CHEMISTRY 109 – Help Sheet #12
Organic (Part I); Petroleum

Do the topics appropriate for your lecture

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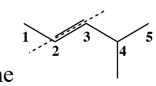
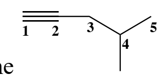
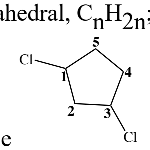
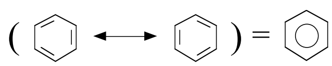
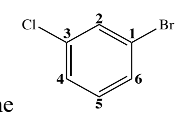
https://clc.chem.wisc.edu (Resources page)

Nuggets: *Functional Groups (Part I); Drawing Organic Molecules; Addition Reactions (alkenes); Naming Molecules; Isomers (only geometric)*

FUNCTIONAL GROUPS (Part I)

Functional Group	Suffix	Formula	Other Info
Alkane	ane	C–C	saturated; tetrahedral; sp^3; 109.5˚; $\mathbf{C_nH_{2n+2}}$; free rotation around C-C σ-bond (see page 3 for naming examples); alkanes are ***not defined*** as a functional group and were added here simply for organizational reasons
Alkene	ene	C=C	unsaturated; trigonal planar; 120˚; sp^2; $\mathbf{C_nH_{2n}}$; geometric isomers (*cis*/*trans*); alkene has a σ + π bond in the double bond; can't rotate thru C=C → π bond;  Naming: e.g., *trans*-4-methyl-2-pentene
Alkyne	yne	C≡C	unsaturated; linear; sp; 180˚; $\mathbf{C_nH_{2n-2}}$; σ + 2π bonds in the triple bond; can't rotate  Naming: e.g., 4-methyl-1-pentyne
Cyclic	cyclo + (ane, ene, or yne)		cycloalkane: unsaturated, strained tetrahedral, C_nH_{2n}; not planar  Naming: e.g., 1,3-dichlorocyclopentane
Aromatic	benzene	C_6H_6 	planar; triangular planar geometry at each C; sp^2 at each C; 120˚; resonance  Naming: e.g., 1-bromo-3-chlorobenzene

Hydrocarbon (H and C only) Functional Groups

Alkanes: only C–C ***single bonds*** = σ bonds; ***formula:*** C_nH_{2n+2}; often denoted as "R"; C–C bond ***can rotate***; saturated molecules (saturated means no more H atoms can be added)

Alkenes: at least one C=C ***double bond*** = σ + π bonds; ***formula:*** C_nH_{2n} (for one double bond); R=R';
C=C double bond ***can't rotate because π bond would need to be broken***; *cis/trans geometric isomers*; unsaturated molecule (unsaturated means more H atoms could be added if multiple bond was broken)

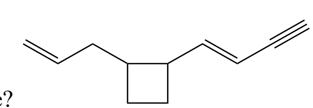
Alkynes: at least one C≡C ***triple bond*** = σ + 2π bonds; ***formula:*** C_nH_{2n-2} (for one triple bond); R≡R';
C≡C triple bond ***can't rotate because π bonds would need to be broken***; unsaturated molecule

Cyclic: ***ring compounds***; ***formula:*** C_nH_{2n} (for one ring); 3-membered ring unstable; 4-membered ring somewhat stable; 5-membered ring stable and almost planar; 6-membered ring stable puckered; unsaturated molecules

Aromatic: the focus is on benzene, C_6H_6, or a derivative of benzene; all C–C bonds equivalent;
$BO_{C–C}$ = 1.5; planar molecule; unsaturated molecule

Degree of unsaturation (skip if not covered): each double bond or ring = 1 degree of unsaturation; each triple bond = 2 degrees of unsaturation; each degree of unsaturation in effect "removes" 2 H atom from a saturated (C_nH_{2n+2}) molecule;

$$\text{Degree of Unsaturation} = \frac{2C + 2 + N - X - H}{2}$$ where C = #C atoms, N = #N atoms, X = #halogen atoms, H = #H atoms

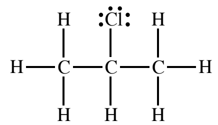
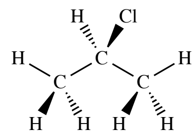
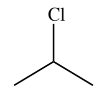
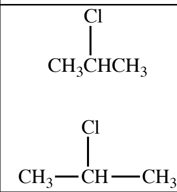


Example 1: How many degrees of unsaturation does this molecule have?

