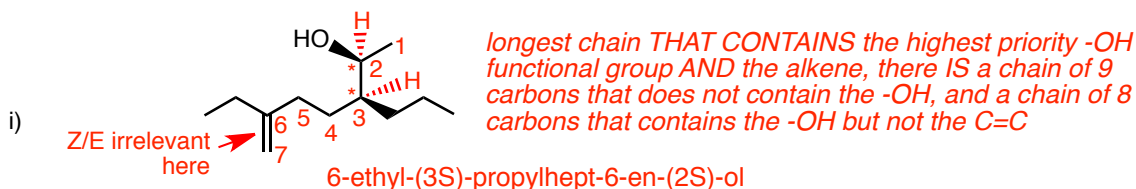
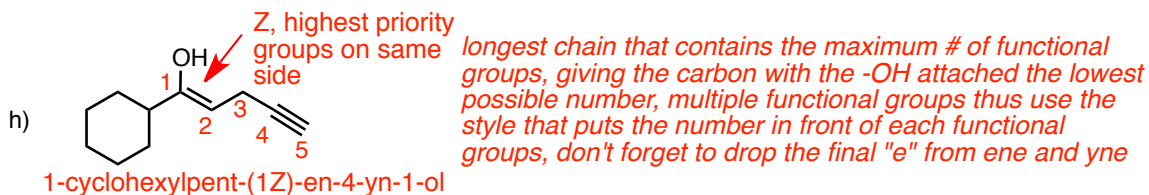
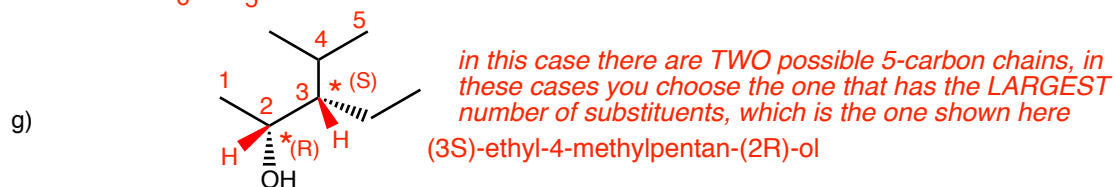
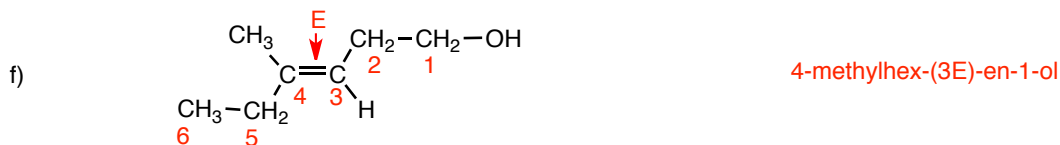
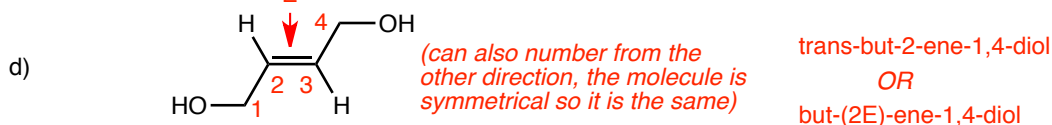
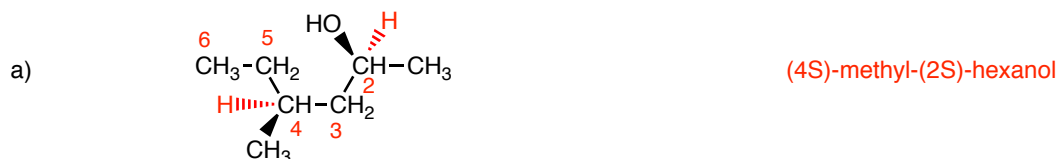


Provide a IUPAC name for the following compounds. Be sure to use cis/trans, E/Z or R/S as appropriate (non-bonding electrons are not shown)



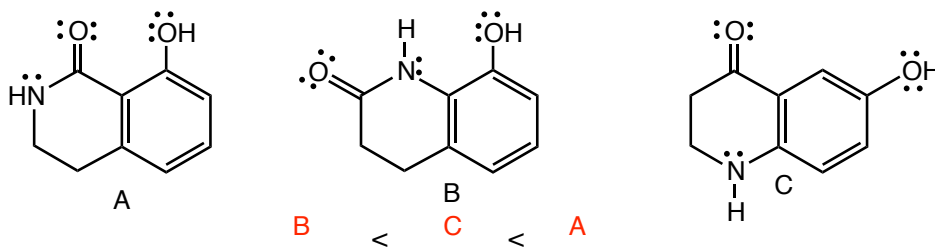
Rank the following in order as requested. Give a BRIEF explanation.

a) increasing Bronsted acidity

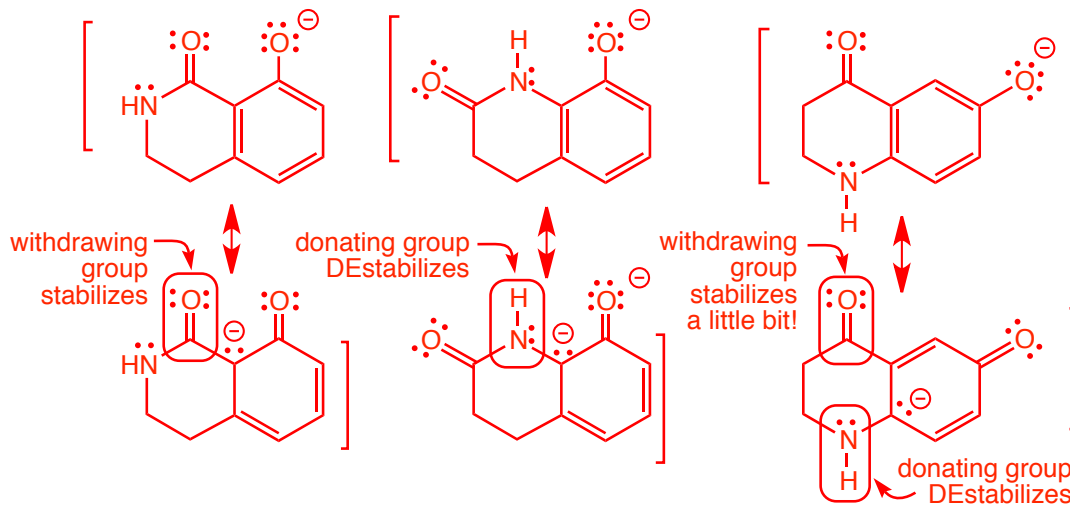


The amide anion can deprotonate a terminal acetylide, water protonates an acetylide, thus $B < A < D$. This question is unusual in that **you could NOT have worked out the answer from first principles**, the answer comes simply (in this case) by knowing the acid/base chemistry of alkynes

b) increasing Bronsted acidity of the -OH group



The anion from A has an electron withdrawing group directly attached to a carbon that carries a formal negative charge in the anion, stabilizing the charge. The anion from B has a donating group that directly destabilizes the negative charge. The anion from C is destabilized by the donating group and slightly, not directly, stabilized by an withdrawing group



(not all resonance structures are shown, only the "first", from deprotonation of the phenol, and the one that makes the stabilization/destabilization of the electrons most clear)

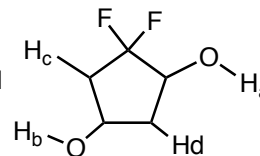
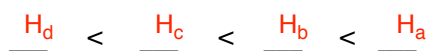
c) increasing bond dissociation energy of the bond in **BOLD**



BDE is a homolytic process determined mainly in these cases by the energies of electrons in the bonds, the more s character in the atomic orbitals that are combined to make the molecular orbitals that characterize the bonds, the stronger the bond. The order goes $\text{sp}^3(\text{C})+\text{sp}^3(\text{C})$ in **D** is weaker than $\text{sp}^3(\text{C})+1\text{s}(\text{H})$ in **A**, weaker than $\text{sp}^2(\text{C})+1\text{s}(\text{H})$ in **B**, weaker than $\text{sp}(\text{C})+1\text{s}(\text{H})$ in **C**.

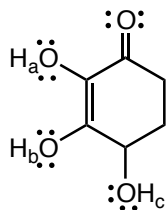
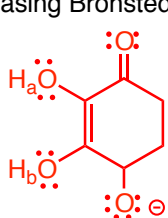
Rank the order requested, give a BRIEF explanation

a) Increasing Bronsted acidity of the hydrogens Ha, Hb, Hc and Hd



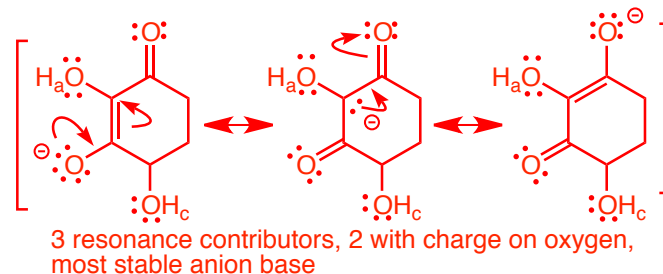
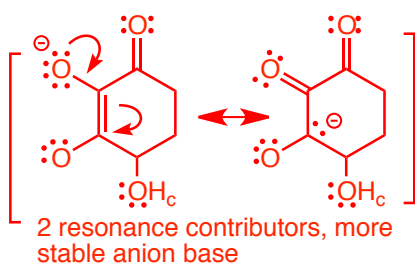
oxygen is more electronegative than carbon and stabilizes the conjugate base anion better, hence Ha and Hb > Hc and Hd. Ha closer to -CF2 group which further stabilizes it base by the INDUCTIVE effect, hence Ha > Hb. Similarly, the conjugate base anion from Hc is more stabilized by the inductive effect than that from Hd. NOTE, ANY EXPLANATION RELATED TO STABILITY MUST EXPLICITELY MENTION THE CONJUGATE BASE ANION, NOT JUST "IT"!

b) Use resonance arguments to rank the following hydrogens Ha, Hb and Hc in order of increasing Bronsted acidity

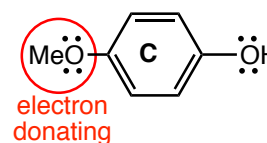
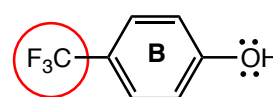
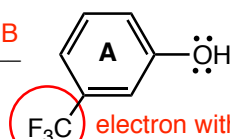


acidity in this case is determined by the extent of resonance stabilization in the conjugate base anions, the more resonance contributors the lower the energy of the non-bonding electrons, more stable the base anion, the more acidic the acid

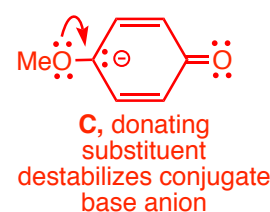
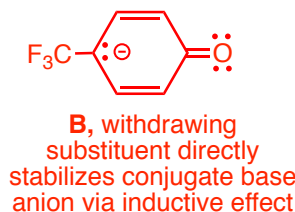
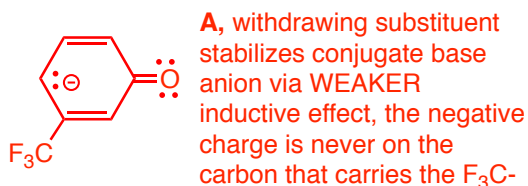
no resonance stabilization, least stable base



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

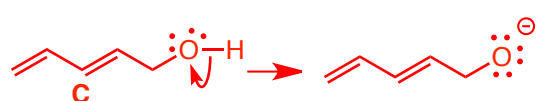
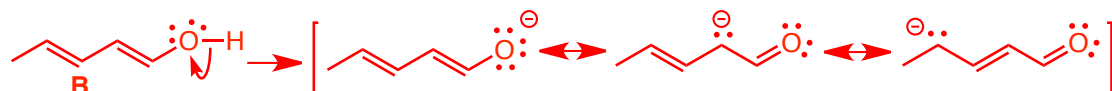
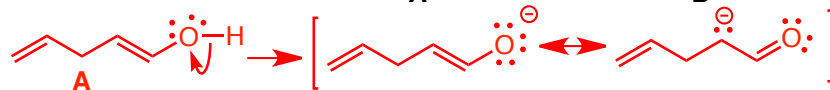
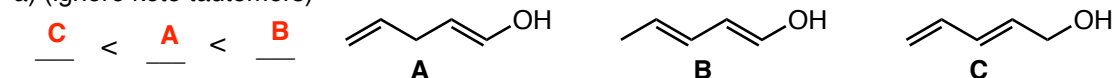


resonance contributors for all conjugate base anions (substituents not shown)



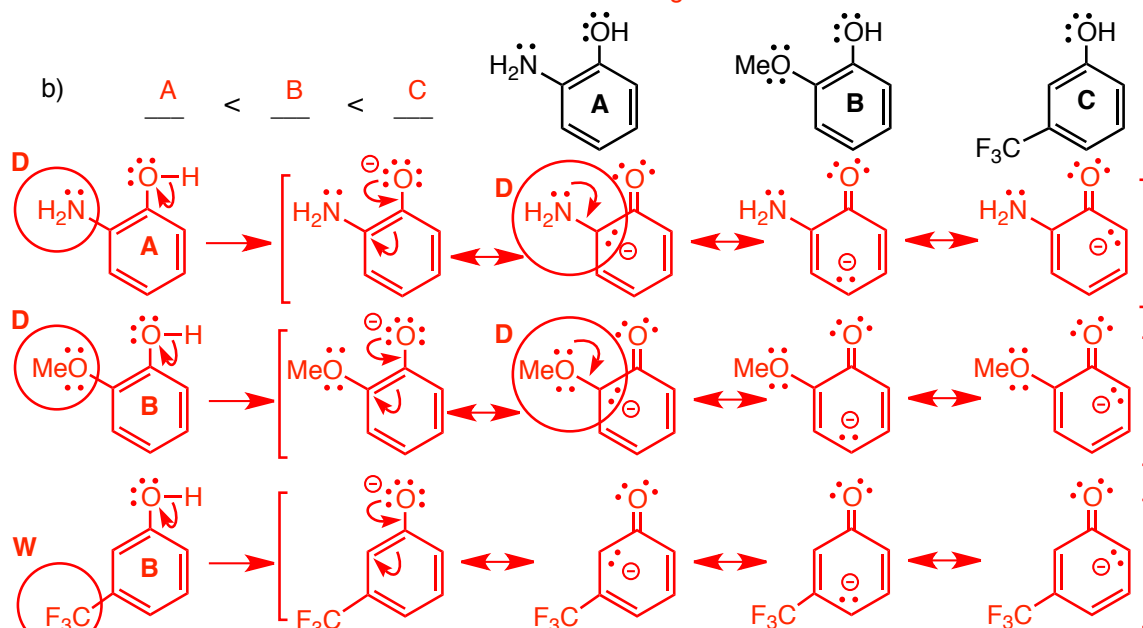
rank in order of increasing Bronsted acidity, give a BRIEF explanation

a) (ignore keto tautomers)



