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FIRST NAME _____PRINTED
LAST NAME _____ASU ID or
Posting ID _____Person on your **LEFT** (or **Aisle**)Person on your **RIGHT** (or **Aisle**)

the exam cover sheets look kind of like this

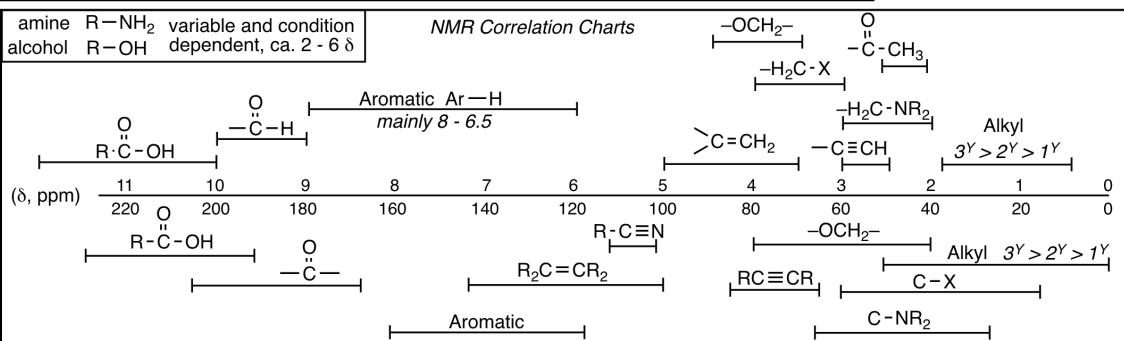
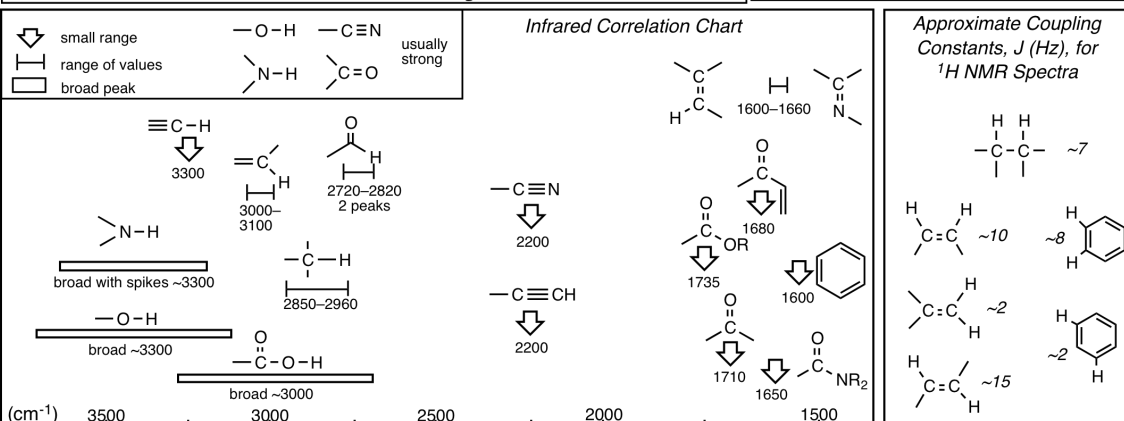
**THIS IS A CHM 234
PRACTICE EXAM****FINAL EXAM
PRACTICE TEST #1**

- **PRINT YOUR NAME ON EACH PAGE!**
- **READ THE DIRECTIONS CAREFULLY!**
- **USE BLANK PAGES AS SCRATCH PAPER**
work on blank pages will not be graded...
- **WRITE CLEARLY!**
- **MOLECULAR MODELS ARE ALLOWED**
- **DO NOT USE RED INK**
- **DON'T CHEAT, USE COMMON SENSE!**

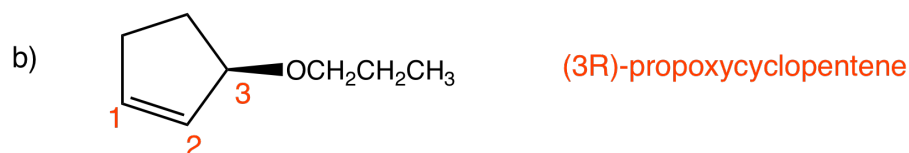
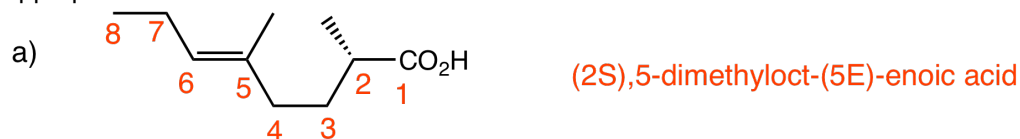
Extra Credit _____/5

Total (incl Extra) _____/375+5

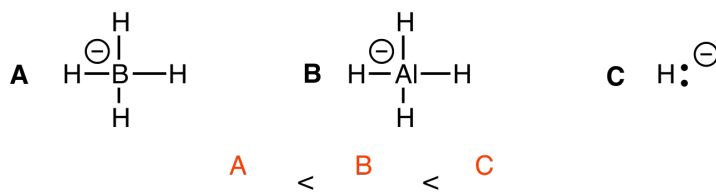
H	He	Interaction Energies, kcal/mol															
Li Be	B C N O F Ne	Eclipsing															
Na Mg	Al Si P S Cl Ar	Gauche															
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn	Ga Ge As Se Br Kr	H/H	-1.0	Me/Me	-0.9												
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd	In Sn Sb Te I Xe	H/Me	-1.4	Et/Me	-0.95												
Cs Ba Lu Hf Ta W Re Os Ir Pt Au Hg	Tl Pb Bi Po At Rn	Me/Me	-2.6	i-Pr/Me	-1.1												
		Me/Et	-2.9	t-Bu/Me	-2.7												



Question Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.

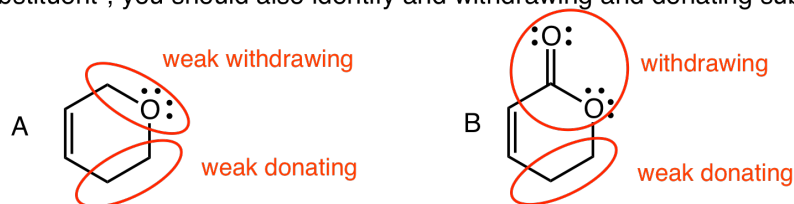


Question 2) Rank the following in order of Lewis base strength, and give a BRIEF explanation



those in C are highest, since they are not in a bond, those in A are lower than in B because the B-H bond is stronger than the Al-H bond, since B is smaller than Al, but is in the same period

Question 3) Indicate which of the following two structures A or B would react fastest with a diene in a Diels-Alder reaction. Give an explanation that includes the following terms: "energy of the HOMO", "energy of the LUMO", and also "withdrawing substituent" and "donating substituent", you should also identify and withdrawing and donating substituents

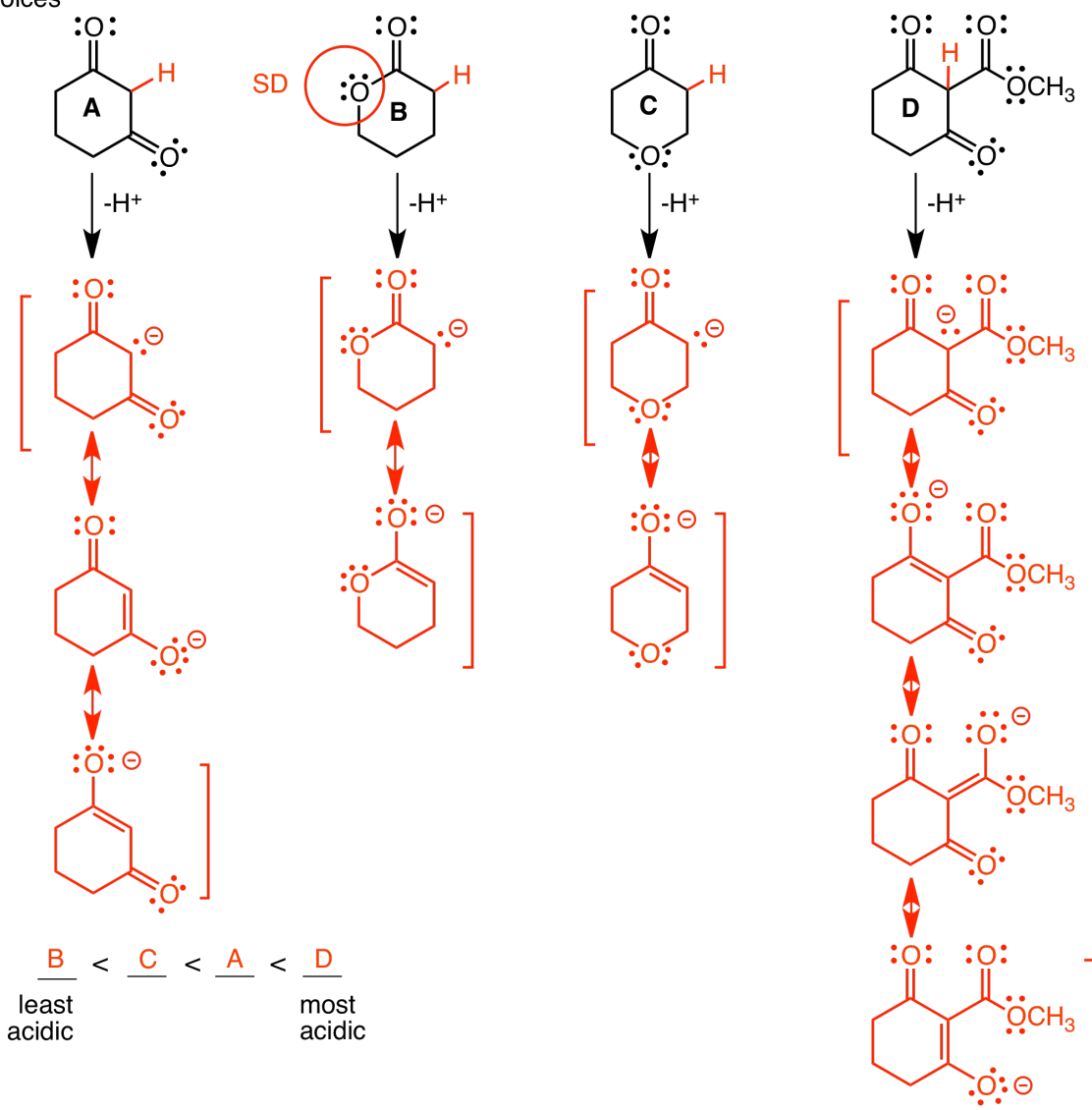


B will react faster, it has an electron withdrawing group (the ester) and a weak donating group (the rest of the ring) attached to the alkene π -system

A also has an electron withdrawing group (the ester) and a weak donating group (the rest of the ring) attached to the alkene π -system, the withdrawing group on A is weaker than that on B since it is due to the inductive effect of the oxygen only, whereas the withdrawing effect in B also includes resonance

the rate of the reaction is determined by the energy gap between the energy of the LUMO of the dienophile and the energy of the HOMO of the diene, the stronger withdrawing substituent in B lowers the energy of the LUMO, which decreases the HOMO/LUMO energy gap, increasing reaction rate

Question 4) Rank the following in order of increasing Bronsted acidity. For each, ADD THE MISSING MOST ACIDIC HYDROGEN ATOM to the provided structure and draw the conjugate base anion, include any important resonance contributors and give a brief explanation for your choices



the strongest acid has the most stable conjugate base anion

the larger the number of resonance contributors the more stable the conjugate base anion

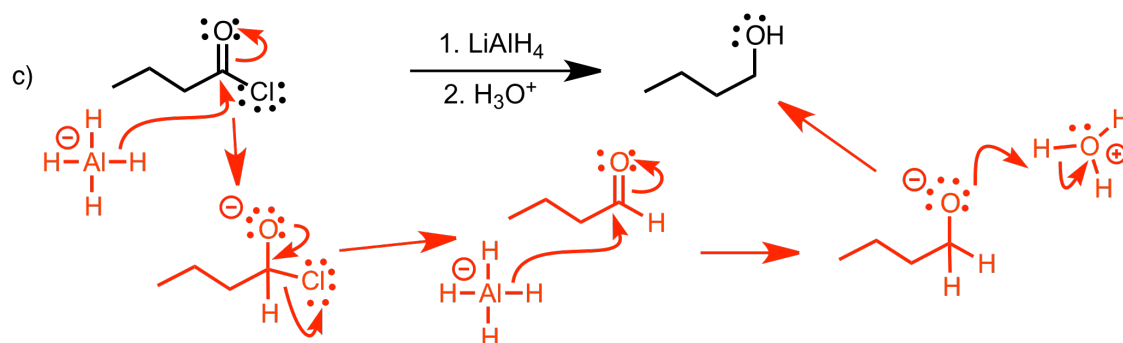
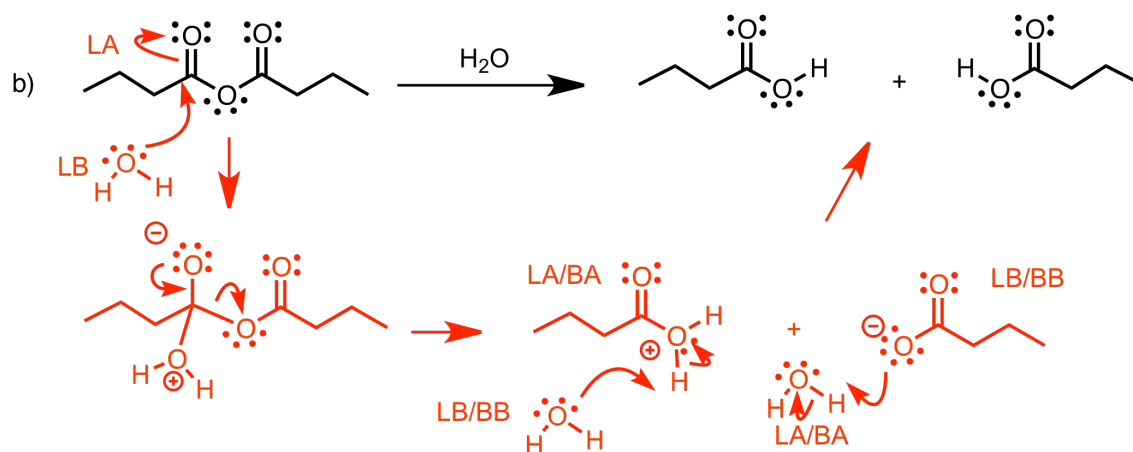
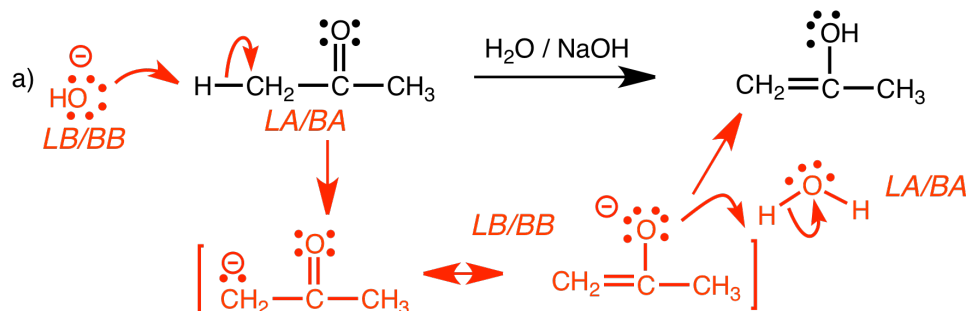
the base anion from D is stabilized by the largest number of resonance contributors, 4

the base anion from A is stabilized by 3 contributors

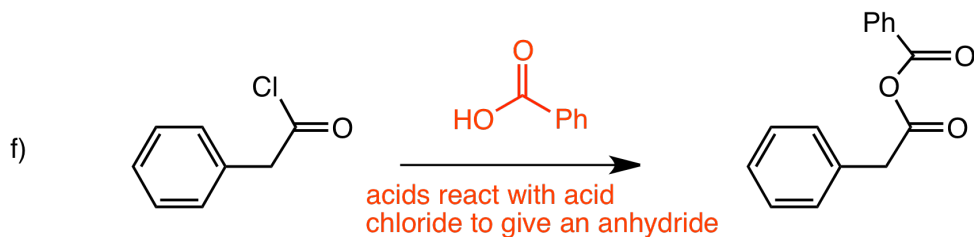
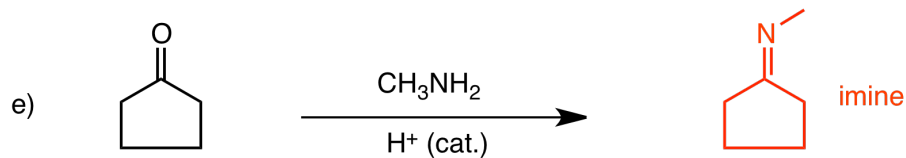
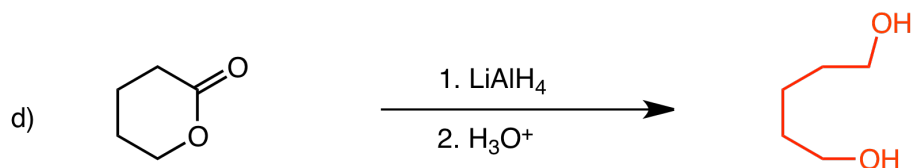
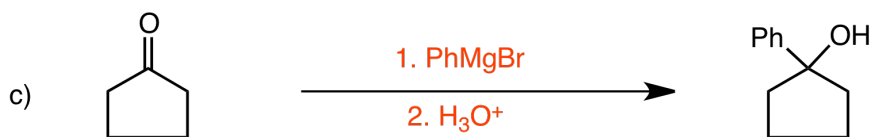
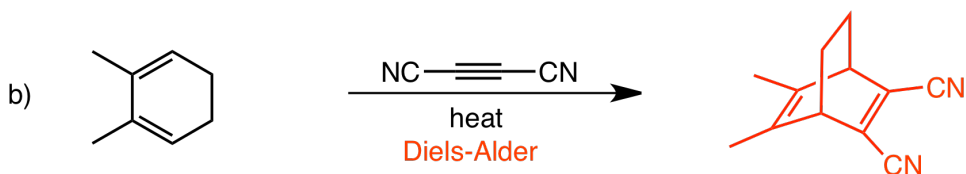
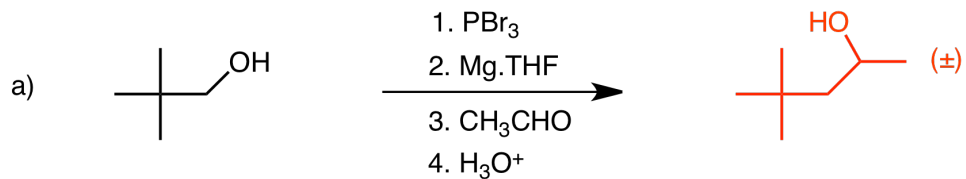
the anion bases in B and C are stabilized by two resonance contributors each, but in B the anion is destabilized by the oxygen (indicated as SD, strong donating group), B is thus the weakest Bronsted acid

