Provide a IUPAC name for the following compounds. Be sure to use cis/trans, E/Z or R/S as appropriate (non-bonding electrons are not shown)

a) 

b) 

c) 

d) 

e) 

f) 

g) 

h) 

i)
Rank the following in order as requested. Give a BRIEF explanation.

a) increasing Bronsted acidity

\[
\text{CH}_3\text{C} \equiv \text{CH} \quad \text{NH}_3 \quad \text{H}_2\text{O} \quad \_ \quad \_ \quad \_ \quad < \quad < \quad <
\]

b) increasing Bronsted acidity of the -OH group

\[
\_ \quad \_ \quad \_ \quad < \quad < \quad <
\]

c) increasing bond dissociation energy of the bond in **BOLD**

\[
\text{H}_3\text{C} \equiv \text{CH}_2\text{H} \quad \text{H}_2\text{C} \equiv \text{CH}_2\text{H} \quad \text{HC} \equiv \text{C} \equiv \text{H} \quad \text{H}_3\text{C} \equiv \text{CH}_3
\]

\[
\_ \quad \_ \quad \_ \quad < \quad < \quad < \quad <
\]
Rank the order requested, give a BRIEF explanation

a) Increasing Bronsted acidity of the hydrogens $H_a$, $H_b$, $H_c$ and $H_d$

$$ _< _< _< _$$

b) Use resonance arguments to rank the following hydrogens $H_a$, $H_b$ and $H_c$ in order of increasing Bronsted acidity

$$ _< _< _$$

c) Use resonance arguments to rank the following in order of increasing Bronsted acidity

$$ _< _< _$$
rank in order of increasing Bronsted acidity, give a BRIEF explanation

a) (ignore keto tautomers)

\[ \text{____ < ____ < ____} \]

\[ \begin{array}{ccc}
  & \text{A} & \\
  & \text{B} & \\
  & \text{C} & \\
\end{array} \]

b) 

\[ \text{____ < ____ < ____} \]

\[ \begin{array}{ccc}
  & \text{A} & \\
  & \text{B} & \\
  & \text{C} & \\
\end{array} \]

c) 

\[ \text{____ < ____ < ____} \]

\[ \begin{array}{ccc}
  & \text{A} & \\
  & \text{B} & \\
  & \text{C} & \\
\end{array} \]
a) Classify the following, when as substituents on a benzene ring, as electron donating or withdrawing:

- $\text{OCH}_3$ donating, withdrawing
- $\text{C} \equiv \text{N}$ donating, withdrawing
- $\text{CH}_2\text{CH}_3$ donating, withdrawing
- $\text{C} \equiv \text{N}(\text{CH}_3)_2$ donating, withdrawing
- $\text{CF}_3$ donating, withdrawing
- $\text{NH} \equiv \text{C} \equiv \text{CH}_3$ donating, withdrawing

b) Rank the following in order of increasing Bronsted acidity and give a BRIEF explanation (hint, convert the condensed $-\text{CHO}$ into a full Lewis structure):

- $\text{A}$
- $\text{B}$
- $\text{C}$
- $\text{D}$

The rankings are:

- $\text{A} < \text{B} < \text{C} < \text{D}$

Me is electron donating, destabilizes the conjugate base anion, in A the Me is directly attached to a carbon with partial negative charge, thus anion A is more destabilized than anion B.

CHO is electron withdrawing, stabilizing the conjugate base anion, in D the -CHO is directly attached to a carbon with partial negative charge, in fact an additional resonance contributor can be drawn, thus anion D is more stabilized than anion C.
In each case, fill in the missing product, reagents or reactants. Note that non-bonding electrons are generally not shown in these structures.

UNLESS INDICATED, pay attention to relative and absolute stereochemistry as appropriate. If several (more than 2) chiral centers are involved you will usually NOT be asked to indicate stereochemistry since such reactions often form mixtures of enantiomers of diastereomers.

When the REACTANT structure is missing, there may be more than one possible correct answer, but there will always be a reaction.