Answer 1: The molecules has 5 degrees of unsaturation; $\text{Degree of Unsaturation} = \frac{2(11) + 2 + 0 - 0 - 14}{2} = \frac{10}{2} = 5$

(Alternatively, the molecule has:
(2 double bonds) x (1 degree of unsat.) + (1 ring) x (1 degree of unsat.) + (1 triple bond) x (2 degrees of unsat.) = 5 degrees of unsat.

DRAWING MOLECULES: C – 4 bonds; N – usually 3 bonds; O – usually 2 bonds; H, F, Cl, Br, I – 1 bond

Molecular formula	Lewis Dot – all bonds and lone pairs of e⁻ drawn	Condensed Structure	Dash-Wedge	Bond Line Notation	Variations: Condensed Structures with some bonds drawn
C_3H_7Cl		$CH_3CHClCH_3$ or $CH_3–CHCl–CH_3$			

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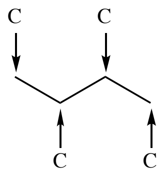
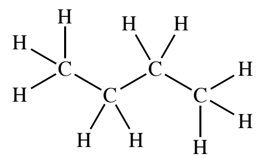
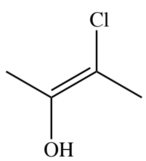
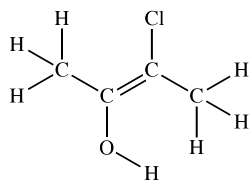
Bond Line Drawings

Example:  =  =  = 

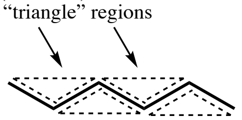
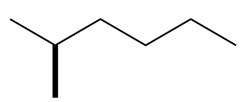
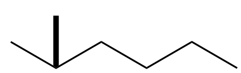
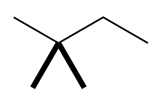
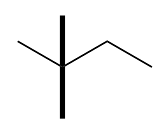
Each point on the line is a C atom; there are 4 C present

Each C must have 4 bonds; add H atoms to each C until each C has 4 bonds

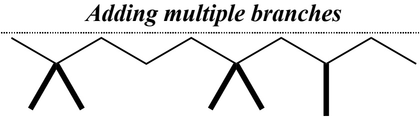
Example:  = 

All atoms drawn; note how the bond connecting the O atom to the C atom does not have a C atom at the end of the line: rather the O atom is there

Adding substituents (branches) off the main chain

Where branches should not be placed	*Adding 1 branch*		*Adding 2 branches*	
no substituents (branches) in these "triangle" regions  **C chain** no substituents (branches) in these "triangle" regions	 Drawn **correctly**; place branch *vertical* relative to the chain, and not in the "triangle" regions	 Drawn **incorrectly**; branch placed in incorrect "triangle" region	 Drawn **correctly**; place branches at an angle relative to the chain (not "vertical") and not in the "triangle" regions	 Drawn **incorrectly**; branches should be on the same side of chain and not in "triangle" regions

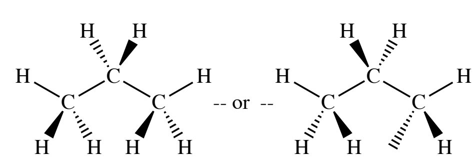
Adding multiple branches



Drawn **correctly**; no branches in the "triangle" regions; single branch is "vertical" from chain; when 2 branches are on the same C atom they are at an angle relative to the chain

3D Drawings:

- Wedge line is ***coming out*** of the plane of the paper towards you
- Dash line is ***going behind*** the plane of the paper away from you
- Regular/thin line is ***in the plane*** of the paper



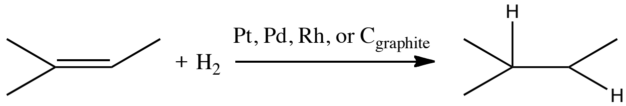
Both structures are **correct**; just drawn from a different perspective