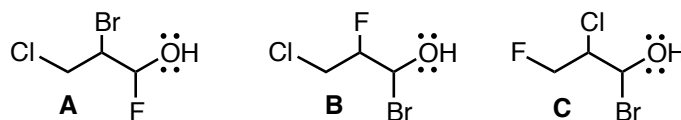
the conjugate base anion for **B** has 3 resonance contributors, the base for **A** 2 contributors and that for **C** no resonance stabilizing contributors at all, the more stable the conjugate base anion the stronger the acid

b) A < B < C



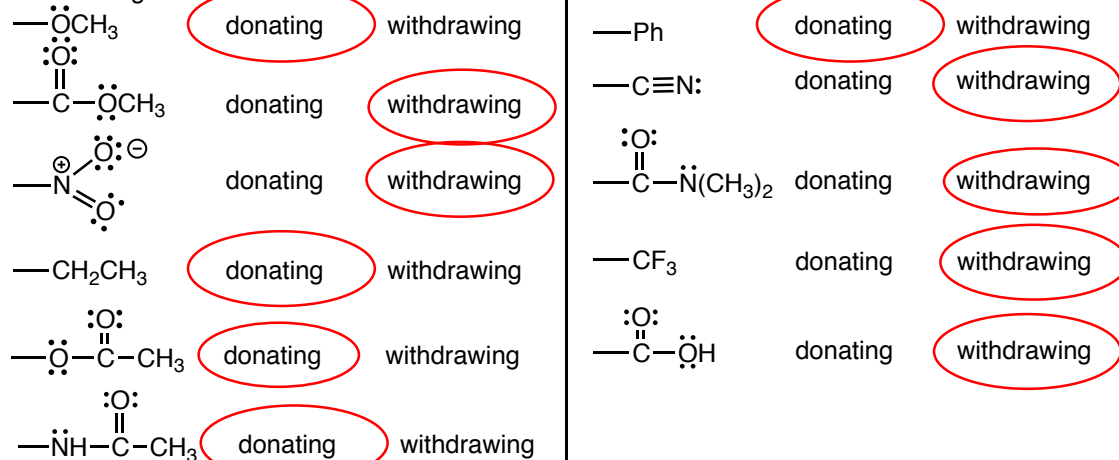
the conjugate base anions from deprotonation of A and B have resonance contributors that are resonance destabilized by resonance donating groups, the charge is on the carbon that carries the donating groups, but -NH₂ is a stronger resonance donating group than -OH (N is less electronegative, the non-bonding electrons on N are higher in energy), the anion from C is somewhat inductively stabilized by -CF₃, even though the charge is never on the carbon with the -CF₃ group, the more stable the base the stronger the acid

c) C < B < A

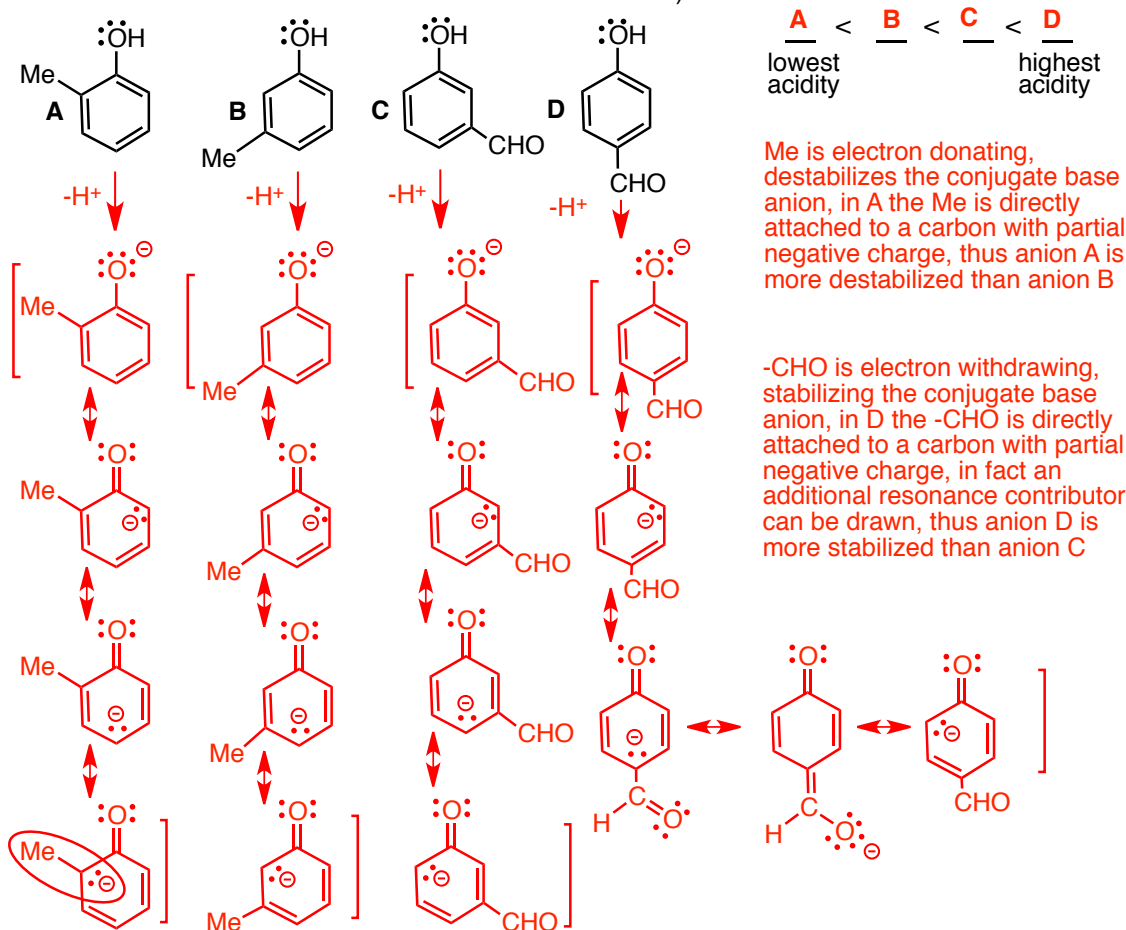


the conjugate base anions formed upon deprotonation the alcohols are more stabilized by the inductive effect by proximity to more electronegative elements, F more electronegative than Cl, more electronegative than Br

a) Classify the following, when as substituents on a benzene ring, as electron donating or withdrawing



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



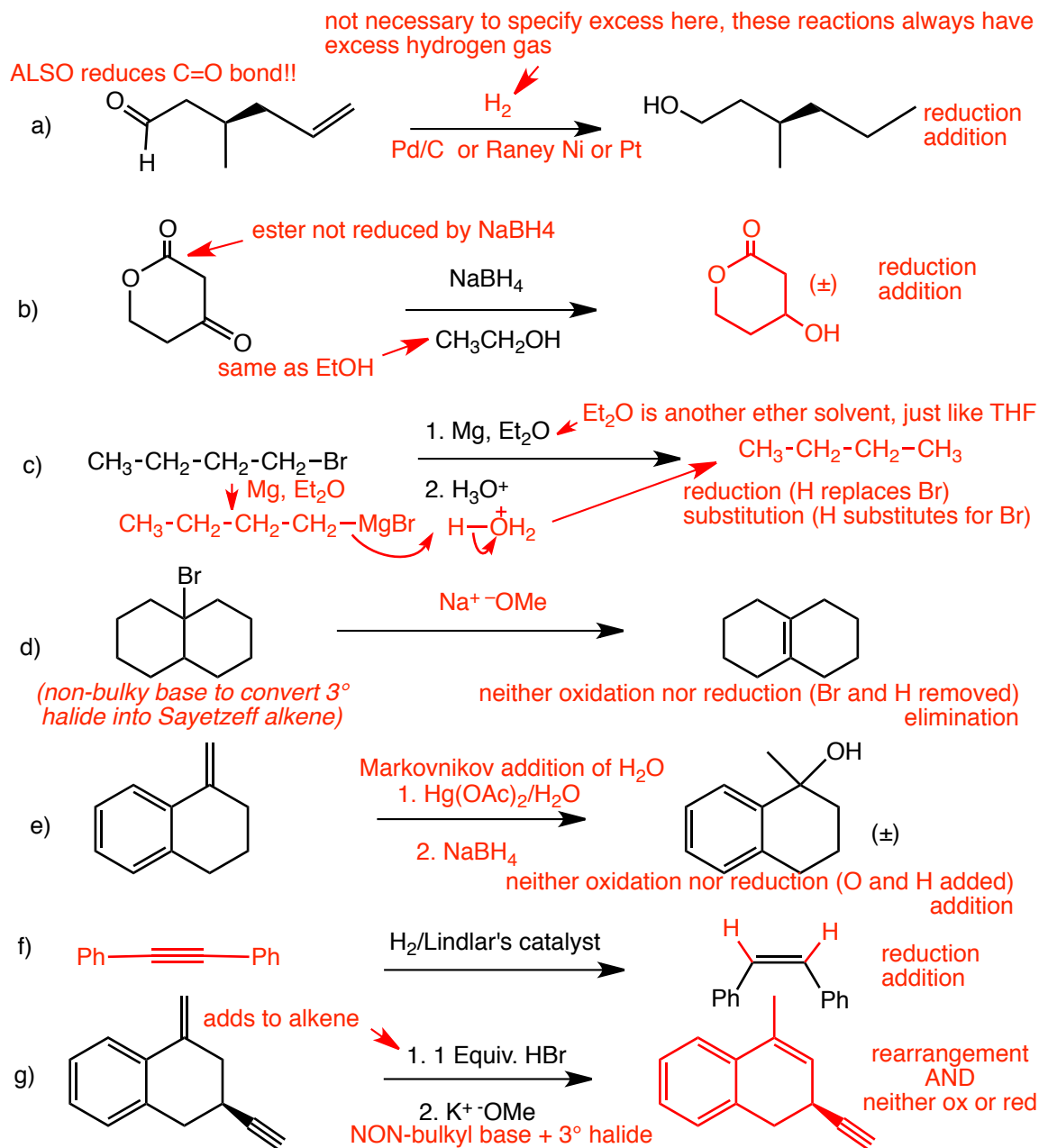
In each case, fill in the missing product, reagents or reactants. Note that non-bonding electrons are generally not shown in these structures.

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

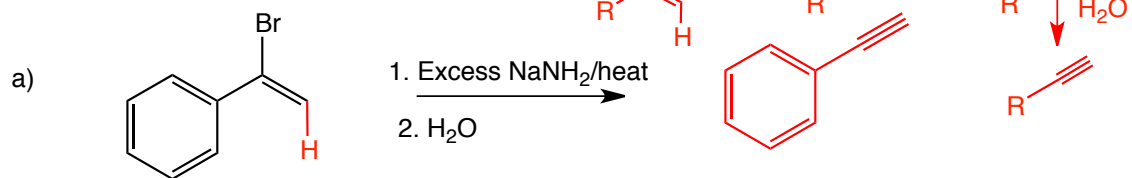
State whether EACH reaction is an **oxidation, reduction or neither**

State whether EACH reaction is an addition, elimination, substitution or rearrangement

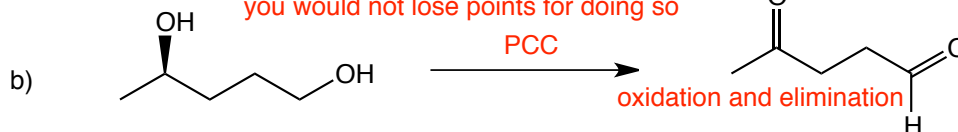


same instructions as previous page

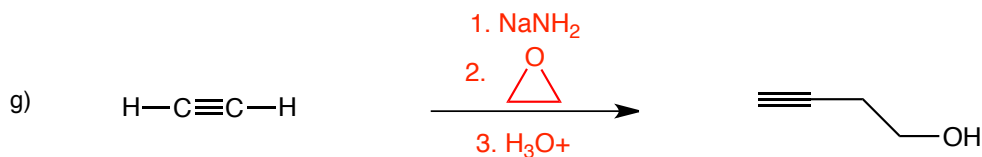
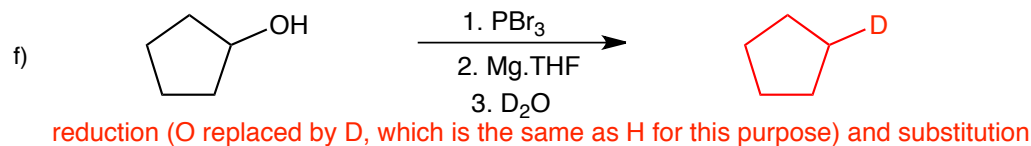
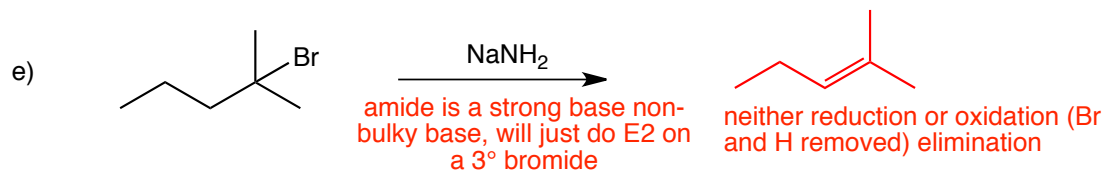
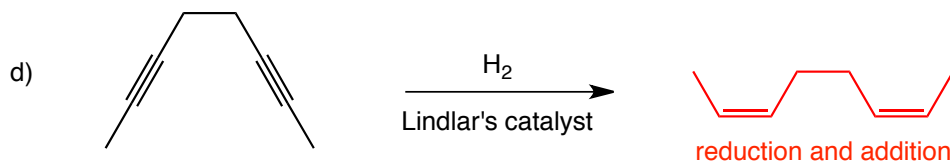
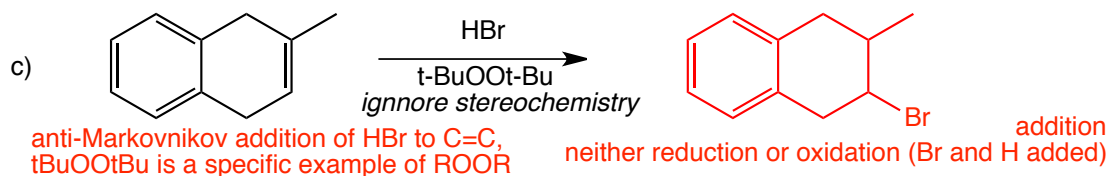
you CAN also start HERE with the vinyl bromide



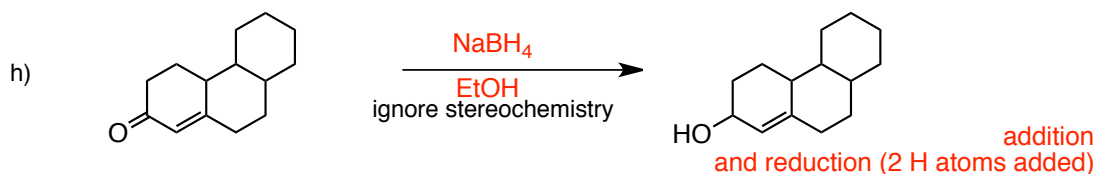
it is not necessary to specify excess here since PCC is always in excess, but you would not lose points for doing so