State whether EACH reaction is an oxidation, reduction or neither.
State whether EACH reaction is an addition, elimination, substitution or rearrangement.

a)  
\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{H} \\
\end{array}
\quad \rightarrow 
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{C} \\
\text{H} \\
\end{array}
\]

b)  
\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\end{array}
\quad \text{NaBH}_4 
\quad \text{CH}_3\text{CH}_2\text{OH}
\]

c)  
\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \\
\quad \text{1. Mg, Et}_2\text{O} \\
\quad \text{2. H}_3\text{O}^+
\]

d)  
\[
\quad \rightarrow 
\]

e)  
\[
\quad \rightarrow 
\quad \text{(±)}
\]

f)  
\[
\quad \text{H}_2/\text{Lindlar's catalyst} 
\]

g)  
\[
\quad \text{1. 1 Equiv. HBr} \\
\quad \text{2. K}^+\text{·OMe} 
\]
same instructions as previous page

a) \[
\begin{align*}
\text{Br} & \quad \text{1. Excess NaNH}_2/\text{heat} \\
\text{C} & \quad \text{2. H}_2\text{O}
\end{align*}
\]

b) \[
\begin{align*}
\text{OH} & \quad \text{HBr}
\end{align*}
\]

\text{ignore stereochemistry}

c) \[
\begin{align*}
\text{PCC} & \quad \text{H}_2\text{O}
\end{align*}
\]

d) \[
\begin{align*}
\text{H}_2 & \quad \text{Lindlar's catalyst}
\end{align*}
\]

e) \[
\begin{align*}
\text{NaNH}_2 & \quad \text{NaBH}_4
\end{align*}
\]

f) \[
\begin{align*}
\text{1. PBr}_3 & \\
\text{2. Mg.THF} & \\
\text{3. D}_2\text{O}
\end{align*}
\]

g) \[
\begin{align*}
\text{H} & \quad \text{C≡C} & \quad \text{H}
\end{align*}
\]

h) \[
\begin{align*}
\text{ignore stereochemistry}
\end{align*}
\]
same instructions as previous pages
EXCEPT DO NOT INDICATE REACTION TYPE OR OX/RED for the problems on this page!!

a) \( \text{Cl} \)  
\[ \text{Excess MgBr} \]

b) \( \text{CH}_3\text{CH}_2\text{C}≡\text{CH} \)  
\[ \rightarrow \text{CH}_3\text{CH}_2\text{CCH}_3 \]

c) \( \text{cyclohexanone} \)  
\[ 1. \text{Excess LiAlH}_4 \]  
\[ 2. \text{H}_3\text{O}^+ \]

d) \( \text{HO} \)  
\[ \text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O} \]

e) \( \text{HO} \)  
\[ \text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O} \]

f) \( \text{HCO} \)  
\[ 1. \text{Excess LiAlH}_4 \]  
\[ 2. \text{H}_3\text{O}^+ \]

g) \( \text{HAl} \)  
\[ 1. \text{CH}_3\text{MgBr} \]  
\[ 2. \text{H}_3\text{O}^+ \]
same instructions as previous page

a) 

b) 

this one is tricky, do 2 consecutive reactions

ignore stereochemistry

c) 

1. \( \text{K}^+ - \text{O-t-Bu} \)

2. \( \text{MCPBA} \)

d) 

e) 

f) 


S\text{OCl}_2

g) 

h) 

1. Excess \( \text{CH}_3\text{MgBr} \)

2. \( \text{H}_3\text{O}^+ \)
same instructions as previous page

a) \[
\text{Cyclohexane} \xrightarrow{\text{conc. } H_2SO_4/\text{heat}} \text{Br-Cyclohexane (±)}
\]

b) \[
\text{Cyclohexanol} \quad \xrightarrow{1. \text{Br}_2} \quad \text{Cyclohexyl bromide}
\]
\[
\quad \xrightarrow{2. \text{NaNH}_2/\text{heat} \ 3. \text{H}_2\text{O}} \quad \text{Cyclohexyl acetylene}
\]

c) \[
\text{tosylated aromatic} \quad \xrightarrow{\text{Na}^+ - \text{CN}} \quad \text{tosylated aromatic}
\]

d) \[
\text{tosylated aromatic} \quad \xrightarrow{\text{OMgBr}} \quad \text{tosylated aromatic with } \text{OMgBr}
\]
\[
\quad \xrightarrow{\text{H}_3\text{O}^+} \quad \text{tosylated aromatic with } \text{H}_3\text{O}^+
\]

e) \[
\text{Phenol} \quad \xrightarrow{\text{OMgBr}} \quad \text{Phenol with } \text{OMgBr}
\]
\[
\quad \xrightarrow{\text{H}_3\text{O}^+} \quad \text{Phenol with } \text{H}_3\text{O}^+
\]

f) \[
\text{tosylated aromatic} \quad \xrightarrow{\text{Na/NH}_3(l)} \quad \text{tosylated aromatic}
\]

h) \[
\text{tosylated aromatic} \quad \xrightarrow{\text{2 HBr / ROOR}} \quad \text{tosylated aromatic}
\]

i) \[
\text{Acetylene} \quad \xrightarrow{1 \text{ Equiv. } \text{HBr}} \quad \text{ignore sterochemistry}
\]

j) \[
\text{Cyclohexanol} \rightarrow \text{Cyclohexyl bromide}
\]

k) \[
\text{Acetylene} \rightarrow \text{Cyclohexyl acetylene}
\]