Question 5 (Give a curved arrow pushing mechanism for the following reactions)

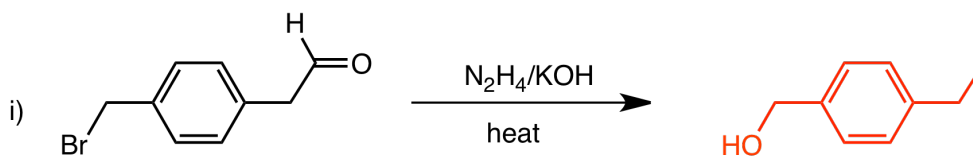
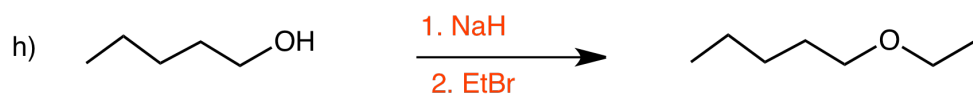
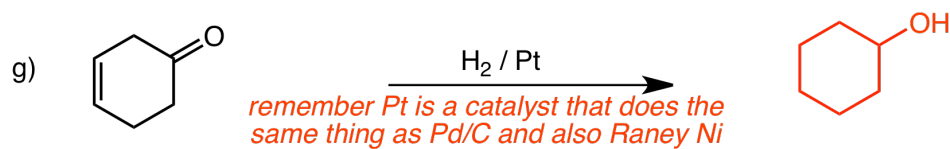
- AS APPROPRIATE, SHOW WHERE ALL PROTONS COMES FROM AND GO TO (no $+H^+/-H^+$)
- DRAW ALL RESONANCE CONTRIBUTORS for the intermediates as appropriate
- At each INTERMOLECULAR step, INDICATE THE Lewis acid and base (LA or LB) and whether they are also Bronsted acids and bases (BA or BB) as appropriate



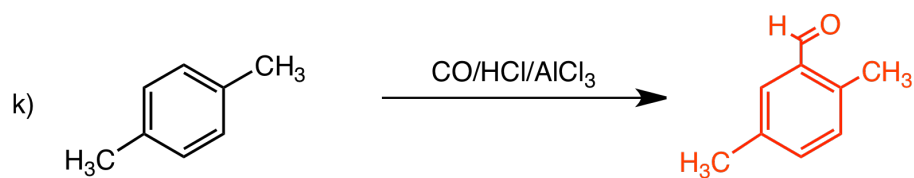
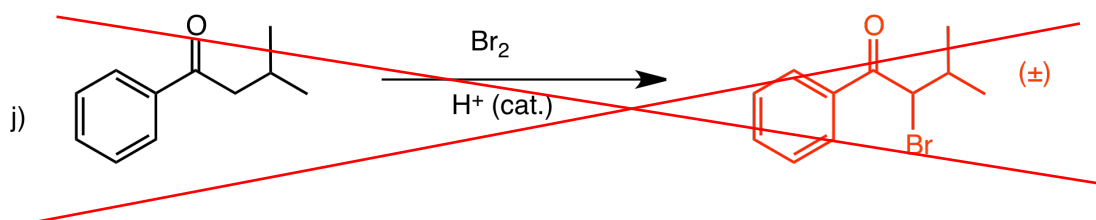
Question 6 Provide the missing major organic products, or reagents/conditions, or organic reactants, as appropriate. **Do not forget to include stereochemistry as appropriate** unless specified otherwise.



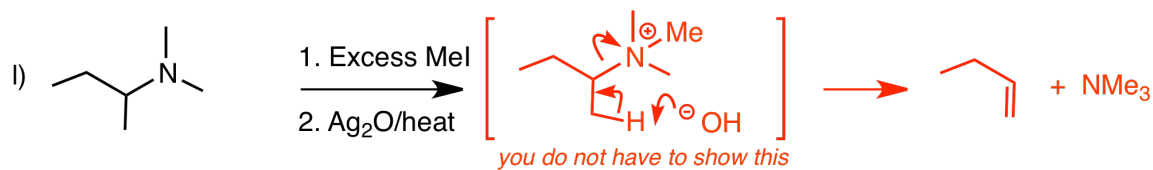
Question 6, contd.



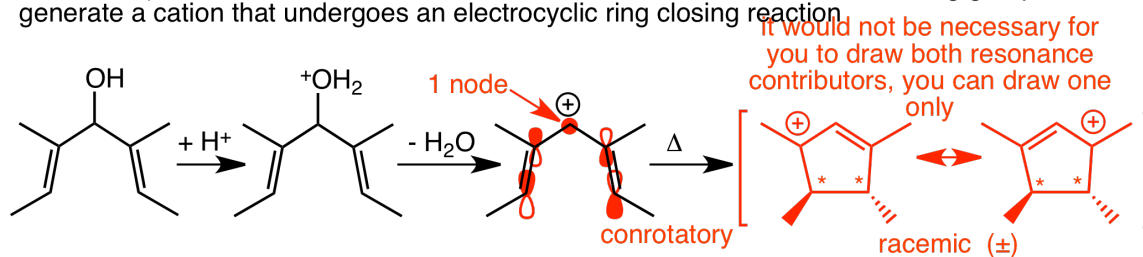
Wolf-Kischner, the -OH from the KOH will also do an SN2 with the benzyl bromide



substitution in any position gives exactly the same product

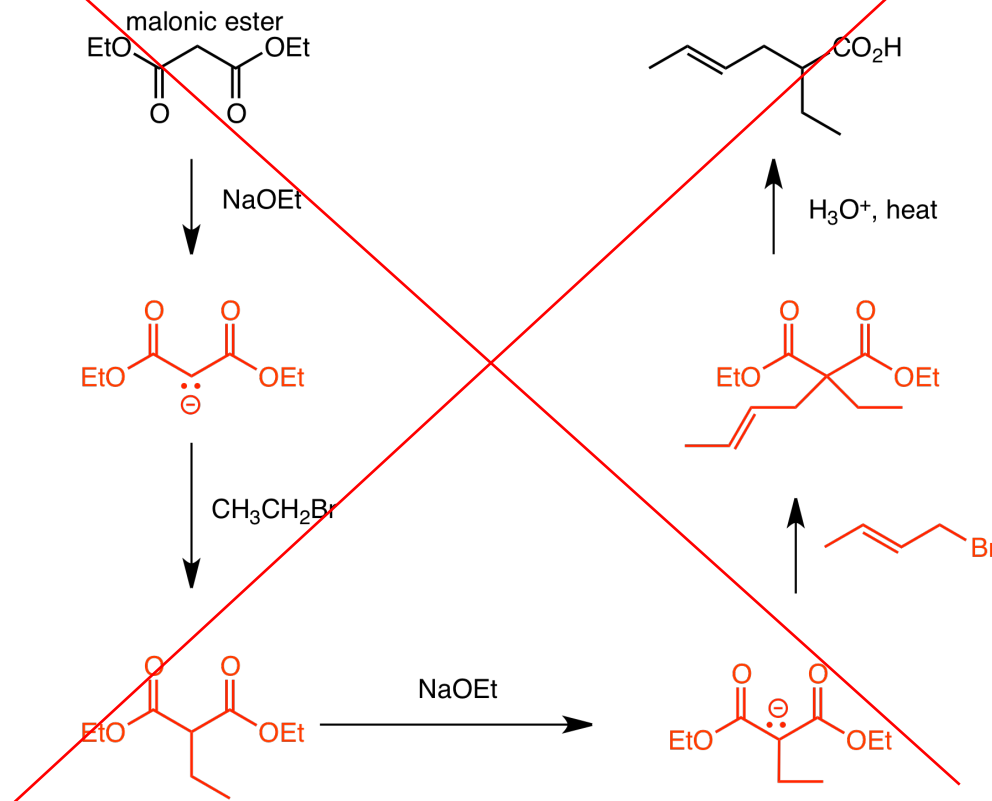


Question 7) Protonation of the alcohol below results in loss of water as a leaving group to generate a cation that undergoes an electrocyclic ring closing reaction.

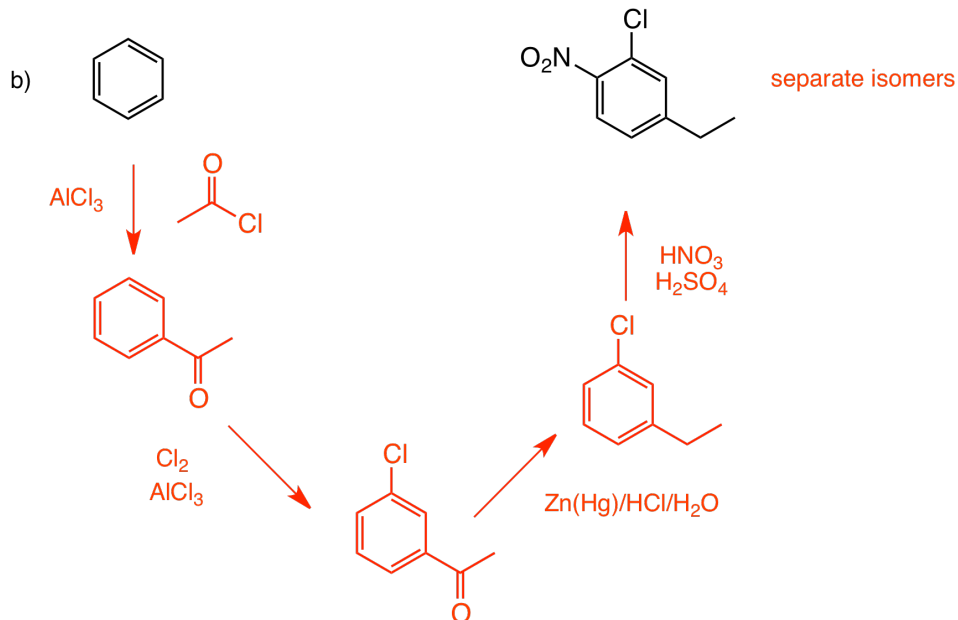
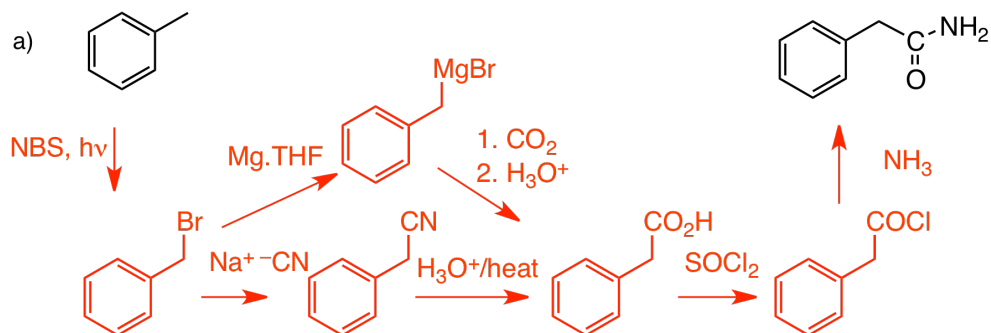


- give the curved arrow-pushing that accounts for electrocyclic reaction
- draw the electrocyclic product, paying special attention to relative stereochemistry of any substituents
- in the product(s), indicate the locations of any chiral (asymmetric) carbons atoms with the* symbol, and state whether the product(s) are racemic, a meso compound or achiral
- ON TOP OF THE CATION STRUCTURE, give a drawing of the HOMO
- state the number of vertical nodes and clearly indicate their positions
- state whether the allowed reaction proceeds via a conrotatory or a disrotatory ring closing

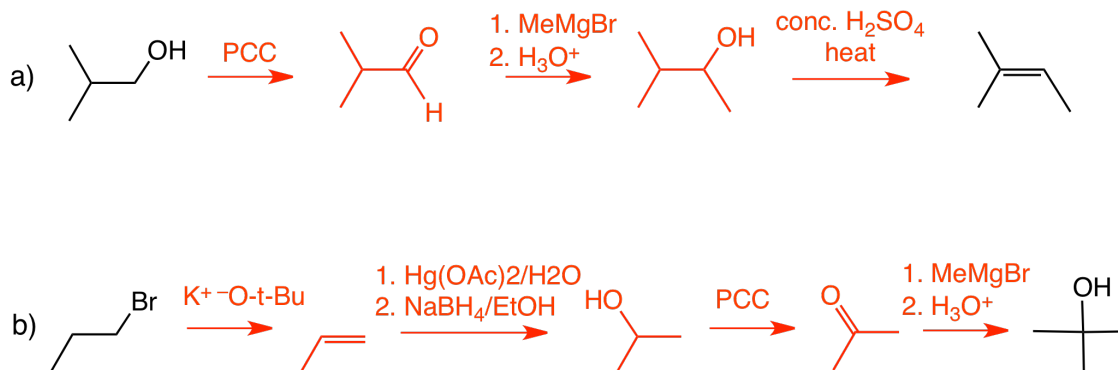
Question 8) Provide the missing structures in the following malonic ester synthesis of a carboxylic acid