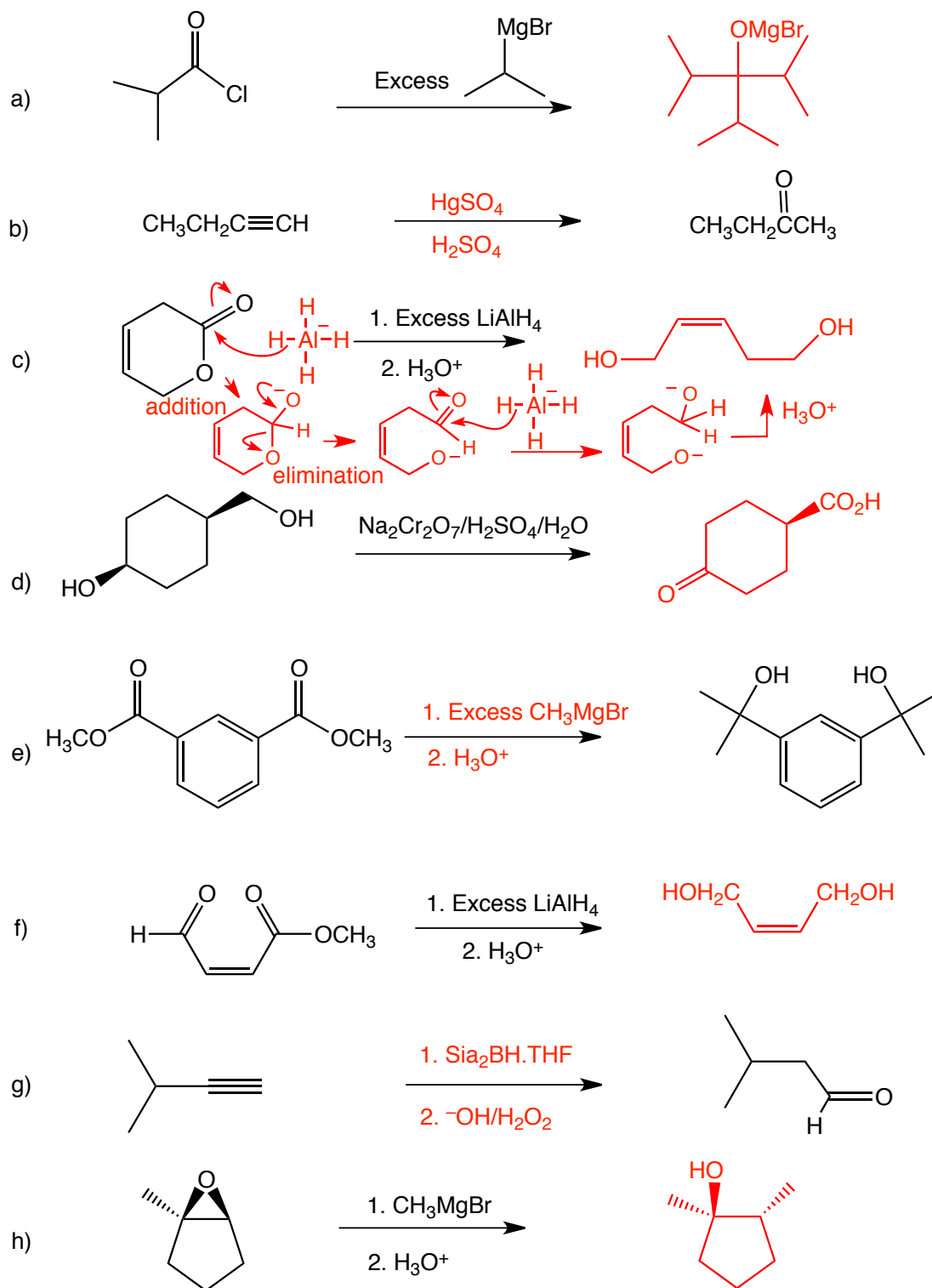
oxidation and elimination



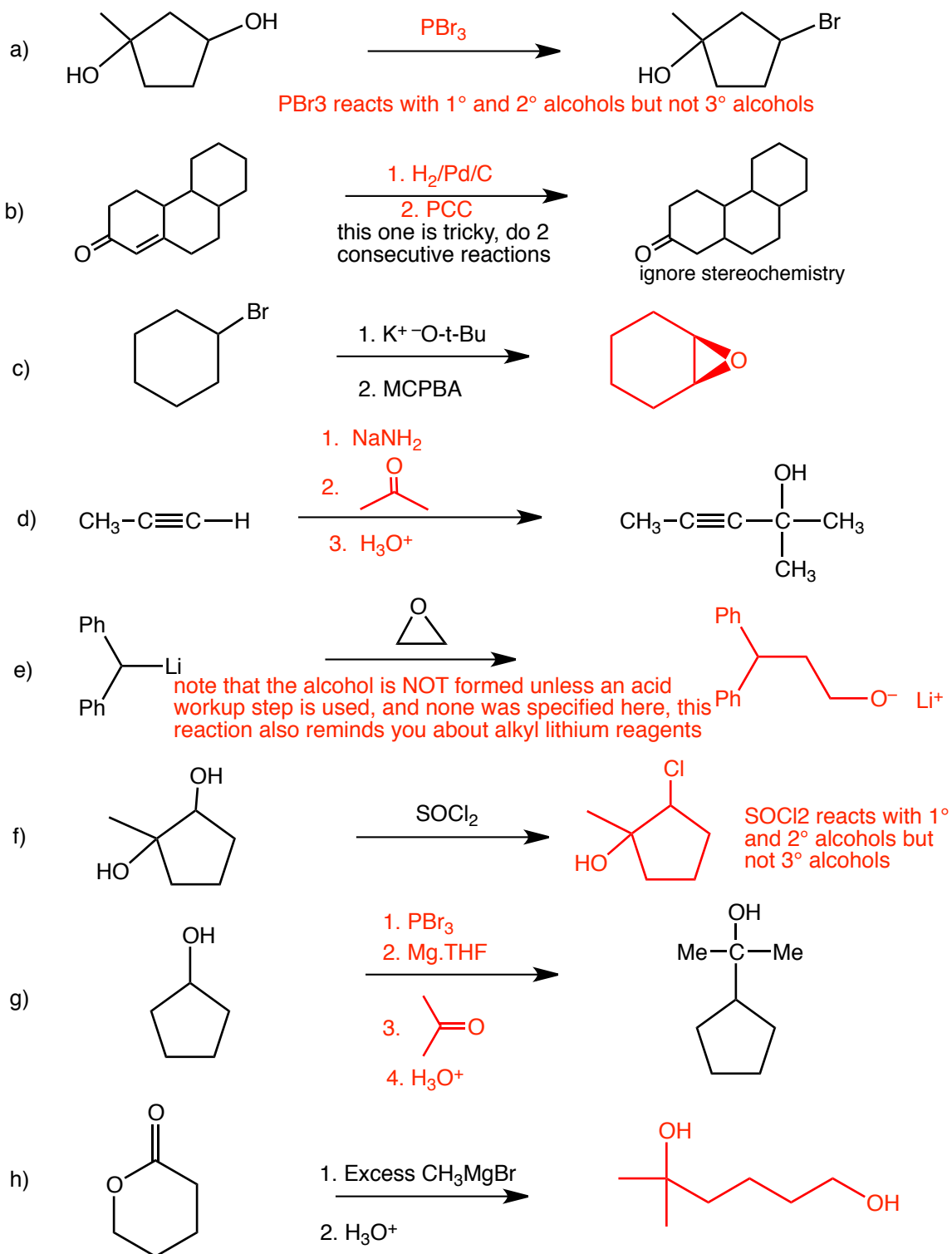
substitution (-H substituted by the -CH2CH2OH) and oxidation, the H is replaced by C (I won't ask something like this on a test!)



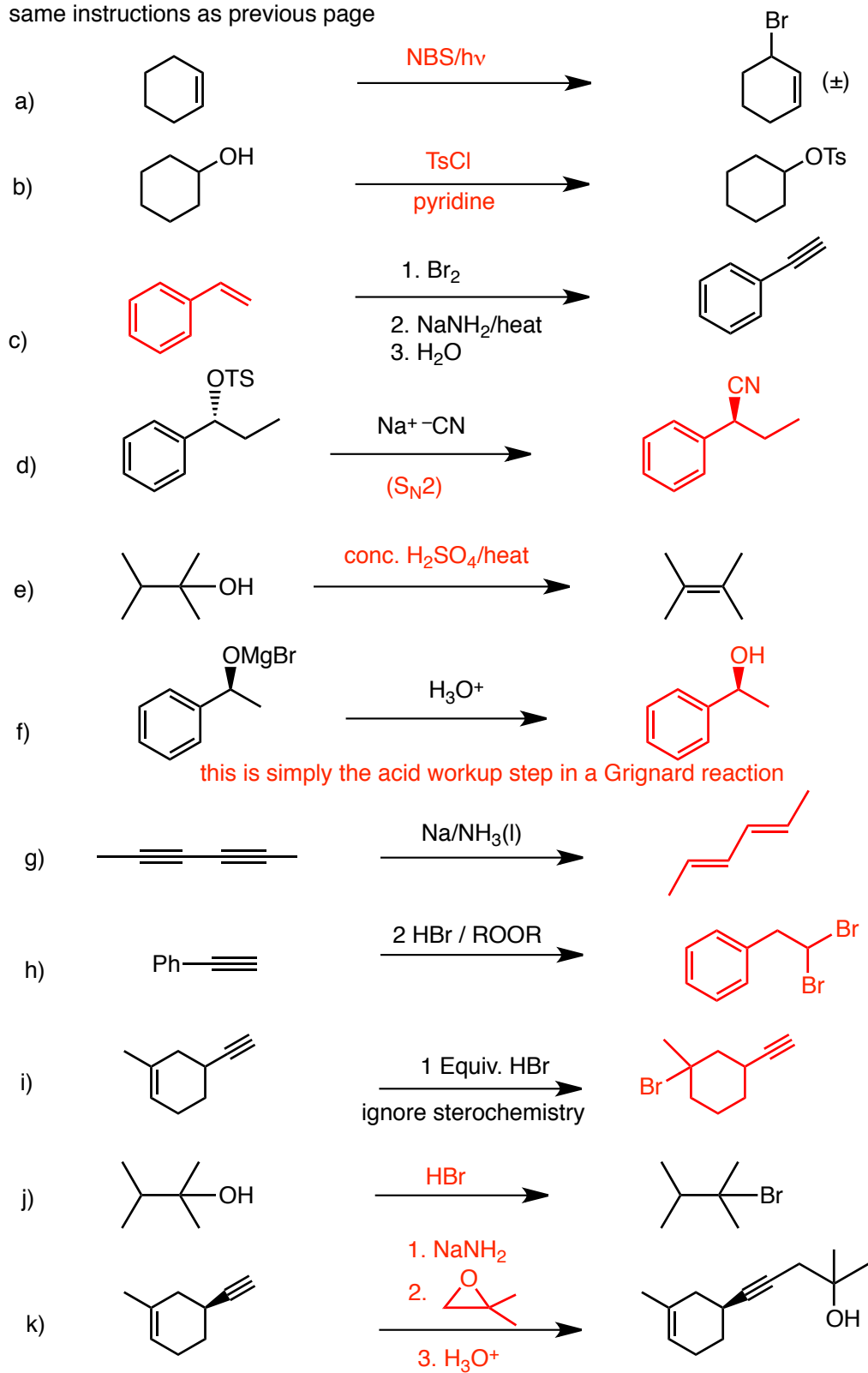
same instructions as previous pages
EXCEPT DO NOT INDICATE REACTION TYPE OR OX/RED for the problems on this page!!



