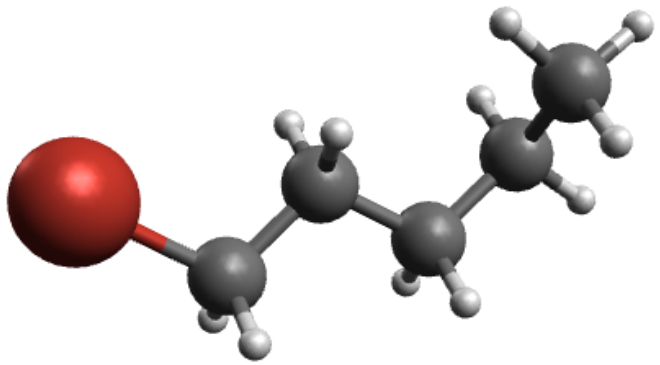
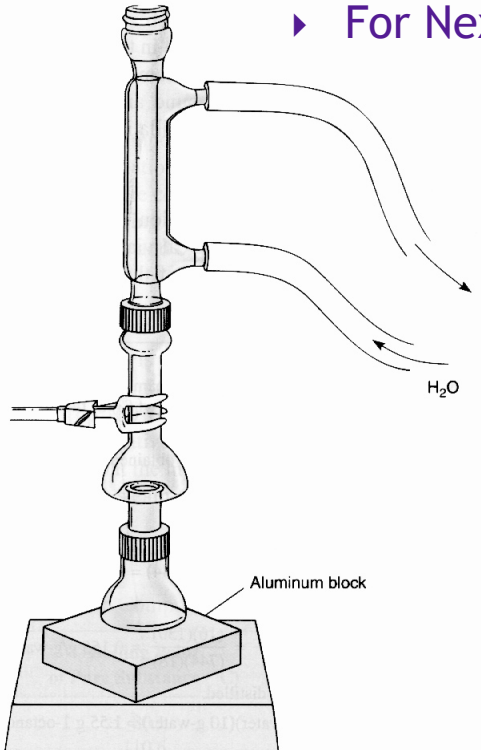
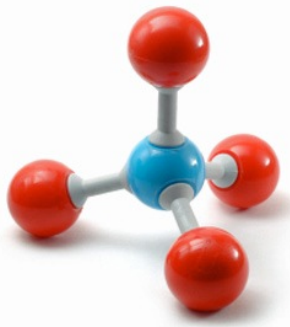
Ex23

Haloalkanes

- Alkyl Halides
  - Uses
  - Structure
    - Classification
  - Properties
  - Applications
- The Experiment
  - Setup
  - Reaction
  - Isolation
  - Purification
  - Analysis
- For Next Week

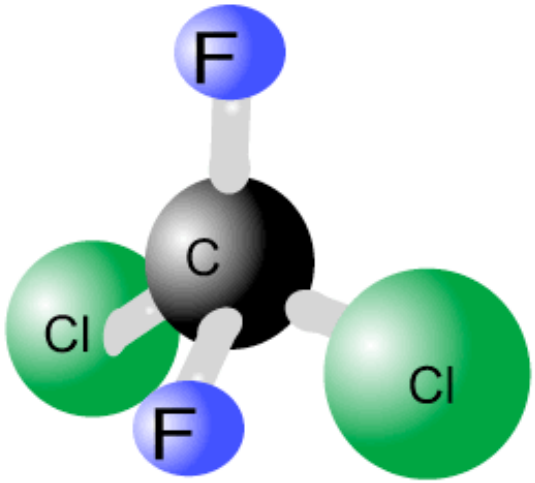




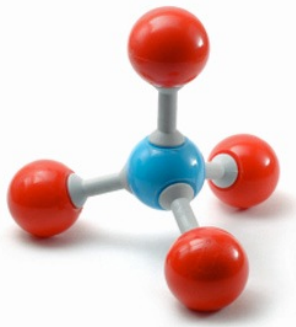


Haloalkanes

- Hydrocarbons are the foundation of organic compounds.
- The first modification to this theme is the replacement of a hydrogen with a halogen.
  - Haloalkanes are alkanes that contain one or more halogen atoms.
  - The halogens found in organic molecules are chlorine, bromine, fluorine, and iodine.
  - Haloalkanes are also called halogenated alkanes or alkyl halides.



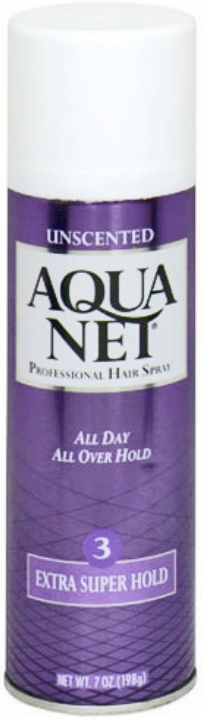
- Halolakanes are much less flammable than alkanes.
  - Because of that reduced flammability they were often used as fire retardants.
  - Halon 1211 bromochlorodifluoromethane (CF_2ClBr) is a very effective fire retardant because it's low molecular weight makes it a gas at room temperature—allowing it to be it's own propellant in pressurized fire extinguishers.

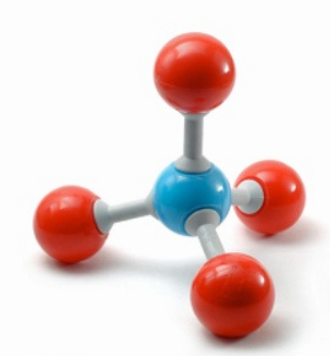


Haloalkanes

- Expanding gas can be used to deliver other substances, like hair spray oils
- Expanding gas also absorbs heat, it's the basis for modern refrigerators.

- Alkanes are a poor choice for these applications because of their flammability.
- Haloalkanes have been used for these purposes instead.





Haloalkanes

- Generically, these low boiling haloalkanes are described as CFC's (chlorofluorocarbons).
- They are also commonly known by the DuPont brand name Freon.
  - The most common representative is dichlorodifluoromethane (R-12 or Freon-12).
  - Many CFCs have been widely used as refrigerants, propellants (in aerosol applications), and solvents.
- Because volatile chlorine containing compounds contribute to ozone depletion in the upper atmosphere, the manufacture of such compounds has been phased out under the Montreal Protocol.
- They are being replaced with other haloalkanes such as hydrofluorocarbons (HFCs).

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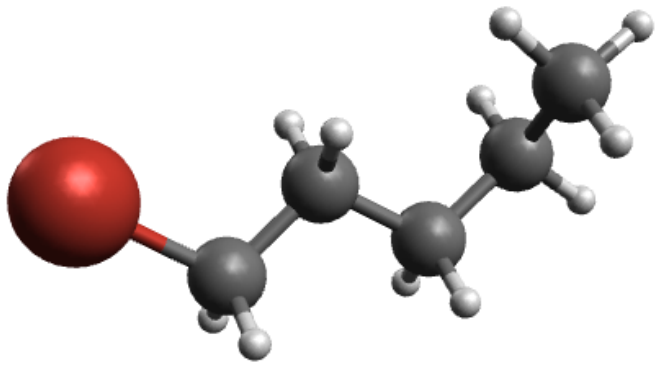
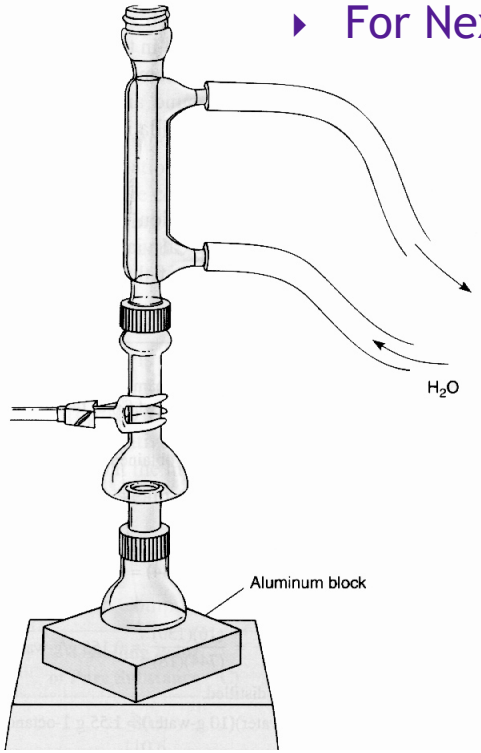
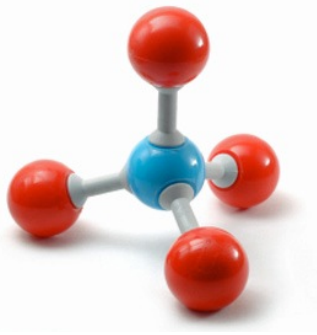
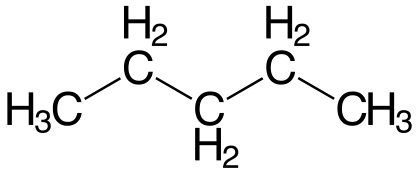


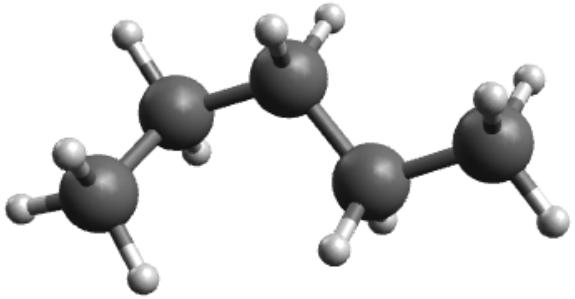


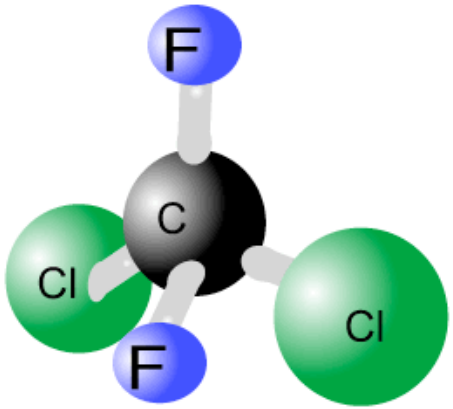


Haloalkanes

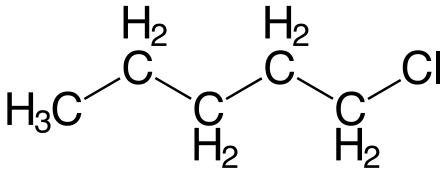
- Hydrocarbons are the foundation of organic compounds.