Page 10
same instructions as previous page

a) \[
\begin{array}{c}
\text{Br} \\
\end{array}
\xrightarrow{HBr}
\]

b) \[
\begin{array}{c}
\end{array}
\xrightarrow{}
\]

c) \[
\begin{array}{c}
\text{D} \\
\end{array}
\xrightarrow{1. BH_3\text{THF}}
\xrightarrow{2. \text{HOH/H}_2\text{O}_2}
\]

d) \[
\begin{array}{c}
\end{array}
\xrightarrow{}
\]

e) \[
\begin{array}{c}
\text{Na} \\
\end{array}
\xrightarrow{}
\]

f) \[
\begin{array}{c}
\end{array}
\xrightarrow{}
\]

g) \[
\begin{array}{c}
\text{MgBr} \\
\end{array}
\xrightarrow{}
\]

h) \[
\begin{array}{c}
\end{array}
\xrightarrow{}
\]

i) \[
\begin{array}{c}
\end{array}
\xrightarrow{\text{Excess HBr}}
\]
same instructions as previous page

a) \[
\begin{align*}
\text{benzene} &\quad \overset{\text{Excess Br}_2}{\rightarrow} \quad \text{benzyl bromide}
\end{align*}
\]

b) \[
\begin{align*}
\text{alkyne} &\quad \overset{\text{H}_2 \text{ with Lindlar catalyst}}{\rightarrow} \quad \text{alkene}
\end{align*}
\]

c) \[
\begin{align*}
\text{propyne} &\quad \overset{1 \text{ Equiv. Br}_2}{\rightarrow} \quad \text{propyl bromide}
\end{align*}
\]

d) \[
\begin{align*}
\text{benzyl lithium} &\quad \overset{\text{H}_3\text{O}^+}{\rightarrow} \quad \text{benzyl alcohol}
\end{align*}
\]

e) \[
\begin{align*}
\text{phenol} &\quad \overset{\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O}}{\rightarrow} \quad \text{benzoic acid}
\end{align*}
\]

f) \[
\begin{align*}
\text{cyclohexanol} &\quad \overset{\text{H}_2} {\text{H}_2} \quad \overset{\text{H}_3\text{O}^+}{\rightarrow} \quad \text{cyclohexyl thiocyanate}
\end{align*}
\]

h) \[
\begin{align*}
\text{alkyne} &\quad \overset{1 \text{ Equiv. HCl}}{\rightarrow} \quad \text{alkane}
\end{align*}
\]

ignore stereochemistry

e) \[
\begin{align*}
\text{phenyl acetylene} &\quad \overset{\text{1. PBr}_3} {2. \text{Mg.THF}} \quad \overset{3. \text{O}} {4. \text{H}_3\text{O}^+}{\rightarrow} \quad \text{phenyl Grignard}
\end{align*}
\]

ignore stereochemistry
disconnect the indicated bond according to the method of retrosynthetic analysis, generate the synthons and convert these into "real reagents", or "synthetic equivalents". The first one is done for you so that you can see what to do.

\[
\begin{align*}
\text{synthons} & \quad \text{real reagents/synthetic equivalents} \\
\end{align*}
\]

a) 
\[
\begin{align*}
\text{(structure)} & \quad \text{(structure)}
\end{align*}
\]

b) 
\[
\begin{align*}
\text{(structure)} & \quad \text{(structure)}
\end{align*}
\]

c) 
\[
\begin{align*}
\text{(structure)} & \quad \text{(structure)}
\end{align*}
\]

d) 
\[
\begin{align*}
\text{(structure)} & \quad \text{(structure)}
\end{align*}
\]

e) 
\[
\begin{align*}
\text{(structure)} & \quad \text{(structure)}
\end{align*}
\]
The following retrosynthesis problems can be done in only two steps, they are simpler than you will find on the midterms, they are to build confidence (ignore sterochemistry)

a) 

b) 

c) 

d) 

e) 

f) 

Page 14
Synthesize the (target) molecule on the right from the starting molecule on the left. This cannot be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.

a) ![Structure](image1)

b) ![Structure](image2) do NOT ignore stereochemistry
Synthesize the (target) molecule on the right from the starting molecule the left. This can not be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.

a) \( \text{CH}_3-\text{CH}_2\text{OH} \quad \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH} \)

b) 

\[ \text{benzene} \quad \text{biphenyl} \]

c) 

\[ \text{cyclopropene} \quad \text{1,4-pentadiyne} \]
Synthesize the (target) molecule on the right from the starting molecule on the left. This cannot be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.

a)  

b)  

c)  

This one is tricky, the last step is an intramolecular Grignard. Do the Grignard backwards at the last step to see how to solve this one (ignore stereochemistry).
Synthesize the (target) molecule on the right from the starting molecule the left. This cannot be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.