Question 9) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers**

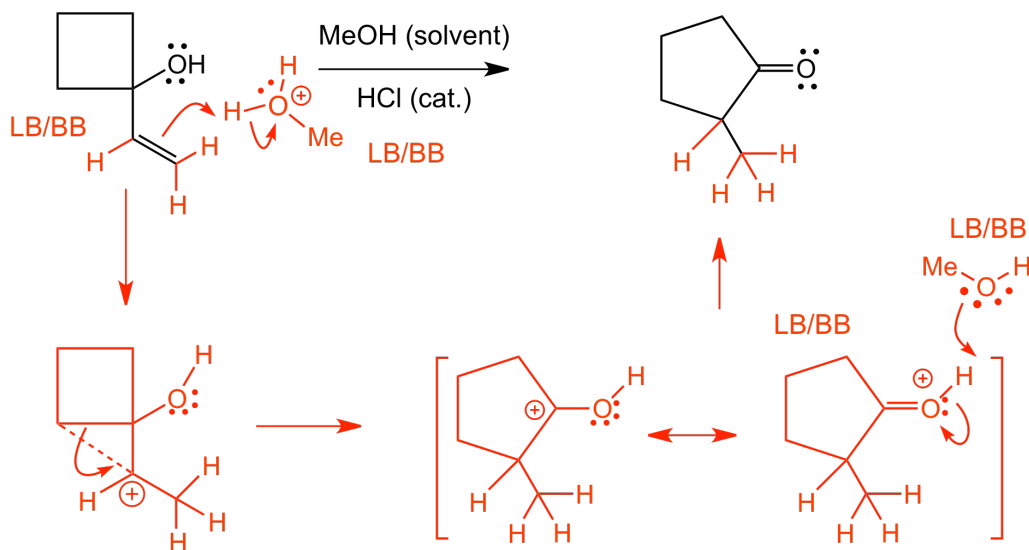


Question 10) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

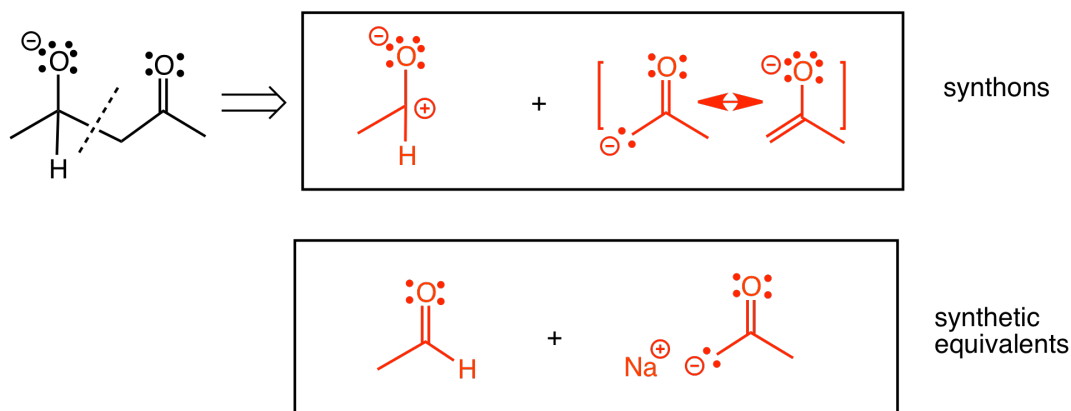


Question 11) Give a curved arrow pushing mechanism for the following reactions

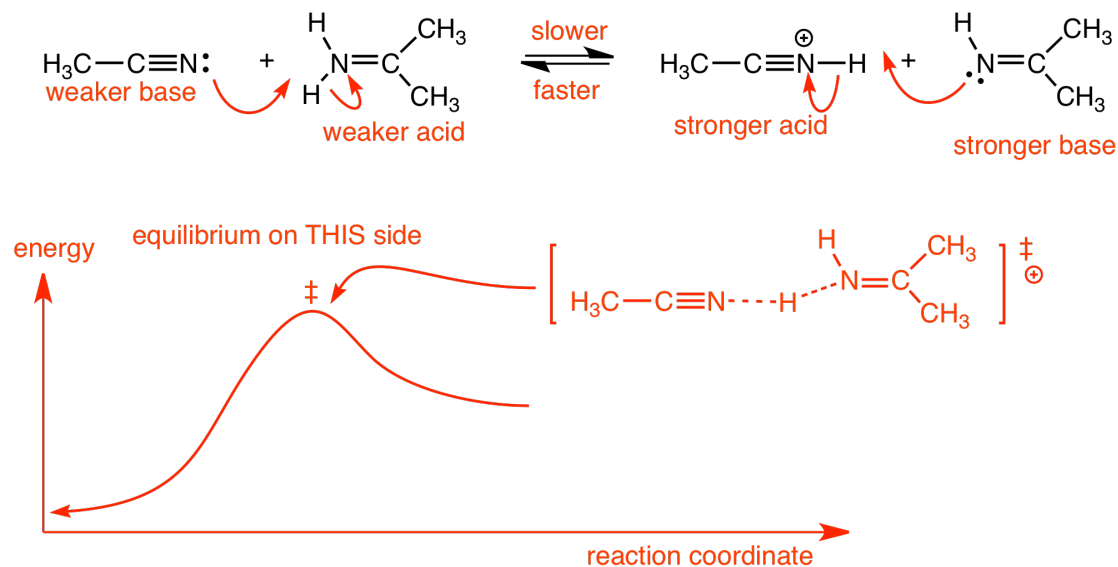
- SHOW WHERE ALL PROTONS COMES FROM AND GO TO (no $+H^+/-H^+$) (assum that H-Cl is completely dissociated in methanol)
- DRAW ALL RESONANCE CONTRIBUTORS for the intermediates as appropriate
- At each INTERMOLECULAR step, INDICATE THE Lewis acid and base (LA or LB) and whether they are also Bronsted acids and bases (BA or BB) as appropriate
- Add hydrogen atoms and non-bonding electrons where appropriate



Question 12) Disconnect the indicated bond according to the method of retrosynthetic analysis, generate the synthons and convert these into "real reagents", or "synthetic equivalents".

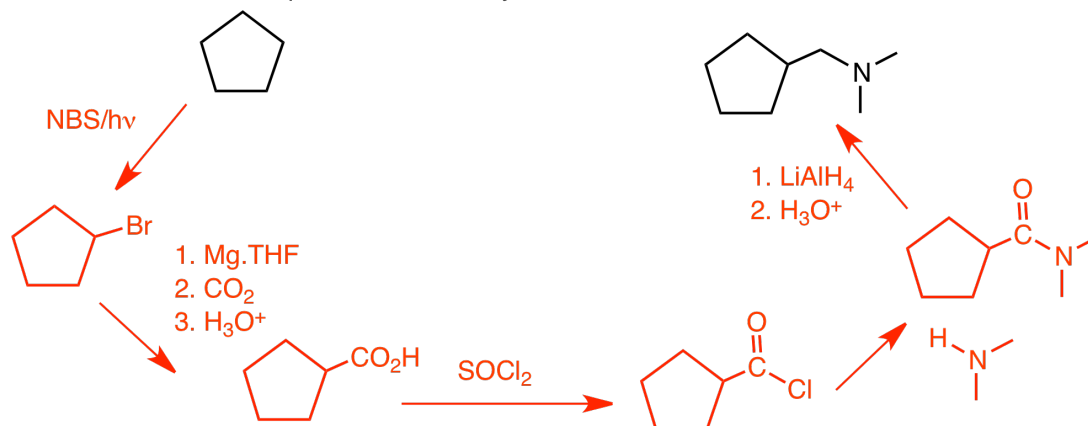


Question 13) For the Bronsted acid/base reaction below, label the acids/bases and which are stronger and give a brief explanation, give the curved arrow-pushing in both directions, draw a reaction energy diagram and include a drawing of the transition state, indicate which reaction is faster (left to right or vica versa) and on which side the equilibrium lies

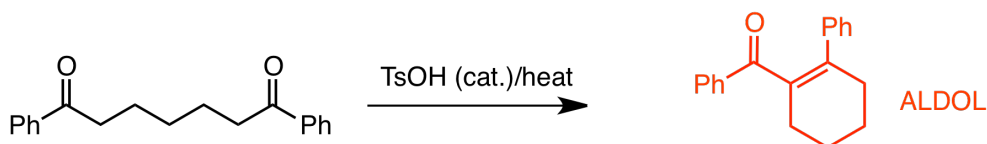


the weaker base has lower energy electrons in an sp hybridized atomic orbital compared to an sp^2 hybridized atomic orbital in the stronger base

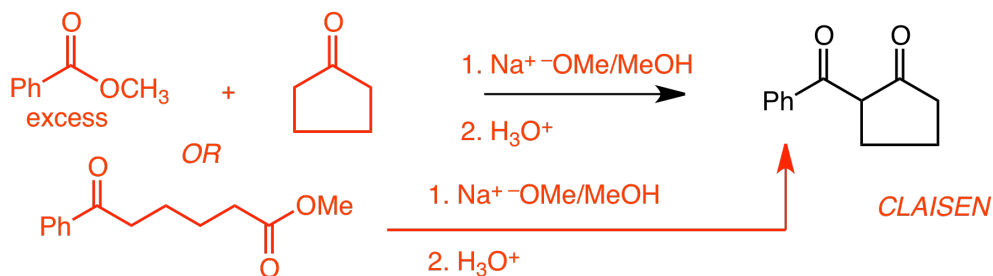
Question 13) Synthesize the (target) molecule on the right from the starting molecule on the left. this can not be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.



Question 14) Provide the major organic product of the following reaction and classify it as an Aldol or a Claisen reaction



Question 15) Provide the reactants/reagents/conditions to for the provided product and state whether the reaction is an Aldol condensation or a Claisen reaction



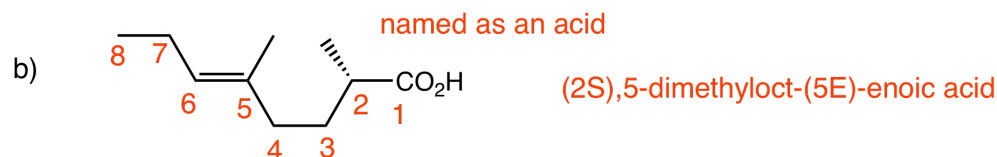
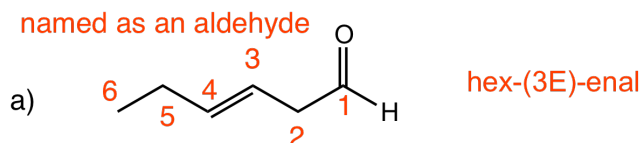
Question 16) Explain why electron donating substituents on a benzene ring increase reactivity in electrophilic aromatic substitution, whereas electron donating groups on a $\text{C}=\text{O}$ generally decrease reactivity in nucleophilic addition, e.g. reaction with Grignards.

in electrophilic aromatic substitution, benzenes are Lewis bases (donate electrons) in the rate determining step, electron donating groups raise the energy of the electrons in the benzene, increasing reactivity

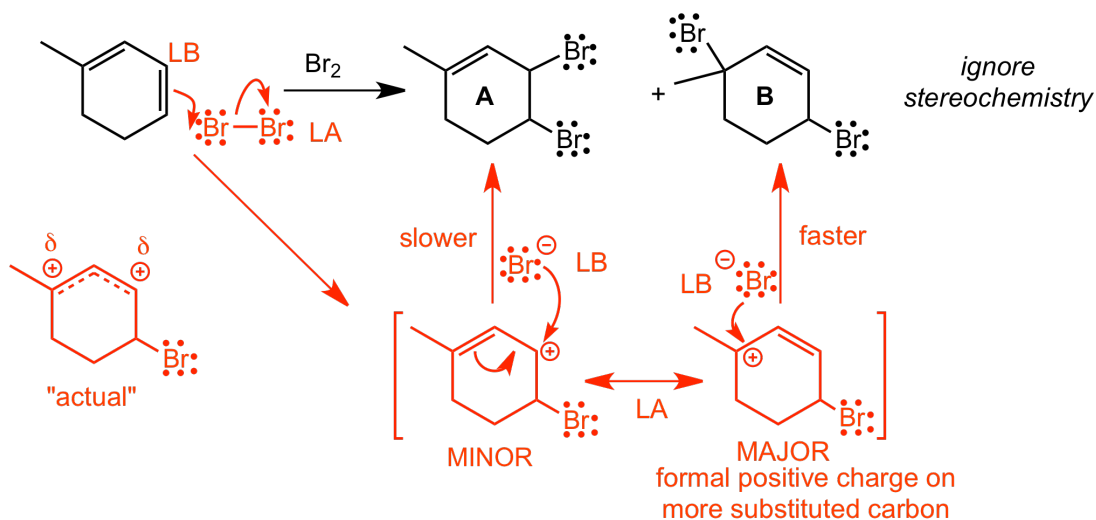
in nucleophilic addition to $\text{C}=\text{O}$, the carbonyl acts as a Lewis acid (accepts electrons), electron donating substituents make the carbonyl carbon a weaker Lewis acid, decreasing reactivity

START OF PRACTICE TEST #2

Question 1) Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.



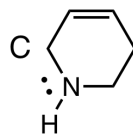
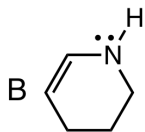
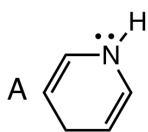
Question 2) Provide a curved arrow pushing mechanism for the following reactions (indicate LB/LA and BB/BA as appropriate). For any resonance stabilized intermediates, include all relevant resonance contributors, INDICATE WHICH IS THE MAJOR CONTRIBUTOR and explain WHY, and draw an "actual" structure using the "delta" notation to indicate partial charges. Indicate which would be the major product under conditions of **kinetic control** and which under thermodynamic control, give a BRIEF explanation for your choice that mentions temperature.



under thermodynamic control, higher temperature, the reactions are reversible, and, even though **B** is formed faster, eventually the more stable (more substituted alkene) product **A** accumulates and becomes the major product

under kinetic control, lower temperature, the faster reaction of the resonance stabilized intermediate gives **B** as the major product, since the reactions are irreversible

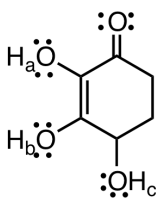
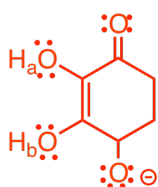
Question 3) Rank in order of increasing basicity and give a brief explanation



A < B < C

basicity is determined by the energy of the non-bonding electrons, the higher the energy the stronger the base, in these cases electron energy is determined by the extent of resonance delocalization, the electrons in C are not delocalized at all, those in B are delocalized via 1 additional minor resonance contributor (not shown), A has 2 additional minor contributors, thus C is the most reactive and A the least

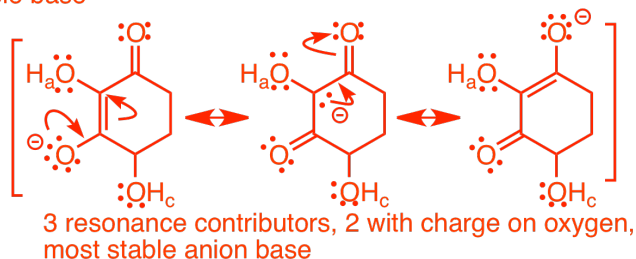
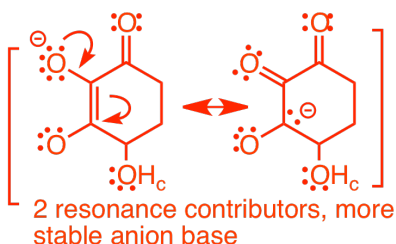
Question 4) Rank the following hydrogens H_a, H_b and H_c in order of increasing Bronsted acidity, draw structures of the relevant conjugate base anions to support your reasoning and give a brief explanation



H_c < H_a < H_b

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

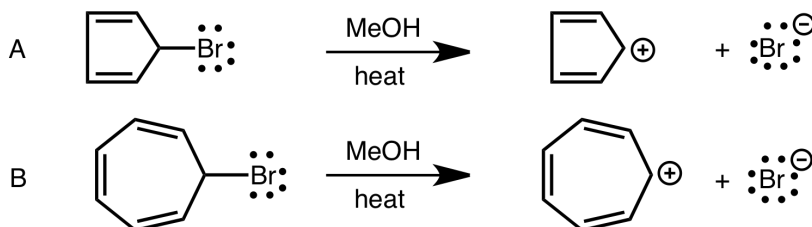
no resonance stabilization, least stable base



Question 5) In what way is the Lewis acid/base description of reactions different from the nucleophile/electrophile description?

the definition of Lewis basicity and acidity is thermodynamic, the most exothermic reaction corresponds to the strongest acid/base, the definition of nucleophilicity/electrophilicity is based on kinetics, the fastest reaction corresponds to the strongest nucleophile/electrophile

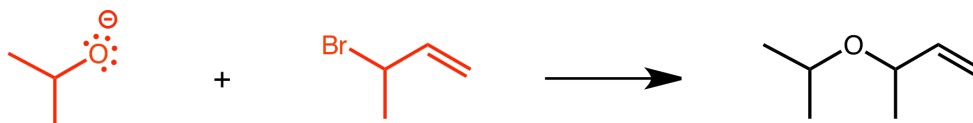
Question 6) Indicate which of the following two reactions, A or B would be faster. **GIVE AN EXPLANATION THAT INCLUDES A DISCUSSION OF THE EXOTHERMICITY OR ENDOTHERMICITIES OF THE REACTIONS** (only 1 point for the correct answer, 9 pts for the explanation, include the term "energy of the electrons" in your explanation)



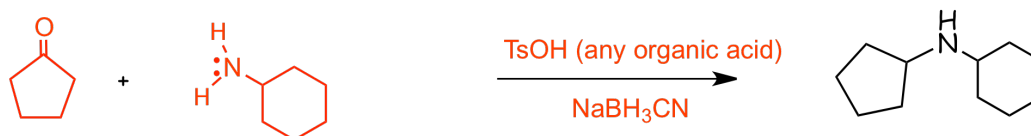
both reactions are endothermic, but reaction A is more endothermic since it makes a less stable ANTI-AROMATIC cation (or non-aromatic if it can twist enough), reaction B is less endothermic since it makes an AROMATIC cation, reaction B is thus faster

Question 7)

a) Give the structures of the best anion and alkyl halide pair that can be used to form the provided ether (this is a Williamson ether synthesis).