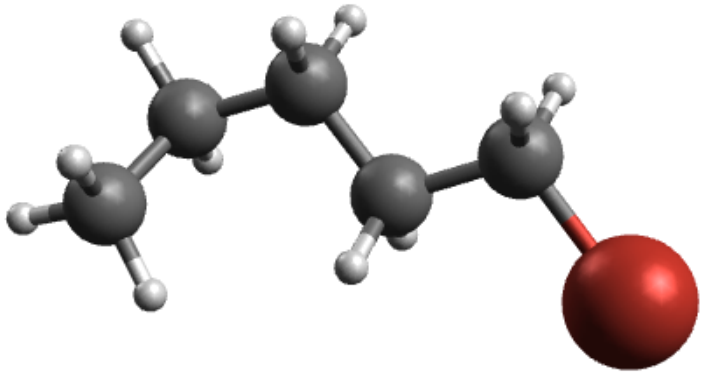


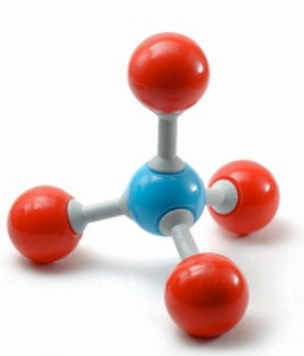




- The first modification to this theme is the replacement of a hydrogen with a halogen—the haloalkane family (also called alkyl halides)

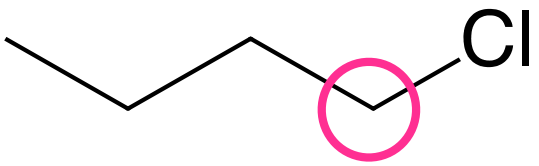




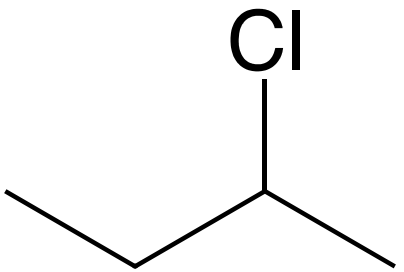


Haloalkanes

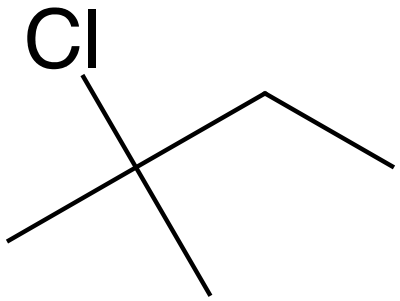
- Halolakanes are substituted hydrocarbons.
  - So are alcohols.
- Simple substituted hydrocarbons are classified by the number of carbon atoms adjacent to the substituted atom.
  - If there is one carbon adjacent, it's a primary haloalkane.



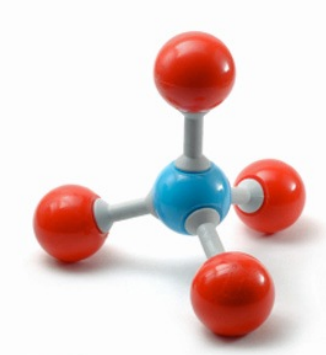
primary (1˚) haloalkane



secondary (2˚) haloalkane



tertiary (3˚) haloalkane



Haloalkanes

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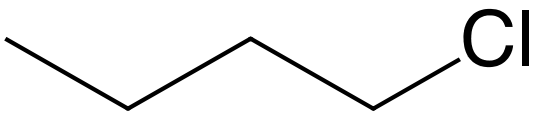
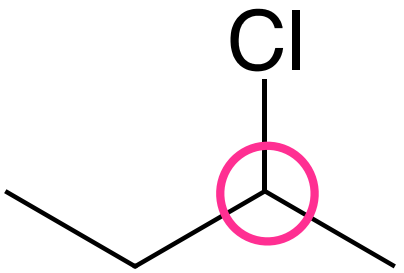
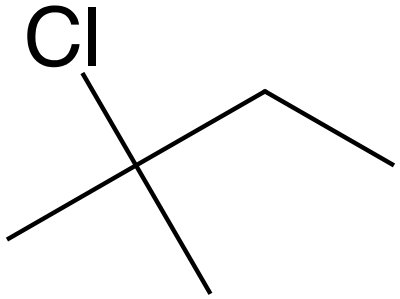
  - If there are two, it's secondary.



primary (1˚) haloalkane



secondary (2˚) haloalkane



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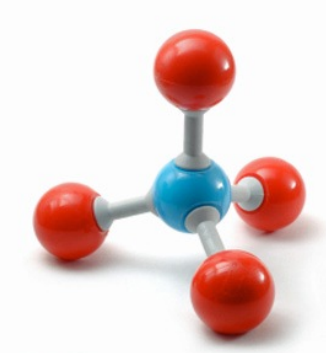

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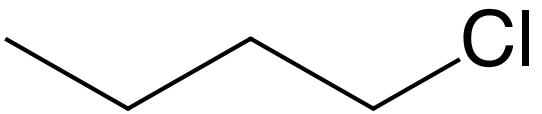
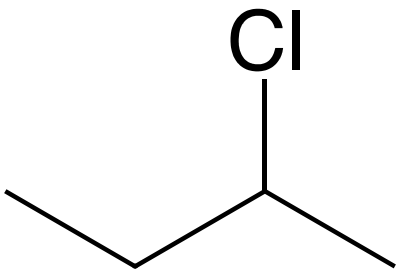
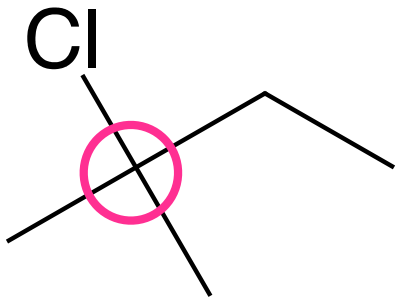
- Simple substituted hydrocarbons are classified by the number of carbon atoms adjacent to the substituted atom.
  - If there is one carbon adjacent, it's a primary haloalkane.
  - If there are two, it's secondary.
  - Tertiary halocarbons have three adjacent carbons.



primary (1˚) haloalkane



secondary (2˚) haloalkane



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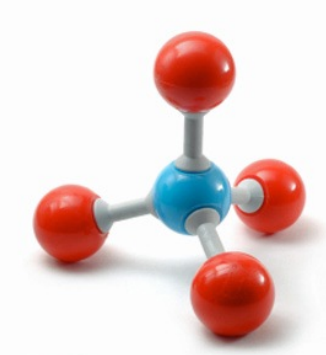

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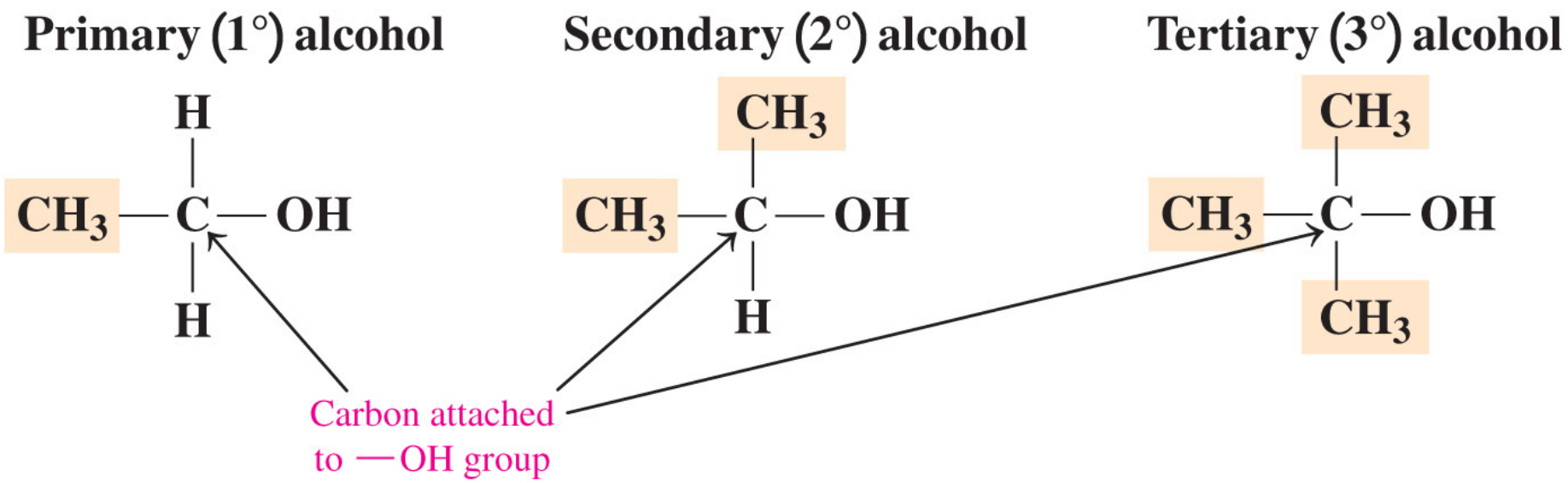
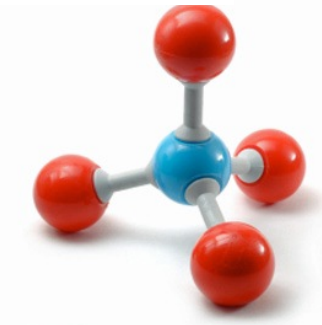
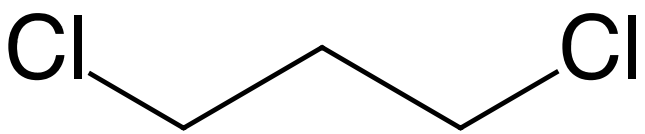