ADDITION REACTIONS ***(skip if topic not covered!)***

Alkenes: add Cl_2/Br_2, H_2, H_2O, or HCl/HBr *across the double bond (chemicals above the arrow are catalysts)*

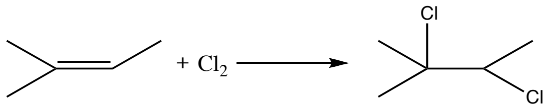
add H_2 (*hydrogenation)*

alkene + H_2 $\xrightarrow{\text{Pt, Pd, Rh, } C_{graphite}}$ alkane



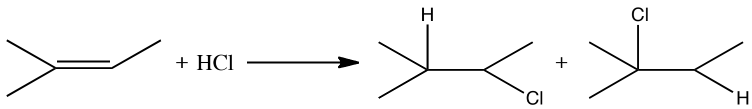
add Cl_2 or Br_2 (*halogenation*)

alkene + X_2 $\rightarrow$ dihaloalkane



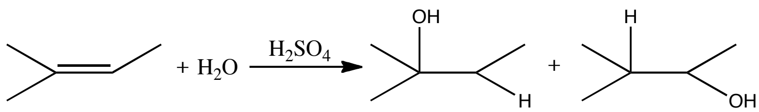
add HCl/HBr ***(skip if not covered)*** (*hydrohalogenation)*; can yield multiple products though one dominates

alkene + HX $\rightarrow$ haloalkane



add H_2O ***(skip if not covered)*** (*hydrolysis*); can yield multiple products though one dominates

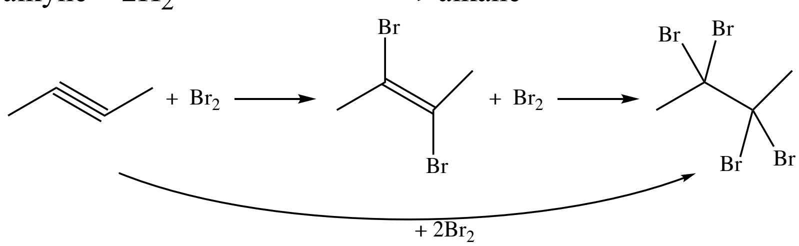
alkene + H_2O $\xrightarrow{H_2SO_4}$ alcohol



Alkynes: *same reactions as alkene addition; can be done in two separate steps or one combined step*

alkyne + H_2 $\xrightarrow{\text{Pt, Pd, Rh, } C_{graphite}}$ alkene + H_2 $\xrightarrow{\text{Pt, Pd, Rh, } C_{graphite}}$ alkane or

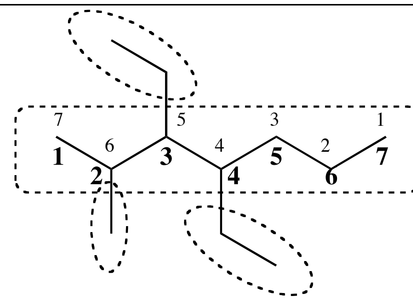
alkyne + $2H_2$ $\xrightarrow{\text{Pt, Pd, Rh, } C_{graphite}}$ alkane



NAMING MOLECULES ***(skip this topic if not covered!)***:

1. Find longest C chain
2. ***Number the longest C chain*** to give smallest numbers for functional group or branches
3. ***Prefix*** = #carbon atoms: *Meth* = 1; *Eth* = 2; *Prop* = 3; *But* = 4; *Pent* = 5; *Hex* = 6; *Hept* = 7; *Oct* = 8; *Non* = 9; *Dec* = 10
4. ***Suffixes*** = functional group: "ane" for alkanes, "ene" for alkenes, "yne" for alkynes; use prefix "cyclo" for cyclic molecules; use "benzene" when a benzene ring is included
5. a. ***Branches***: for C branches: prefix+"yl"; e.g., 1-C branch = meth+yl = methyl; 2-C branch = ethyl; etc.
   b. ***Duplicate branches***: use: di = 2; tri = 3; tetra = 4; e.g., two (di) 1-C (methyl) branches = dimethyl
   c. ***Alphabetize multiple branches***; do not alphabetize on the di, tri, or tetra
      ethyl before propyl; ethyl before dimethyl (alphabetize on "e" and "m" and ignore "di")
   d. ***Every branch and functional group must have a number*** identifying C chain position
   e. Commas between numbers; dashes ("-") between numbers and letters
6. Alkene functional group: check for *cis*/*trans* isomers

