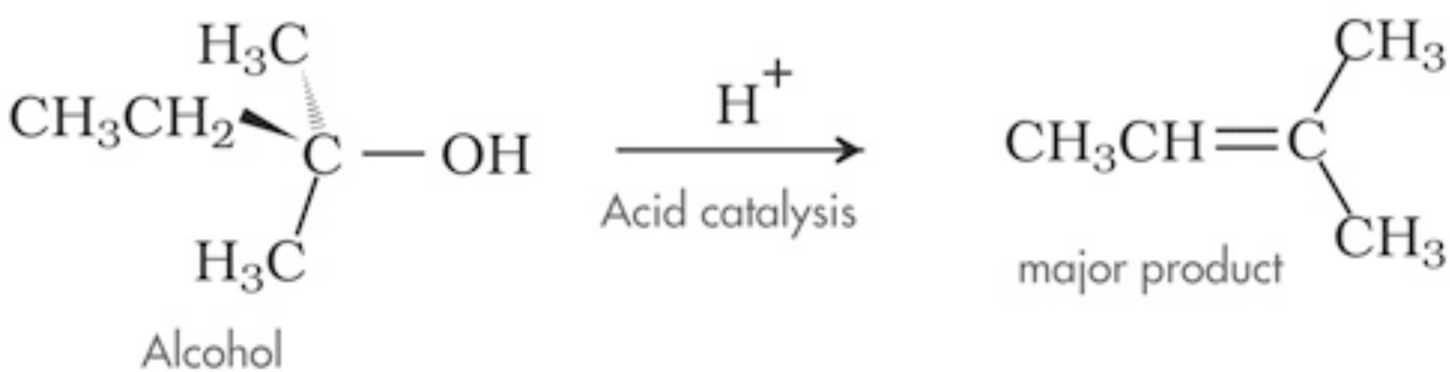




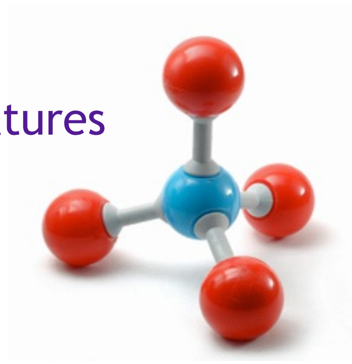


Dehydration

- Alcohols can be converted to olefins by heating them at hight temperature under strongly acidic conditions.
- This process eliminates water.
- Decomposition reactions that produce water are called dehydration reaction.

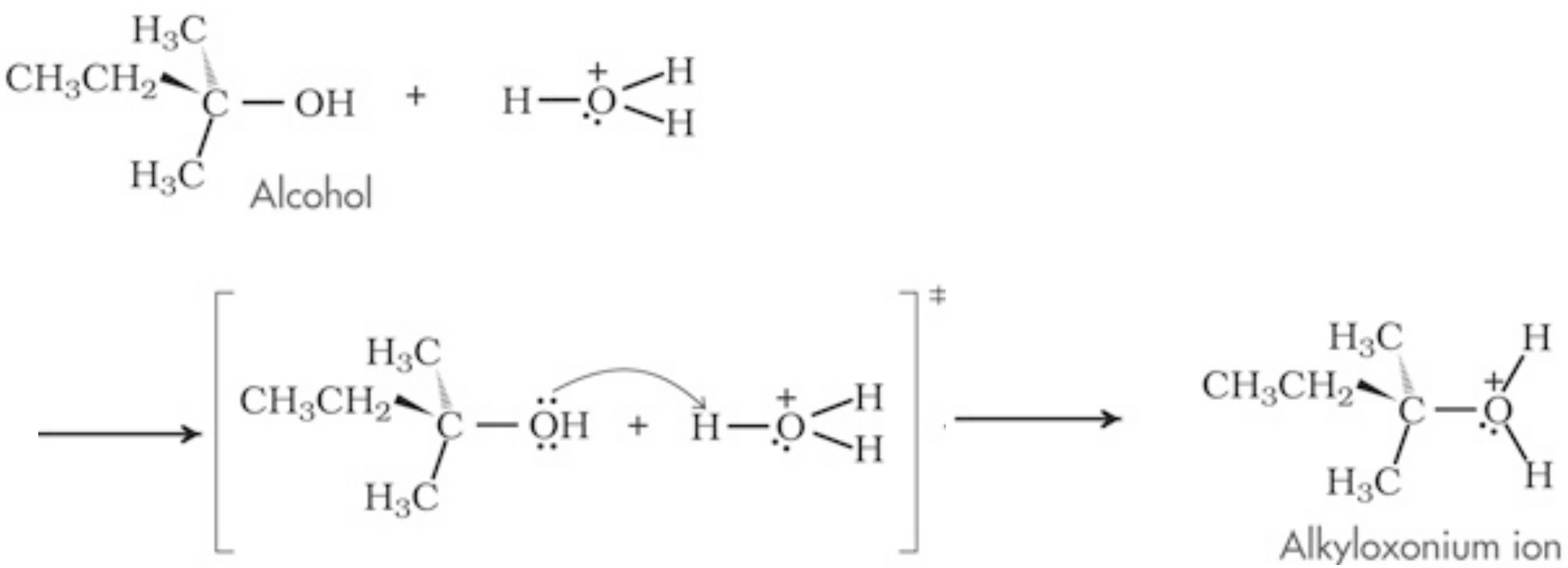


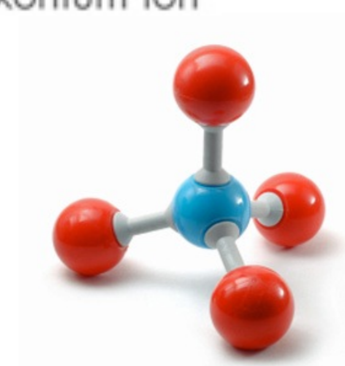
- This reaction is reversible. Dehydration is generally done at hight temperatures to drive the reaction entirely to the olefin product.



Dehydration

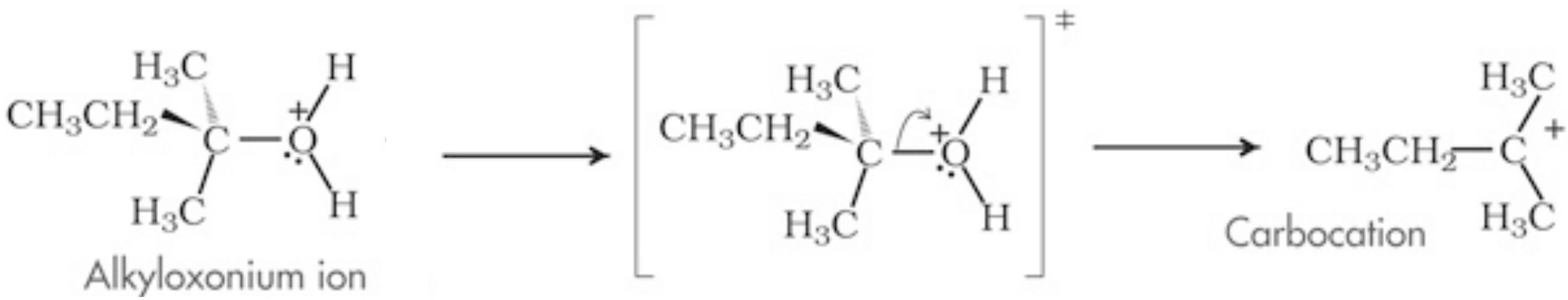
- One path by which this reaction occurs is an E1 mechanism.
- The first step is protonation of the alcohol.



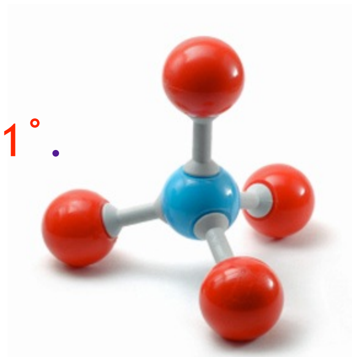


Dehydration

- One path by which this reaction occurs is an E1 mechanism.
- The second step is elimination of water to form a carbocation.