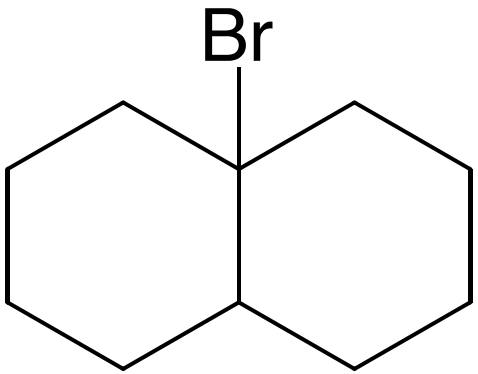


Haloalkanes

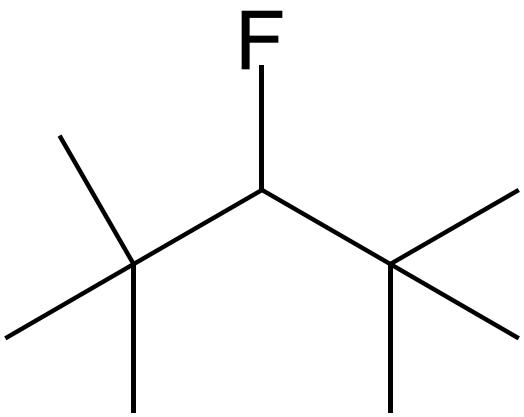
- Can you classify the haloalkane?



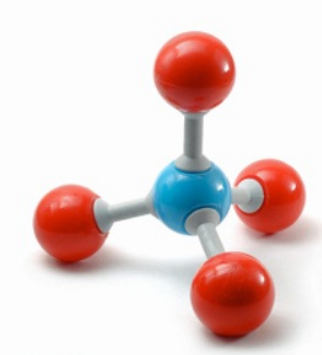
primary (1˚)
haloalkane



tertiary (3˚)
haloalkane



secondary (2˚)
haloalkane



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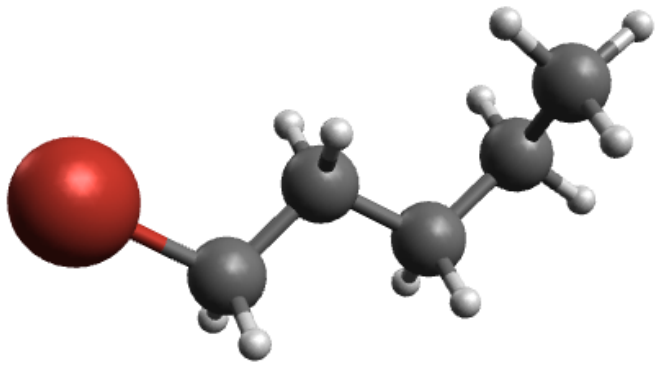
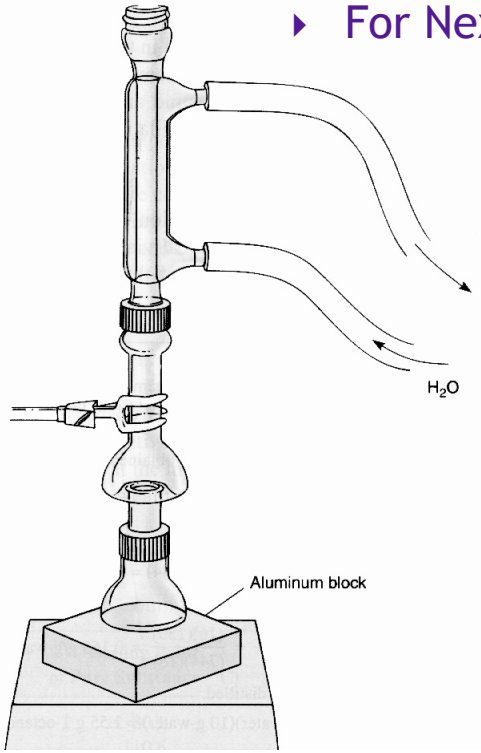
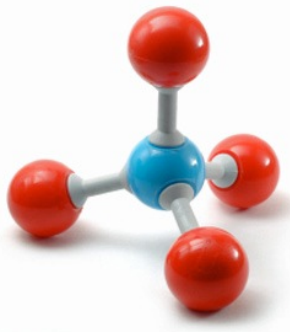
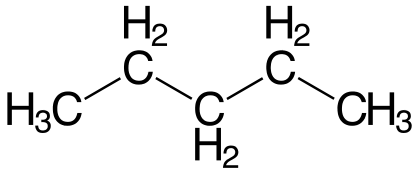


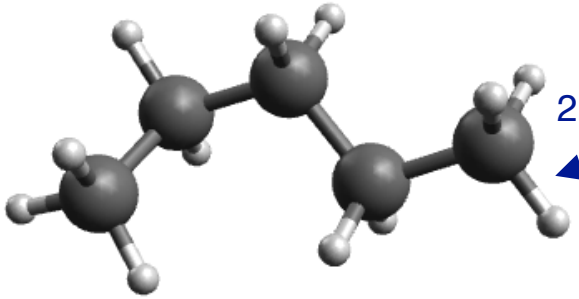




Haloalkanes

- Hydrocarbons are the foundation of organic compounds.
  - They contain no polar covalent bonds. They have no dipoles.

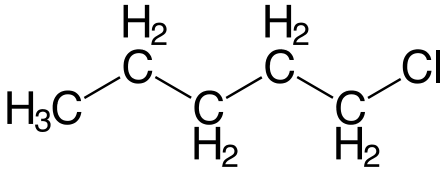


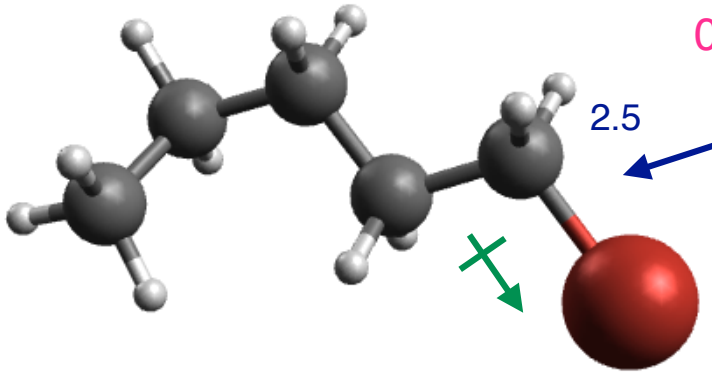


ΔEN 0.4

< 0.5 — purely covalent

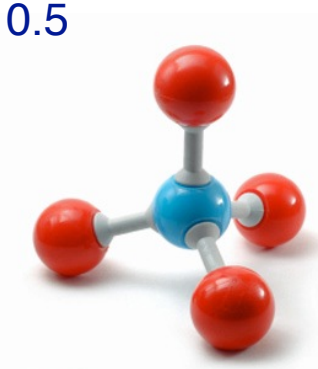
- The first modification to this theme is the replacement of a hydrogen with a halogen—the haloalkane family (also called alkyl halides)
  - Halogens have greater electronegativity and introduce dipoles.





0.5-1.9 — polar covalent

ΔEN 0.5

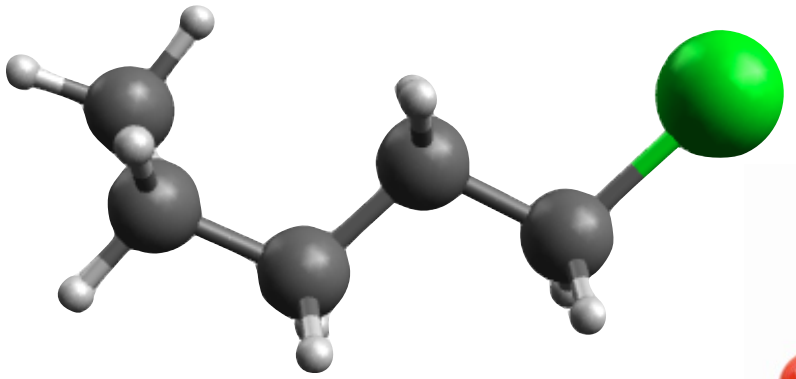


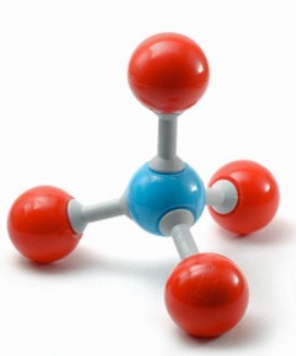
Haloalkanes

- Haloalkanes have a dipole and therefore experience dipole-dipole Van der Waals.
- This additional intermolecular force results in higher boiling points than the corresponding alkane.