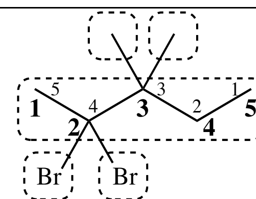
Example 2: Name the molecule shown.



1. Find longest C chain (dashed rectangular box) – **7** carbons long; prefix = **hept**
2. All C–C single bonds (alk**ane**); suffix = **ane**
3. Find branches off C chain (dashed ovals); one branch = 1-C long = **methyl**; two branches = 2-C long = each is **ethyl** – since two identical branches use **diethyl**
4. **Number chain** both ways; choose numbering scheme to yield smaller numbers for branches (bottom bold numbers). Functional groups (e.g., an alcohol) get higher priority in numbering chain; this molecule has no functional group (alkane not considered functional group)
5. **Alphabetize** branches (di**e**thyl before **m**ethyl; alphabetize on "e" and "m").
6. ***Each*** branch gets a number: 2-methyl; 3,4-diethyl (note the 2 numbers: one for each ethyl branch)
7. commas (,) between numbers; dashes (-) between numbers and letters

***Answer 2*: 3,4-diethyl-2-methylheptane**

Example 3: Name the molecule shown.



1. Find longest C chain (dashed rectangular box) – **5** carbons long; prefix = **pent**
2. All C–C single bonds (alk**ane**); suffix = **ane**
3. Find branches off C chain (dashed ovals); two branches = 1-C long = each is **methyl** – since two identical branches use **dimethyl**; two branches = Br = **bromo** – since two identical branches use **dibromo**
4. **Number chain** both ways; choose numbering scheme to yield smaller numbers for branches (bottom bold numbers). Functional groups (e.g., an alcohol), get higher priority in numbering chain; this molecule has no functional group
5. **Alphabetize** branches (di**b**romo before di**m**ethyl; alphabetize on "b" and "m").
6. ***Each*** branch gets a number: 2,2-dibromo (note the 2 numbers: one for each Br); 3,3-dimethyl (note the 2 numbers: one for each methyl)
7. commas (,) between numbers; dashes (-) between numbers and letters

***Answer 3*: 2,2-dibromo-3,3-dimethylpentane**

ISOMERS (Part I) – Molecules with the ***same formula*** but different bonding or different arrangements in space; (molecules that have ***different formulas***, e.g., C_6H_{12} and C_6H_{14}, ***are not*** isomers)

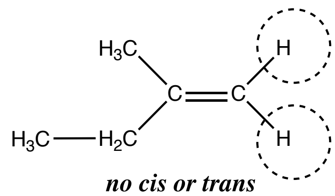
Geometric Isomers: same formula, same bonding/connectivities and *different spatial arrangements (positions) of the atoms* to yield *cis* versus *trans* isomers

Criteria:

1. ***Does it contain a C=C*** (a double bond)
2. On ***each C*** of the C=C, there must be 2 *different groups*.

Both criteria must be true for a molecule to have *cis/trans* isomers.

The molecule below ***does not*** have *cis/trans* isomers.



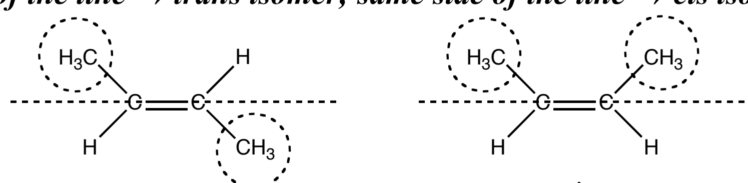
no cis or trans

{Above molecule has a double bond and meets the first criteria. The left C of the C=C bond has 2 different groups (a $–CH_3$ and a $–CH_2CH_3$ group) but the right C of the C=C has two H atoms (same groups; needs different groups on ***each*** C of the C=C).}

If molecule has geometric isomers, is it cis or trans?