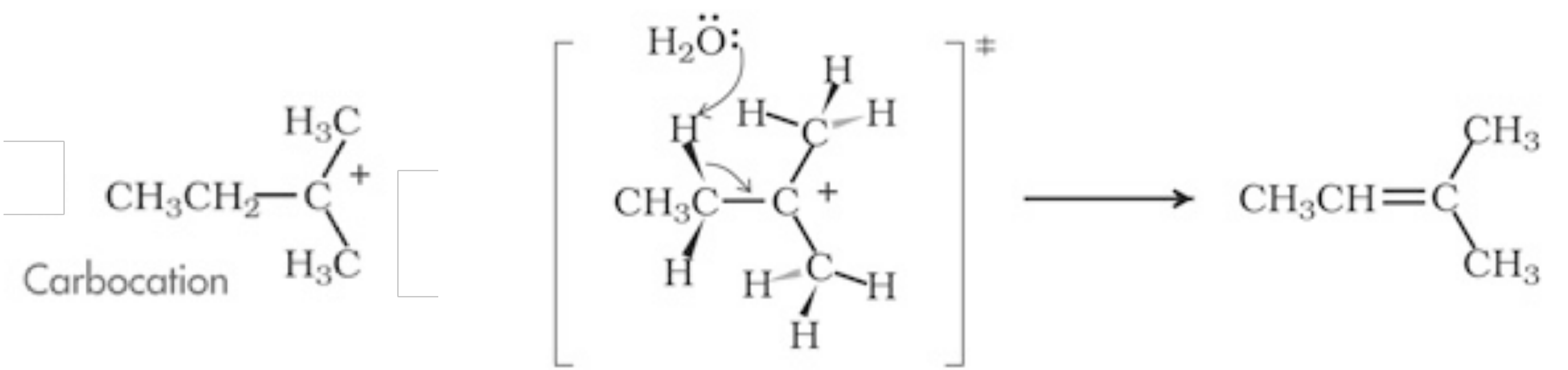


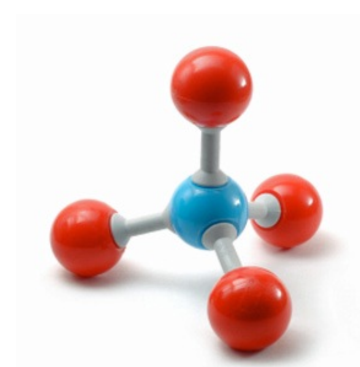
- Alkyl groups are electron donors and will stabilize the carbocation.
- As a result, dehydration occurs more readily with 3˚ alcohols than 2˚ than 1˚.



Dehydration

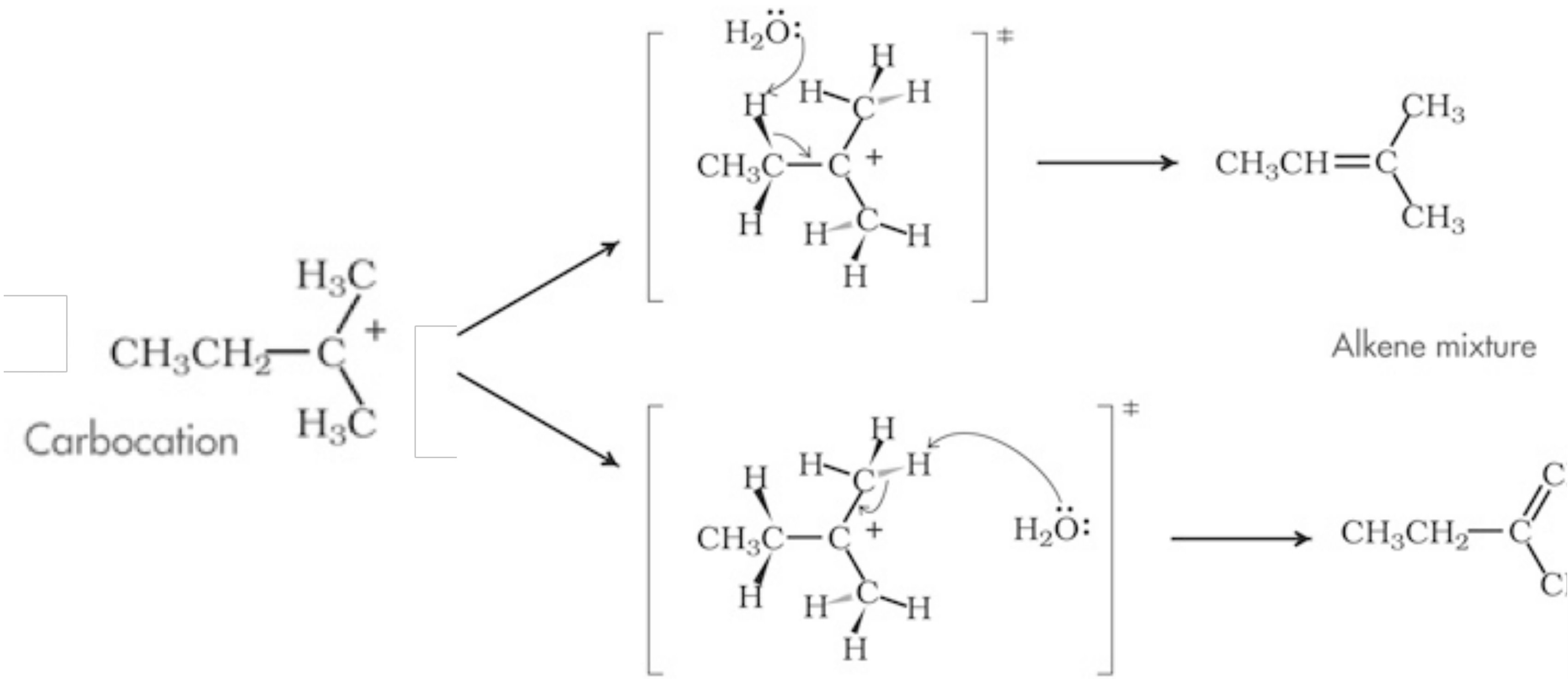
- One path by which this reaction occurs is an E1 mechanism.
- The third step is deprotonation of an alpha hydrogen to form the olefin.

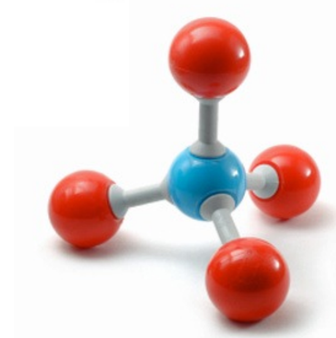




Dehydration

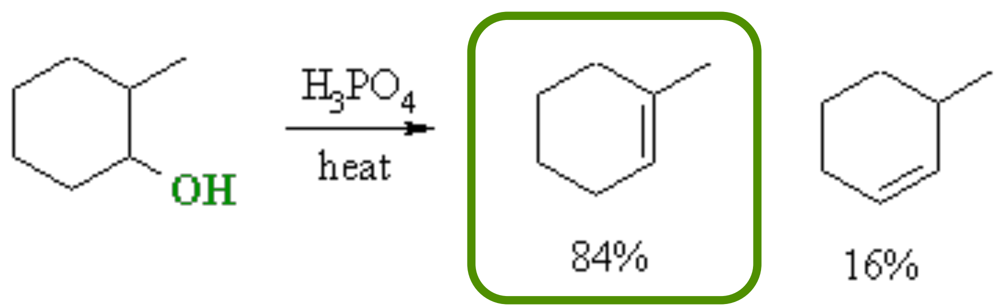
- In the third step, there is more than one kind of alpha hydrogen.
- More than one product is possible.