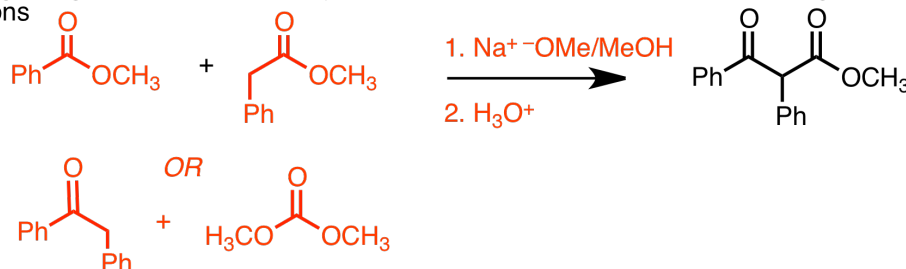


b) Give the structures of the amine and the carbonyl compound that can be used to make the provided amine in a reductive amination, you should also add the reagents/conditions to the reaction arrow (you can specify reagents for either an indirect or a direct reductive amination)

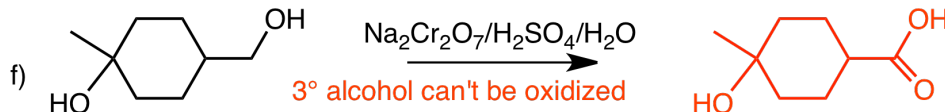
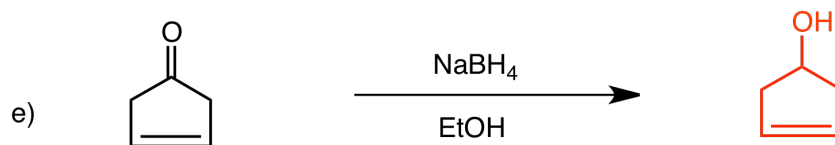
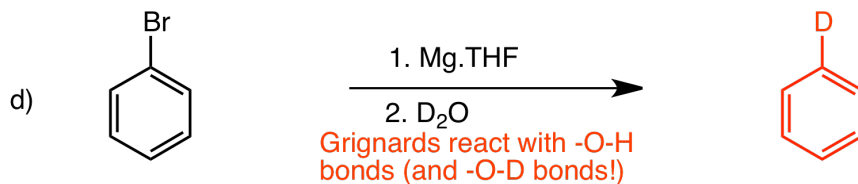
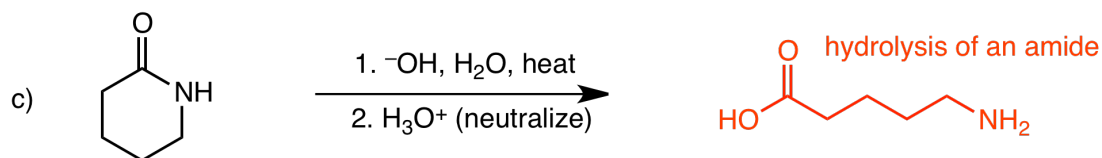
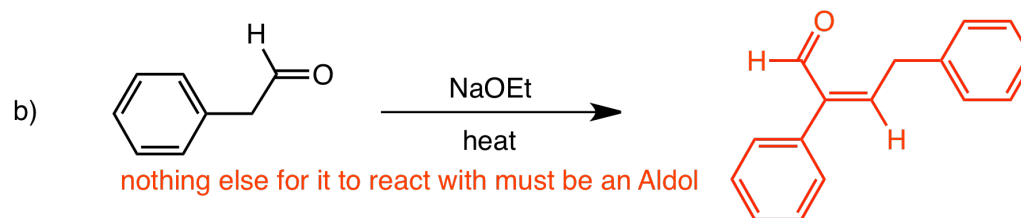
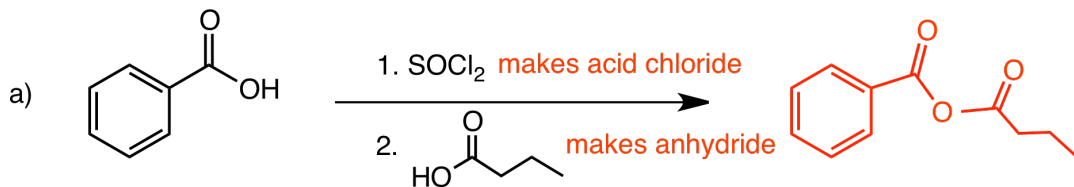


or for an INDIRECT reductive amination the reagents would be:
1. H⁺ (cat.) 2. any of several reducing agents such as H₂/Pd/C etc

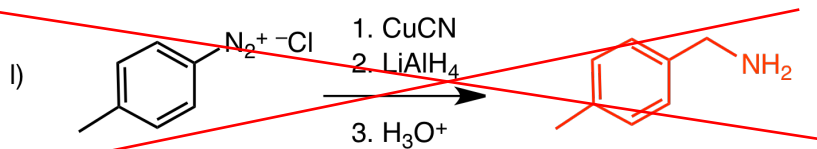
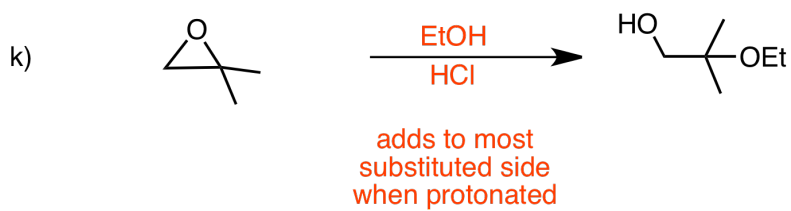
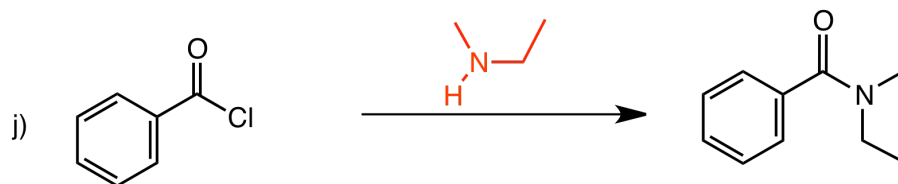
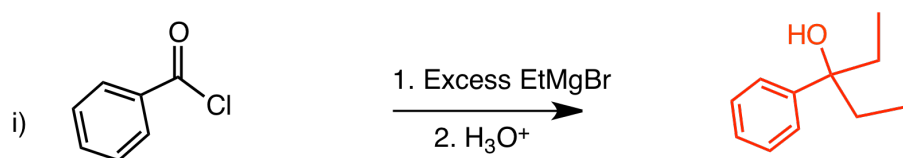
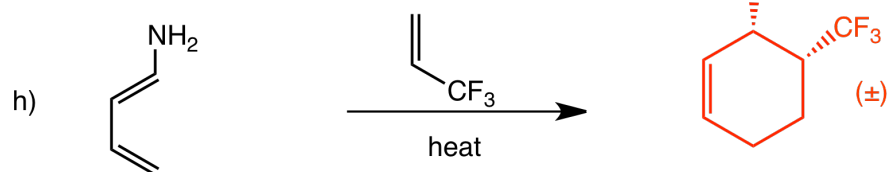
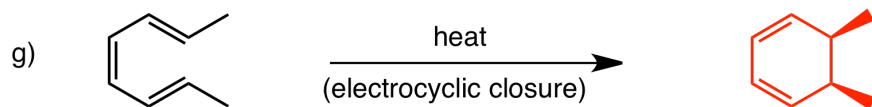
c) Give the structures of carbonyl compounds which could be used to prepare the following using an Aldol or Claisen type reaction and also provide example reagents and conditions



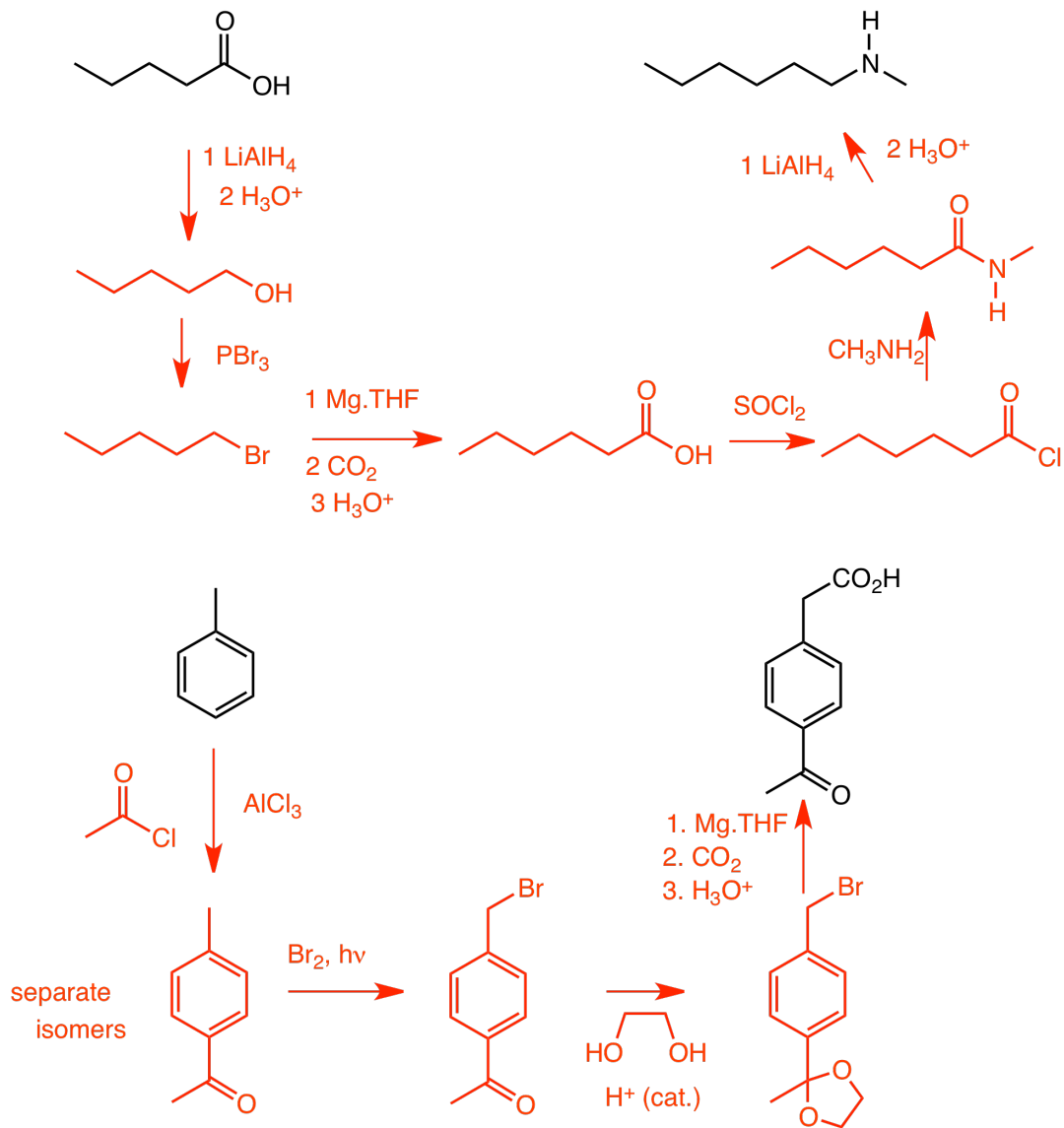
Question 8) Provide the missing major organic products, or reagents/conditions, or organic reactants, as appropriate. **Do not forget to include stereochemistry as appropriate** unless specified otherwise.



Question 8, contd.

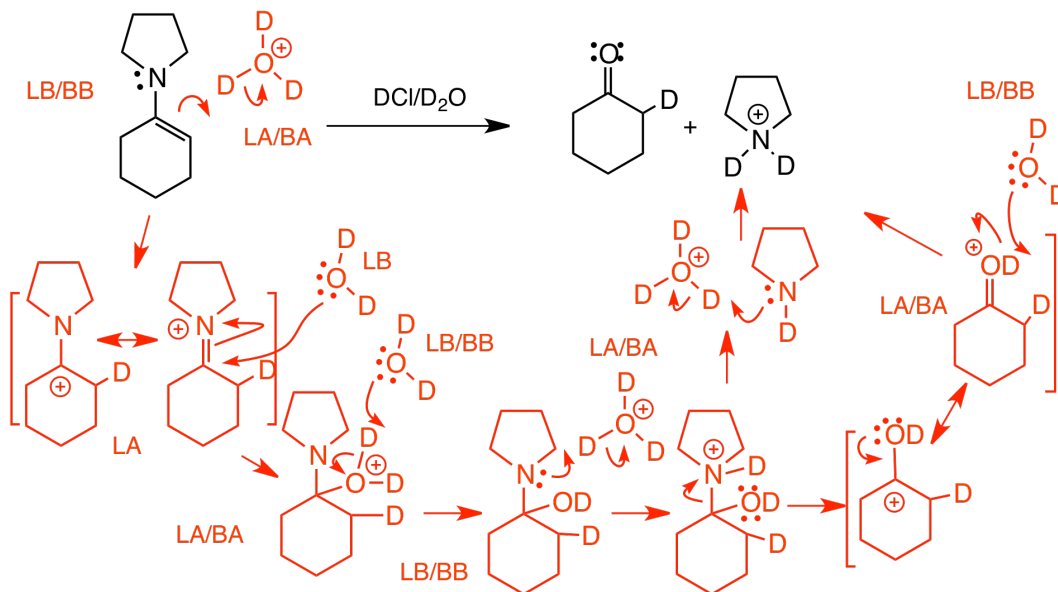


Question 9) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers**

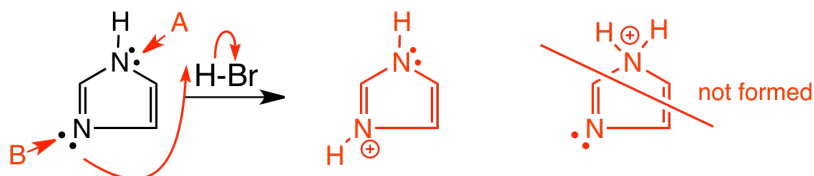


Question 10) Draw the complete arrow pushing mechanism for the following reaction. Indicate the Lewis acid/base at each step, and if they are also Brønsted acids/bases. Add non-bonding electrons as necessary. Draw the **ALL important** resonance structure of the intermediates

DCI/D₂O = deuterated HCl in heavy water, D₂O, acts just like any acid in water, but shows you which protons come from the aqueous acid medium

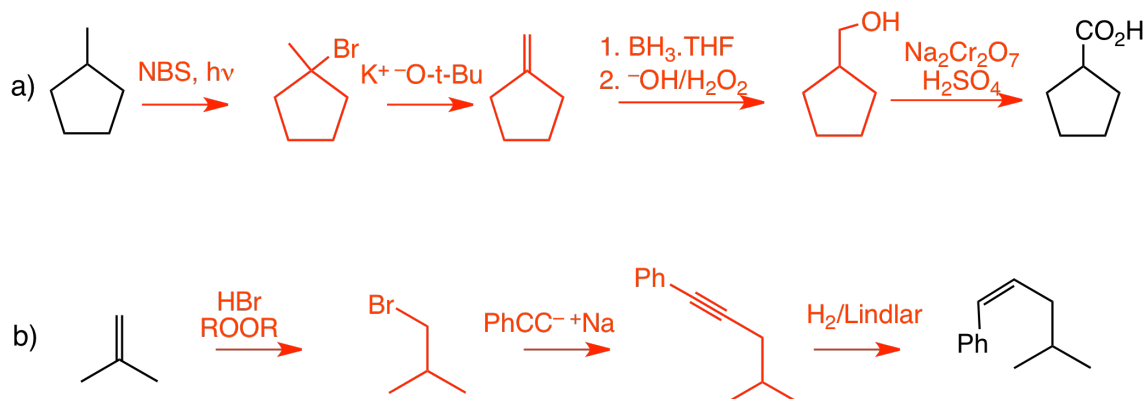


Question 11) Give the product of the following Bronsted acid/base reaction, give the curved arrow pushing and give a BRIEF explanation for your choice of reaction product

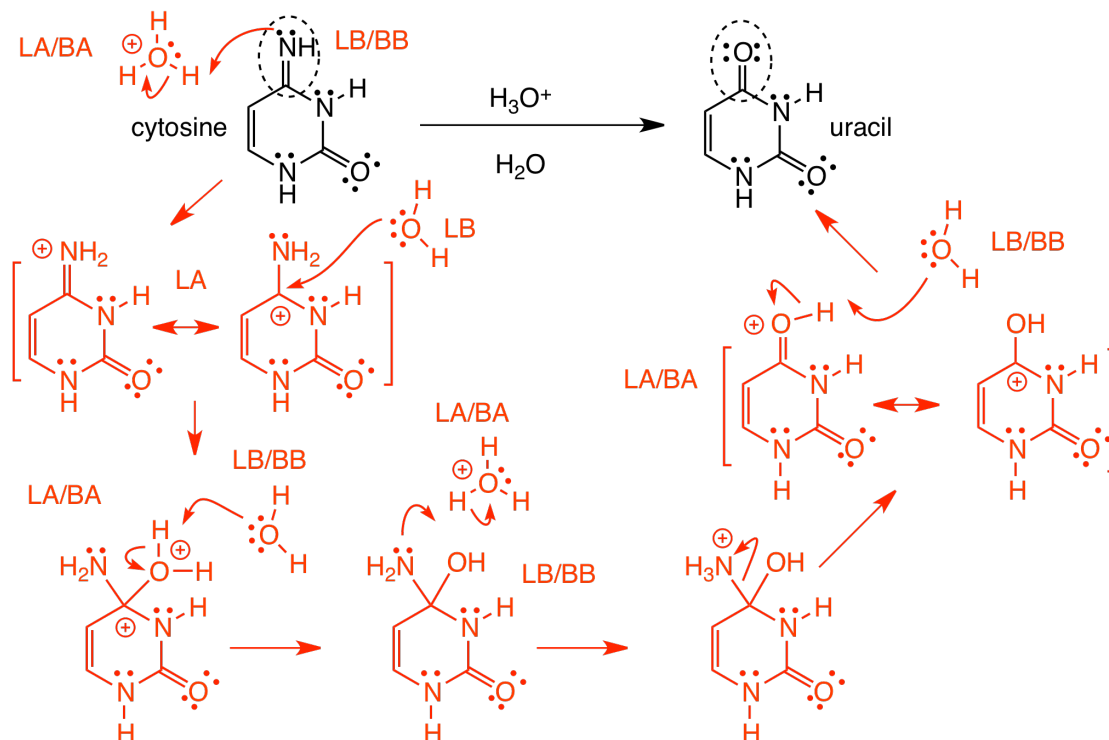


the non-bonding electrons A are part of the aromatic system and are thus less reactive than the electrons B, the product of reaction of electrons A is non-aromatic and higher in energy than the product of reaction of the B electrons

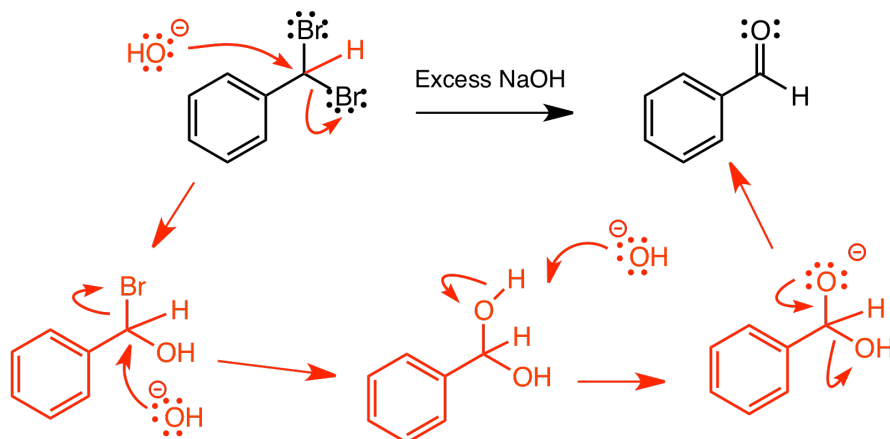
Question 12) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