Molecule below has a double bond (satisfies the first criteria) and each C of the C=C has two different groups (*each* C has a –H and a $–CH_3$ group – these are different groups; satisfies the second criteria)

1. Draw a line through C=C bond
2. Find the 2 groups ***that are the same*** on the two C atoms of the C=C and circle them; if they're on the ***different sides of the line → trans isomer; same side of the line → cis isomer***



trans ***cis***

PETROLEUM

Petroleum or crude oil: a mixture of alkanes, alkenes, cycloalkanes, and aromatic compounds; there are ~20,000 chemicals found in crude oil

Distillation: a chemical separation technique that separates chemicals based on boiling points; in general, larger molecules have higher boiling points

Petroleum fraction: a mixture of chemicals separated from distillation with a similar range of boiling points

Hydrocarbons in petroleum:

C_1-C_4 (gases; bp < 20˚C);

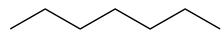
C_5-C_{12} (gasoline – motor fuels and solvents; bp: 20-200˚C);

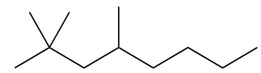
C_{12}-C_{16} (kerosene – diesel fuel and kerosene; bp: 175-275˚C);

C_{15}-C_{18} (fuel oil – heating oil and diesel fuel; bp: 250-400˚C);

C_{16}-C_{20} (lubricating oils; bp > 400˚C)

Octane number: a measure of how efficiently gasoline burns in an engine

Heptane ($CH_3(CH_2)_5CH_3$): octane rating = 0; 

Isooctane (2,2,4-trimethylpentane, $CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$): octane rating = 100; 

Common gasoline (e.g., octane rating = 83): burns similarly to a mixture of 83% isooctane + 17% heptane

Catalytic cracking: chemical process using a catalyst, and high T and P to break large hydrocarbons into smaller ones

Catalytic reforming: chemical process to change straight-chain hydrocarbon molecules into branched molecules or into aromatic molecules; branched molecules have higher octane ratings than straight-chain molecules

Octane enhancers: chemicals added to gasoline to increase octane ratings; common: $Pb(C_2H_5)_4$, tetraethyllead (no longer used); toluene; methanol; ethanol; 2-methyl-2-propanol

Oxygenated gasoline: gasoline with oxygen-containing additives (e.g., ethanol, methanol, etc.) are used to reduce CO emissions in winter

Reformulated gasoline (RFG): oxygen-containing additives (e.g., ethanol, methanol, etc.) added to gasoline that has a different composition of hydrocarbons for a cleaner burn

US Energy Consumed

Natural gas: mixture of C_1-C_4 hydrocarbons (70-90% CH_4); hydraulic fracturing (fracking) – high pressure fluid injected into wells that crack subterranean shale formations and release natural gas and oil

Coal: partially hydrogenated six-membered carbon rings

Topics in organic can vary with course and instructor; do only the appropriate questions for your course.

1. From each of the following condensed molecular structures, draw the
   a) Lewis dot structure,
   b) bond line notation, and
   c) dash-wedge 3D structures.

I. $CH_3CH_2CH_2CH_2CH_2CH_3$ II. $(CH_3)_2CHCH(CH_3)_2$ III. $CHCCH_3$ IV. $CH_3CH_2CH(OH)CH_3$

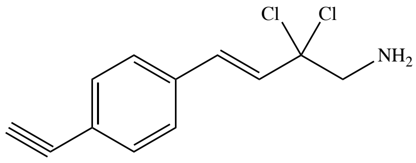
2. Which functional group could the molecule, $C_{35}H_{70}$, contain?

a. alkane b. alkene c. alkyne d. alcohol e. more info needed

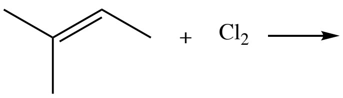
3. Which molecule could contain a ***triple bond***?