R—X

Boiling Points of Haloalkanes (°C)		
R	X = H	F
CH_3	-161.7	-78.4
CH_3CH_2	-88.6	-37.7
$CH_3(CH_2)_2$	-42.1	-2.5
$CH_3(CH_2)_3$	-0.5	32.5
$CH_3(CH_2)_4$	36.1	62.8
$CH_3(CH_2)_7$	125.7	142.0



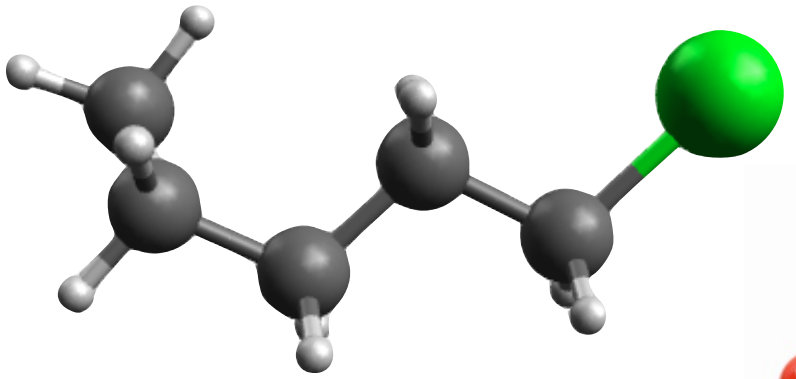


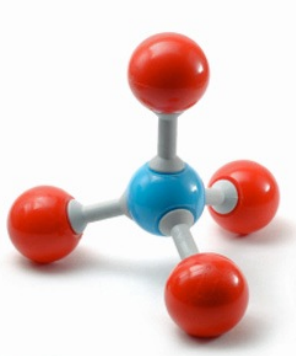
Haloalkanes

- Haloalkanes have a dipole and therefore experience dipole-dipole Van der Waals.
- This additional intermolecular force results in higher boiling points than the corresponding alkane.
- Boiling points also increase with higher period halides.
- Why?

R—X

Boiling Points of Haloalkanes (°C)					
R X =	H	F	Cl	Br	I
CH_3	-161.7	-78.4	-24.2	3.6	42.4
CH_3CH_2	-88.6	-37.7	12.3	38.4	72.3
$CH_3(CH_2)_2$	-42.1	-2.5	46.6	71.0	102.5
$CH_3(CH_2)_3$	-0.5	32.5	78.4	101.6	130.5
$CH_3(CH_2)_4$	36.1	62.8	107.8	129.6	157.0
$CH_3(CH_2)_7$	125.7	142.0	182.0	200.3	225.5

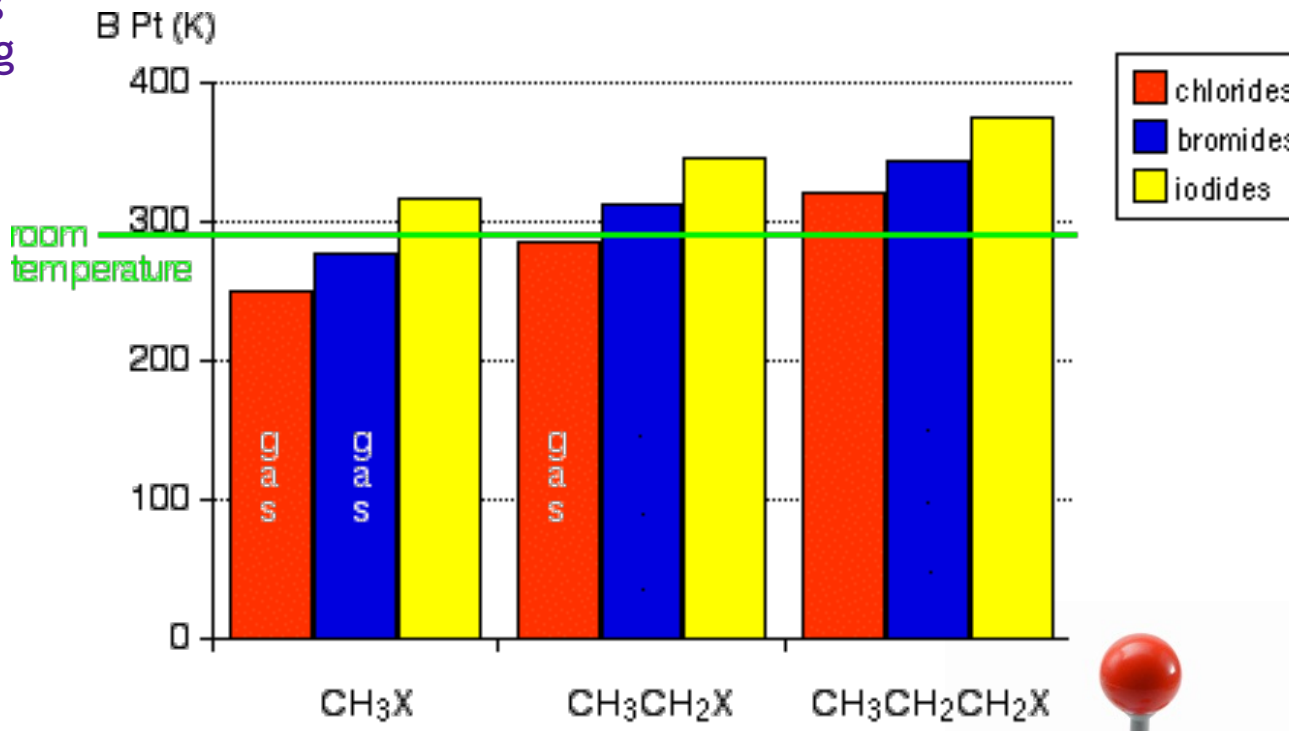


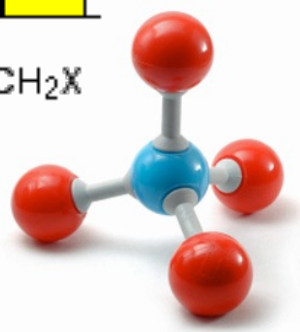


Haloalkanes

- Haloalkanes have a dipole and therefore experience dipole-dipole Van der Waals.
- This additional intermolecular force results in higher boiling points than the corresponding alkane.
- Boiling points also increase with higher period halides.
- Atomic radius increases with higher period elements.
- Greater atomic radius means greater London-Dispersion forces.

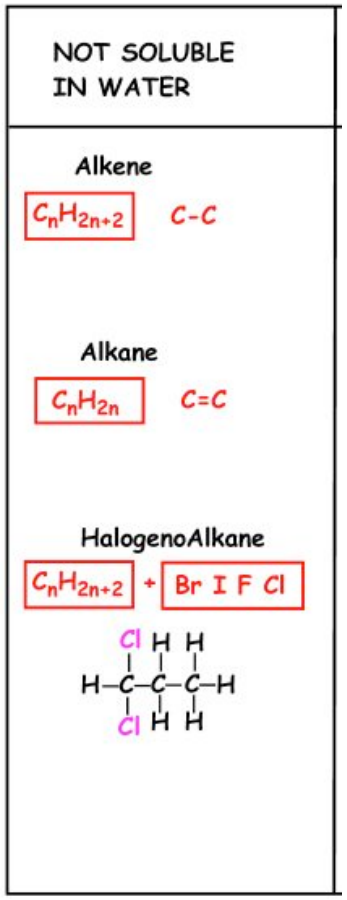
R—X

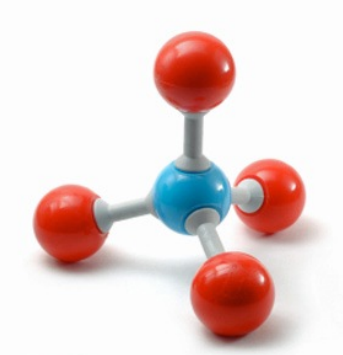




Water Solubility

- Unlike other polar functional groups, haloalkanes cannot participate in hydrogen bonding.
- Halogenated solvents are generally not soluble in or miscible with water.

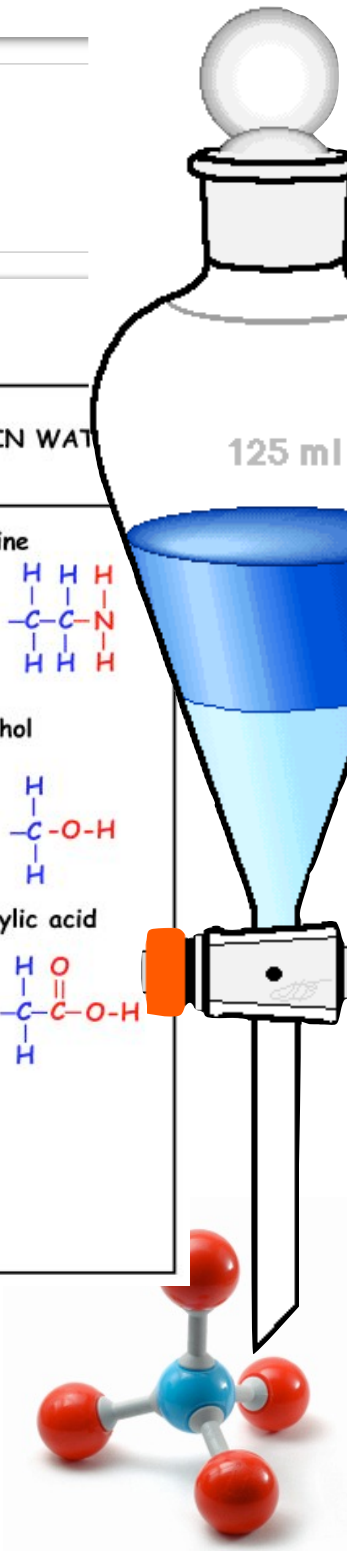




Water Solubility

- Unlike other polar functional groups, haloalkanes cannot participate in hydrogen bonding.
- Halogenated solvents are generally not soluble in or miscible with water.
- Halogenated solvents are therefore a useful extraction choice in getting polar organics out of aqueous solutions.