Question 13) Draw the complete arrow pushing mechanism for deamination of cytosine to give uracil. Indicate the Lewis acid/base at each step, and if they are also Brønsted acids/bases. Add non-bonding electrons as necessary. Draw the **ALL important** resonance structures of the intermediates. This is an acid hydrolysis mechanism that is very similar to many we covered in class



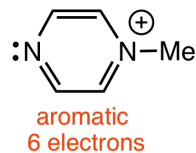
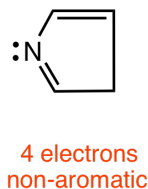
Question 14) Draw the complete arrow pushing mechanism for the following reaction. Even though we have not seen this one it just uses principles that we have seen. (hint: start by doing two consecutive S_N2 reactions at the benzylic carbon)



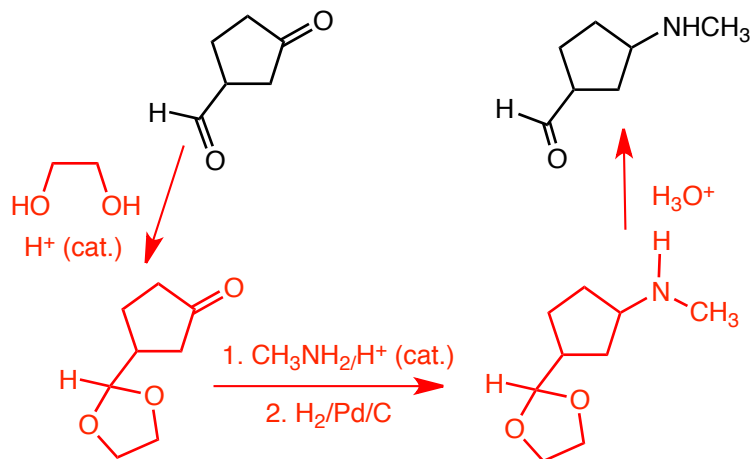
Question 15) For the following cation, draw all reasonable additional resonance contributors including appropriate curved arrow pushing, and on TOP of the provided structure, draw the HOMO using "p A.O." notation we used in class and CLEARLY INDICATE ANY VERTICAL NODES, AND state the number of p A.O.s involved, the TOTAL number of pi-molecular orbitals that are possible and the number of electrons in the pi-system



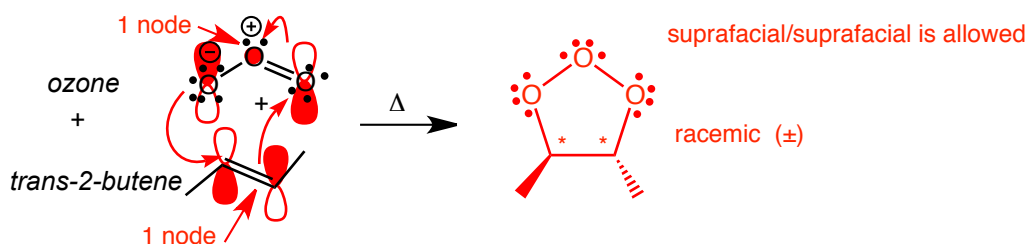
Question 16) Assign the following structures as aromatic, non-aromatic or anti-aromatic and give the number of electrons associated with the conjugated systems, assume that the structures are as planar as possible



Question 17) Synthesize the (target) molecule on the right from the starting molecule on 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.



Question 18) Alkenes react with ozone, O_3 , to form an ozonide, an example reaction with trans-2-butene is shown below.

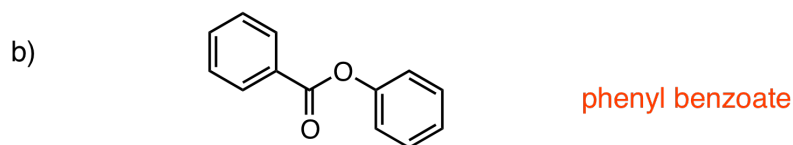
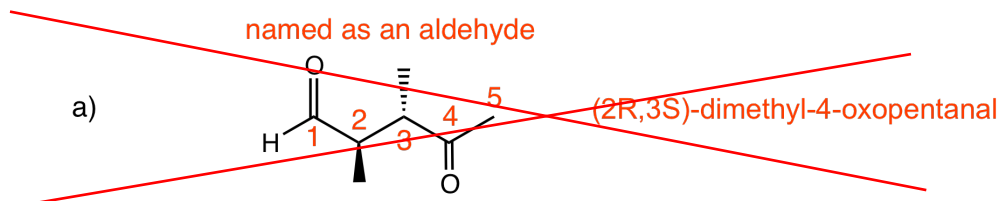


- give the curved arrow-pushing that accounts for formation of the ozonide
- draw the ozonide, paying special attention to relative stereochemistry of any substituents
- indicate the locations of any chiral (asymmetric) carbons atoms with the * symbol, and state whether the ozonide is racemic, a meso compound or achiral
- give drawings of the HOMO and LUMO, ON TOP OF OZONE and trans-2-BUTENE, respectively
- state the number of vertical nodes for each MO and clearly indicate their positions
- state whether the allowed reaction is suprafacial/suprafacial or suprafacial/antarafacial and give a brief explanation

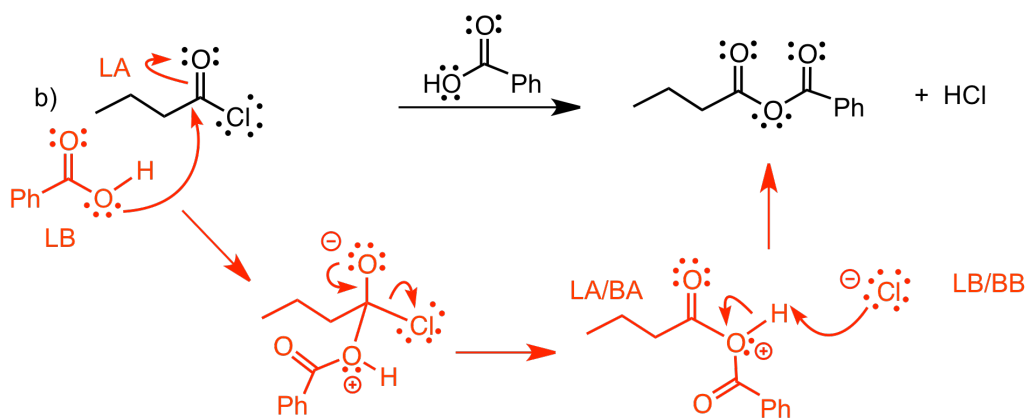
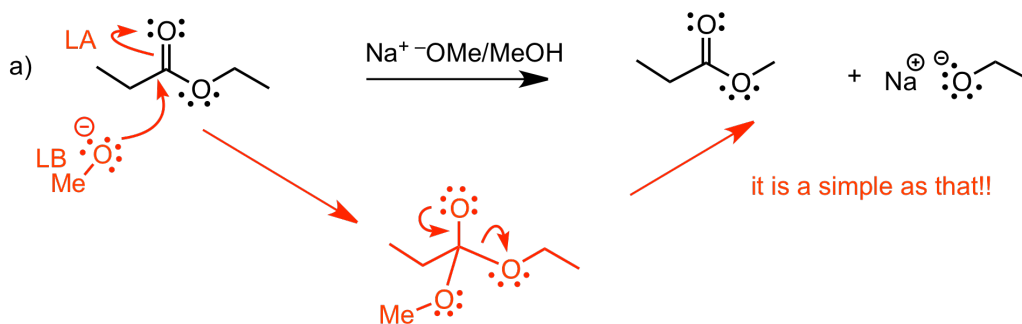
suprafacial/suprafacial is allowed because this allows bonding interactions (i.e. in phase, shaded overlapping with shaded and non-shaded overlapping with non-shaded) to make both new sigma bonds at the same time in a concerted reaction

START OF PRACTICE TEST #3

Question 1) Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.

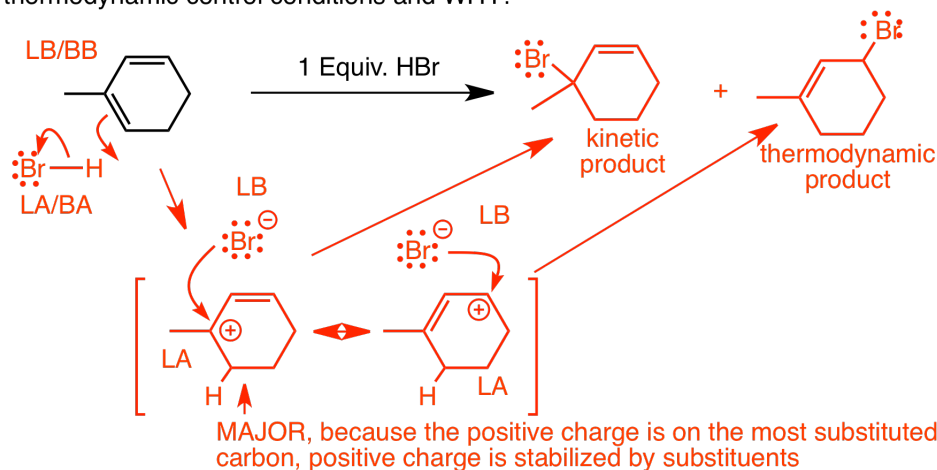


Question 2) Give curved arrow-pushing mechanisms for the following reactions. Indicate the Lewis acid and base and Bronsted acid and base at each step as appropriate. Show where every proton comes from and goes to (i.e. no $+H^+$ and $-H^+$). The first reaction is a transesterification (we mentioned this in class but did not really cover it properly, until now!). Transesterification transforms one ester into another, as shown.



Question 3)

a) Give a curved arrow-pushing mechanism that describes formation of the two reaction products, indicate the Lewis and Bronsted acids and bases at each step as appropriate and identify which product is more likely to be formed under kinetic control conditions and which under thermodynamic control conditions and WHY!



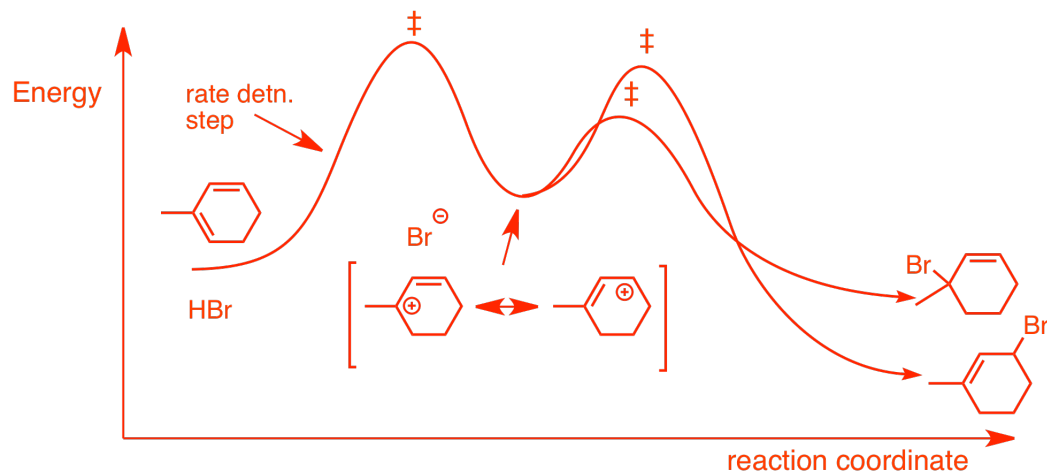
the thermodynamic product is more stable because the alkene is more substituted, the kinetic product is formed faster because there is more positive charge in the intermediate cation on the carbon the bromide adds to to form this product

b) Include resonance contributors for intermediates as appropriate, and indicate the MAJOR CONTRIBUTOR and WHY it is the major contributor

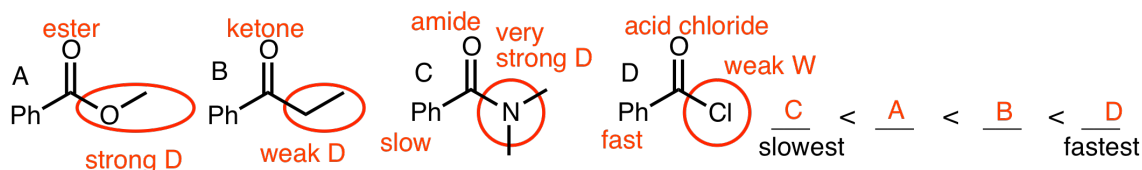
Indicate which would be the major product at high and low temperature conditions and state WHY

kinetic product favored a low temperature because under these conditions the reactions are more likely to be IRREVERSIBLE, and so the product that is formed fastest forms in the highest concentration. At higher temperatures the reactions are more likely to be REVERSIBLE, and under these conditions the more stable thermodynamic product will eventually accumulate

c) Draw a properly labelled reaction energy diagram for these reactions ON THE SAME DIAGRAM identify the positions of the starting structure, the intermediates, locate the positions of the transition states but do not draw them and indicate the rate determining step

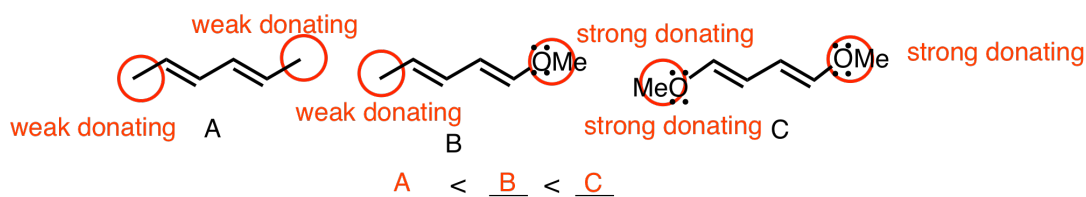


Question 4) Rank in order of increasing rate of reaction with a Grignard reagent and give a brief explanation, AND ASSIGN EACH FUNCTIONAL GROUP



Grignards are Lewis bases/nucleophiles and will add to the carbonyl carbon, C=O. The carbonyl carbon thus accepts electrons in this reaction. The C=O is a simple pi-system with substituents. Donating substituents decrease the ability of this carbon to accept electrons, withdrawing substituents increase the ability of this carbon to accept electrons. The acid chloride is most reactive, fastest, due to the -Cl withdrawing group, followed by the ketone with 2 weak donating groups, followed by the ester with a stronger -OR donating group, the slowest is the amide which has the strong -NR₂ donating group.

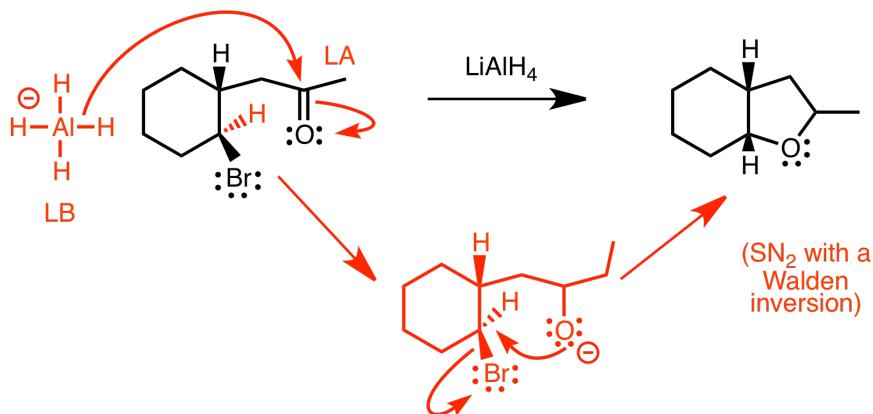
Question 5) Rank in order of increasing rate of reaction in a Diels-Alder reaction and give an explanation that includes the terms HOMO and LUMO



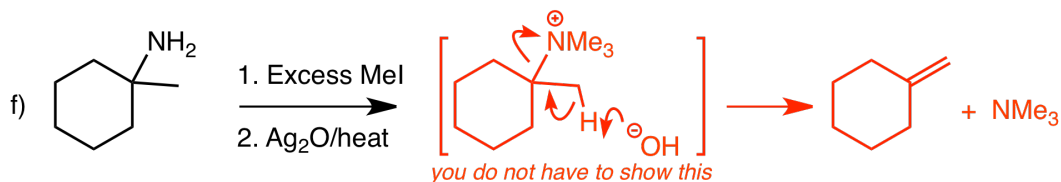
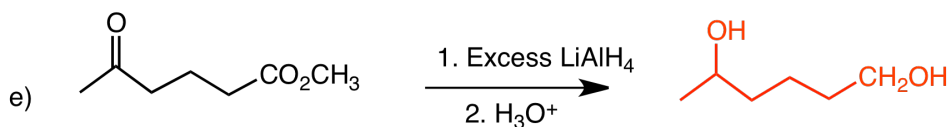
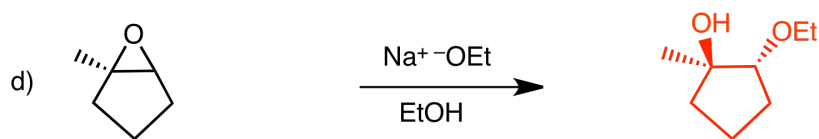
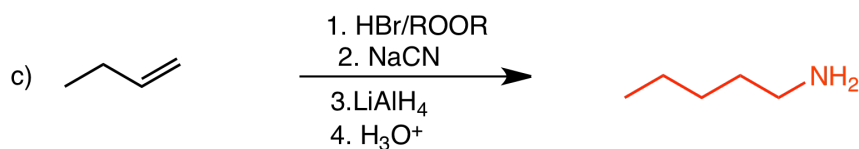
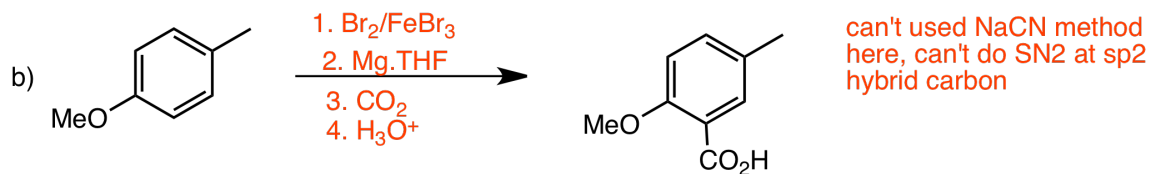
Diels-Alder reactions go faster with stronger donating groups attached to the conjugated pi-diene, donating groups raise the energy of the electrons in the HOMO of the diene, decrease the energy gap between the HOMO and the LUMO of the dienophile