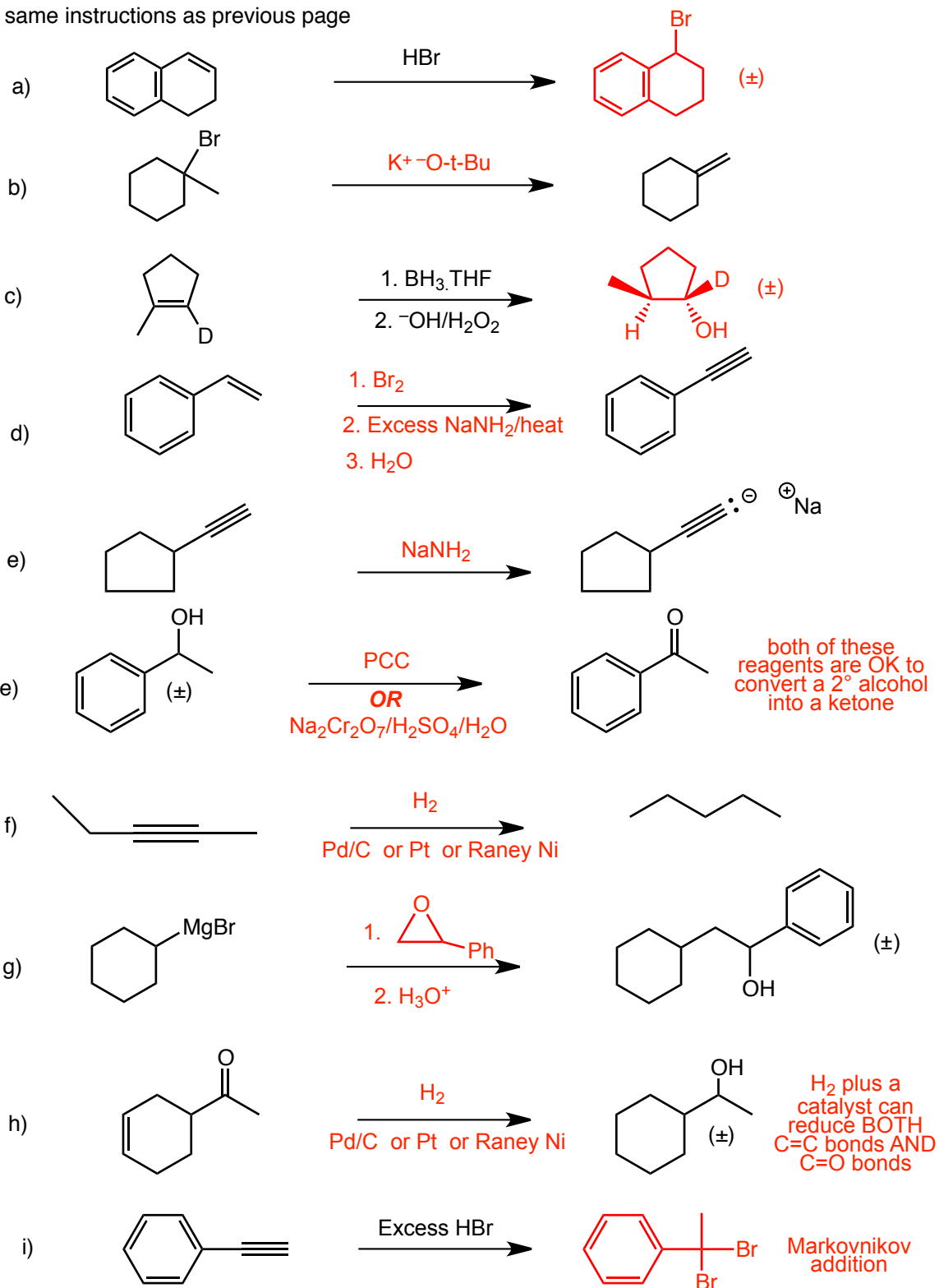
same instructions as previous page



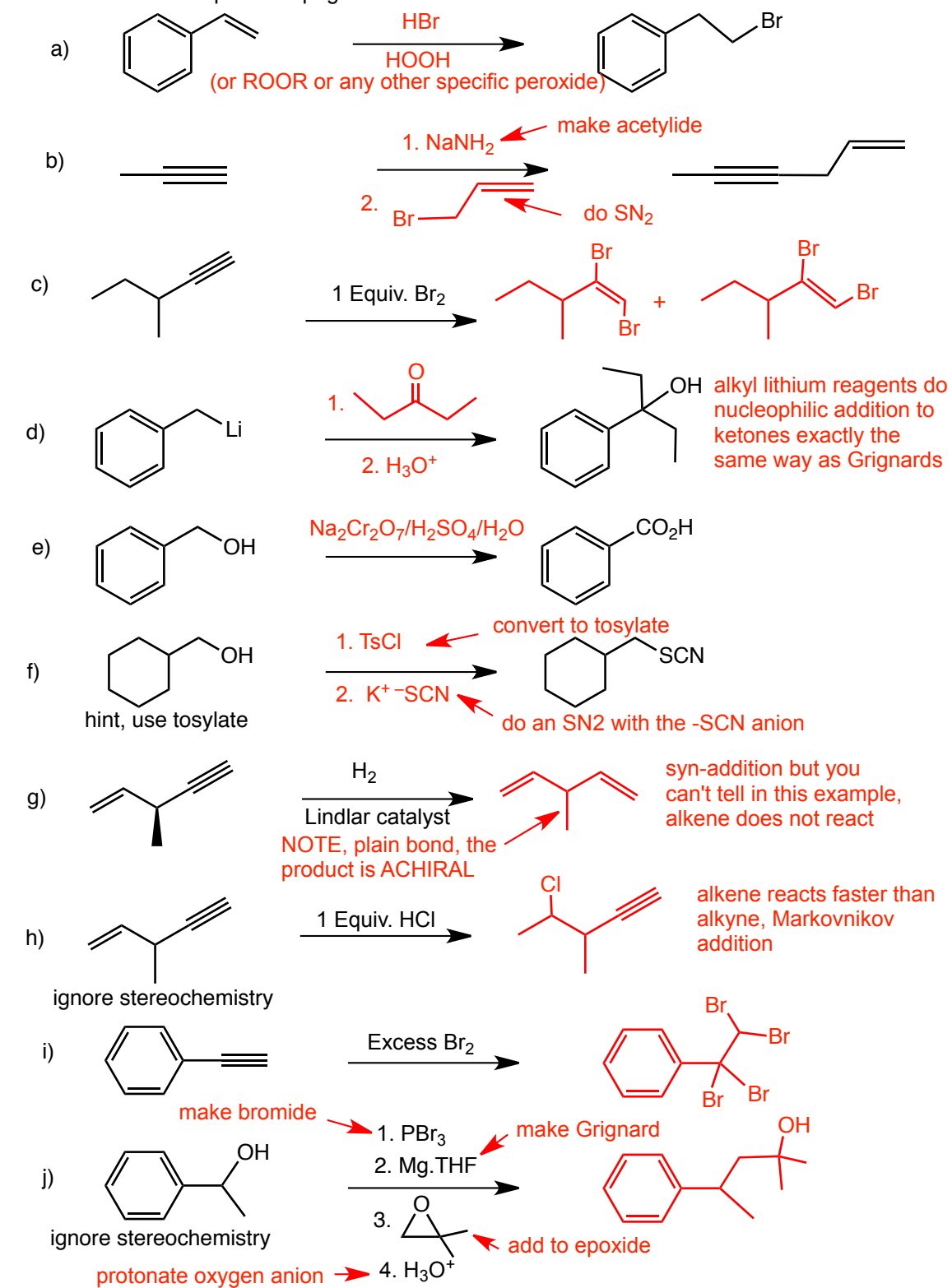
same instructions as previous page



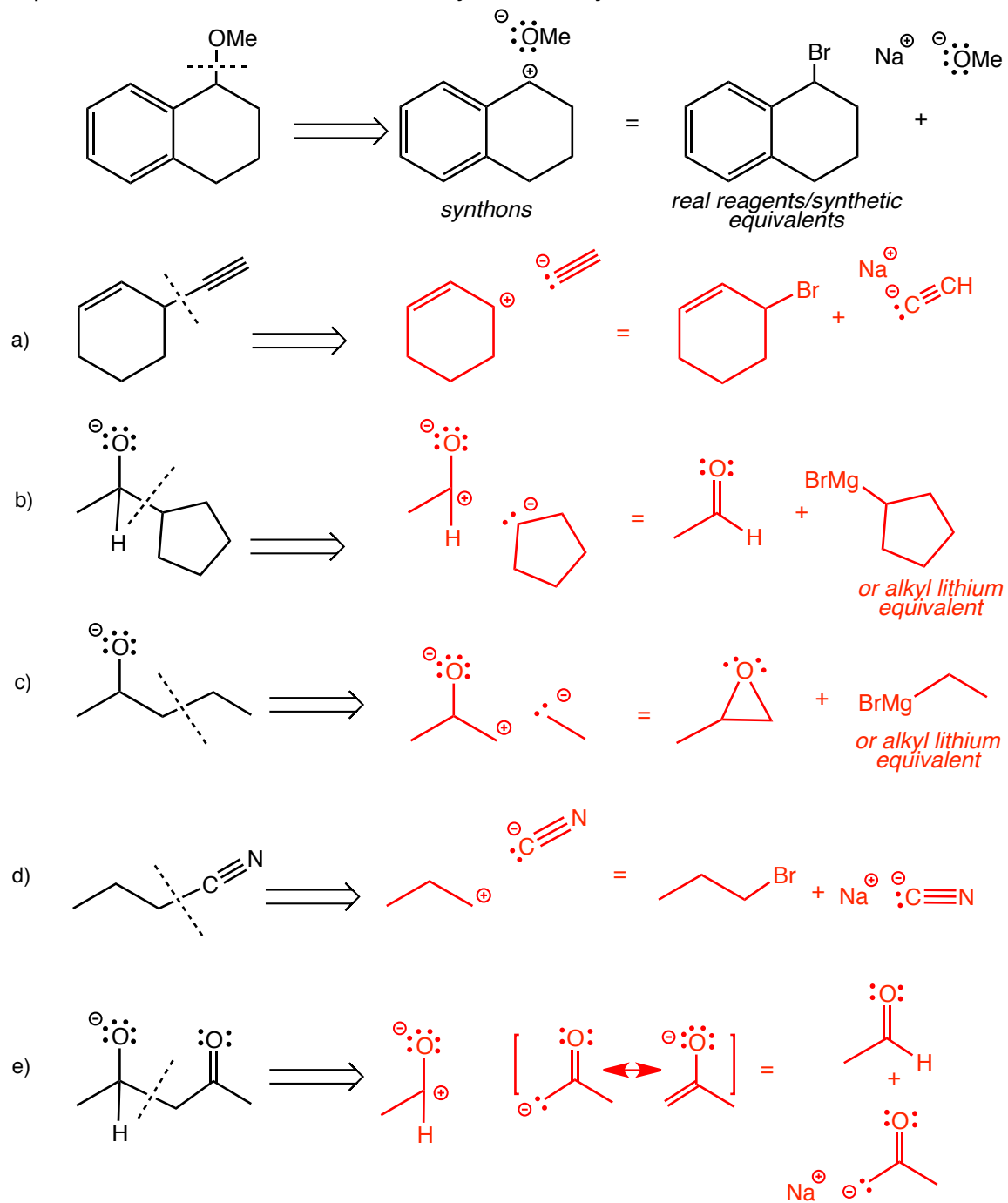
same instructions as previous page



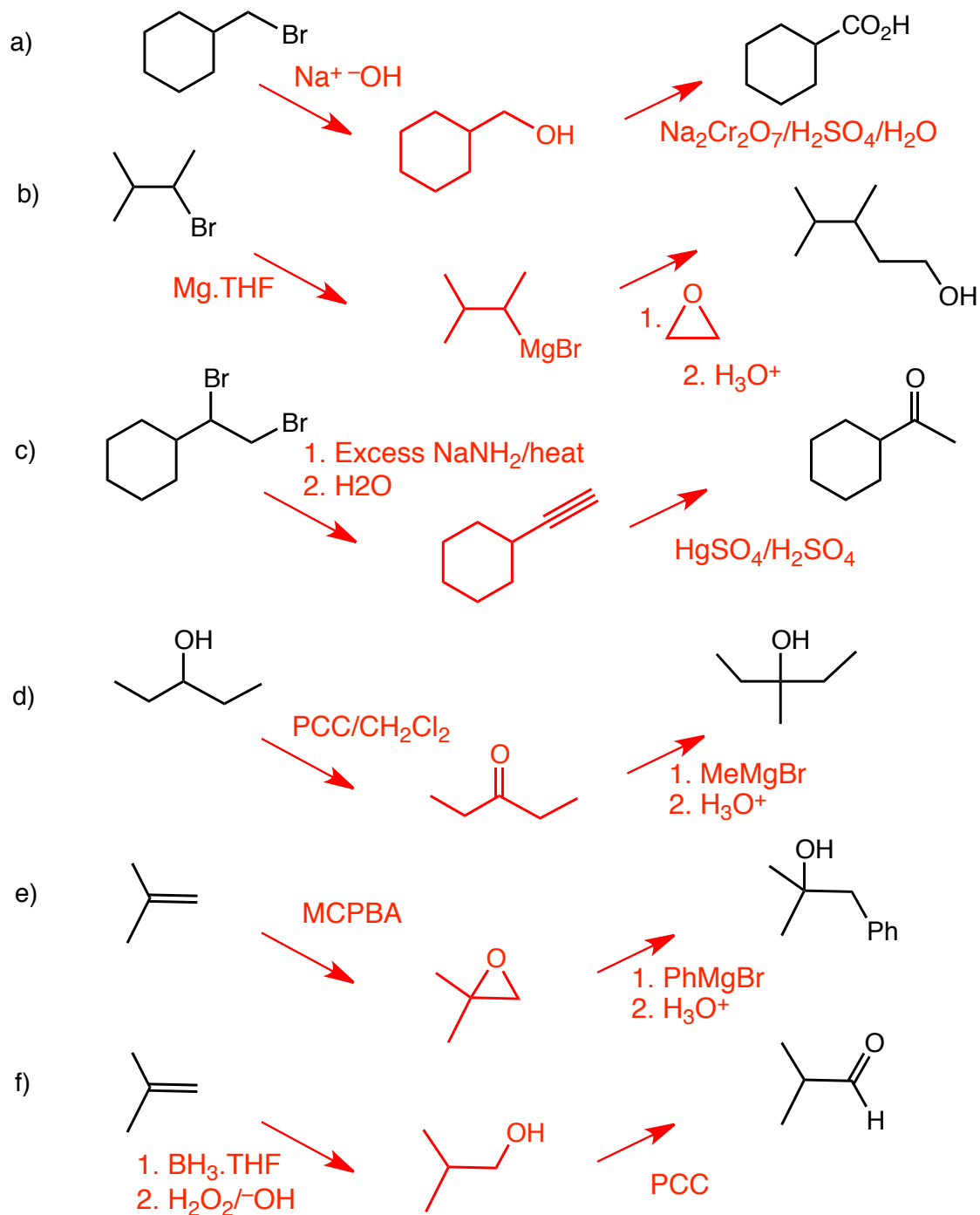
same instructions as previous page



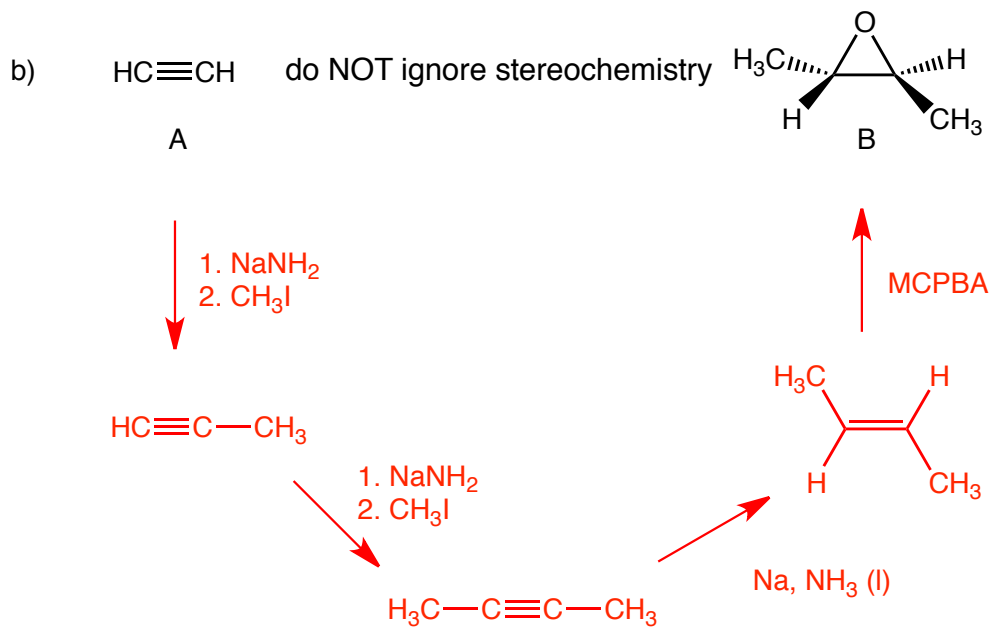
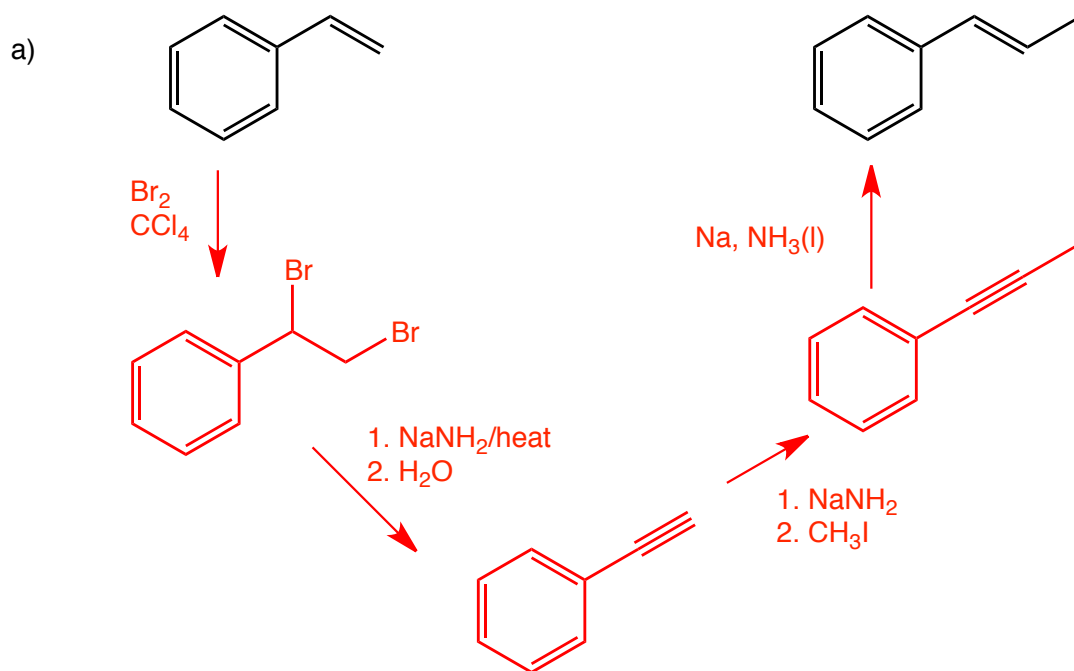
disconnect the indicated bond according to the method of retrosynthetic analysis, generate the synthons and convert these into "real reagents", or "synthetic equivalents". The first one is done for you so that you can see what to do.



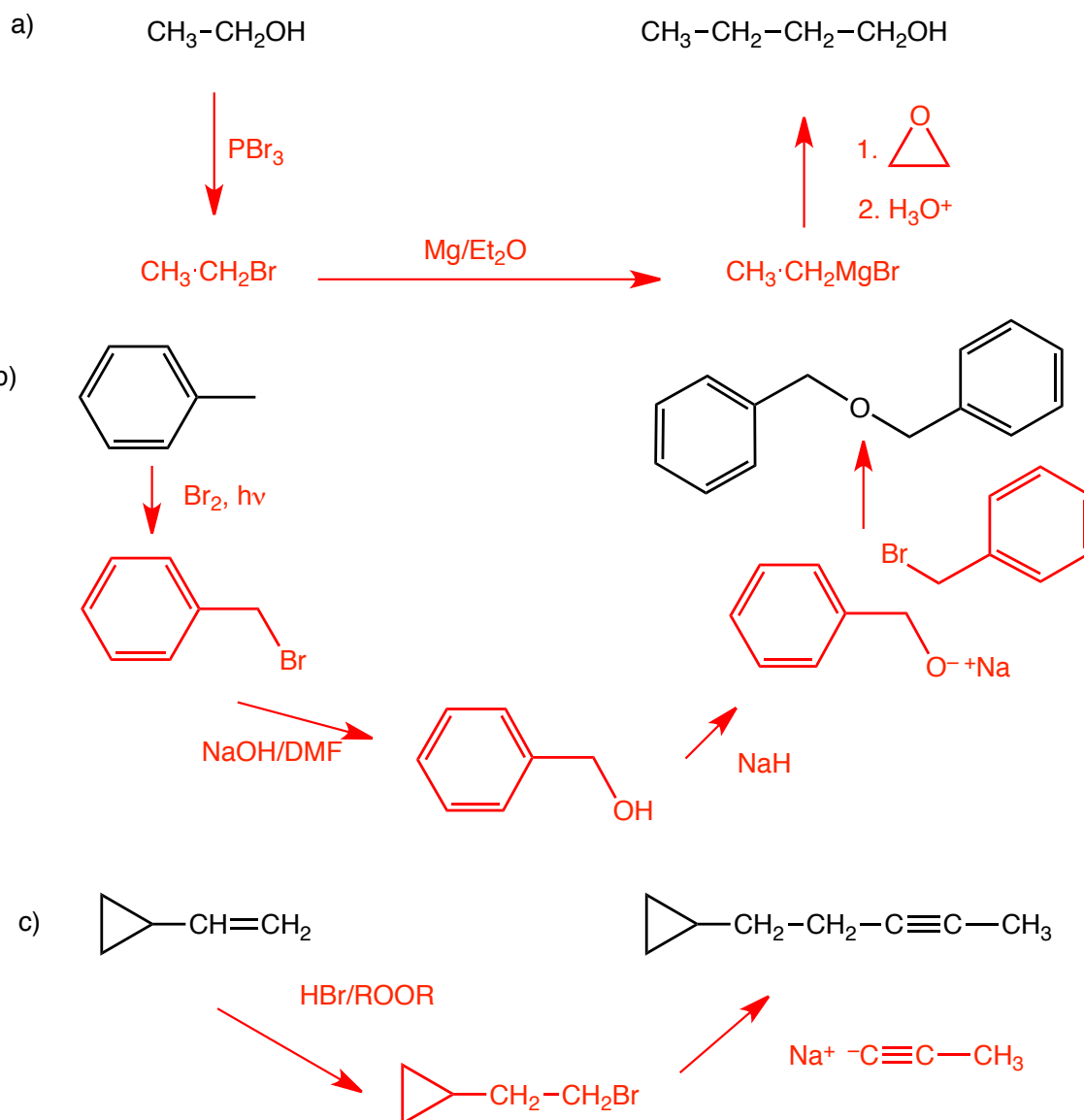
The following retrosynthesis problems can be done in only two steps, they are simpler than you will find on the midterms, they are to build confidence (ignore stereochemistry)