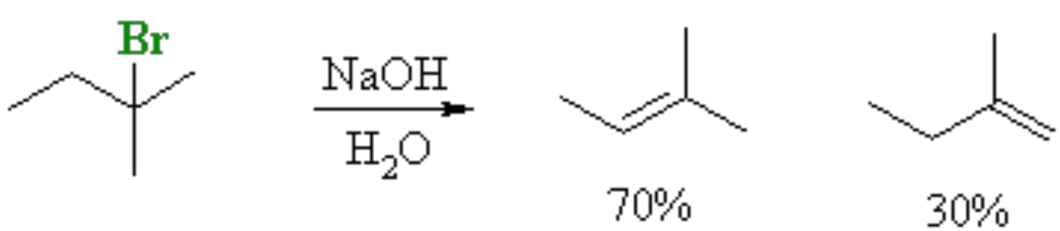


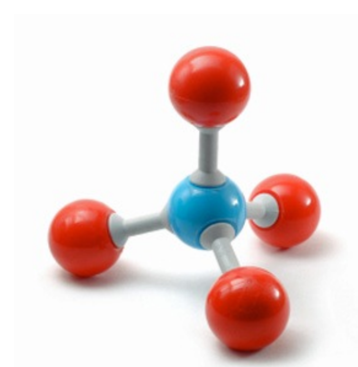


Dehydration

- At high temperatures, E1 elimination favors more substituted double bonds.
- Zaitsev's rule states that when more than one regioisomeric product is possible, the more substituted double bond is favored.
- Zaitsev’s rule applied to many olefin forming reactons, including dehydration of alcohols.

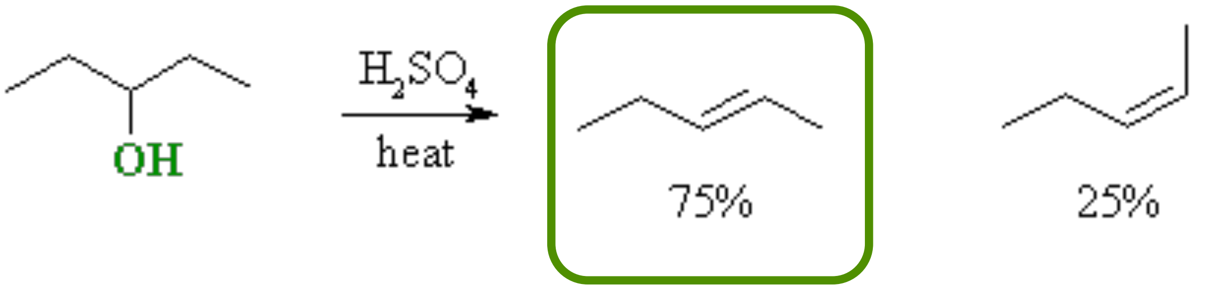


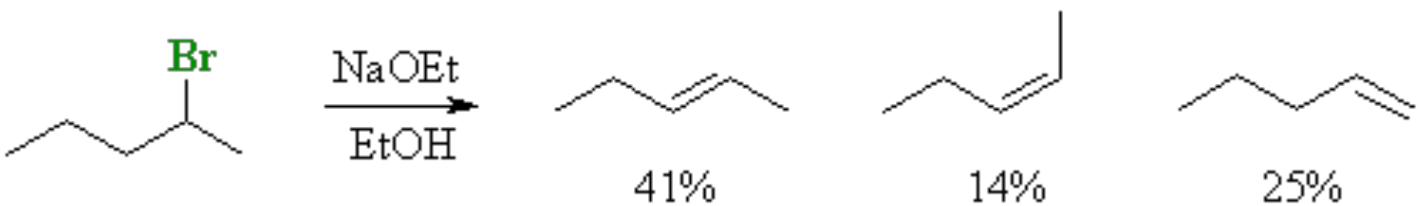


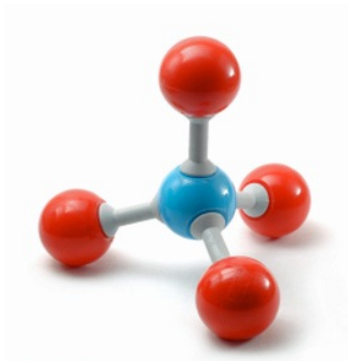


Dehydration

- Multiple stereoisomers may be possible as well.
- In forming a double bond cis or trans isomers may be possible.
- At higher temperatures, E1 eliminations favors trans double bonds.
  - Other types of elimination (E2) may not follow this rule.

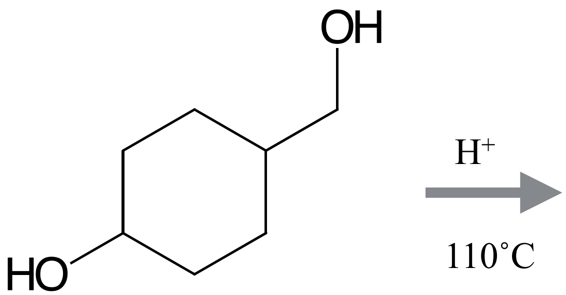




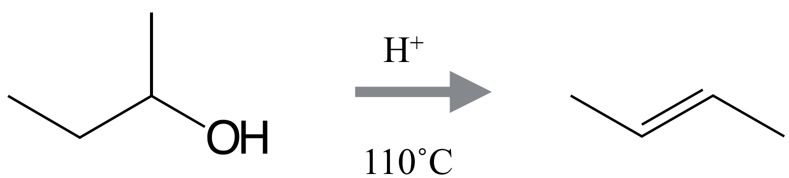


Dehydration

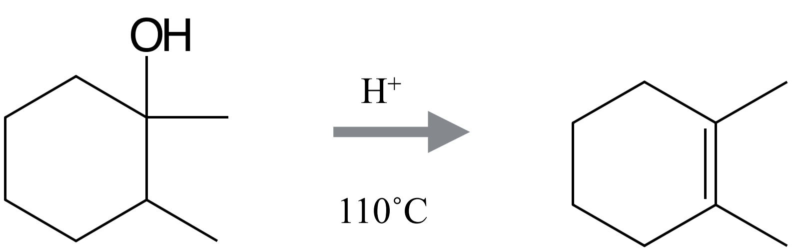
- Predict which olefin forms (assume only one double bond is formed).