NOT SOLUBLE IN WATER	SOMEWHAT SOLUBLE IN WATER	SOLUBLE IN WAT
Alkene C_nH_{2n+2} C-C	Aldehyde CHO	Amine NH_2
Alkane C_nH_{2n} C=C	Ketone COC	Alcohol OH
HalogenoAlkane C_nH_{2n+2} + Br I F Cl	Amide CON	Carboxylic acid COOH
	Ester COOC	



Density

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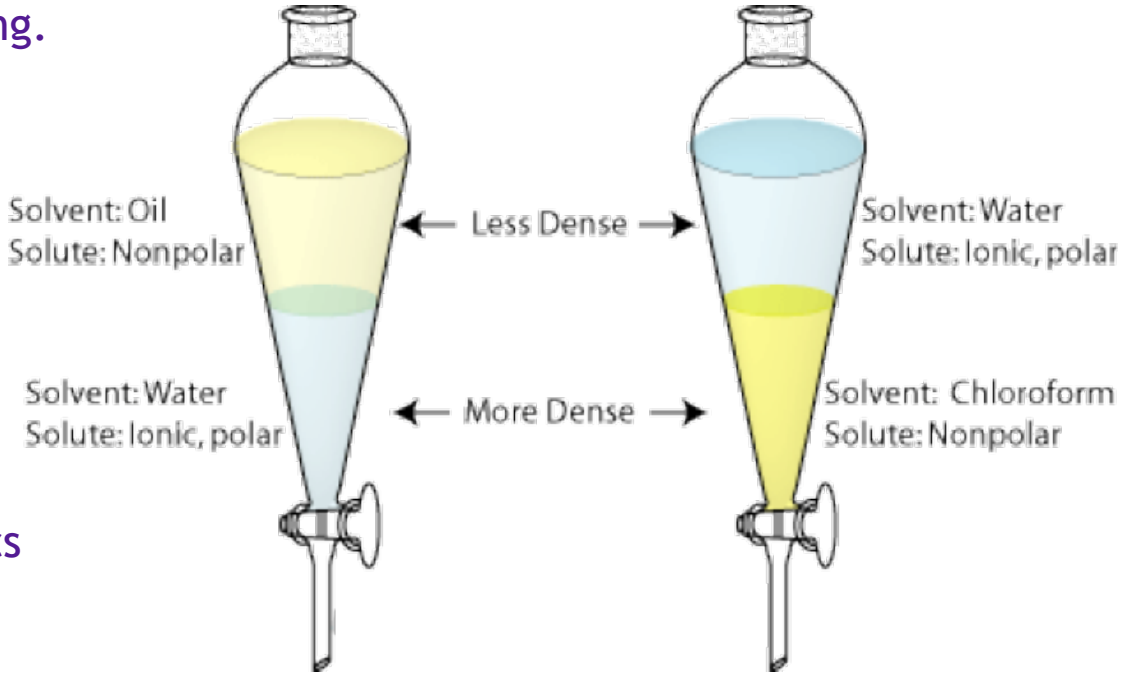
- Because halogens tend to be heavy, haloalkanes tends to be more dense than water.
  - Unlike other extraction solvents, haloalkanes tend to sink in water.



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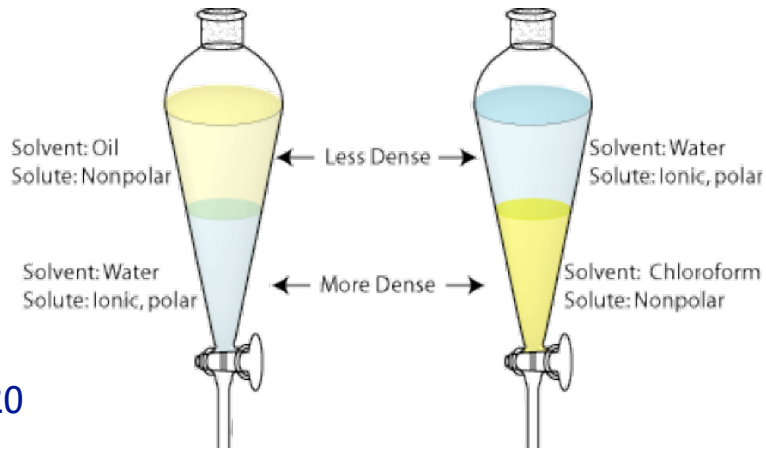

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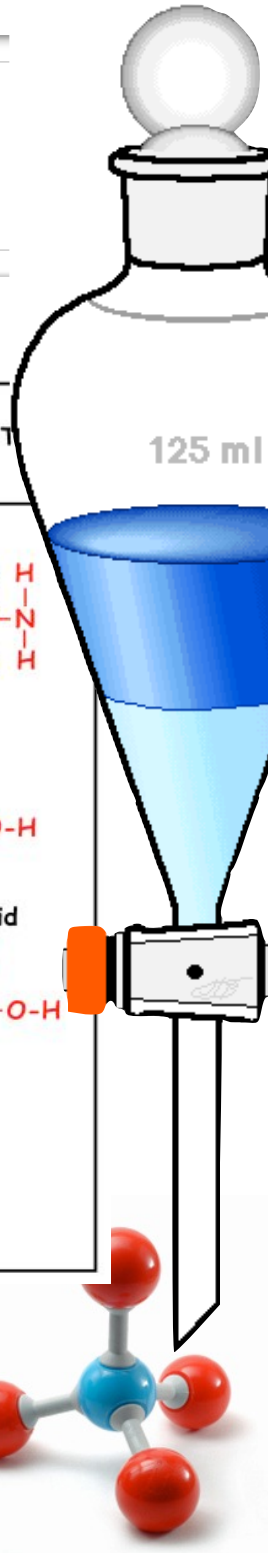


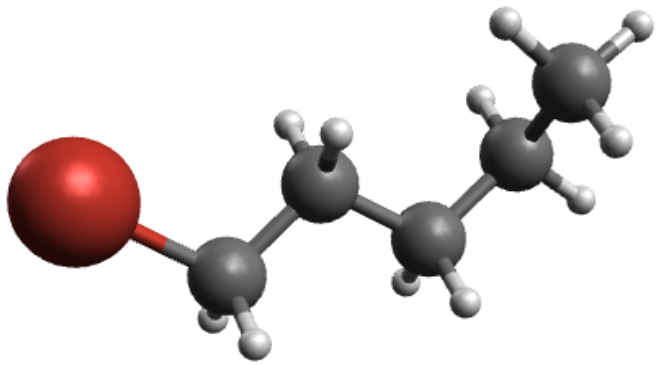
Ex23

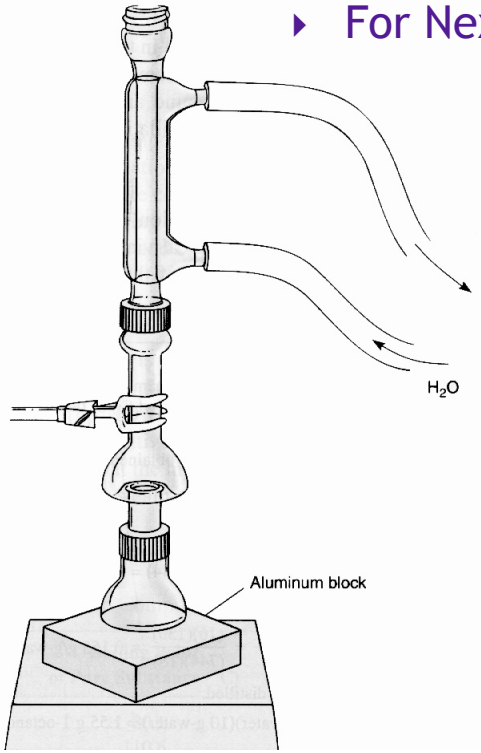
Haloalkanes

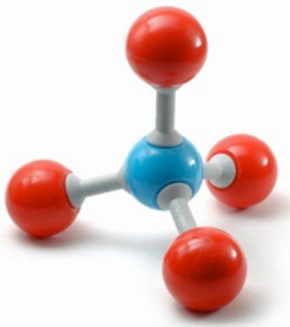
- Alkyl Halides
  - Uses
  - Structure
    - Classification
  - Properties
  - Applications

- The Experiment
  - Setup
  - Reaction
  - Isolation
  - Purification
  - Analysis