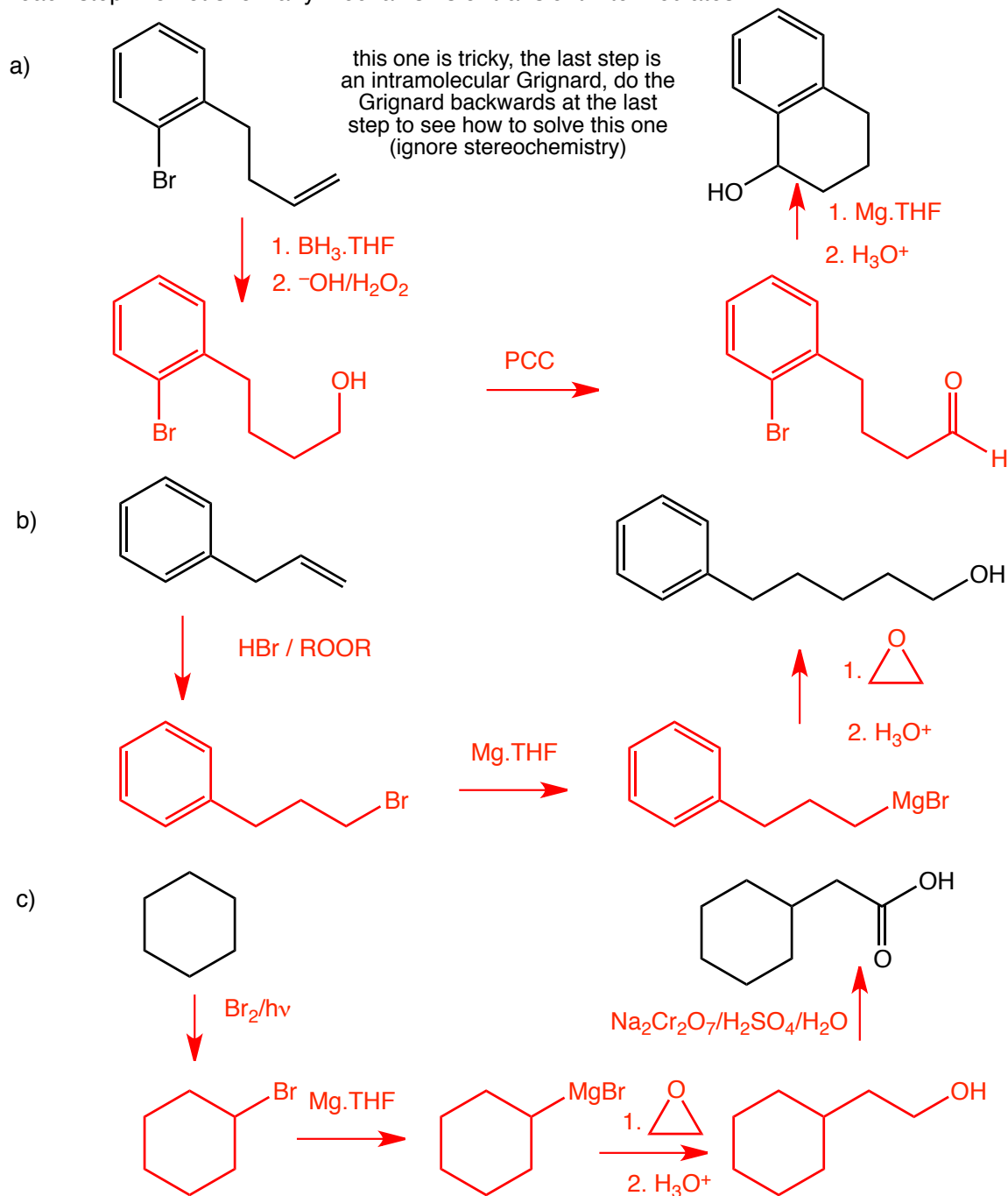
Synthesize the (target) molecule on the right from the starting molecule the left. this can not be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.



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.



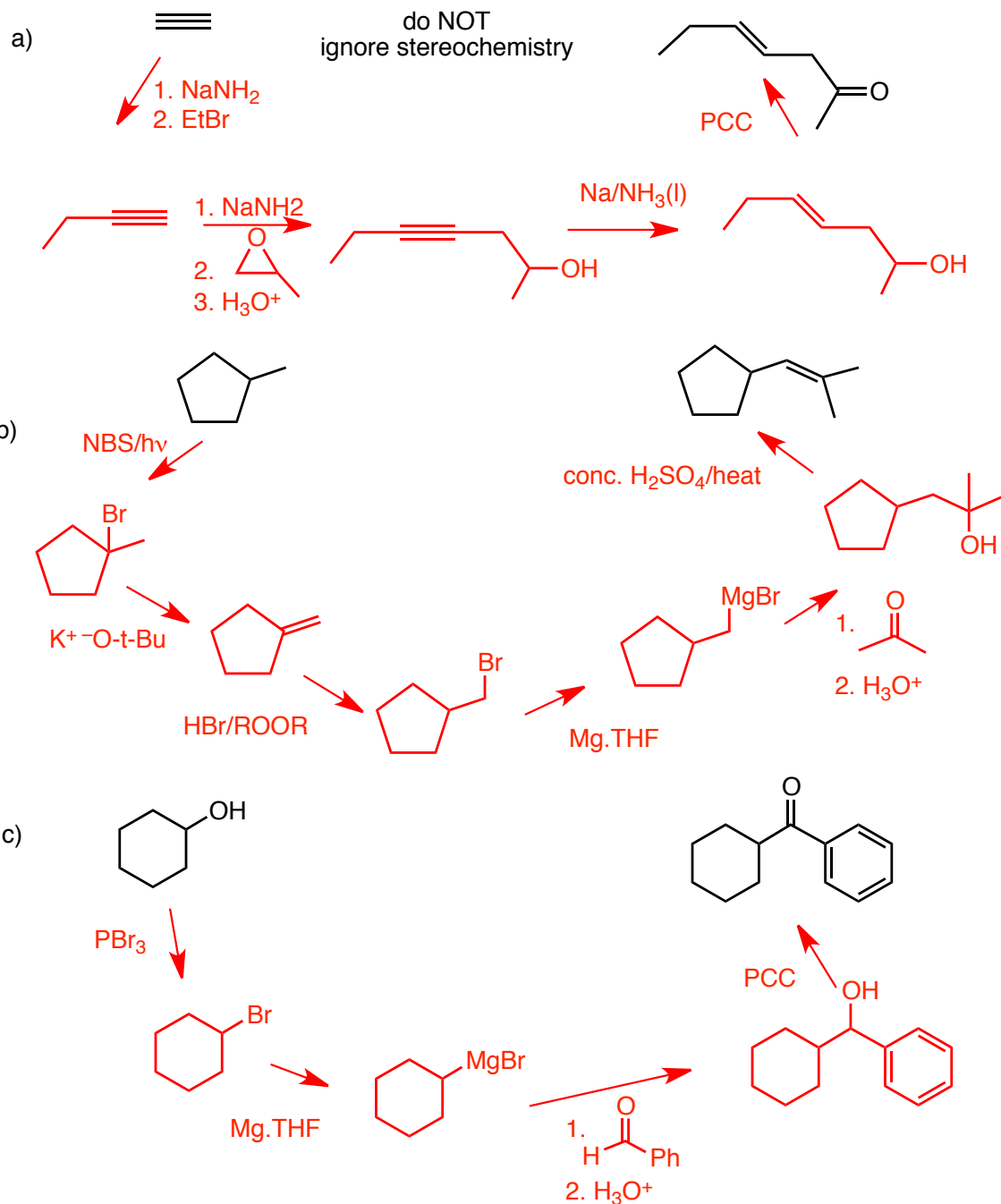
Synthesize the (target) molecule on the right from the starting molecule the left. this can not be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.



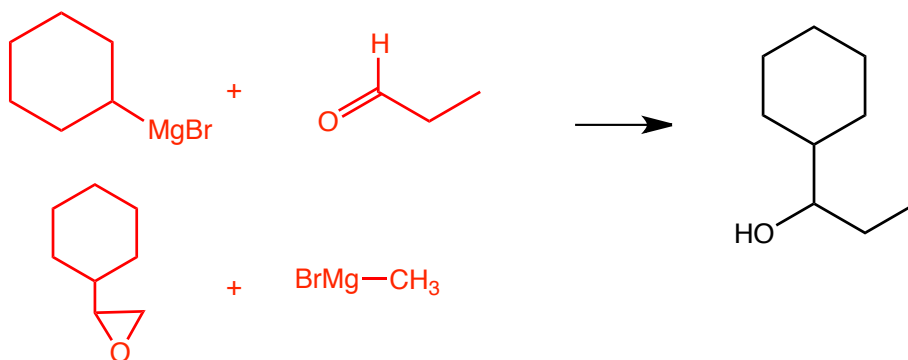
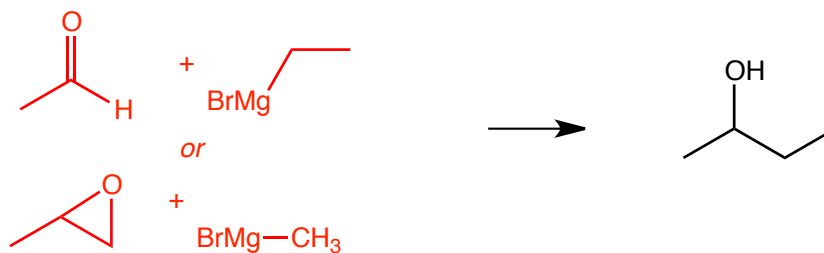
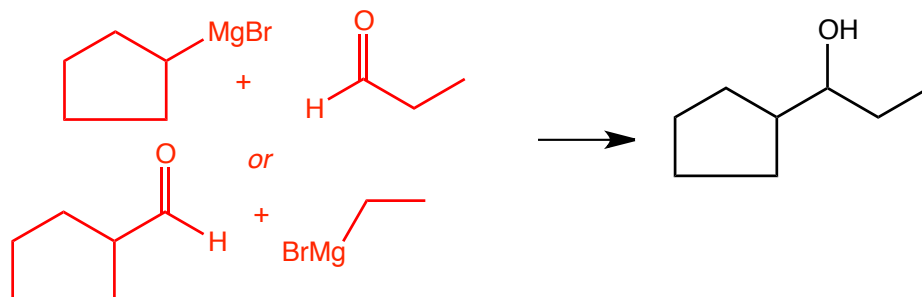
page seventeen

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.

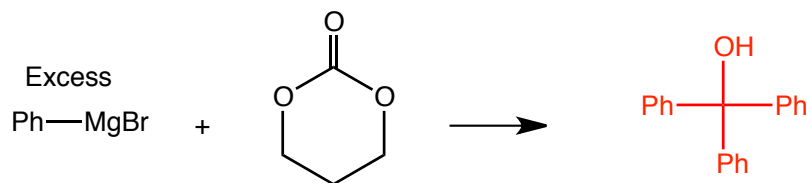
These problems are considered difficult



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

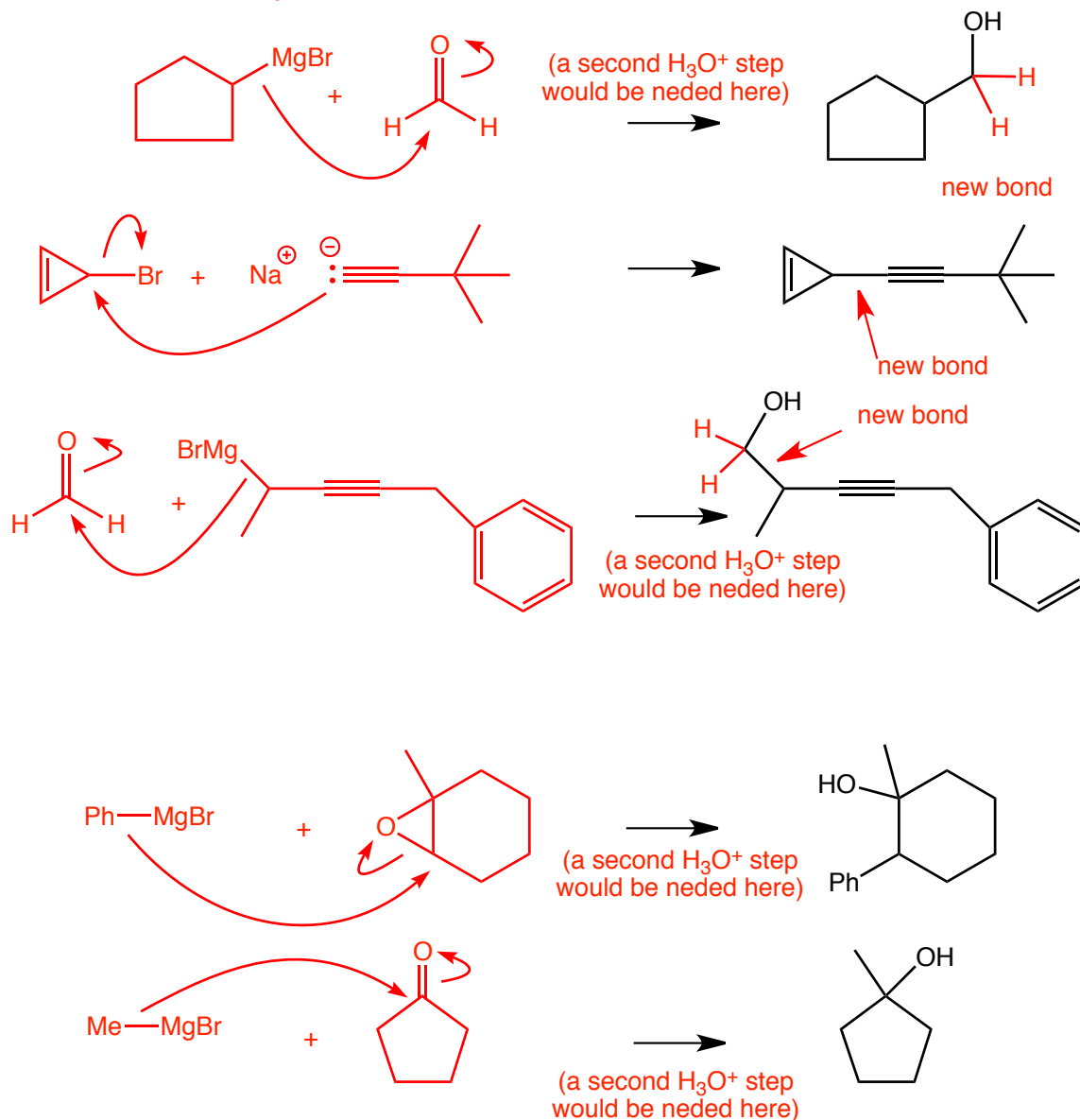


Give the product of addition of this Grignard reagent to this cyclic compound, after workup with dilute aqueous acid (addition of H_3O^+).