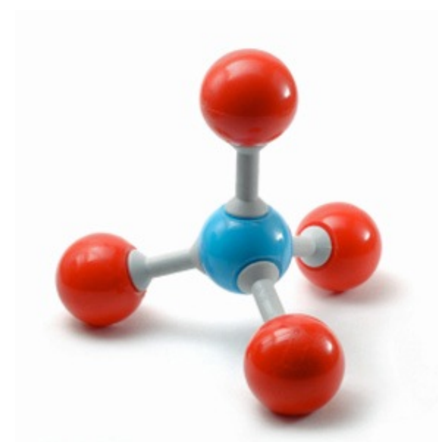
2˚ more reactive than 1˚



trans is favored over cis



most substituted olefin is favored



Ex24

Dehydration

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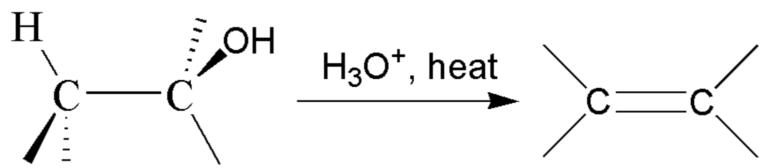
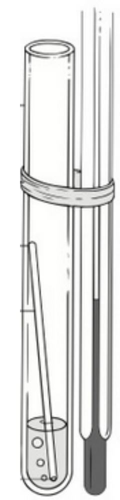
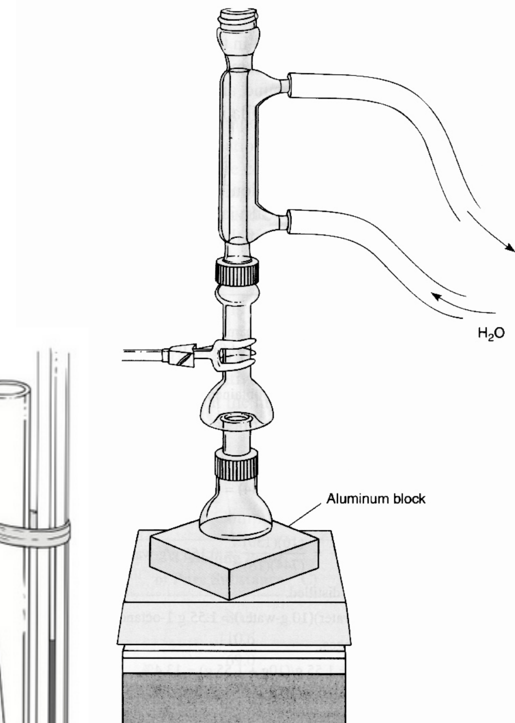
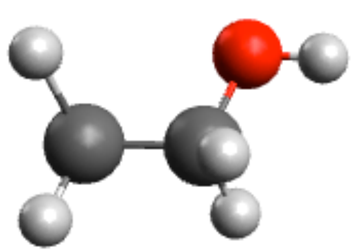
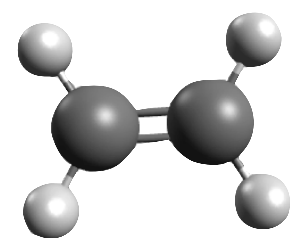
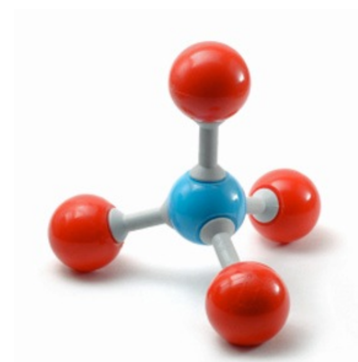






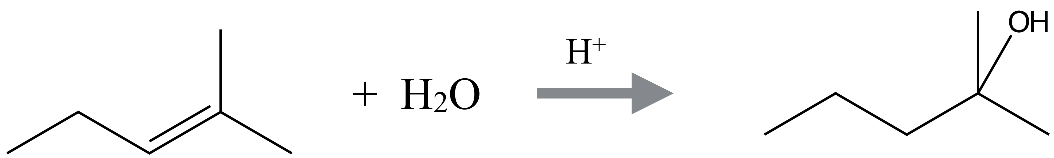


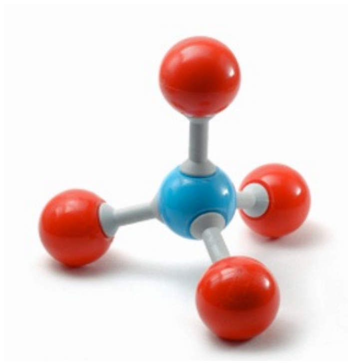




Hydration

- This reaction is reversible.
- With excess water, acidic conditions covert an olefin to an alcohol.
- Hydration reactions are the reverse of a dehydration reaction.

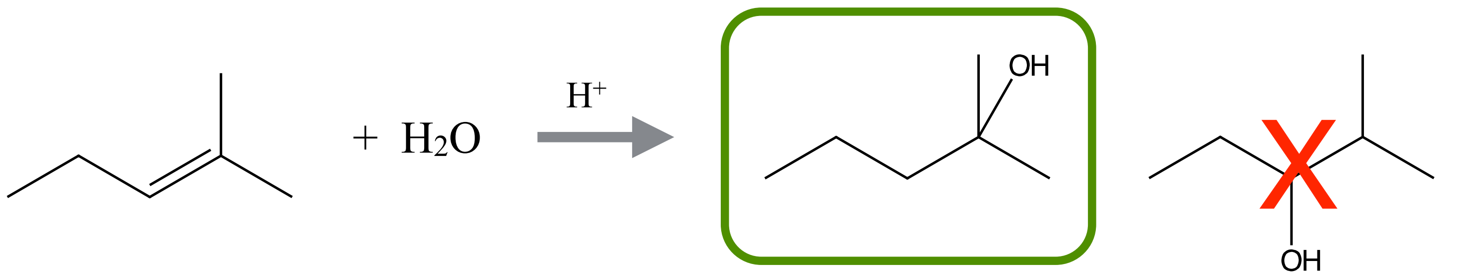




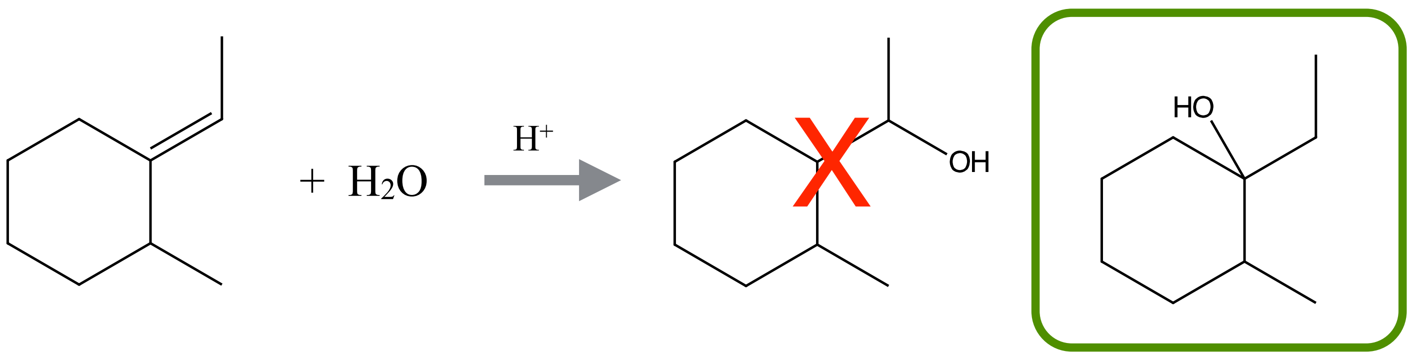
Hydration

- The same carbocation stability effects hydration.
- More substituted alcohols are formed preferentially.

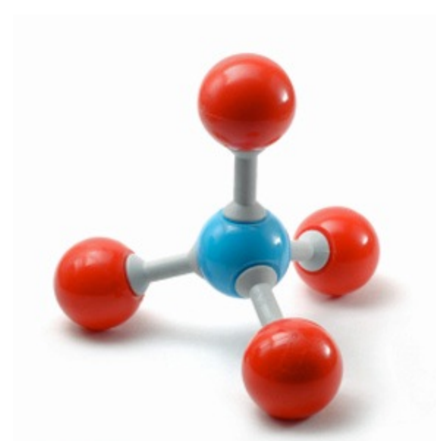
3° > 2° > 1° Alcohols from double bonds.



Tertiary (3°) Secondary (2°)

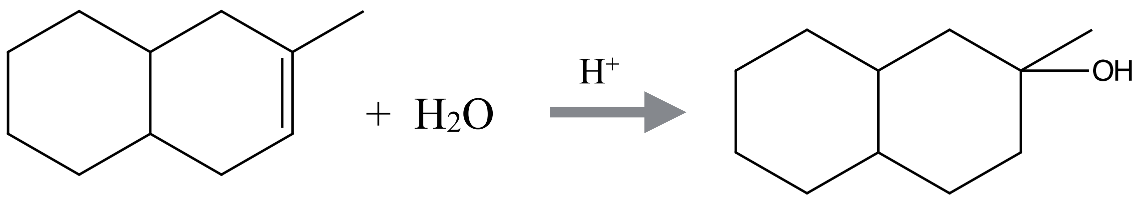


Secondary (2°) Tertiary (3°)

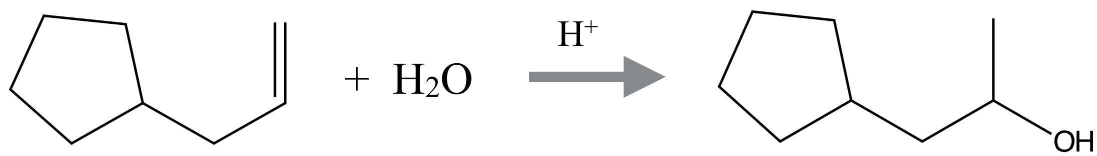


Hydration

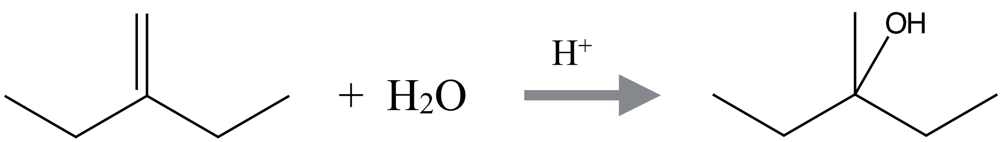
- Predict Which alcohol forms. Indicate whether it's a primary, secondary, or tertiary alcohol.