- For Next Week



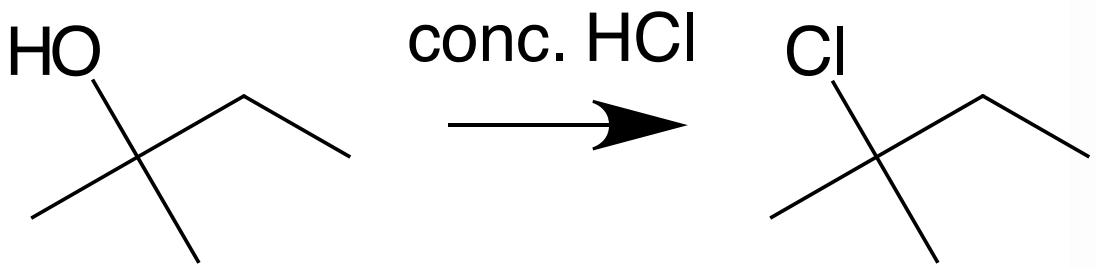




Preparation of *tert*-Pentyl Chloride

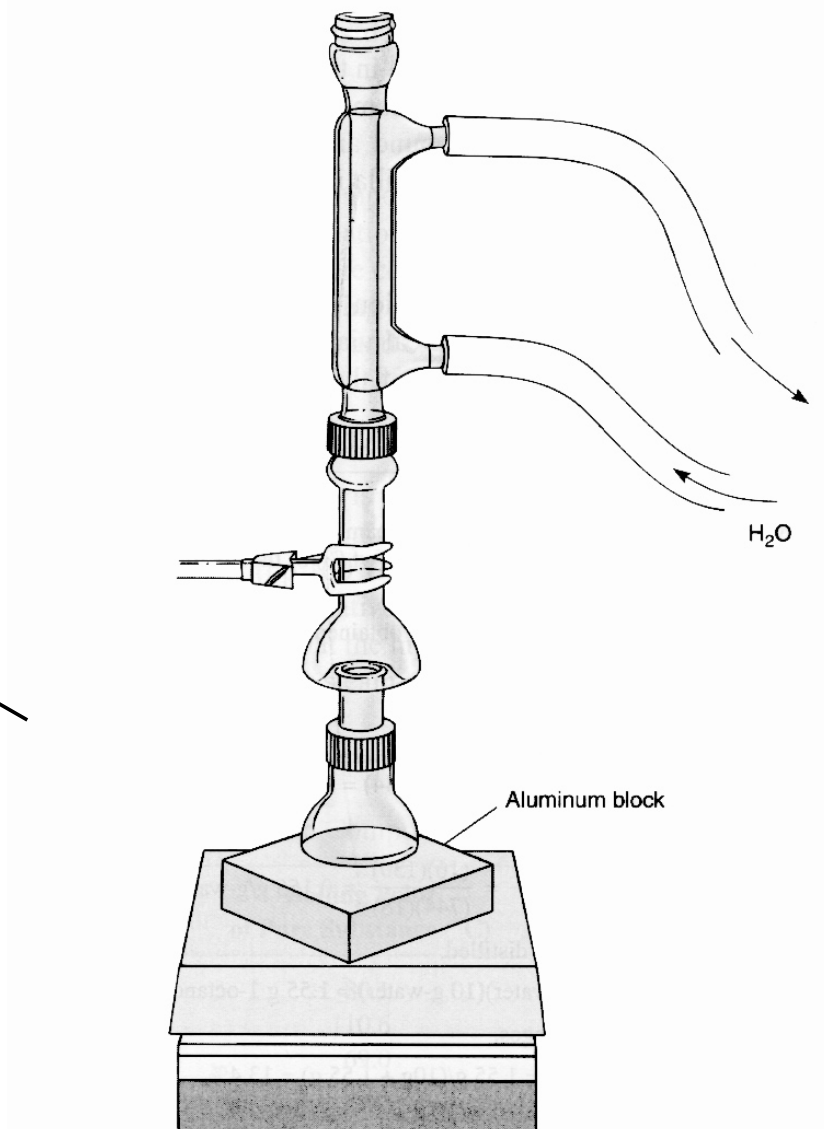
- OBJECTIVE: To prepare, isolate, purify and characterize *tert*-pentyl chloride.

- GOAL: To accomplish our first preparation of a new organic compound and apply our techniques for isolation, purification and characterization.



bp 102 ˚C

bp 85-86 ˚C

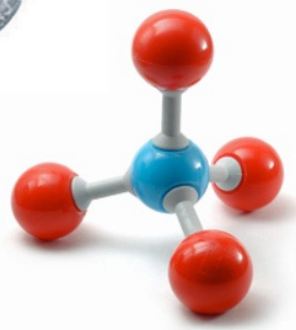


Preparation of *tert*-Pentyl Chloride

- Setup
  - Pre-weigh a 5 mL conical via.
  - By pipet add:
    - 1.0 mL tetra-pentyl Alcohol
      - d = 0.865 g/mL
    - 2.5 mL concentrated HCl (aq)

CAUTION: this is phantom of the opera level stuff.

It can scar-blind-hurt you.

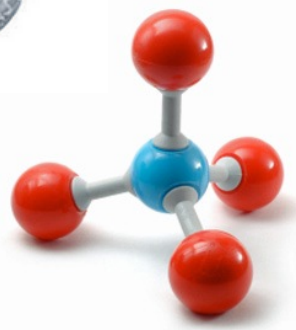


Preparation of *tert*-Pentyl Chloride

- Reaction
  - Cap vial — be sure vial is secure
    - CAREFULLY shake vial.
  - If secure, shake more vigorously for 1 min
    - Losen cap to vent.
  - Secure cap. Shake 3 more minutes.
    - vent occasionally.
  - Let stand to allow layers to separate.
  - Add drop of HCl to identify layers.

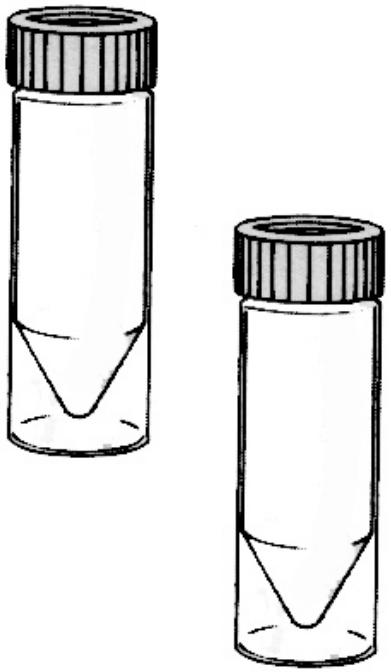
CAUTION: this is phantom of the opera level stuff.

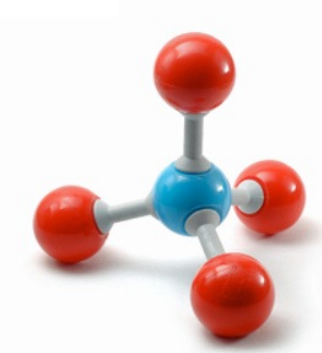
It can scar-blind-hurt you.



Preparation of *tert*-Pentyl Chloride

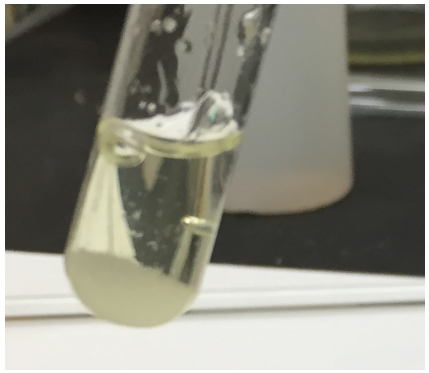
- Separate & Extract
  - Once layers have separated & organic layer has been confirmed.
  - Add to separate test tubes:
    - 1.0 mL d H2O (A)
    - 1.0 mL 5% sodium bicarbonate (B)
  - Wash organic layer with 1 mL d H2O (A)
    - Cap and shake to mix. Let separate.
    - Remove & discard aqueous layer with pipette
  - Wash organic layer with 1 mL 5% sodium bicarbonate (B)
    - Gently stir with glass stir rod.
    - Cap and shake to mix (vent occasionally).
    - Let separate.
    - Remove & discard aqueous layer with pipette
  - Transfer organic layer to new, dry vial or test tube.

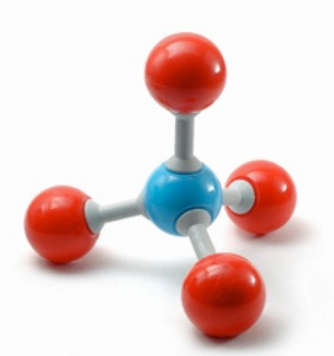




Essence of Cloves

- Drying:
  - Using the small end of the spatula, add one measure of sodium sulfate (Na_2SO_4) to your extracts.
    - Look for clumping of sodium sulfate (swirl tube or stir with clean dry micro spatula).
  - Continue adding small quantities of Na_2SO_4 until clumping occurs.
  - You will probably need 2-5 small measures of the drying agent.
    - If you use too much, you may have difficult removing the dried liquid and will get a poor yield.
  - Let solution dry at least 15 minutes.
    - Stir slightly every 2-3 minutes to increase the exposure to the drying agent.
  - Remove the dried solution by pipet to a try pre-weighted 5 mL conical flask or RB.





Ex23

Haloalkanes

- Alkyl Halides
  - Uses
  - Structure
  - Properties
  - Applications
- Preparation
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    - Free Radical Addition
    - SN1 Addition
    - SN2 Displacement
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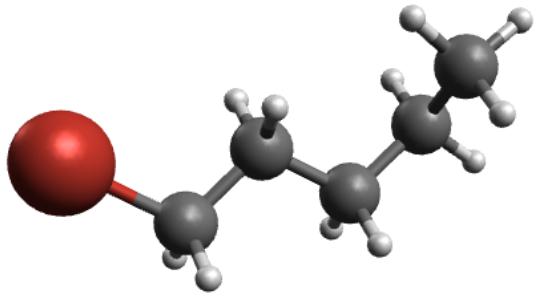
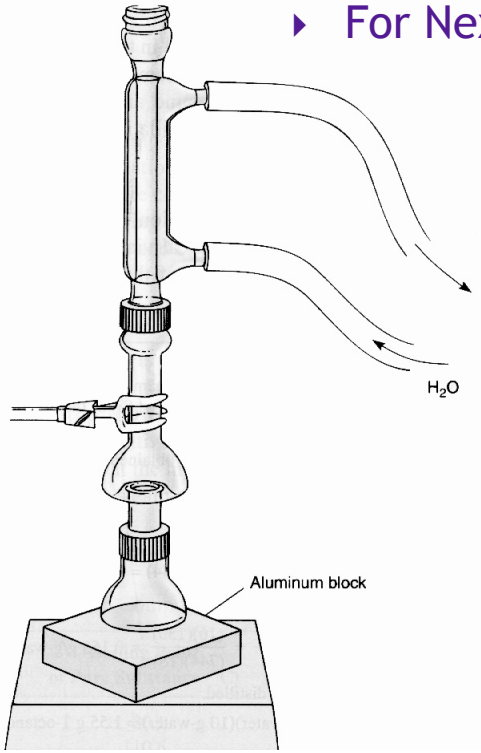
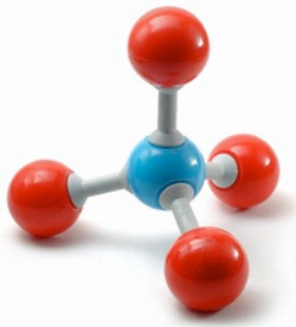
- For Next Week