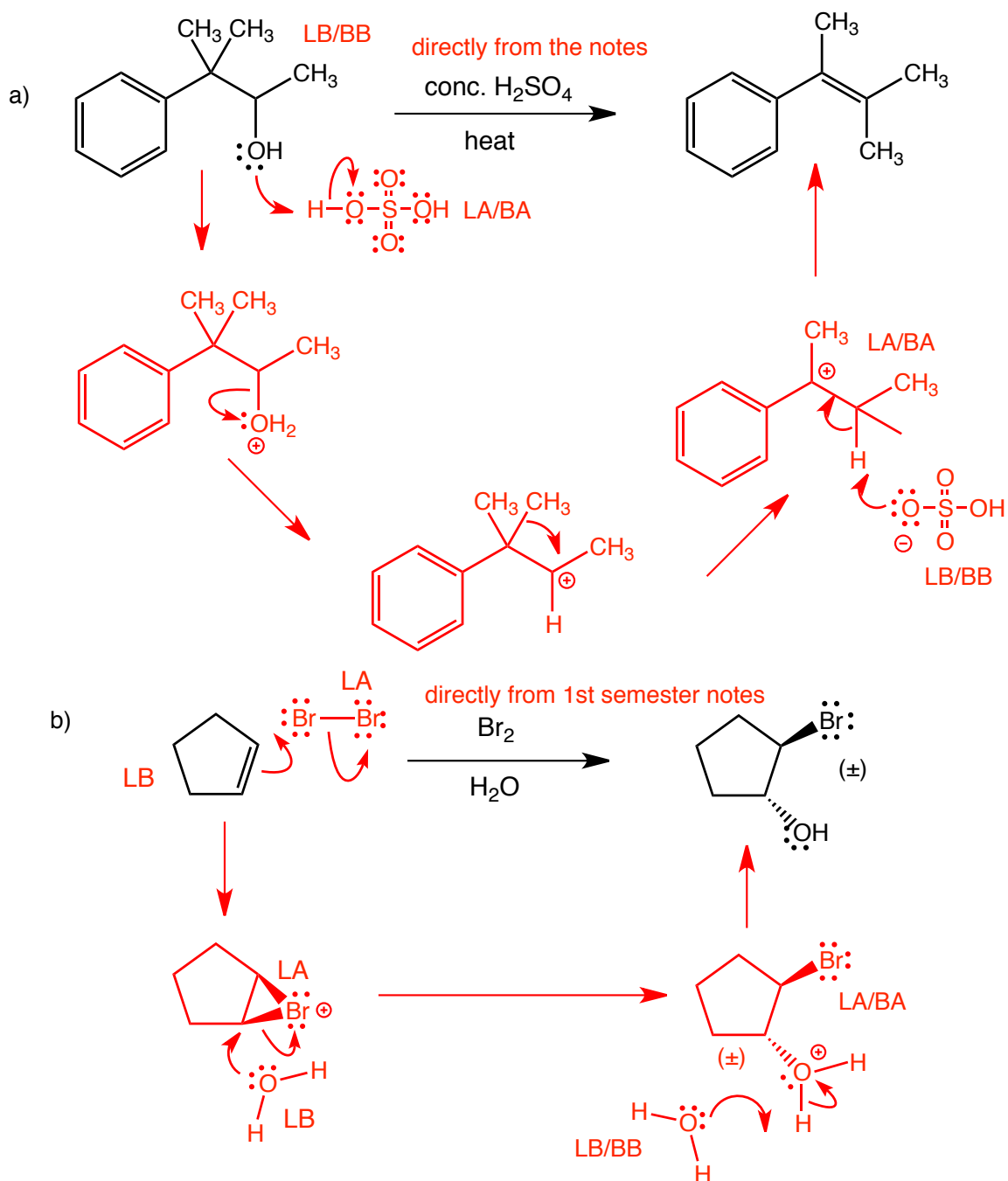
In each case, provide ONE SET of reactants/reagents/conditions that can react to make a new C-C bond for each provided structure (an acid workup step can be assumed, if necessary, you do not need to include it). In each case there may be more than two possible answers, but only 1 is shown here

on a test it would not be necessary to show the curved-arrow pushing, it is included here so that you can see how the reactions work



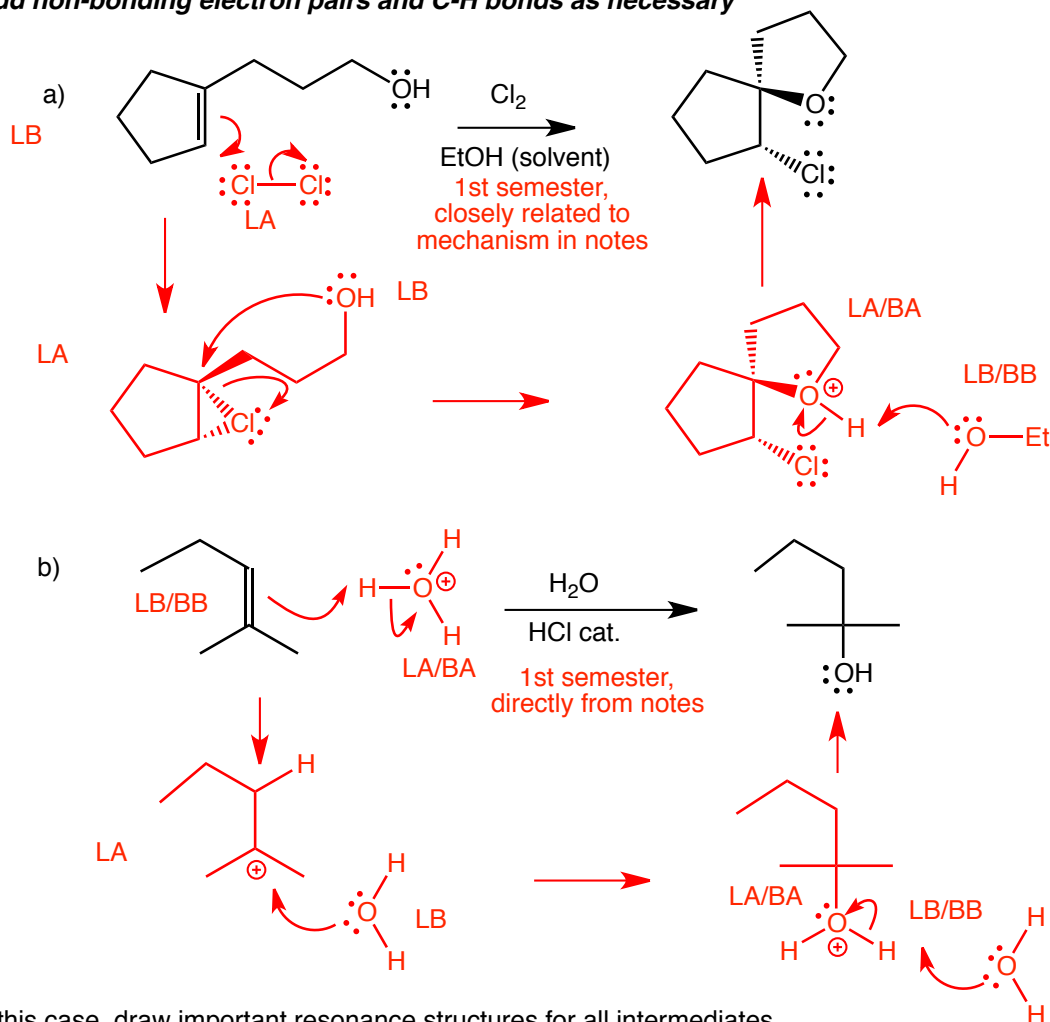
Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

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

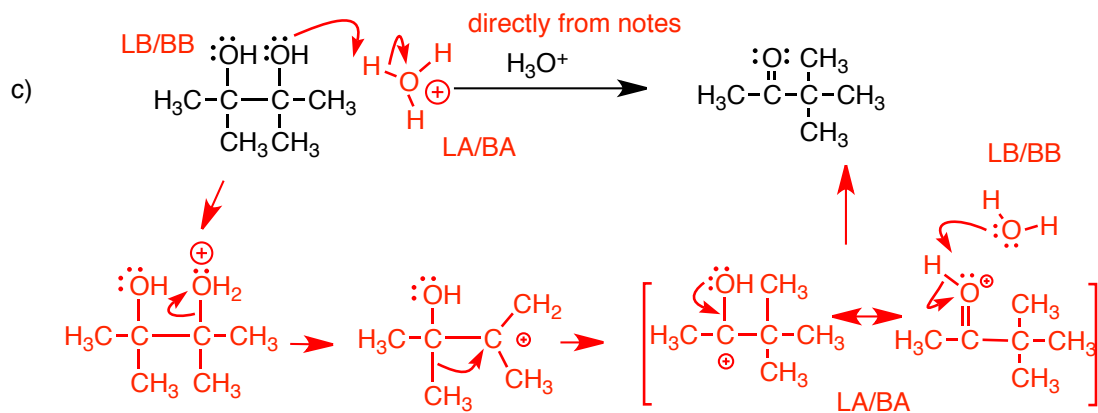


Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

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



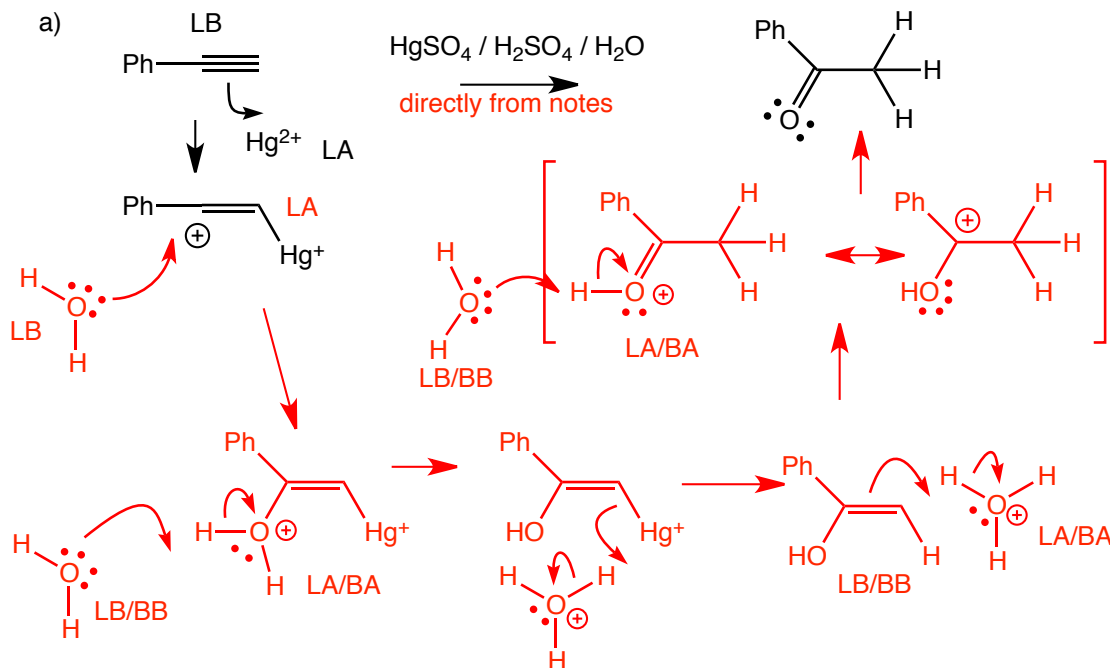
In this case, draw important resonance structures for all intermediates



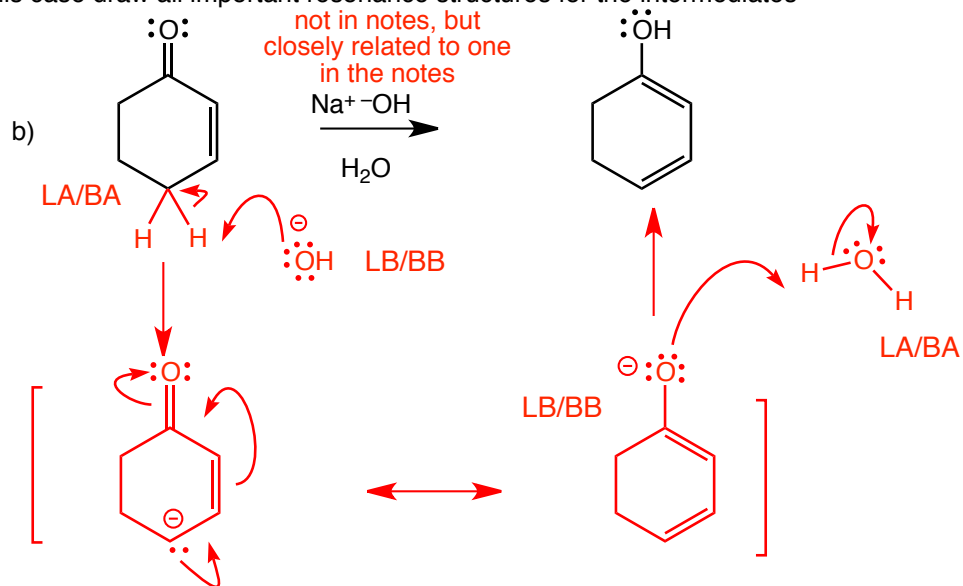
Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

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



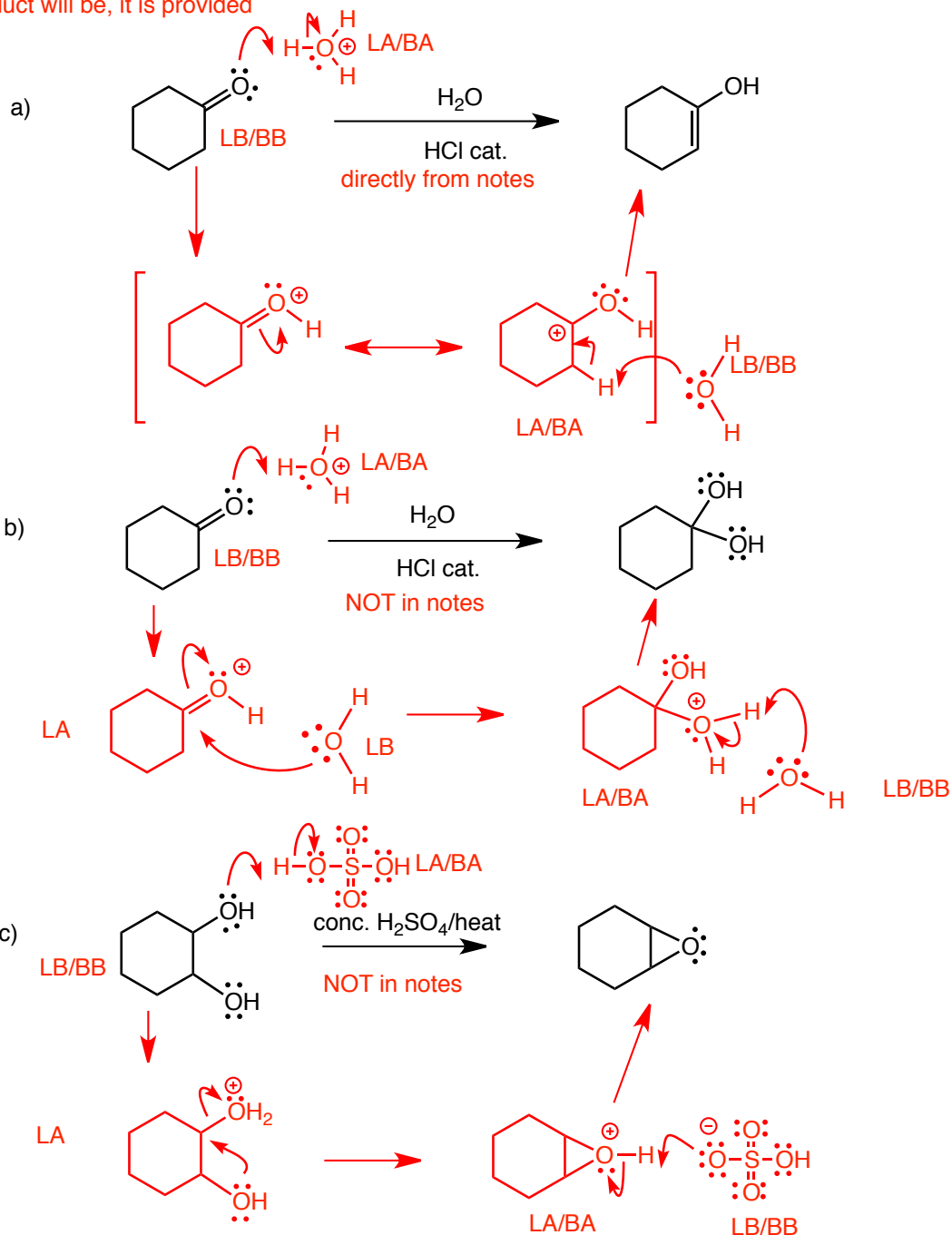
In this case draw all important resonance structures for the intermediates