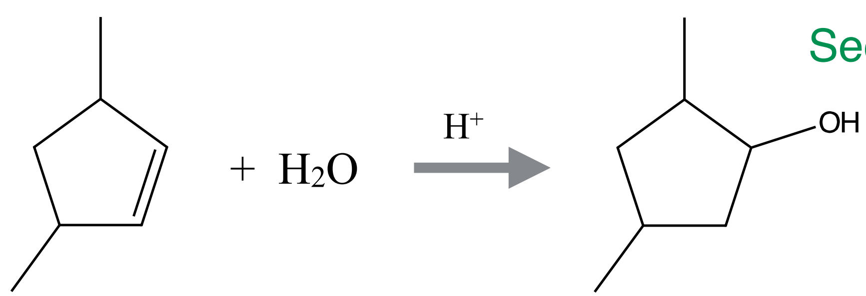
Tertiary (3˚)



Secondary (2˚)



Tertiary (3˚)



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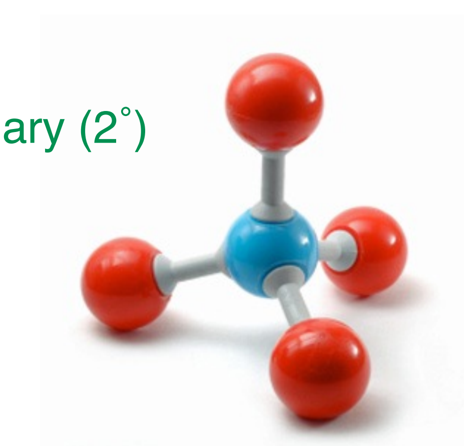

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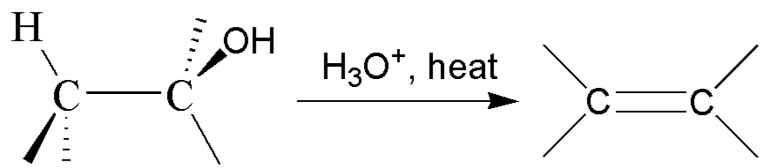
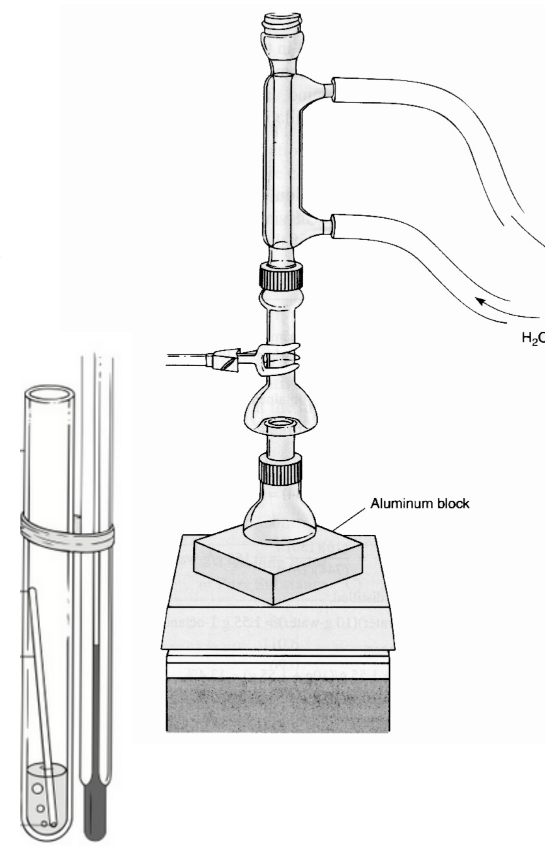
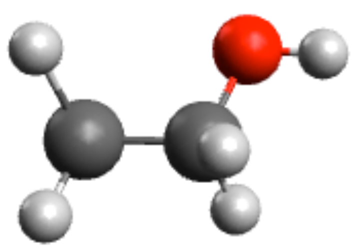
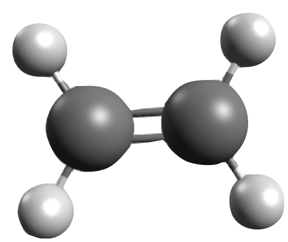
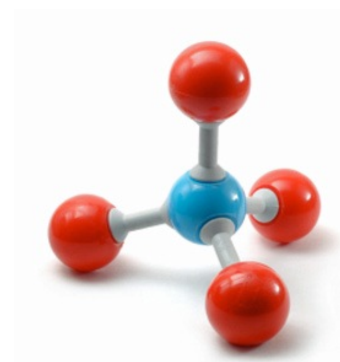






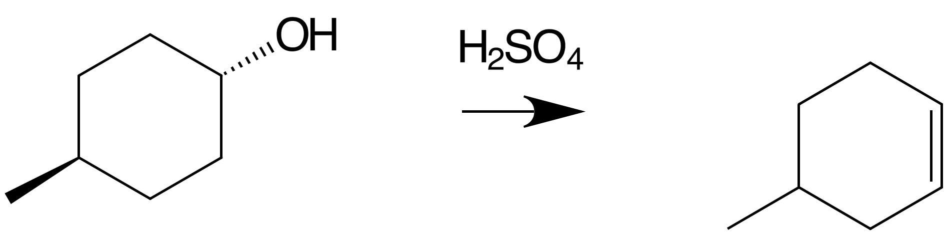




Preparation of 4-Methylcyclohexene

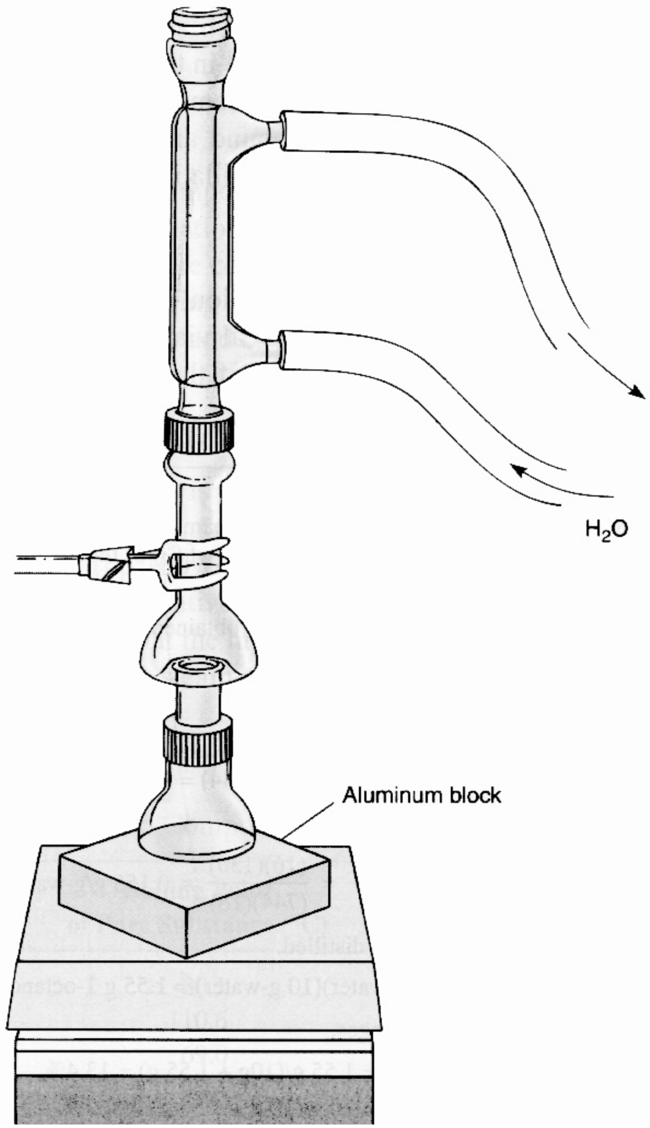
- OBJECTIVE: To prepare, isolate, purify and characterize 4-methyl cyclohexene.