-OCH₃ is stronger than -CH₃, thus C faster than B which is faster than A

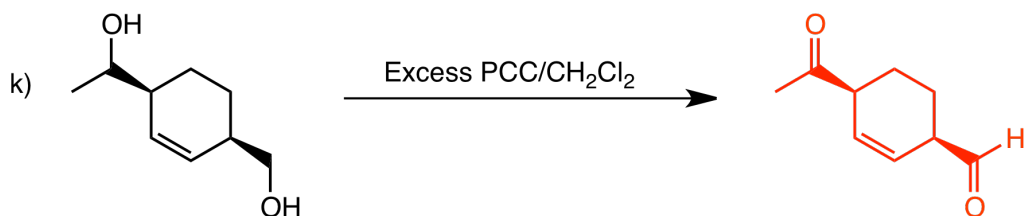
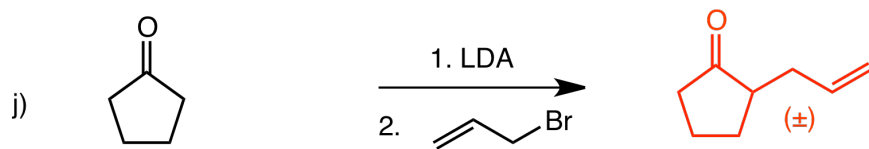
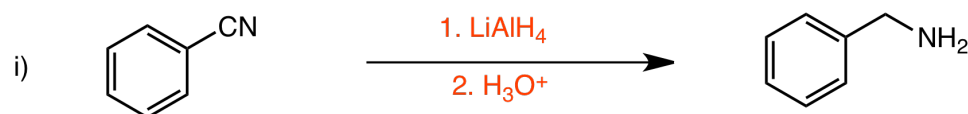
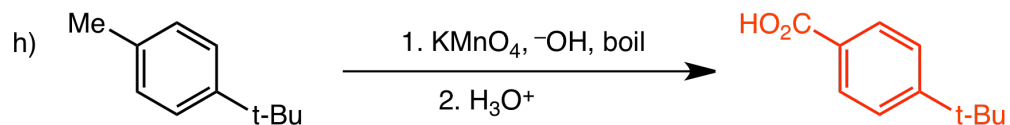
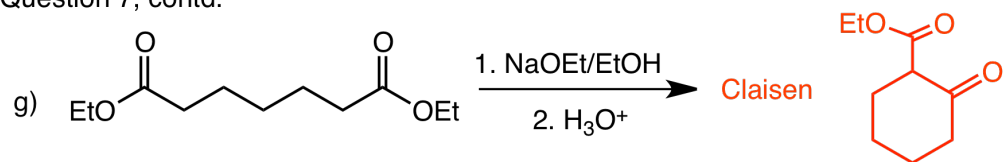
Question 6) Draw the complete arrow pushing mechanism for the following reaction. Indicate the Lewis acid/base for each INTERMOLECULAR step, and if they are also Brønsted acids/bases. Add non-bonding electrons as necessary.



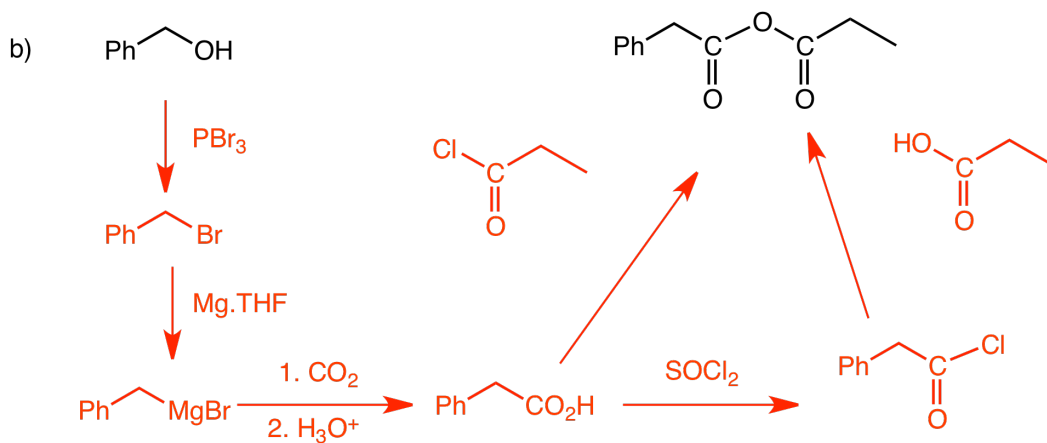
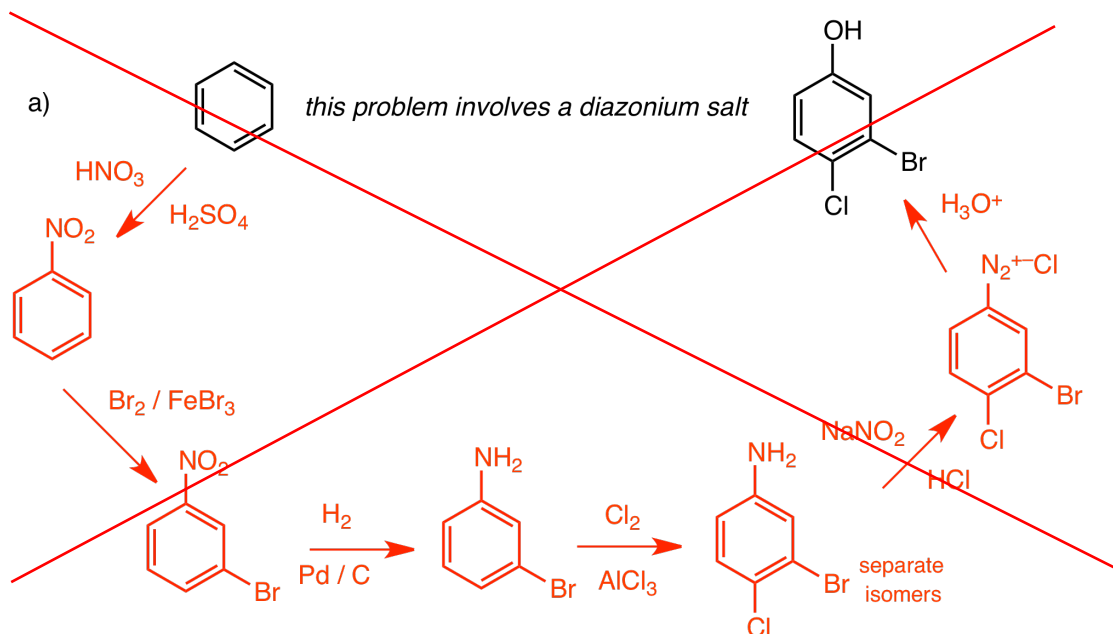
Question 7) Provide the missing major organic products, or reagents/conditions, or organic reactants, as appropriate. **Do not forget to include stereochemistry as appropriate** unless specified otherwise.



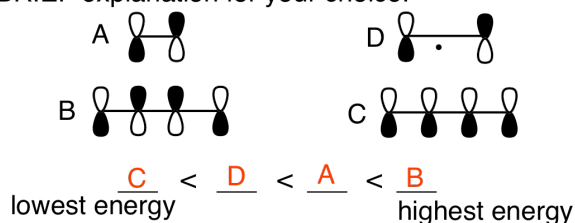
Question 7, contd.



Question 8) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers**

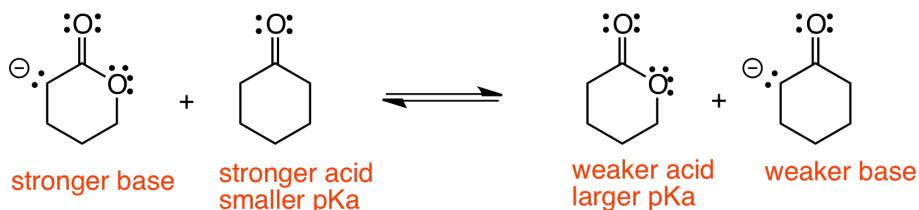


Question 9.) Rank the energies of an electron in each of the following π -molecular orbitals. Give a BRIEF explanation for your choice.



an electron will be lower in energy the bonding interactions in the molecular orbital, and higher in energy the more antibonding interactions, orbital D is non-bonding

Question 10) On each side of the following equilibrium, identify the stronger and weaker acid and base, identify which acid would have the LOWER pKa, indicate on which side the equilibrium would lie, and give a brief explanation for your choices.

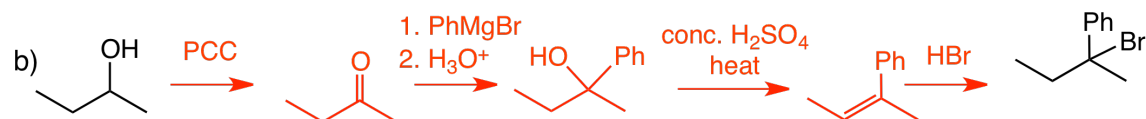
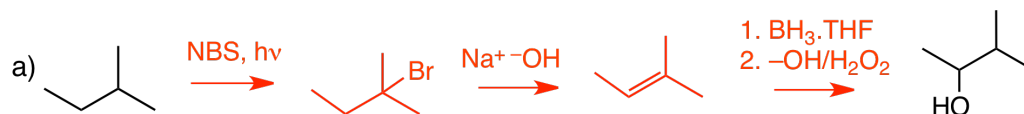


The pair of nonbonding electrons on the deprotonated ester are destabilized by additional oxygen atom that acts as a donating group to destabilize the enolate anion, compared to the weaker alkyl group in the ketone. The enolate anion from the ester thus has higher energy more reactive electrons is thus the stronger base, corresponding to the weaker acid.

Question 11) Why do two hydrogen atoms react to make a hydrogen molecule? This is one of my favorite questions to ask at a chemistry PhD oral defence you would be surprised how few satisfactory answers I get!

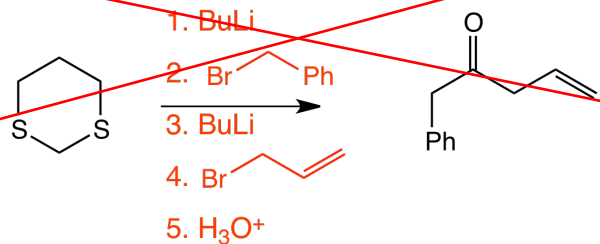
in the molecule the electrons are in a bond, in a bond they have lower (kinetic) energy

Question 12) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

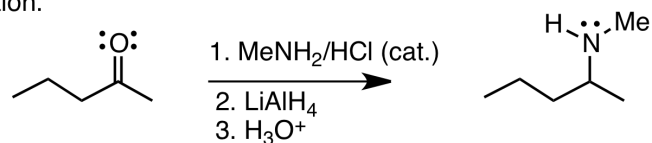


Question 13) Give the reagents/conditions you would use to make the following ketone using a dithiane synthesis

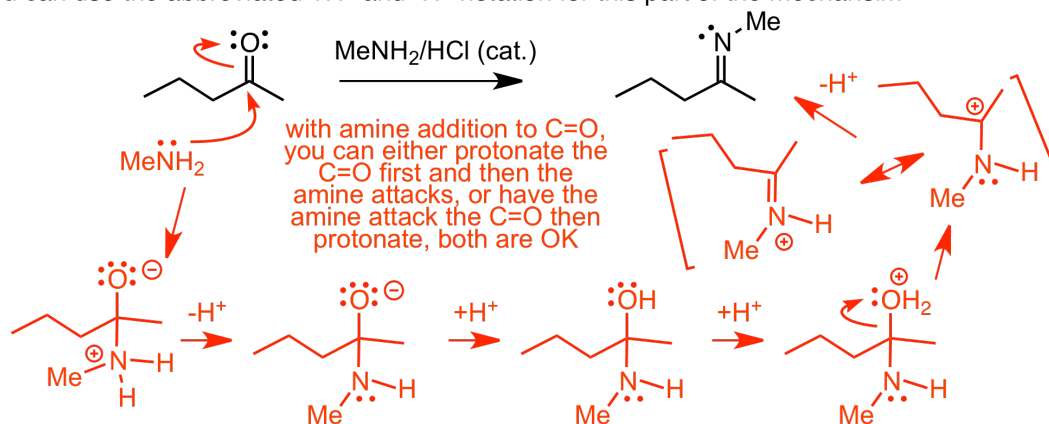
the order of addition of the bromides could be reversed



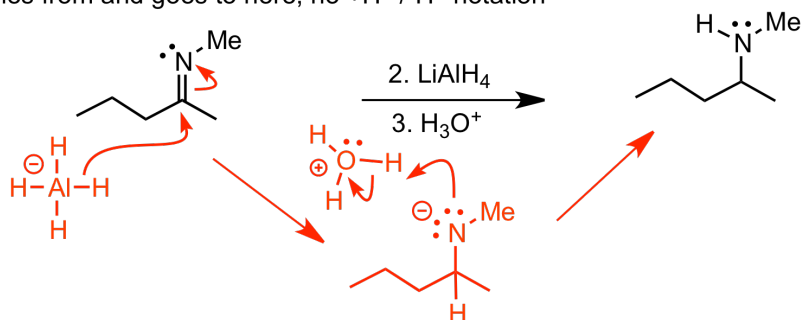
Question 15) Give a curved arrow-pushing mechanism for the two parts of the following indirect reductive amination.



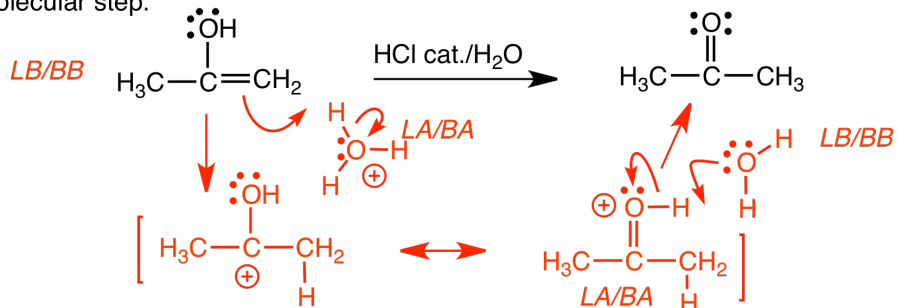
a) First, the mechanism of formation of the imine intermediate structure (i.e. the reaction below), you can use the abbreviated $+\text{H}^+$ and $-\text{H}^+$ notation for this part of the mechanism



b) Second, the reduction to the amine, shown below, you MUST show exactly where each proton comes from and goes to here, no $+\text{H}^+/-\text{H}^+$ notation

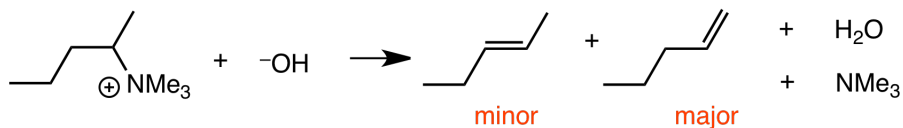


Question 16) Give a curved arrow-pushing mechanism for the following reaction, show where every proton comes from and goes to, no $+\text{H}^+/-\text{H}^+$, indicate the Lewis and Bronsted acids/bases for each INTERmolecular step.