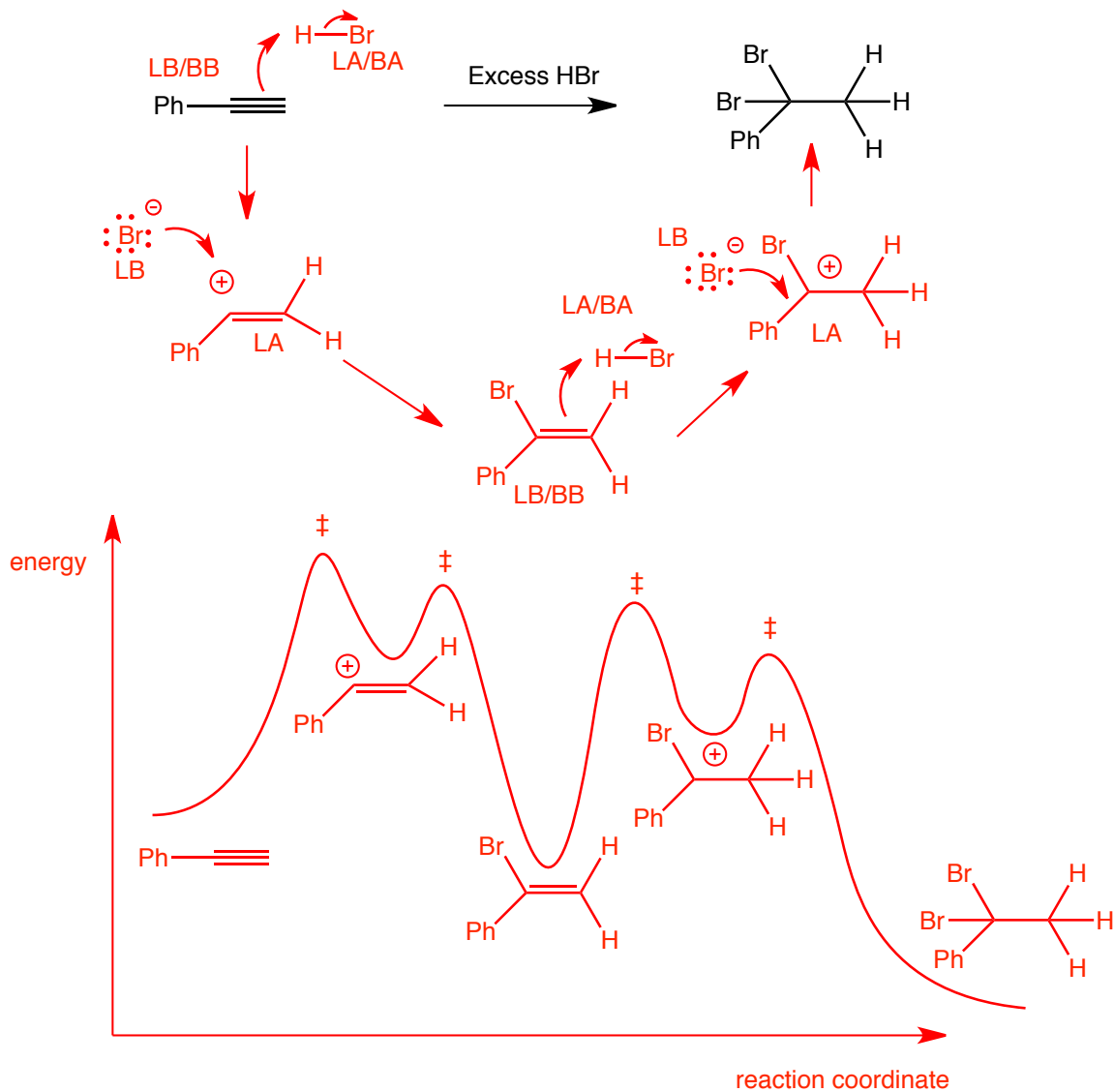
Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

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

NOTE, these are mechanism problems, which means that you do not have to work out what the product is (e.g. problem a versus problem b on this page, it is provided, so even though there are (at least) 2 possible reactions for a ketone plus aqueous acid/ you don't have to work out what the product will be, it is provided)



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.

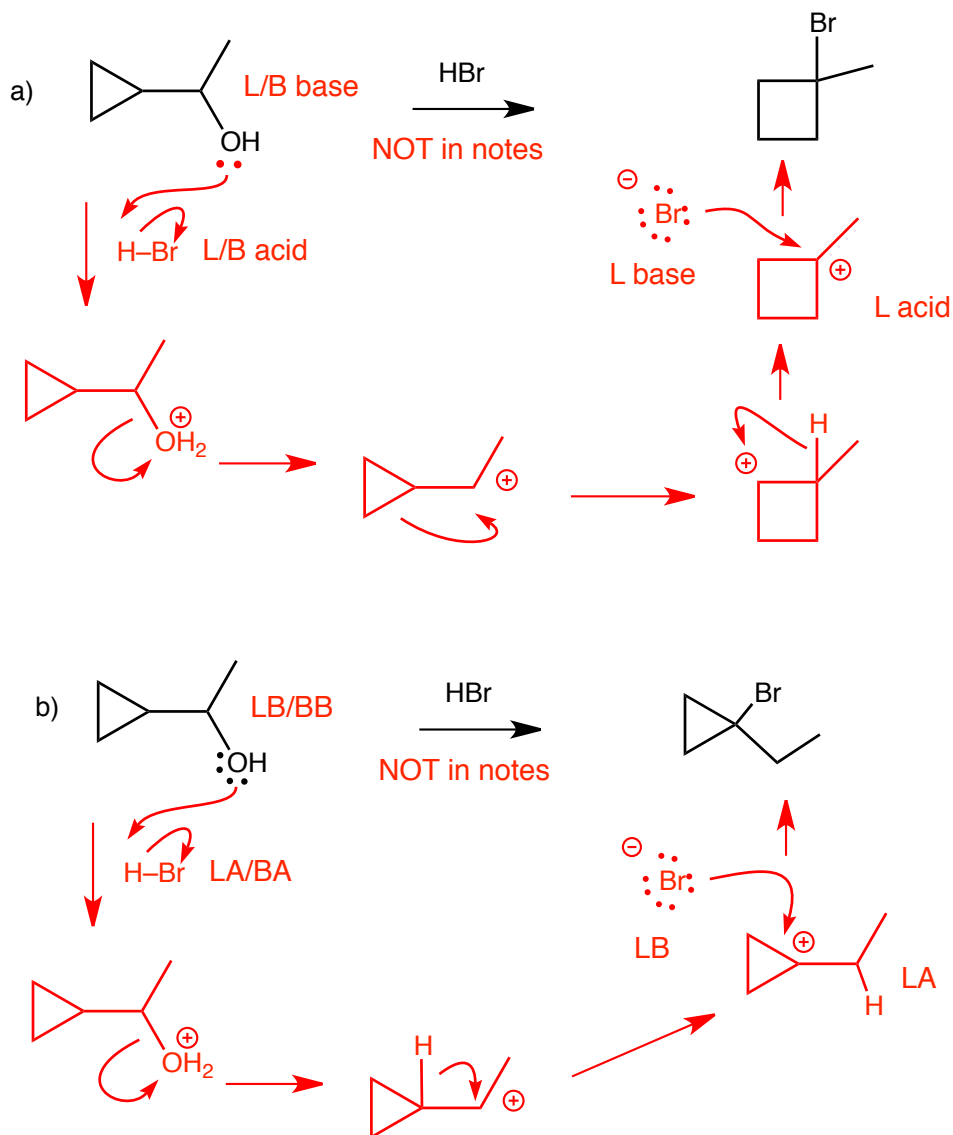


Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

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

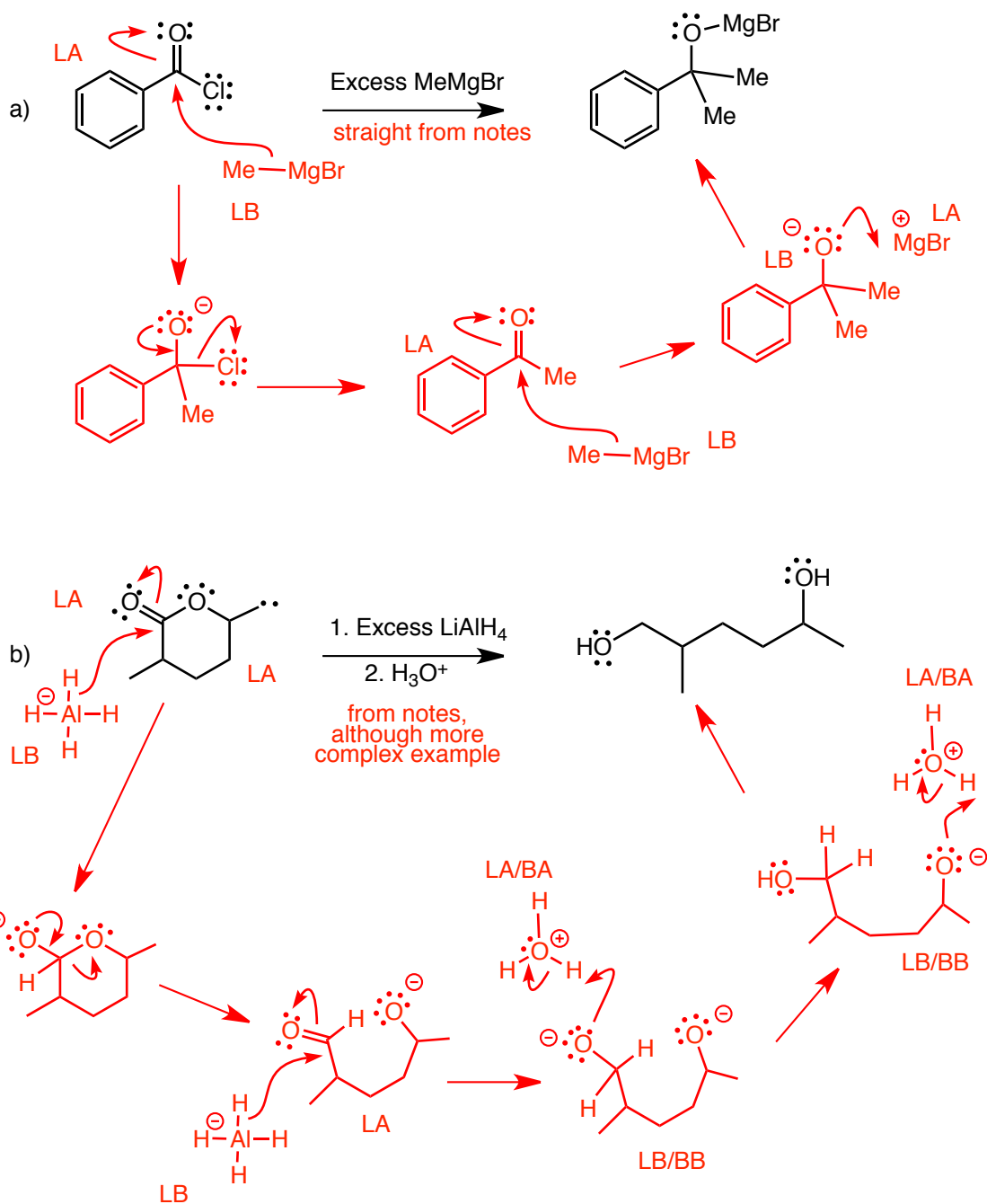
these are a little bit tricky, but use what you know about LA/LB reactions and cation rearrangements to solve them

NOTE, these are mechanism problems, which means that you do not have to work out what the product is, so even though there are (at least) 2 possible products for this reaction, you don't have to work out what the product is in each case, it is provided

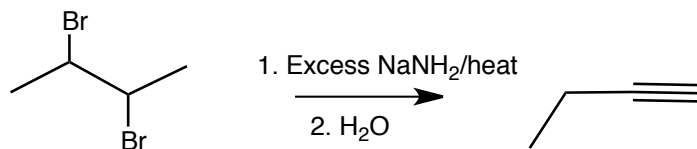


Provide detailed (arrow pushing) mechanisms for the following transformations. Where appropriate, indicate the Lewis acids and bases for each step, and whether they are also Brønsted acids and bases (LB/BA, LA/BA etc.)

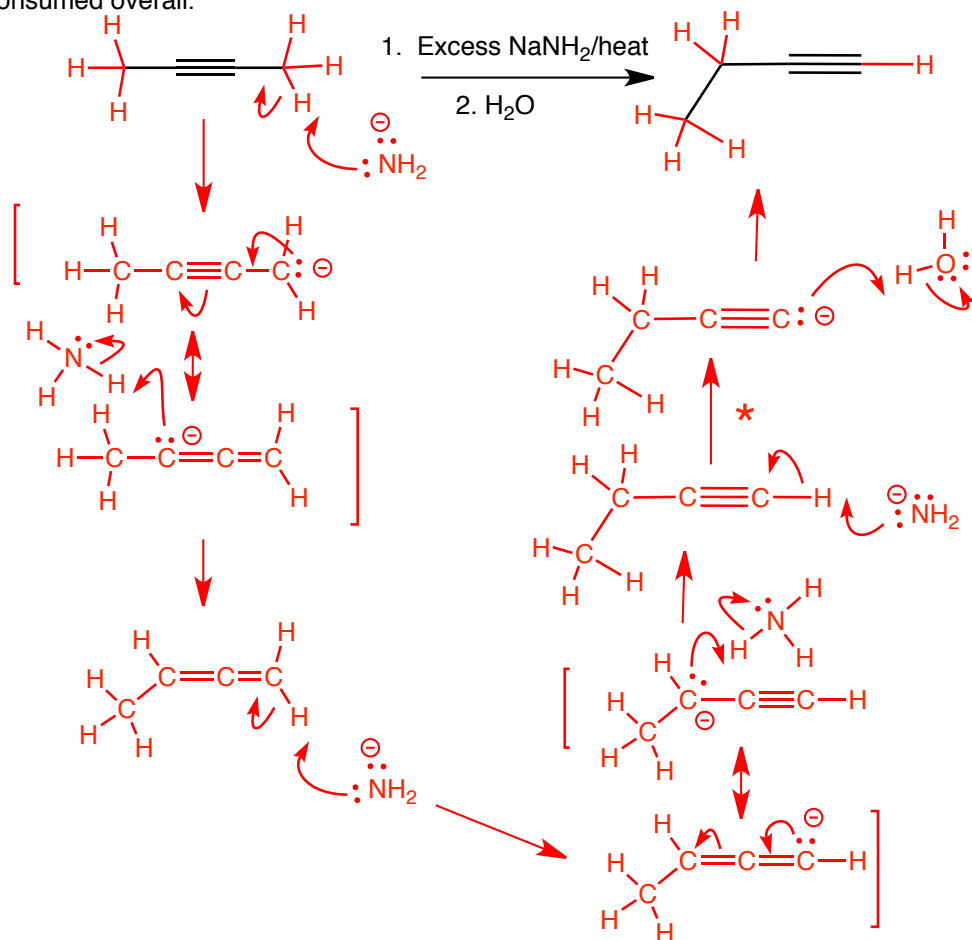
Add non-bonding electron pairs and C-H bonds as necessary



In class we learned that dehydrohalogenation of a dibromide is only useful for preparation of a terminal alkyne, in fact the following reaction occurs.....