- GOAL: To accomplish understand and implement the transformation of an alcohol to an olefin. To practice and refine our techniques for isolation, purification and characterization of an oil.



bp 173 ˚C

bp 104 ˚C

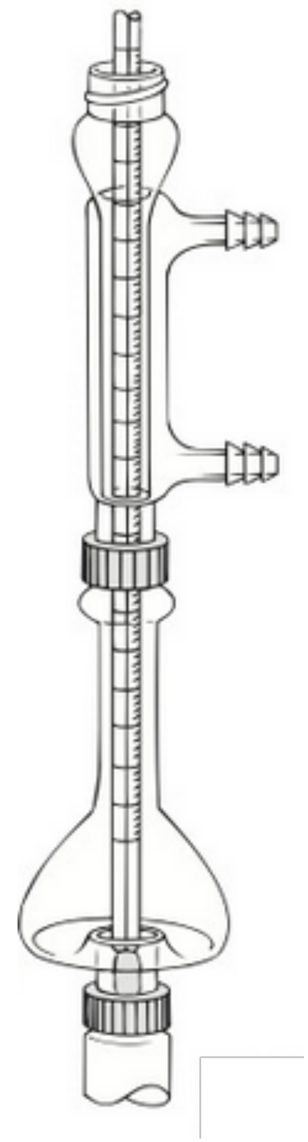


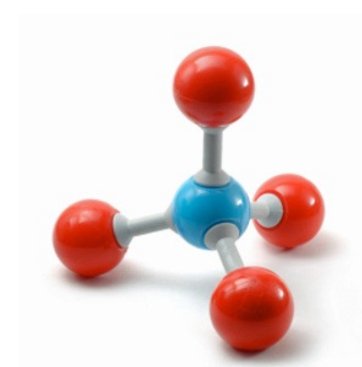
Preparation of 4-Methylcyclohexene

- Setup
  - Prepare a sand bath with electronic thermometer in the hood.
  - Prepare a water condenser for reflux.
  - Prepare a Hickman distillation head.

  - Pre-weigh a 5 mL conical flask.
    - Add 1.5 mL 4-methyl cyclohexanol
      - d = 0.92 g/mL mm 114.19 mg/mol
    - Reweigh reaction vessel to get weight of starting material.
    - Add boiling chip.

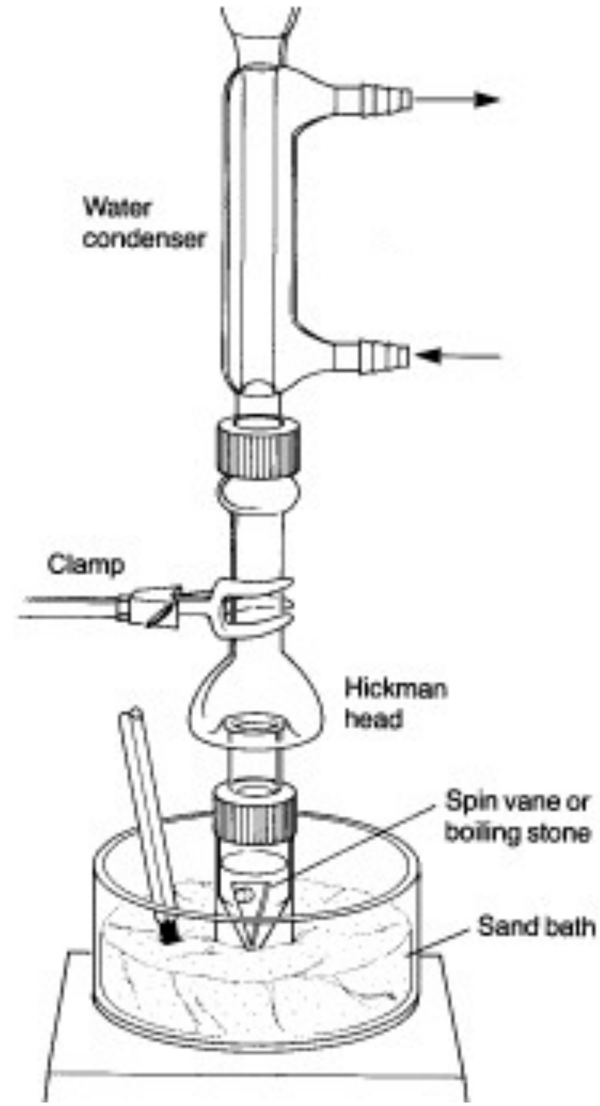
  - By pipet add:
    - 0.40 mL concentrated (85%) H_3PO_4
    - Add six drops concentrated H_2SO_4
      - CAUTION:
        This is 18 M sulfuric acid. It will hurt you.





Preparation of 4-Methylcyclohexene

- Reaction
  - Install the reaction flask in the sand bath.
    - Sand should cover upper curve of flask.
  - Equip the distillation head to the flask.
  - Equip the condenser to the head.
  - Begin circulating water through the condenser.
  - Heat the sand bath to between 160-180˚C
    - You may need to add aluminum foil.
  - Collect distillate until no further reflux is observed.
    - When liquid in flask stops boiling, reflux will cease.



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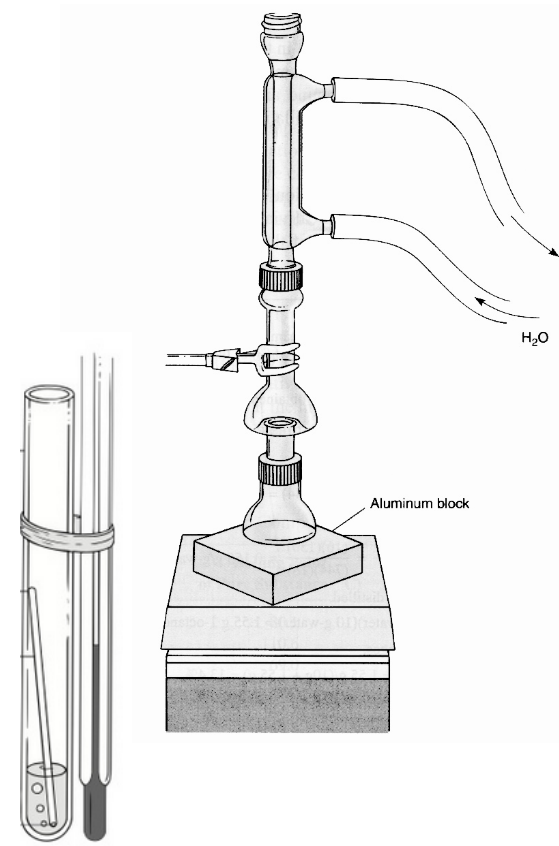
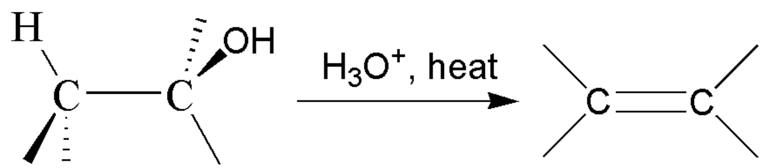
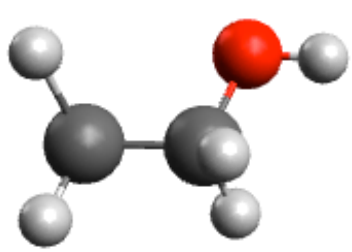
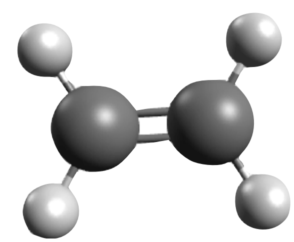
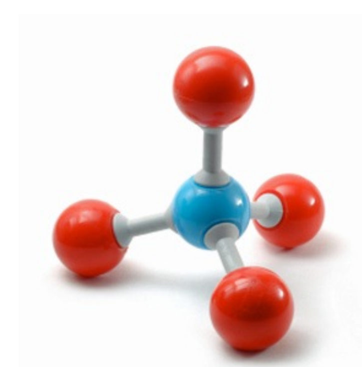