*These problems are considered difficult*

a) do NOT ignore stereochemistry

b) 

c)
In each case, provide TWO DIFFERENT SETS of reactants that when they undergo a Grignard reaction give the provided structure as the product (after acid workup). In each case there are more than two possible answers, but only 2 answers will be provided in the answer key.

\[ \text{OH} \quad \rightarrow \quad \text{ } \]

\[ \text{OH} \quad \rightarrow \quad \text{ } \]

Give the product of addition of this Grignard reagent to this cyclic compound, after workup with dilute aqueous acid (addition of H}_2\text{O}^+\text{.}

\[ \text{Excess } \]
\[ \text{Ph—MgBr} + \quad \text{O—O} \quad \rightarrow \]

Page 19
In each case, provide ONE SET of reactants/reagents/conditions that can react to make a new C-C bond for each provided structure (an acid workup step can be assumed, if necessary, you do not need to include it). In each case there may be more than two possible answers, but only 1 is shown here.

- OH
  + MgBr
  →
  ...

- OH
  + Ph MgBr
  →
  ...

- OH
  + Me MgBr
  →
  ...

- HO
  + Ph
  →
  ...

Page 20
Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

*Add non-bonding electron pairs and C-H bonds as necessary*

a)

\[
\begin{array}{c}
\text{CH}_3\text{CH}_3\text{CH}_3
\end{array}
\quad \text{conc. H}_2\text{SO}_4 \quad \text{heat}
\begin{array}{c}
\text{CH}_3\text{CH}_3
\end{array}
\]

b)

\[
\begin{array}{c}
\text{Br}_2
\end{array}
\quad \text{H}_2\text{O}
\begin{array}{c}
(\pm)
\end{array}
\]

Page 21
Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

*Add non-bonding electron pairs and C-H bonds as necessary*

a) 

\[
\begin{array}{c}
\text{EtOH (solvent)} \\
\text{Cl}_2
\end{array}
\]

b) 

\[
\begin{array}{c}
\text{H}_2\text{O} \\
\text{HCl cat.}
\end{array}
\]

In this case, draw important resonance structures for all intermediates

c)
Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

**Add non-bonding electron pairs and C-H bonds as necessary**

In this case draw all important resonance structures for the intermediates, this mechanism has been started for you:

a) 

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Hg}^+ & \quad \text{Hg}^+ \\
\text{Hg}^{2+} & \quad \text{LA} \\
\text{LB} & \quad \text{HgSO}_4 / \text{H}_2\text{SO}_4 / \text{H}_2\text{O} \\
\end{align*}
\]

b) 

\[
\begin{align*}
\text{Na}^+ & \quad \text{OH} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
\end{align*}
\]
Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

*Add non-bonding electron pairs and C-H bonds as necessary*

---

**a)**

\[
\begin{align*}
\text{HCl cat.} & \\
\text{H}_{2}\text{O} & \\
& \\
\end{align*}
\]

\[
\text{cyclohexanone} \rightarrow \text{cyclohexanol}
\]

---

**b)**

\[
\begin{align*}
\text{HCl cat.} & \\
\text{H}_{2}\text{O} & \\
& \\
\end{align*}
\]

\[
\text{cyclohexanone} \rightarrow \text{cyclohexanediol}
\]

---

**c)**

\[
\begin{align*}
\text{conc. H}_2\text{SO}_4/\text{heat} & \\
\text{cyclohexanol} & \\
& \\
\end{align*}
\]

\[
\text{cyclohexanone} \rightarrow \text{cyclohexene}
\]
Give the curved-arrow pushing mechanism for the following reaction, at each step identify the Lewis acid/Lewis Base (LA/LB), indicate whether any reaction is also a Brønsted acid/base reaction (BA/BB). Draw a reaction energy diagram for the mechanism, clearly indicating the relative energies of all the intermediates, starting material, product. Do not draw any transition states BUT INDICATE THEIR POSITIONS ON THE DIAGRAM. Do not draw resonance contributors for the intermediates.
Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Bronsted acids and bases (LB/BA, LA/BA etc.)