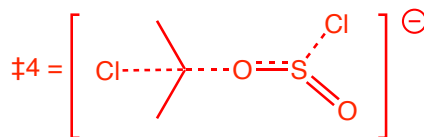
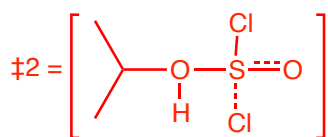
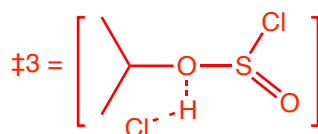
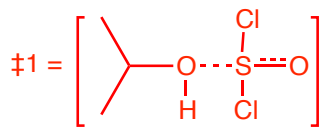
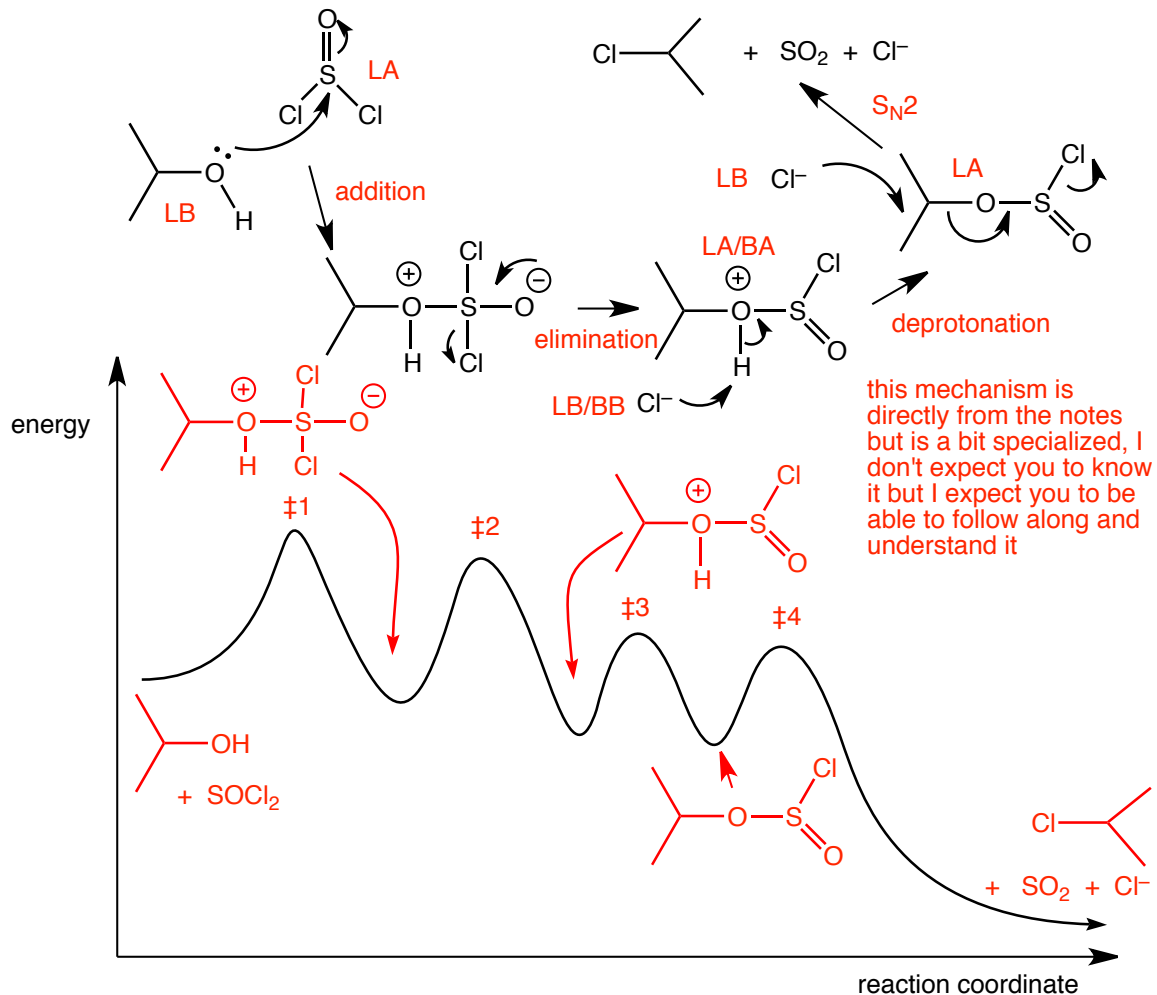


the internal alkyne is formed initially, but it isomerizes to the terminal alkyne, as shown below. Give a mechanism for this isomerization. Solve the problem using the strategy we talked about in class, look at what C-H bonds you have to break and which you have to make, and simply do them in the correct 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.

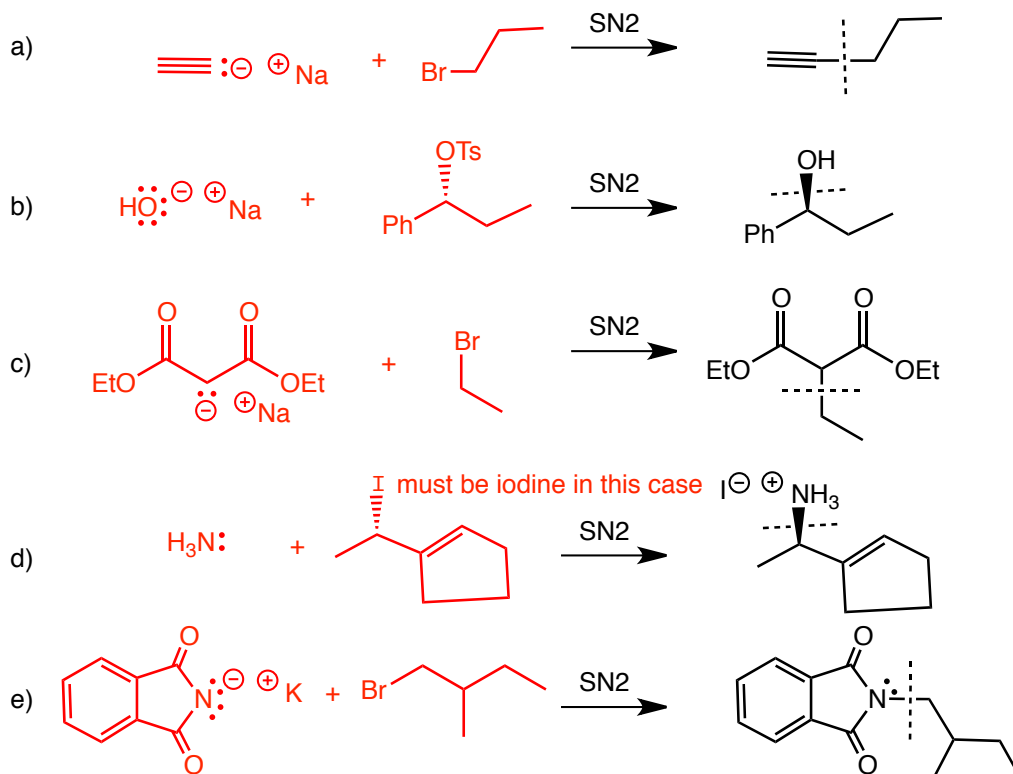


* this last deprotonation by the -NH_2 is unavoidable, and is why the H_2O is needed as step 2, in fact the position of the C-C triple bond can "wander" up and down the chain, most of the steps are reversible, but when it reaches the terminal position this final deprotonation of the terminal alkyne is irreversible, which "traps" the alkyne in the terminal position

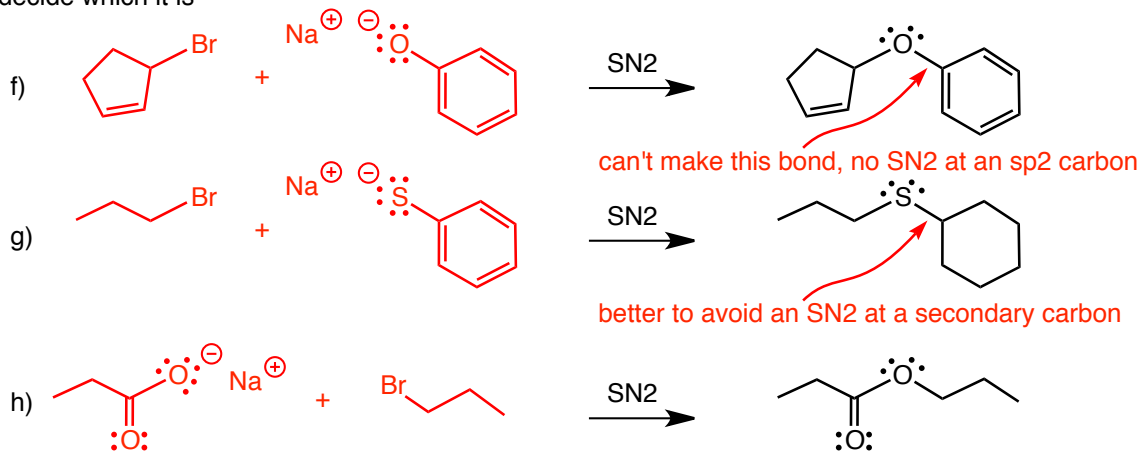
For each step in the following mechanism as appropriate, identify the Lewis acid/Lewis Base (LA/LB) and indicate whether each is also a Brønsted acid/base reaction (BA/BB). Identify each step as either an S_N1, S_N2, E1, E2, addition, elimination, protonation or deprotonation. Draw a reaction energy 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



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

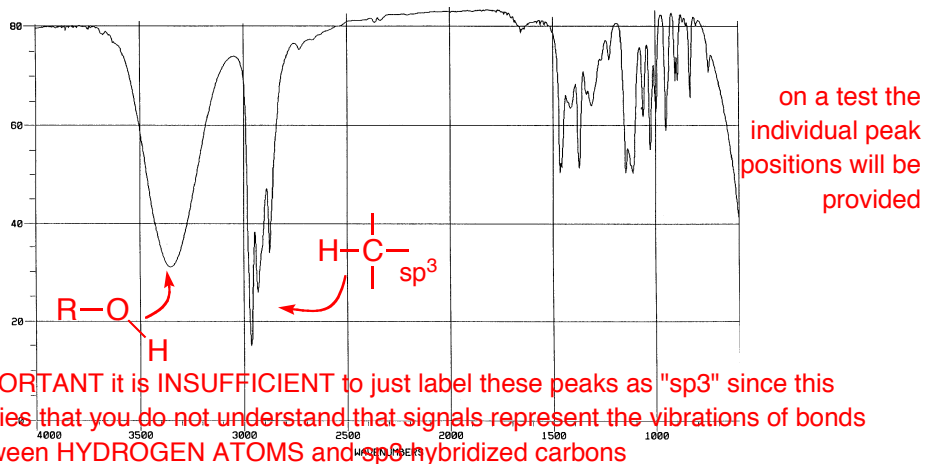


THIS IS THE FORMAT OF THE SPECTRUM QUESTION YOU WILL SEE ON AN EXAM

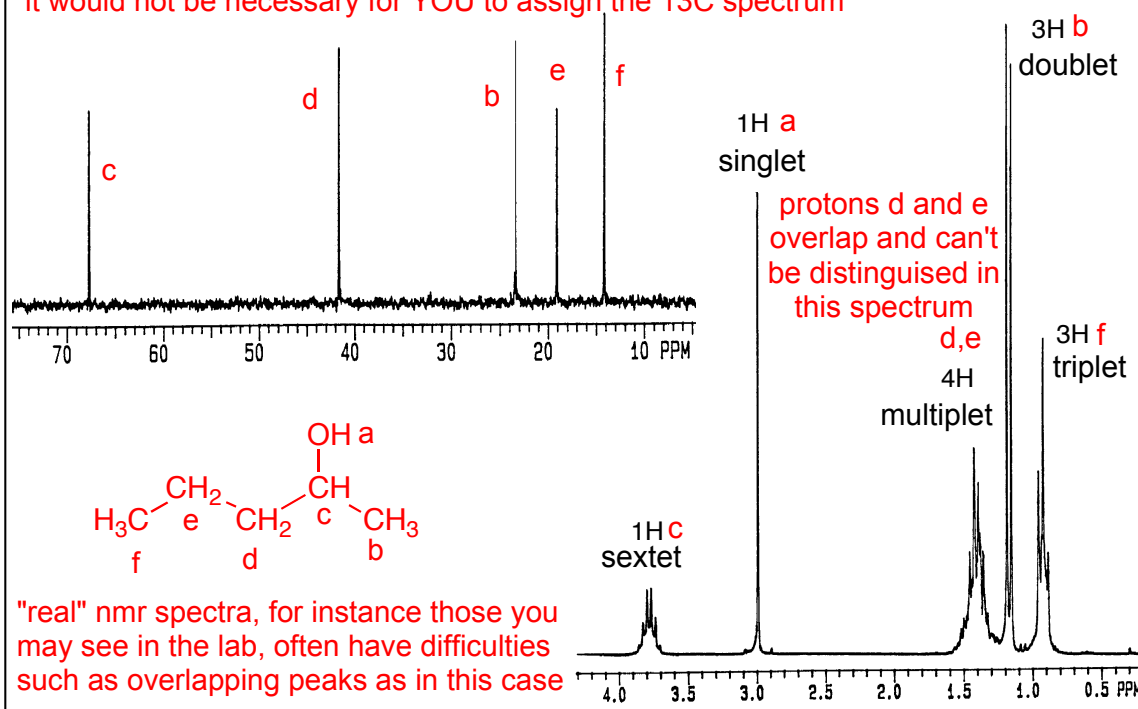
Provided are spectra for a compound with molecular formula $C_5H_{12}O$

a) Give the degrees of unsaturation 0 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.



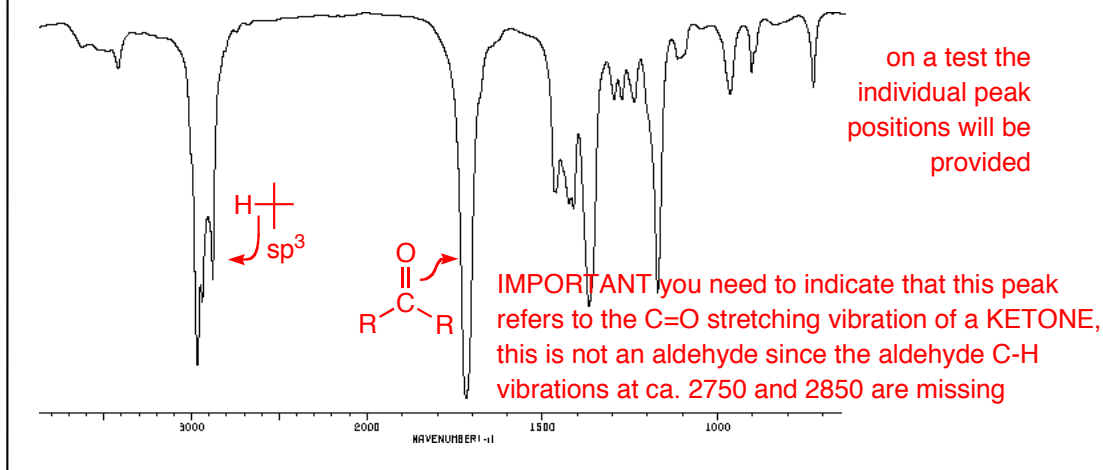
c) draw the structure and clearly indicate which hydrogens correspond to which signals in the proton nmr spectrum ONLY
it would not be necessary for YOU to assign the ^{13}C spectrum



Provided are spectra for a compound with molecular formula $C_5H_{10}O$

a) Give the degrees of unsaturation 1° 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.



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