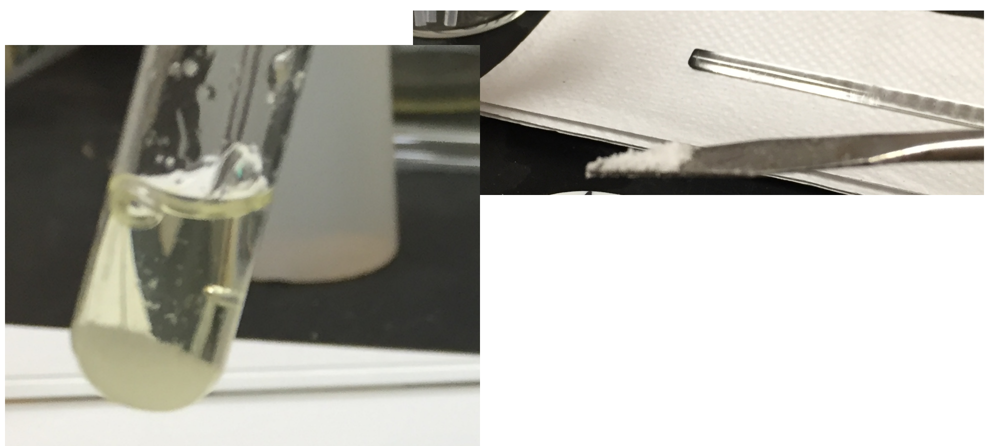






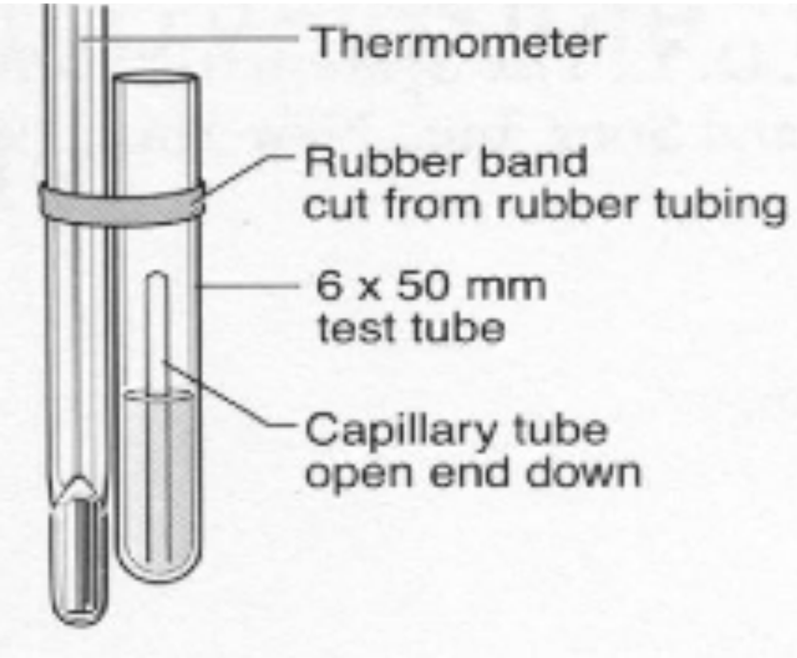
Preparation of 4-Methylcyclohexene

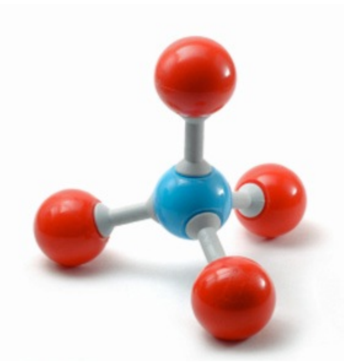
- Isolation & Drying:
  - After system cools to room temperature.
    - Transfer distillate to a clean dry 3 mL conical vial.
    - Wash walls of Hickman head carefully with 1.0 mL saturated NaCl solution.
    - Collect and add wash to 3 mL conical vial.
  - Allow layers to separate.
  - Pipette aqueous later (bottom) to a clean dry test tube.
  - Add minimal amount of sodium sulfate
  - Stopper and let dry 15 minutes.



Preparation of *tert*-Pentyl Chloride

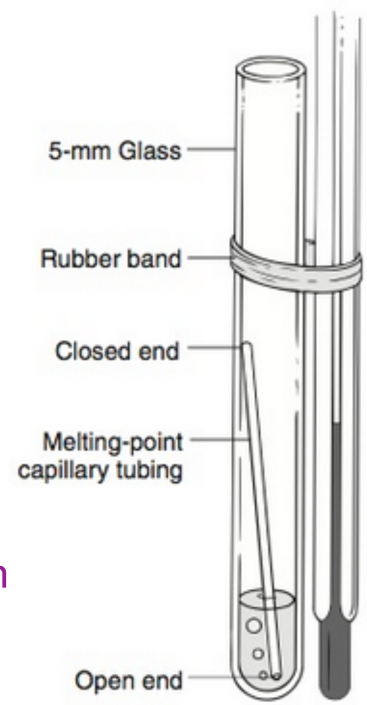
- Analysis:
  - Determine the purity of the sample you have collected.
  - Place about 1 cm depth of your collected product in a 50 mm test tube.
  - Attach a glass thermometer to the tube with a small rubber band.
  - Place a melting point capillary—open end down—in the liquid.

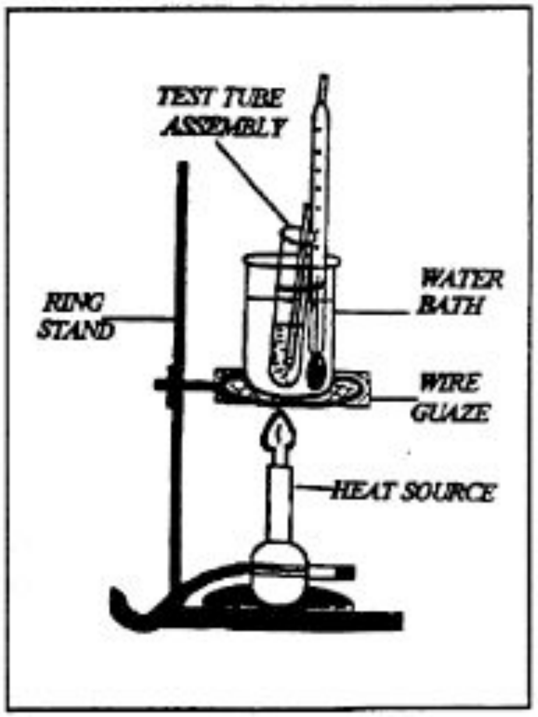


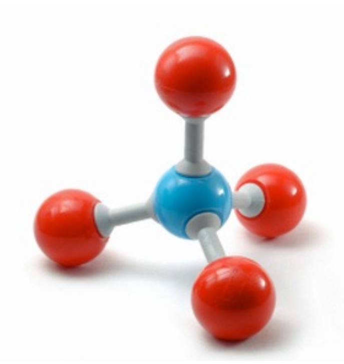


Preparation of *tert*-Pentyl Chloride

- Analysis:
  - Determine the purity of the sample you have collected.
  - Place about 1 cm depth of your collected product in a 50 mm test tube.
  - Attach a glass thermometer to the tube with a small rubber band.
  - Place a melting point capillary—open end down—in the liquid.
  - Secure the tube in a 150 mL beaker of water and slowly heat until a steady stream of bubbles is coming from the tip of the capillary.