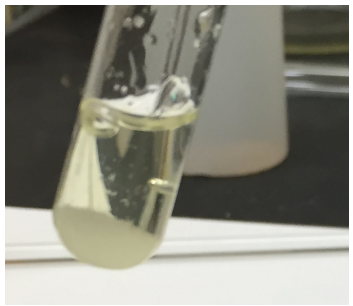


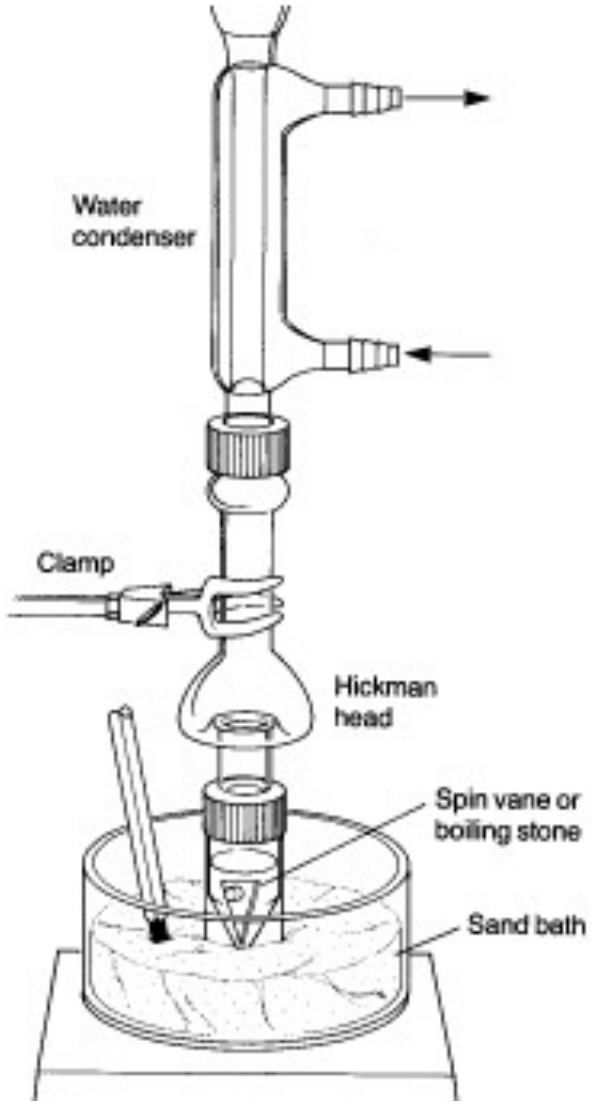




Preparation of *tert*-Pentyl Chloride

- Distillation
  - Preheat a sand bath to 50˚C
    (use electronic thermometer for sand)
  - Using a pipette transfer the crude tert-pentyl chloride to a 5 mL round bottom or conical vial.

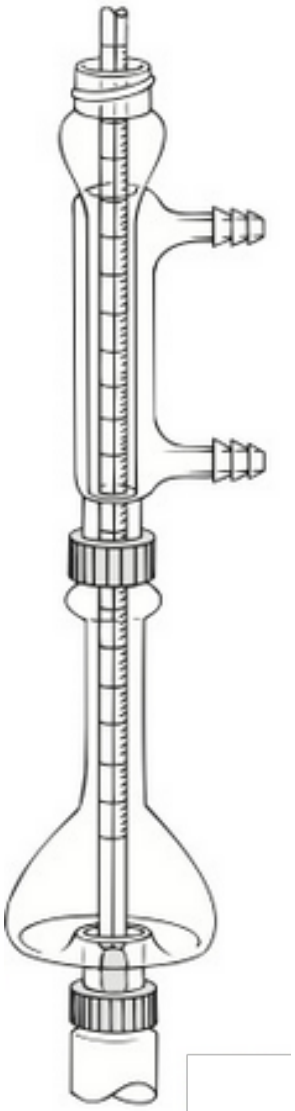


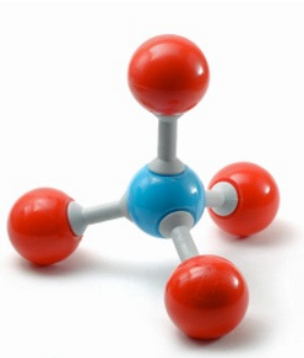


  - Add stir bar or boiling chip.
  - Attach a Hickman distillation head.
  - Attach a water condenser above the Hickman head.

Preparation of *tert*-Pentyl Chloride

- Distillation
  - Secure a glass thermometer inside the distillation head.
  - The glass thermometer will identify the temperature of the gas you are distilling.
  - Begin slowly raising the temperature of the sand.
  - As you reach 85˚C look for a condensation ring forming.
  - Raise heat as needed to bring the condensation ring into the Hickman head.
  - Hold the sand temperature when you see gas condensing at 85˚C.





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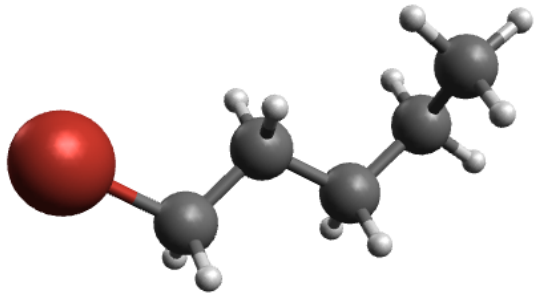
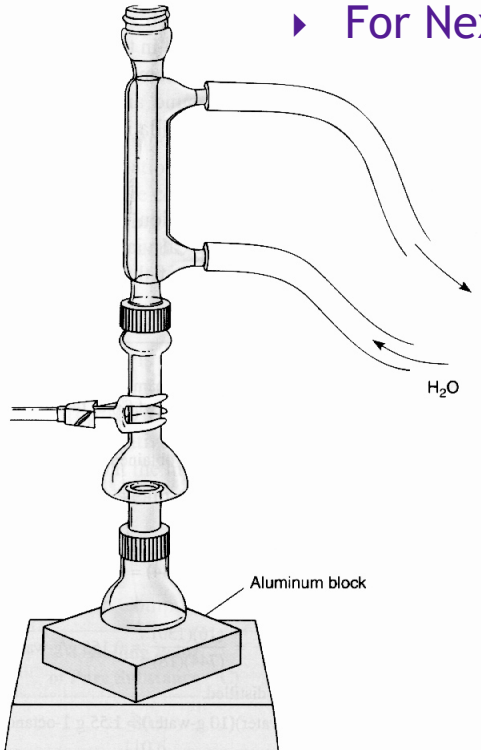
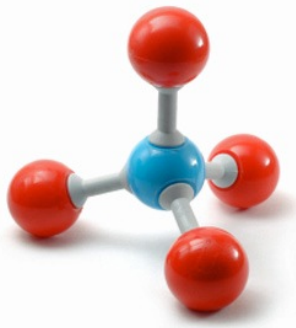
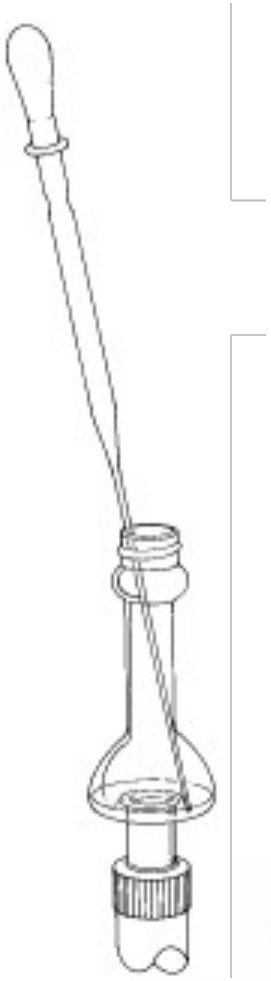


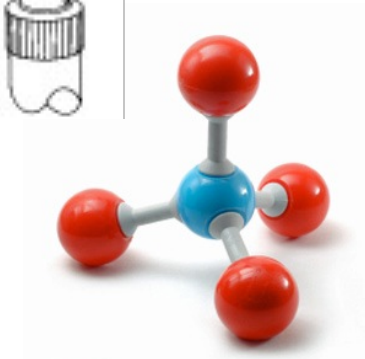




Preparation of *tert*-Pentyl Chloride

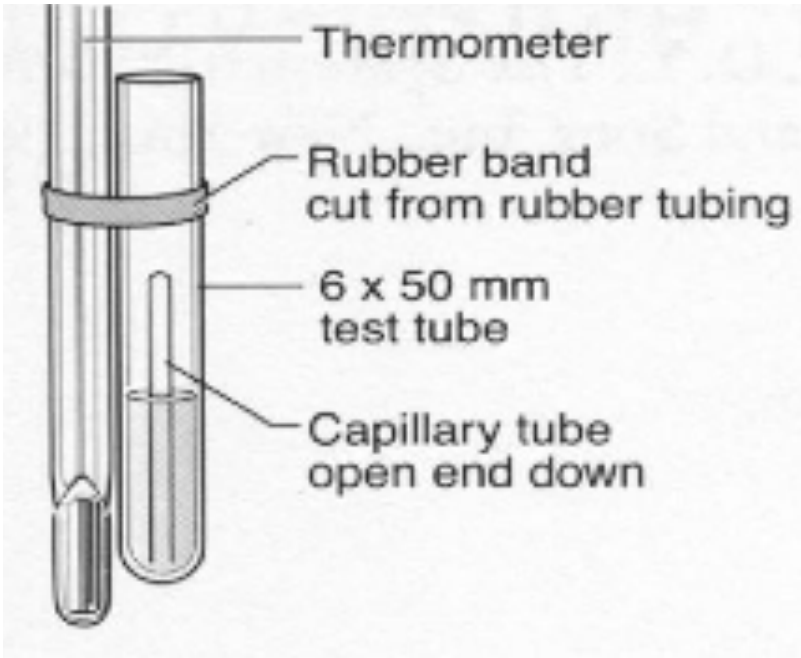
- Analysis
  - When condensation of the 85˚C sample ceases stop heating.
  - Remove distillation system from sand.
  - Let glass cool.
  - After system has cooled remove the condenser and glass thermometer.
  - Collect the distillate using a pasteur pipette into a pre-weighed vial.
  - Determine the yield and boiling point of the