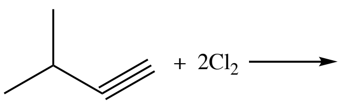
a. C_2H_6 b. C_6H_6 c. C_4H_8 d. C_3H_8 e. None of these

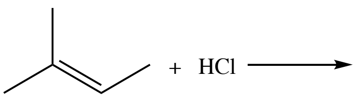
4. *(Skip this question if degrees of unsaturation not covered)* Given the following molecule how many degrees of unsaturation does it contain?



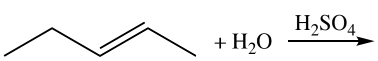
5. ***(Skip this question if addition reactions were not covered!)*** Complete each reaction by drawing the product(s).

a. 

b. 

c. 

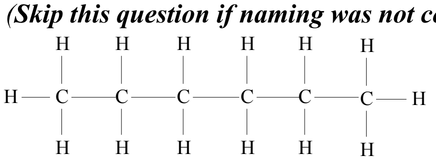
(hint: 2 products)

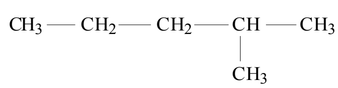
d. 

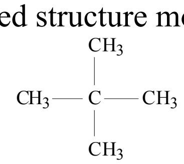
(hint: 2 products)

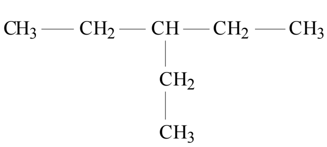
The next 3 questions are practice naming molecules or drawing molecules given their names. ***Skip these questions if naming is not covered.***

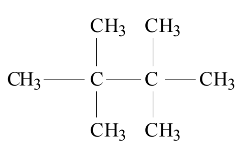
6. ***(Skip this question if naming was not covered)*** Name each of the following condensed structure molecules.

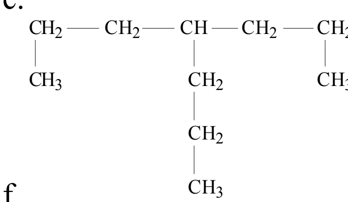
a. 

b. 

c. 

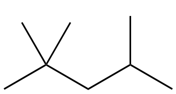
d. 

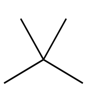
e. 

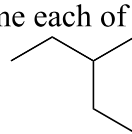
f. 

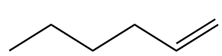
7. ***(Skip this question if naming was not covered)*** Draw the organic molecules in ***bond line notation*** given their names.
a. 2,2,4-trimethylpentane b. 2,2-dimethylbutane c. 4-ethyl-3,5-dimethylheptane d. 1,1,2-trichlorohexane
e. 2,3-dimethyl-1-pentene f. 4-methyl-2-hexyne

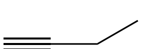
8. ***(Skip this question if naming was not covered)*** Name each of the following bond line structure molecules.

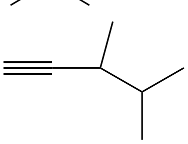
a. 

b. 

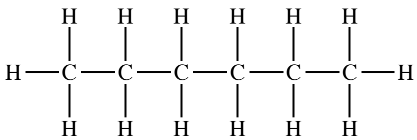
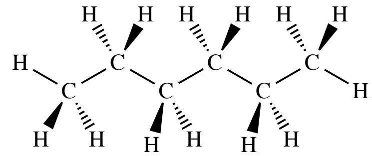
c. 

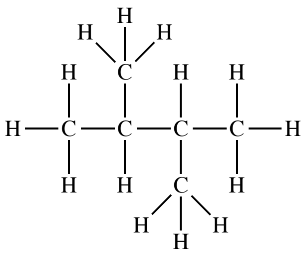
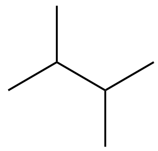
d. 

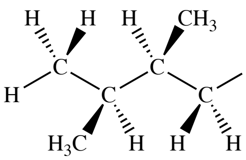
e. 

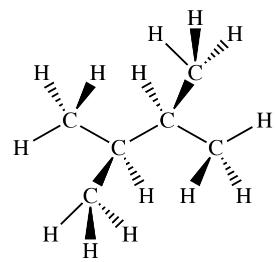
f. 