Question 17) For the following elimination reactions

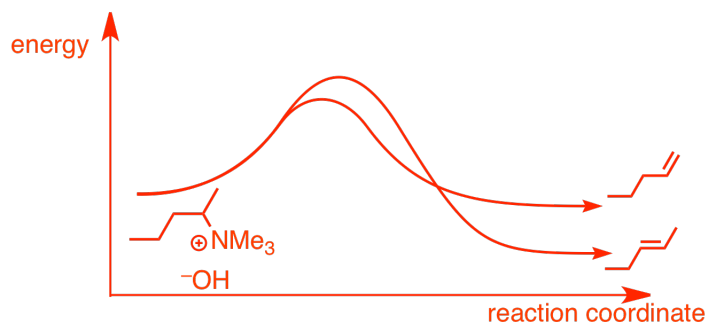
a) Indicate which is the major and which the minor alkene product



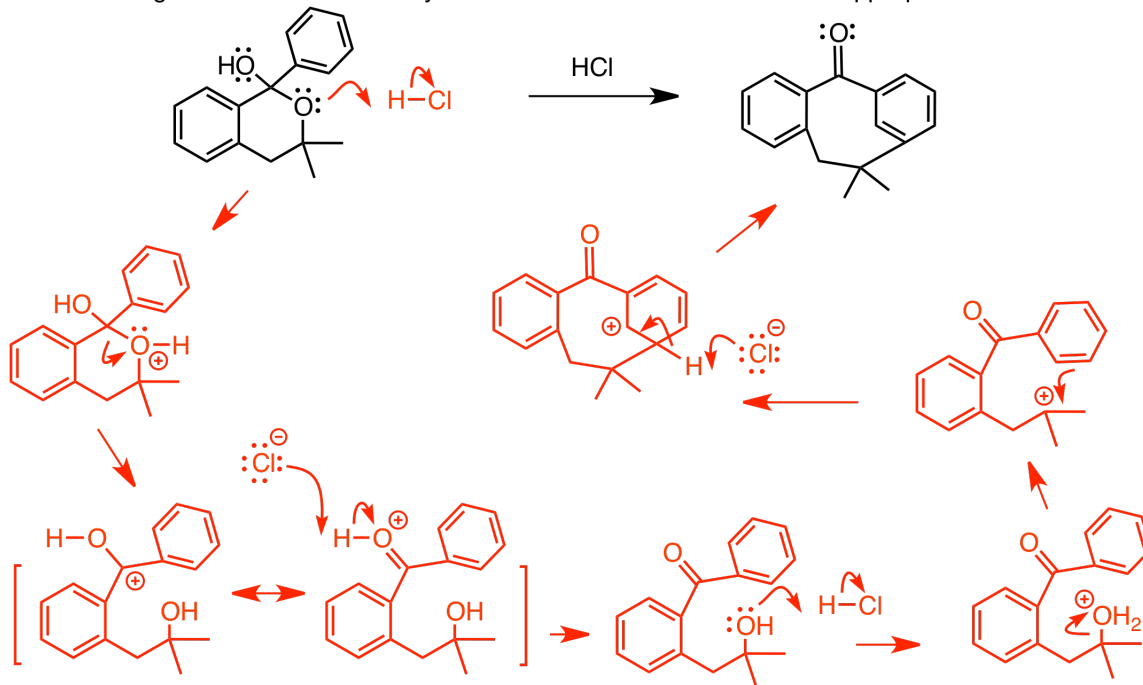
b) State whether the major product is formed as a result of kinetic control or thermodynamic control, give a BRIEF one-sentence explanation

kinetic - the less stable alkene forms because it proceeds via the lower energy transition state, i.e. the one that puts the negative charge on the least substituted carbon

c) Draw a reaction energy diagram for formation of both products on the SAME diagram



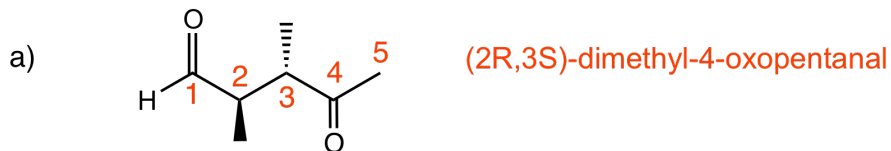
Question 18) Draw the complete arrow pushing mechanism for the following reaction. Add non-bonding electrons as necessary. Draw the resonance structures as appropriate



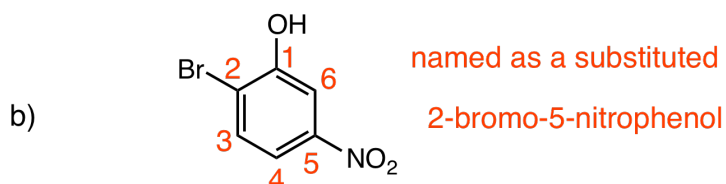
START OF PRACTICE TEST #4

Question 1) Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.

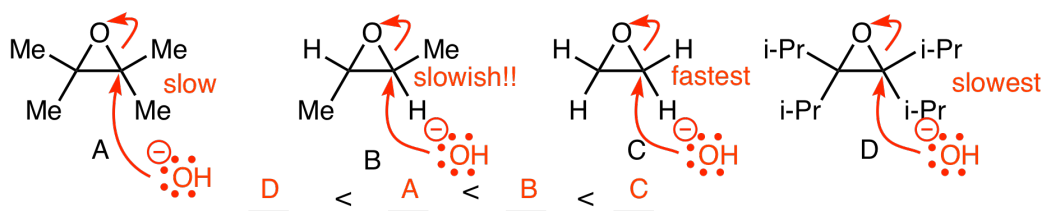
named as an aldehyde



named as a substituted phenol

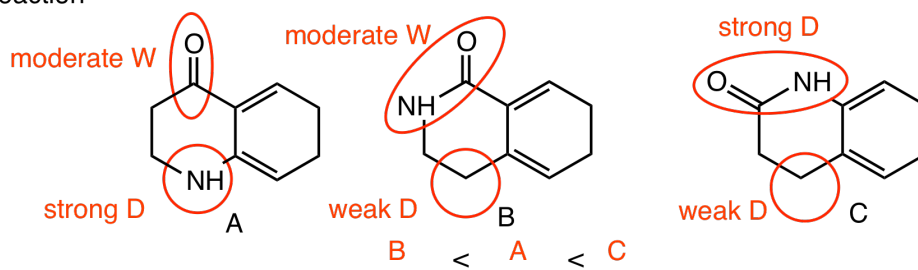


Question 2) Rank the following in terms of increasing rate of reaction in a base catalyzed hydrolysis reaction (addition of water in the presence of hydroxide) and give a brief explanation



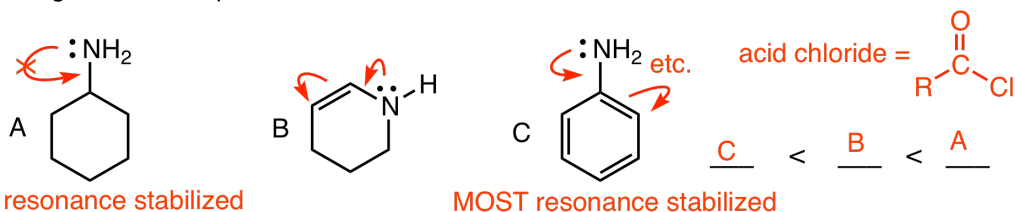
The rate determining step is reaction of hydroxide as Lewis base in an S_N2 type attack on carbon of the Lewis acid epoxide. This process is subject to steric hinderance, hence the order given.

Question 3) Rank the following in terms of increasing energy of an electron in the HOMO of the following dienes. Give an explanation which also states which would react faster in a Diels-Alder reaction



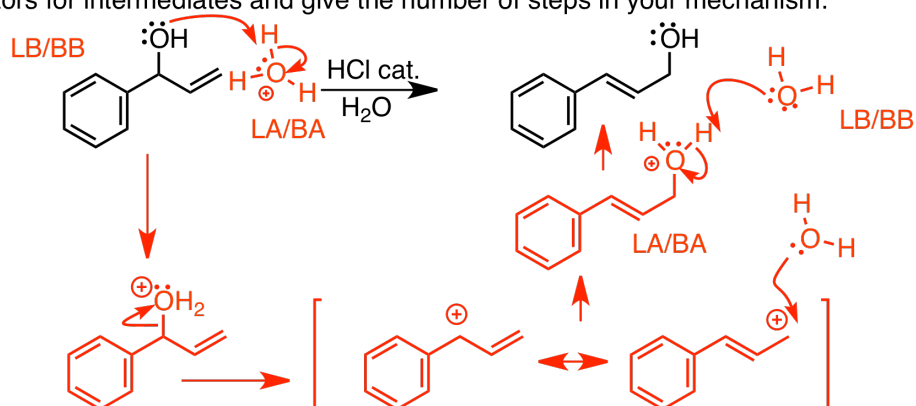
Each diene is substituted by either electron donating (D) or withdrawing groups (W) as indicated. Donating groups raise the electron energy, W decrease electron energy in the dienes. has the highest energy HOMO, would react fastest in a Diels-Alder reaction

Question 4) Rank in order of increasing rate of reaction with an acid chloride to make an amide, give a brief explanation.



this is a reaction between an amine and an acid chloride to make an amide, the amine is the LB/nucleophile, the acid chloride the LA/electrophile, from $A > B > C$ the non-bonding electrons on the N are increasingly resonance stabilized, less Lewis basic, less nucleophilic, less reactive, react slower

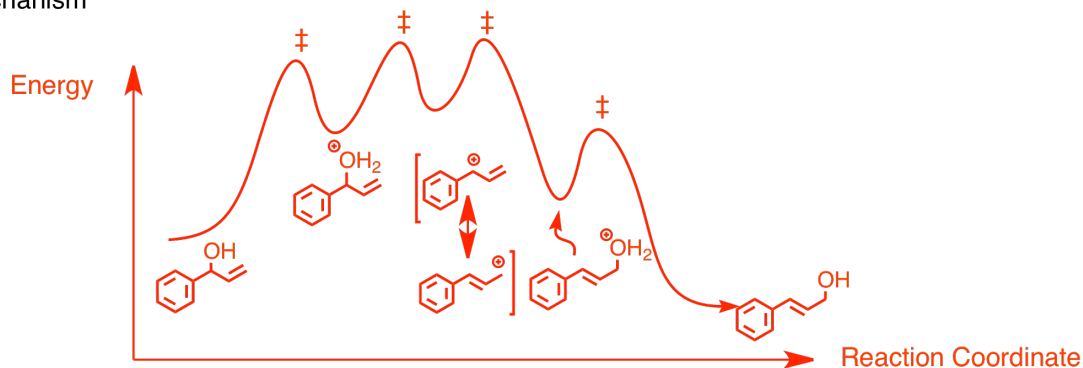
Question 5) Give a curved arrow-pushing mechanism for the following reaction, indicate the Lewis and Bronsted acids/bases for each INTERmolecular step, include all important resonance contributors for intermediates and give the number of steps in your mechanism:



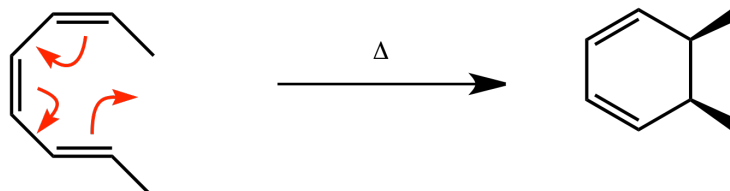
b) Is this reaction exothermic? Give a brief explanation

Yes, because the conjugation in the system increases (the double bond becomes conjugated with the benzene ring) and also because the alkene becomes more substituted

Draw a properly labelled reaction energy diagram for this reaction, identify the locations of the transition states (do not draw them) and the locations of the various intermediates in your mechanism



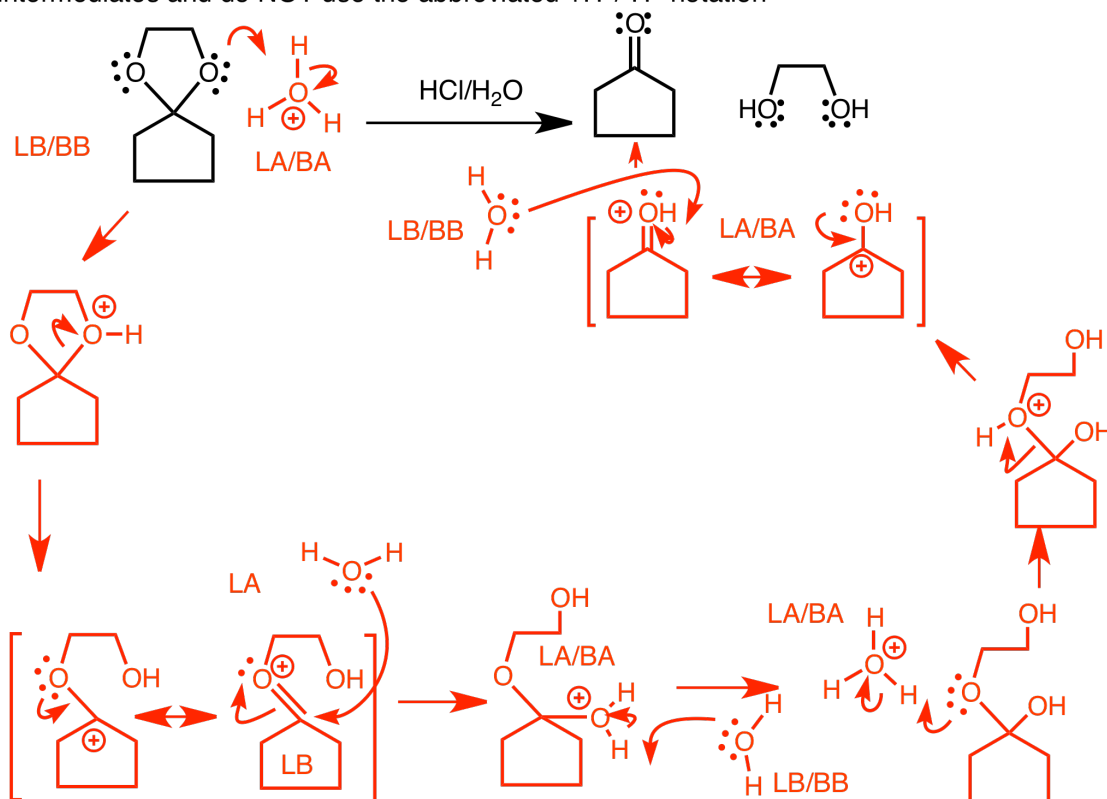
Question 6) The purpose of this question is to determine whether the provided product is allowed or forbidden.



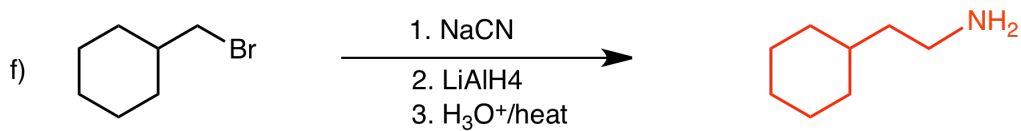
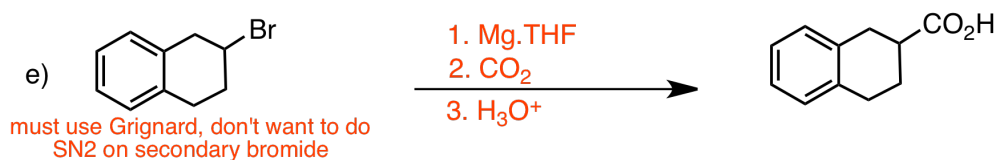
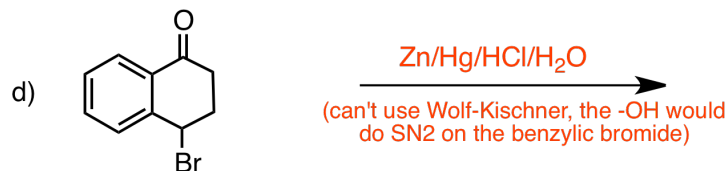
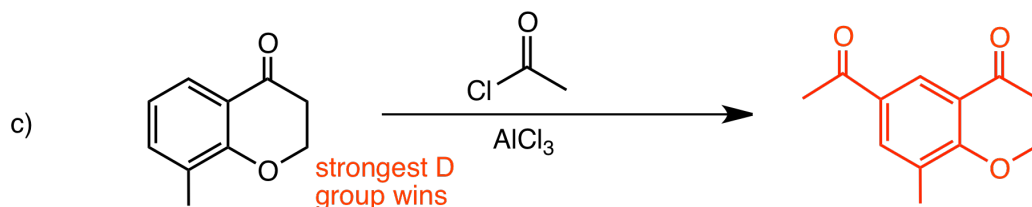
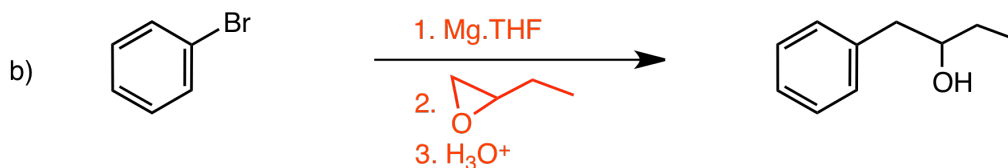
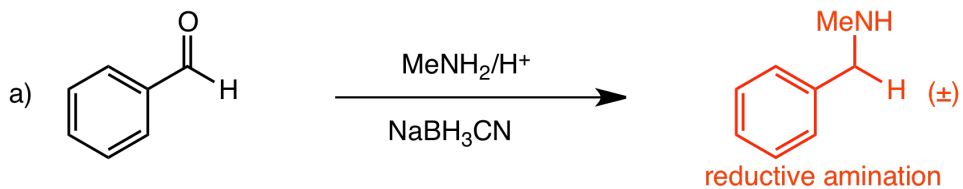
- 1) draw the arrow-pushing that describes formation of the product
- 2) How many electrons are involved in the reaction? **6 electrons**
- 3) FOR THE REACTION SHOWN (which may or may not be allowed), would the ring closing be disrotatory or conrotatory? **Conrotatory**
- 4) FOR THE REACTION SHOWN (which may or may not be allowed), would the transition state be Hückel or Möbius? **Möbius**
- 5) Is THE REACTION SHOWN allowed or forbidden? **Forbidden**

Note that that these questions ask whether the reactions SHOWN go via Hückel or Möbius transition states. To form the product above the reaction would have to go conrotatory and Möbius transition state, whereas the allowed reaction is disrotatory and Hückel.