*Add non-bonding electron pairs and C-H bonds as necessary*

*These are a little bit tricky, but use what you know about LA/LB reactions and cation rearrangements to solve them*

---

**a)**

\[
\begin{align*}
\text{OH} & \quad \text{HBr} \\
\rightarrow & \\
\text{Br}
\end{align*}
\]

**b)**

\[
\begin{align*}
\text{OH} & \quad \text{HBr} \\
\rightarrow & \\
\text{Br}
\end{align*}
\]
Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

*Add non-bonding electron pairs and C-H bonds as necessary*

\[\text{Excess MeMgBr}\]

\[\text{Excess LiAlH}_4\]

\[\text{H}_3\text{O}^+\]
In class we learned that dehydrohalogenation of a dibromide is only useful for preparation of a terminal alkyne, in fact the following reaction occurs.....

\[
\begin{align*}
\text{Br} & \quad \text{1. Excess } \text{NaNH}_2/\text{heat} \\
\text{Br} & \quad \text{2. } \text{H}_2\text{O}
\end{align*}
\]

the internal alkyne is formed initially, but it isomerizes to the terminal alkyne, as shown below. Give a mechanism for this isomerization. Solve the problem using the strategy we talked about in class, look at what C-H bonds you have to break and which you have to make, and simply do them in the correct order! It will be helpful to use the common trick of adding the hydrogens to the line-angle formula before you start. Remember that you are in the presence of a strong base, so you should do a DEprotonation first. In the presence of a base, you are unlikely to have any positively charged intermediates. Draw the important resonance contributors for any intermediates. Finally, it will be helpful to note that the amide anion catalyzes the reaction, it is not consumed overall.

\[
\begin{align*}
\quad & \quad \text{1. Excess } \text{NaNH}_2/\text{heat} \\
\quad & \quad \text{2. } \text{H}_2\text{O}
\end{align*}
\]
For each step in the following mechanism as appropriate, identify the Lewis acid/Lewis Base (LA/LB) and indicate whether each is also a Brønsted acid/base reaction (BA/BB). Identify each step as either an SN1, SN2, E1, E2, addition, elimination, protonation or deprotonation. Draw a reaction energy diagram for the overall process. Identify the locations of the starting structures, the products and the intermediates on the provided energy diagram and provide a drawing of each transition state and indicate their locations on the diagram.
Provide detailed reactants that can be used to make the indicated bonds (dashed line) in an SN2 reaction. Unless the leaving group is implied in the product, the leaving group can be either bromide, iodide or tosylate, your choice (my answers will interchange among these randomly to remind you that you can use more than just bromide), you do not have to specify the solvent, it doesn't matter which counterion you use, but if you need one you must specify an example one.

a) 

b) 

c) 

d) 

e) 

Give the reactants to synthesize the provided structures in an SN2 reaction. One of the bonds in each structure is the obvious one to make in an SN2 reaction, in these problems you will have to decide which it is.

f) 

g) 

h) 

page 30
THIS IS THE FORMAT OF THE SPECTRUM QUESTION YOU WILL SEE ON AN EXAM

Provided are spectra for a compound with molecular formula C₈H₁₂O

(a) Give the degrees of unsaturation

(b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including C(sp³)-H). Indicate BOTH the functional group, and where appropriate, the specific BOND in the functional that corresponds to the peak.

(c) Draw the structure and clearly indicate which hydrogens correspond to which signals in the proton nmr spectrum ONLY.
Provided are spectra for a compound with molecular formula $\text{C}_5\text{H}_{10}\text{O}$

a) Give the degrees of unsaturation

b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including C(sp$^3$)-H). Indicate BOTH the functional group, and where appropriate, the specific BOND in the functional that corresponds to the peak.

-- Image of infrared spectrum --

**ppm**

\begin{align*}
\text{200} & \quad 180 \\
\text{160} & \quad 140 \\
\text{120} & \quad 100 \\
\text{80} & \quad 60 \\
\text{40} & \quad 20 \\
\end{align*}

3H singlet

3H triplet

2H triplet

2H sextet

**ppm**

\begin{align*}
\text{4} & \quad 3 \\
\text{2} & \quad 1 \\
\text{0} & \quad -1 \\
\end{align*}

c) draw the structure and clearly indicate which hydrogens correspond to which signals in the proton nmr spectrum ONLY

\begin{align*}
\text{ppm} & \quad 8 \quad 7 \\
\text{ppm} & \quad 6 \quad 5 \\
\text{ppm} & \quad 4 \quad 3 \\
\text{ppm} & \quad 2 \quad 1 \\
\text{ppm} & \quad 0 \\
\end{align*}