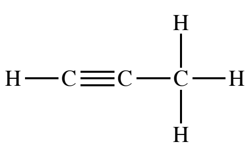
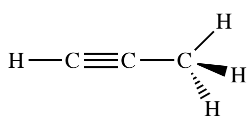
ANSWERS

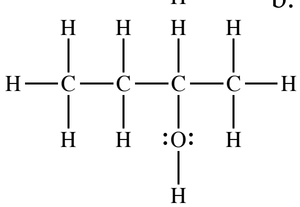
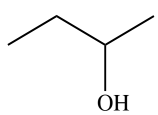
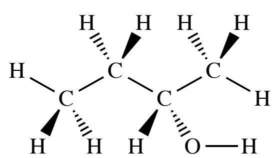
1. I. a.  b.  c. 

II. a.  b. 

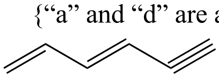
c.  (note how the two CH_3 side chains were kept as a group to simplify the structural drawing);

can also draw it more complicated as follows (not usually required for Chem 104!): 

III. a.  b. c. 

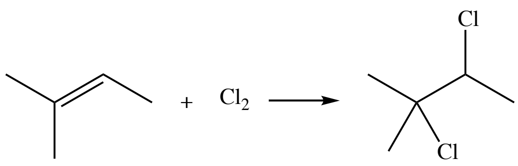
IV. a.  b.  c. 

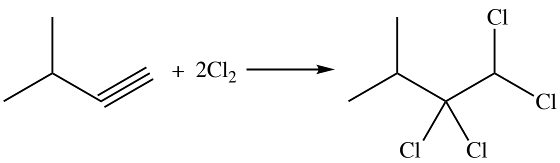
2. b

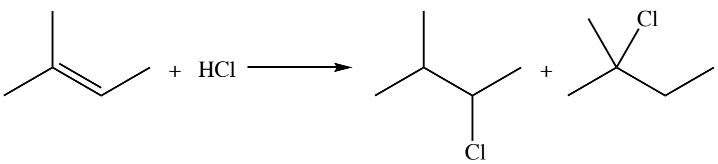
3. b {"a" and "d" are alkanes – C_nH_{2n+2}; "c" is either a ring or an alkene – C_nH_{2n}; "b" could contain a triple bond; e.g., )

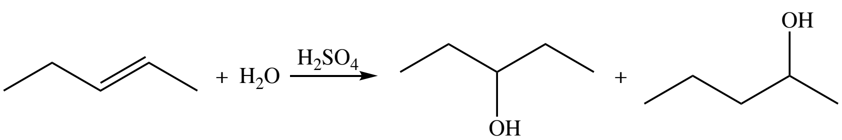
4. 7 { Degree of Unsaturation $= \frac{2(12)+2+1-2-11}{2} = \frac{14}{2} = 7$; alternatively:

(4 double bonds) x (1 degree of unsat.) + (1 ring) x (1 degree of unsat.) + (1 triple bond) x (2 degrees of unsat.) = 7 degrees of unsat.

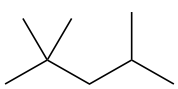
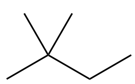
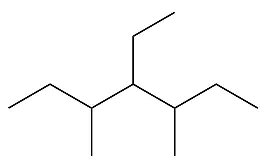
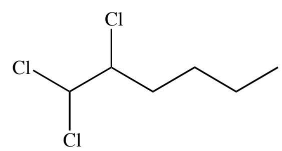
5. a. 

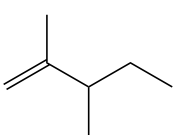
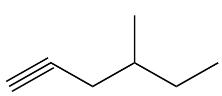
b. 

c. 

d. 

6. a. hexane b. 2-methylpentane c. 2,2-dimethylpropane
d. 3-ethylpentane e. 2,2,3,3-tetramethylbutane f. 4-propylheptane

7. a.  b.  c.  d. 

e.  f. 

8. a. 2,2,4-trimethylpentane b. 2,2-dimethylpropane c. 3-methylpentane
d. 1-hexene e. 1-butyne f. 3,4-dimethyl-1-pentyne