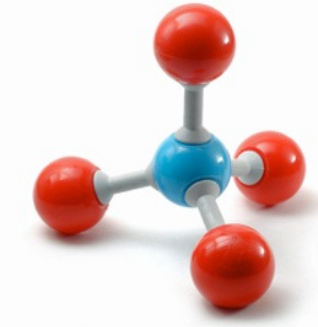




Preparation of *tert*-Pentyl Chloride

- 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.





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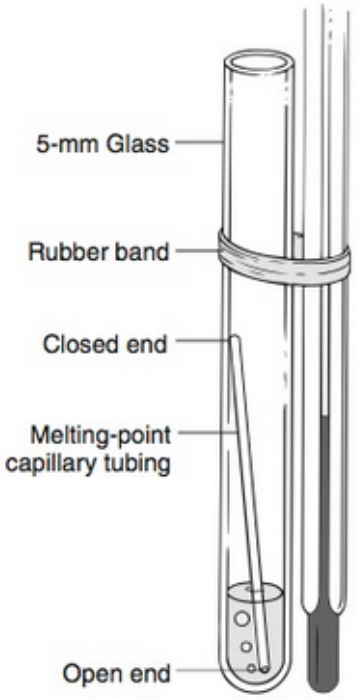
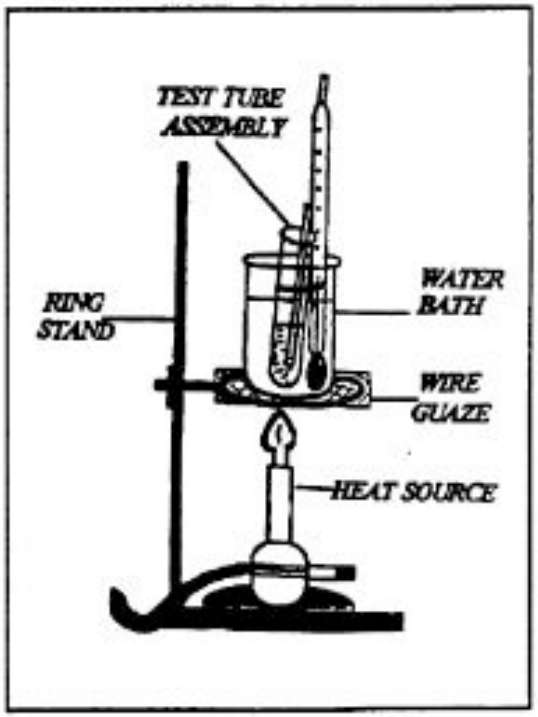
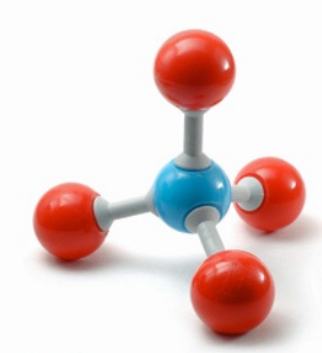
  - Secure the tube in a 150 mL beaker of water and slowly heat until a steady stream of bubbles is coming from the tip of the capillary.

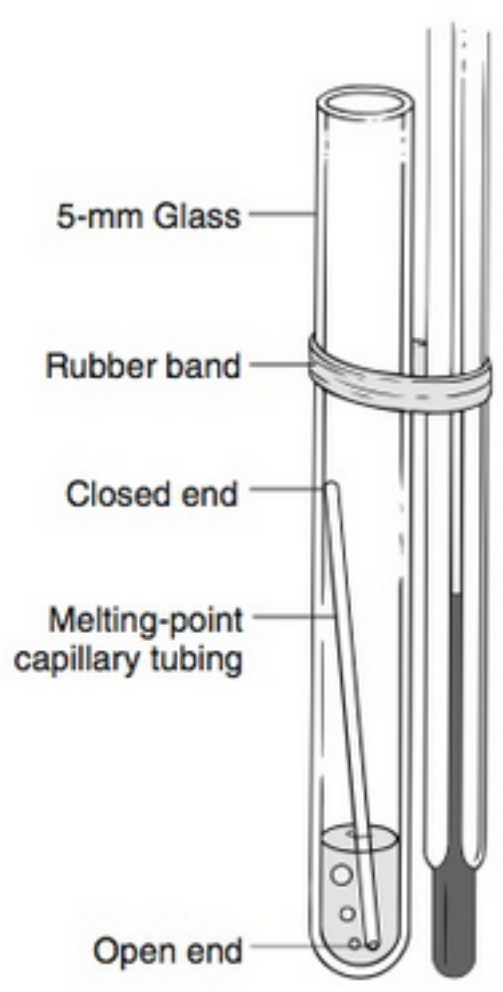


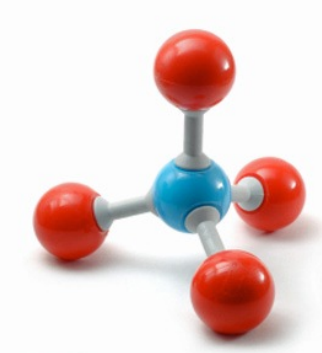




Preparation of *tert*-Pentyl Chloride

- 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.





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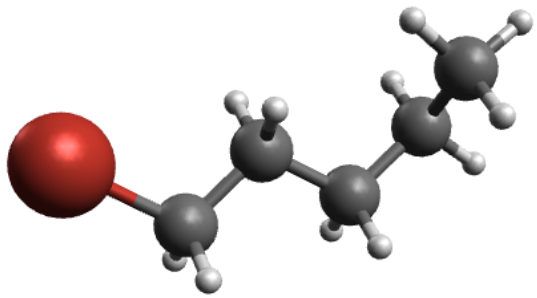
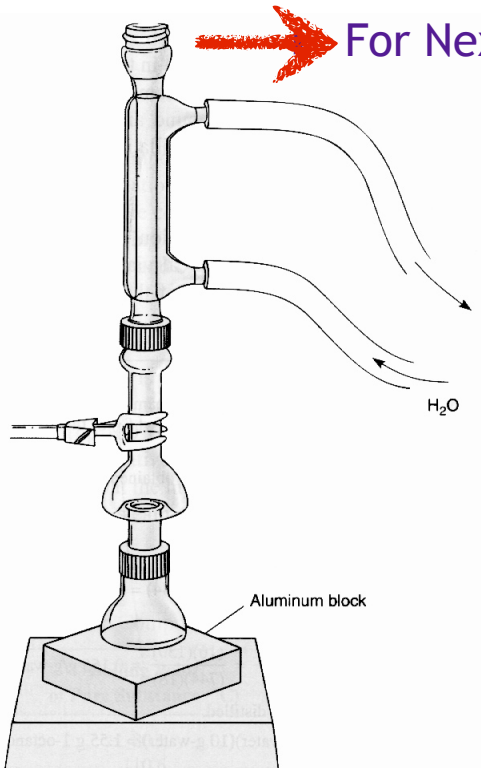
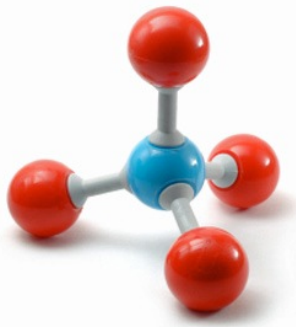
For Next Week

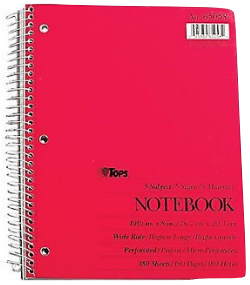


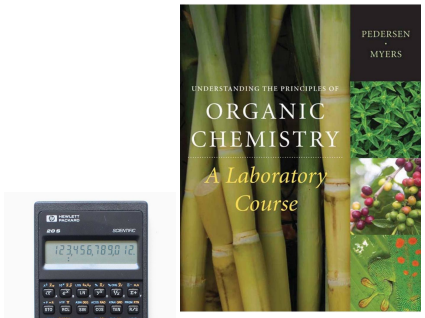


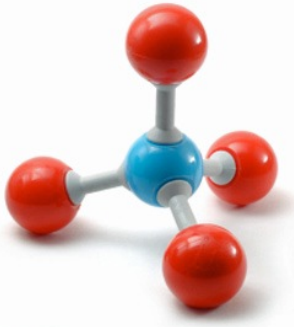


Next Meeting

- 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 24: Deyhdration of an Alcohol
    - Alcohol Dehydration reaction in your lecture
  - Produce and bring to class:
    - Your pre-lab for exp 24 (p209)
    - Your procedure summary for exp 24







Questions?