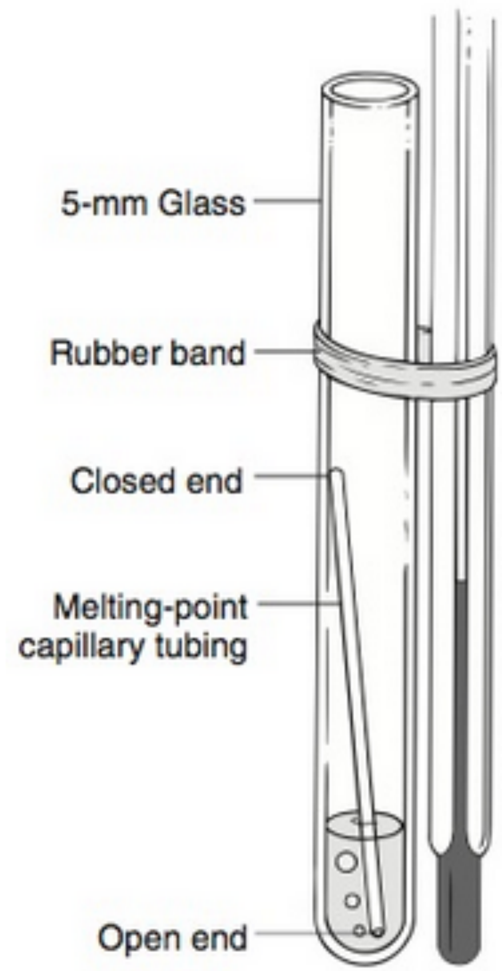


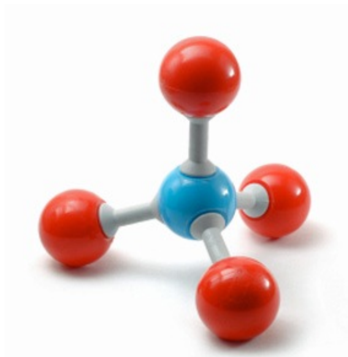




Preparation of *tert*-Pentyl Chloride

- Analysis:
  - Continue heating for one minute.
  - At this point the capillary will be filled with your unknown in gas state.
  - Remove the heat.
  - Bubbles will slowly stop.
  - When the last bubble comes out, your product in the capillary will turn liquid.
  - Record the temperature at which the last bubble comes out, that's your boiling point.
  - Report yield and boiling point.



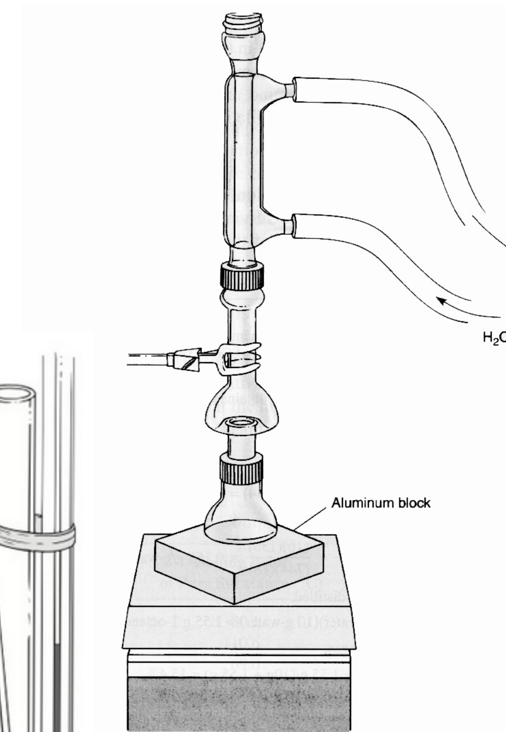


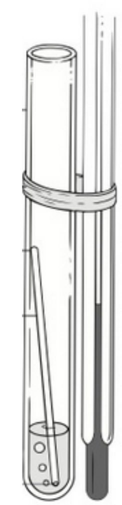
Ex24

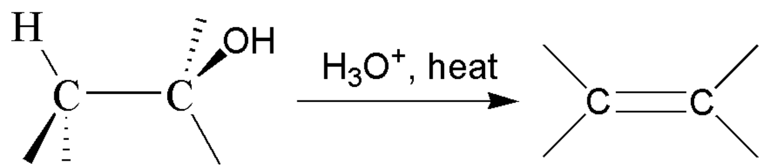
Dehydration

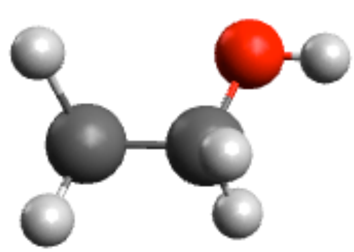
- Substances Explored
  - Olefin Properties & Structure
    - Differences in Olefins
  - Alcohol Properties & Structure
    - Differences in Alcohols
- Dehydration of an Alcohol
  - Conditions
  - Mechanism
  - Selectivity
  - Reverse Reaction
    - Hydration
- The Experiment
  - Setup
  - Reaction
  - Isolation & Drying
  - Analysis

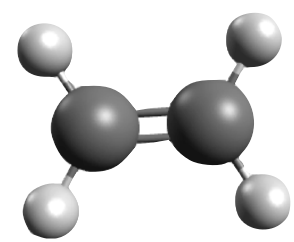
For Next Week

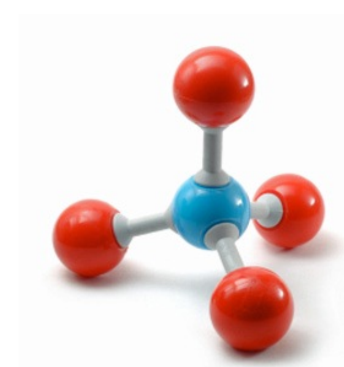






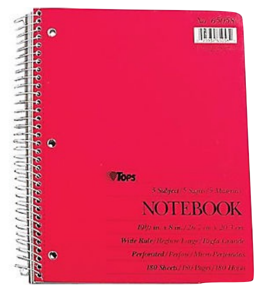


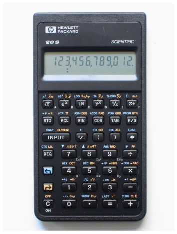


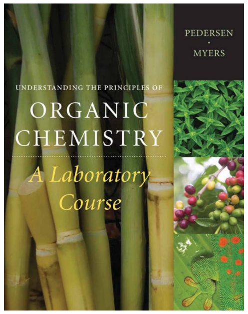


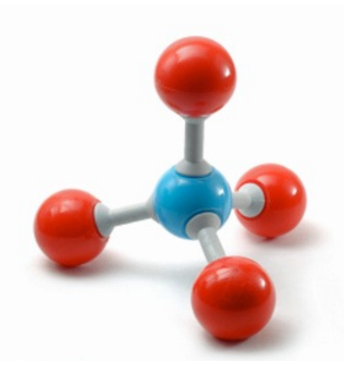
Next Meeting

- For next Meeting:
  - Bring to class:
    - Notebook
      - You will not be turning in notebooks, but this permanent record of your preparations, observations and notes will be essential to success in this class.
    - Textbook, calculator, pencils (yes, you can use pen)
    - Safety Glasses
      (you cannot participate without them)
  - Read through and take notes on:
    - Experiment 09: Synthesis of Aspirin
    - Esterification reactions in your lecture text
  - Produce and bring to class:
    - Your pre-lab for exp 09 (p71)
    - Your procedure summary for exp 09









Questions?