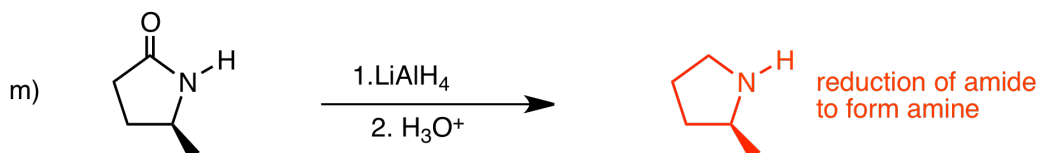
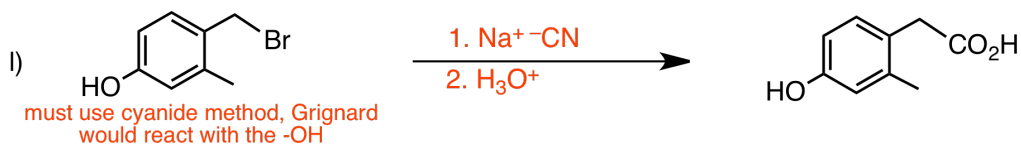
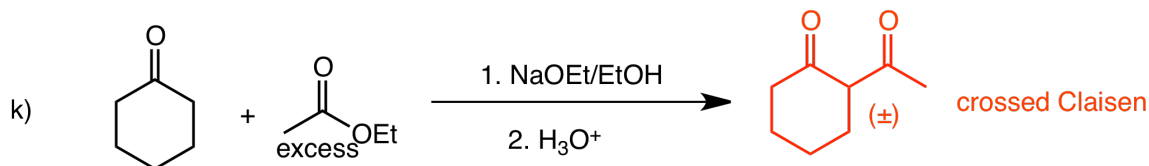
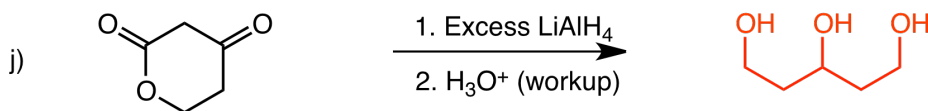
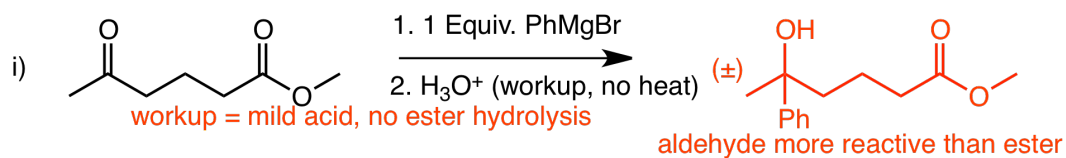
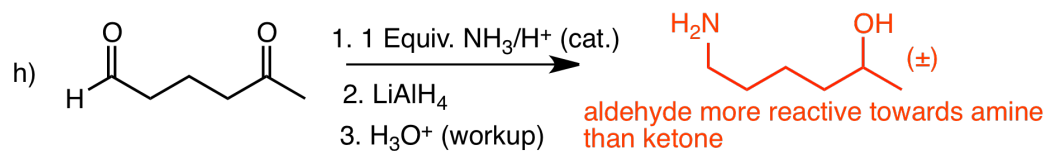
Question 7) Draw the complete arrow pushing mechanism for the following reaction. Indicate the Lewis acid/base at each step, and if they are also Brønsted acids/bases. Add non-bonding electrons as necessary. Draw the **ALL important** resonance structure of the intermediates and do NOT use the abbreviated $+H^-/-H^+$ notation



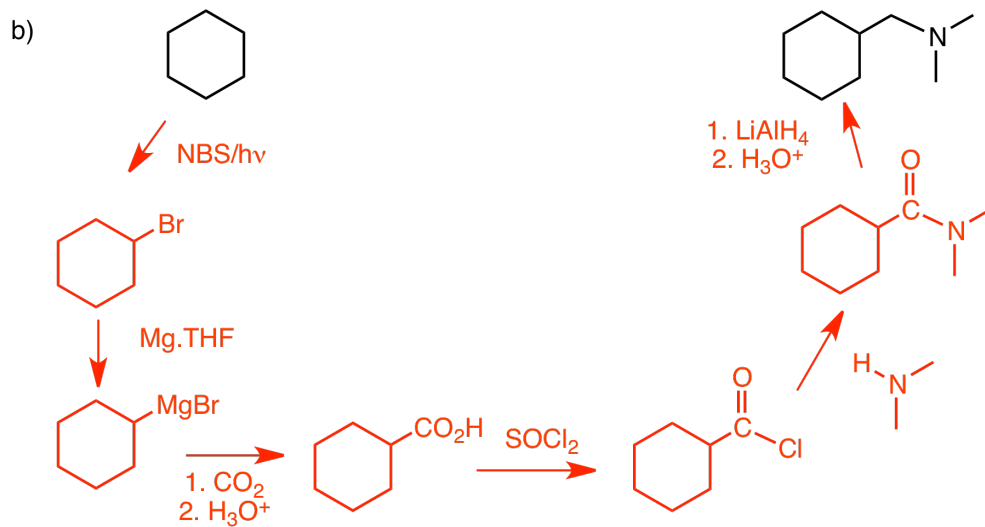
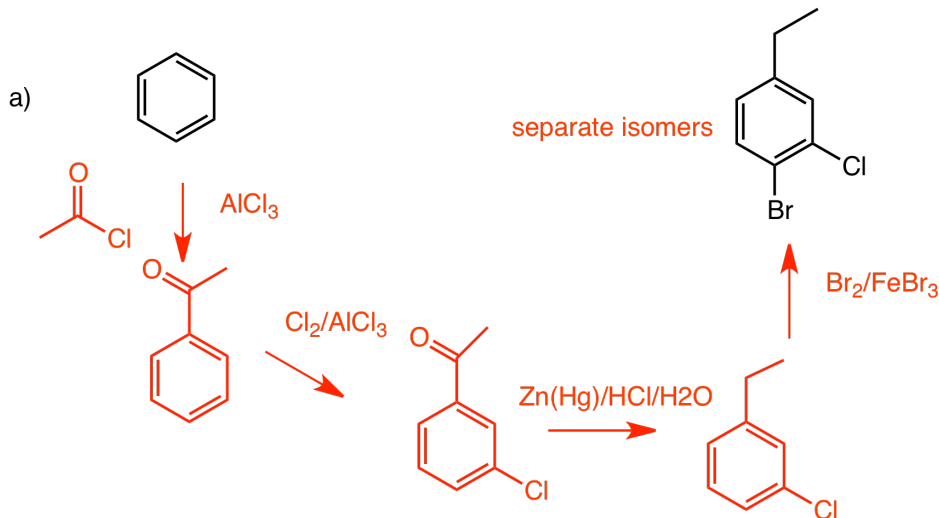
Question 8) Provide the missing major organic products, or reagents/conditions, or organic reactants, as appropriate. **Do not forget to include stereochemistry as appropriate** unless specified otherwise.



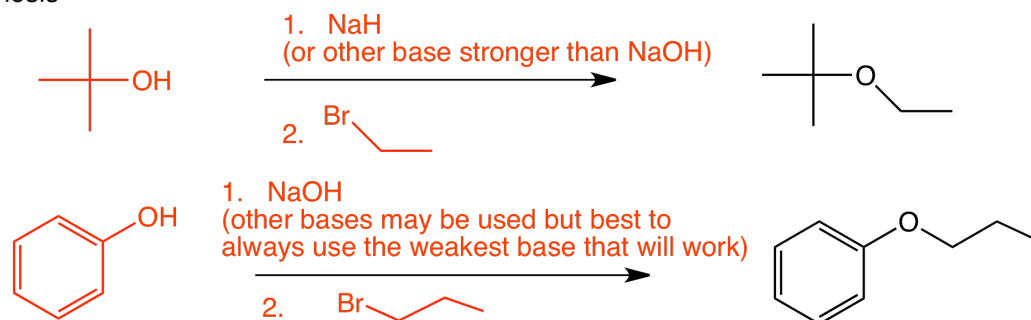
Question 8) contd.



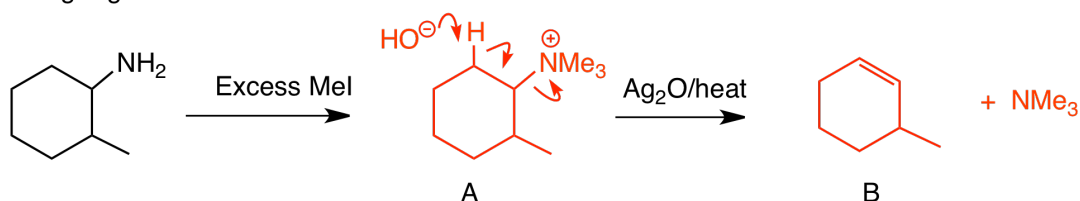
Question 9) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers**



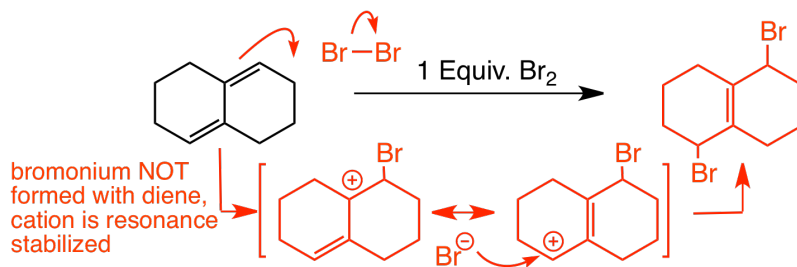
Question 10) Provide the ALCOHOL and the bromide and all other reagents/reactants in proper sequence to synthesize the following ethers using a Williamson ether synthesis



Question 11) The following reaction sequence represents a Hofmann elimination, give the missing organic structures A and B.



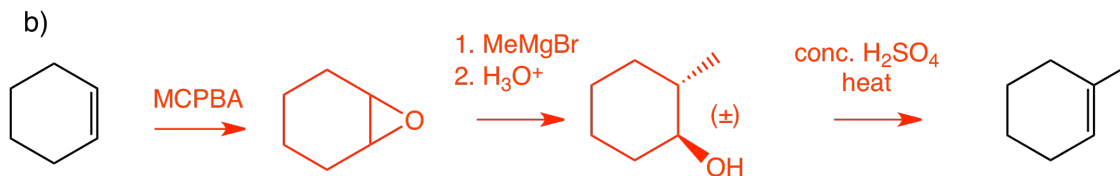
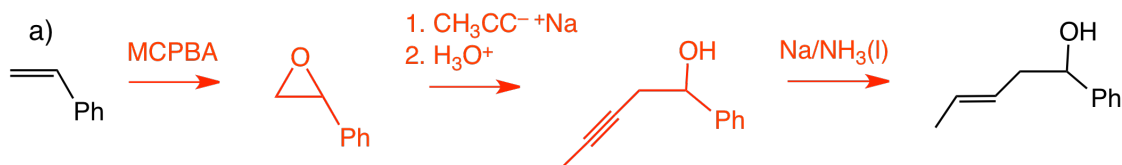
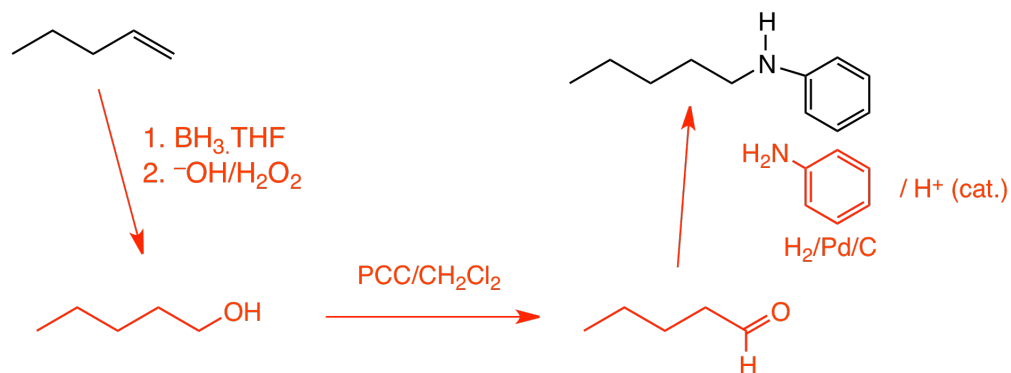
Question 12) Give the major organic product of the following reaction, assume THERMODYNAMIC CONTROL (ignore stereoisomers)



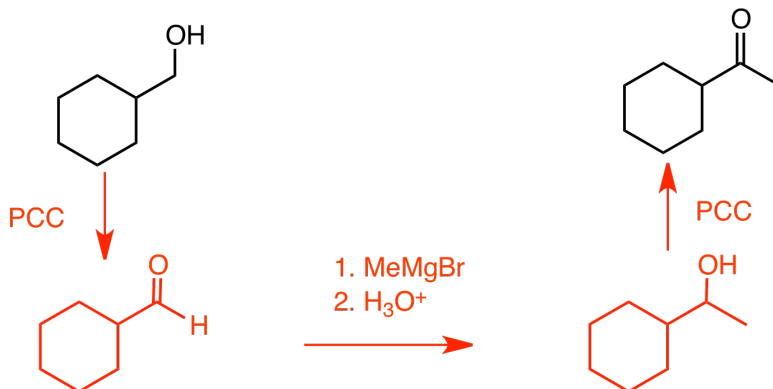
Question 13) When we say that reactions are controlled mainly by the energy of the electrons, how do we understand this statement in terms of reaction free energy?

reactions are controlled by free energy, which is divided into enthalpy and entropy, in most organic reactions enthalpy dominates and electron energy is the major contributor to enthalpy

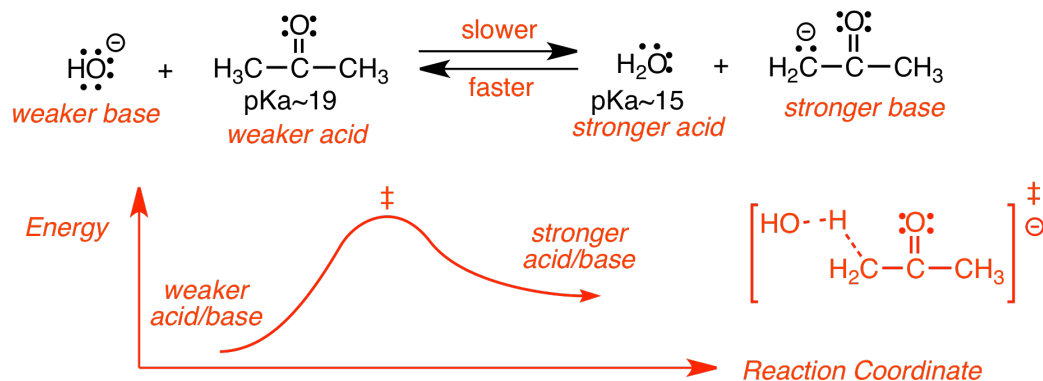
Question 14) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



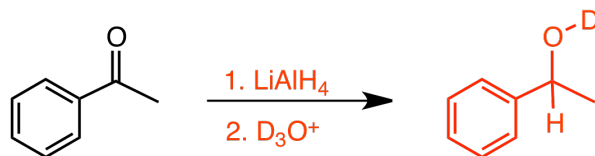
Question 15) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



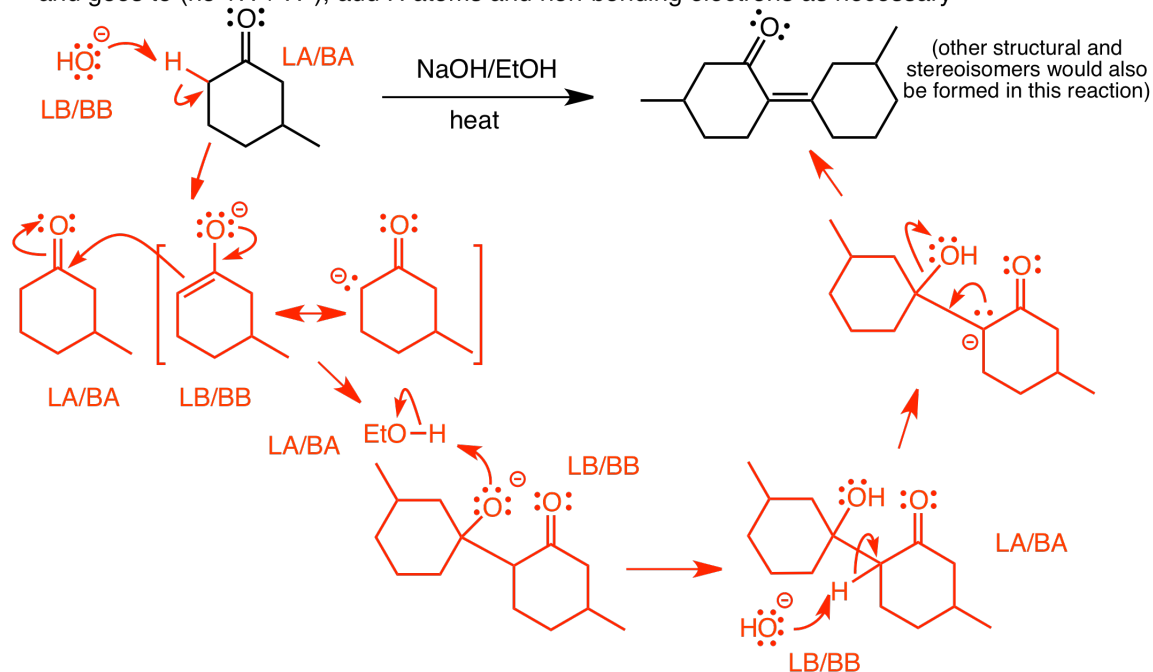
Question 6) For the following equilibrium, indicate the strongest acid and base on EACH side (use the provided pK_a values), indicate which reaction is faster and which slower, and draw a reaction energy diagram for the equilibrium, include a drawing of the transition state



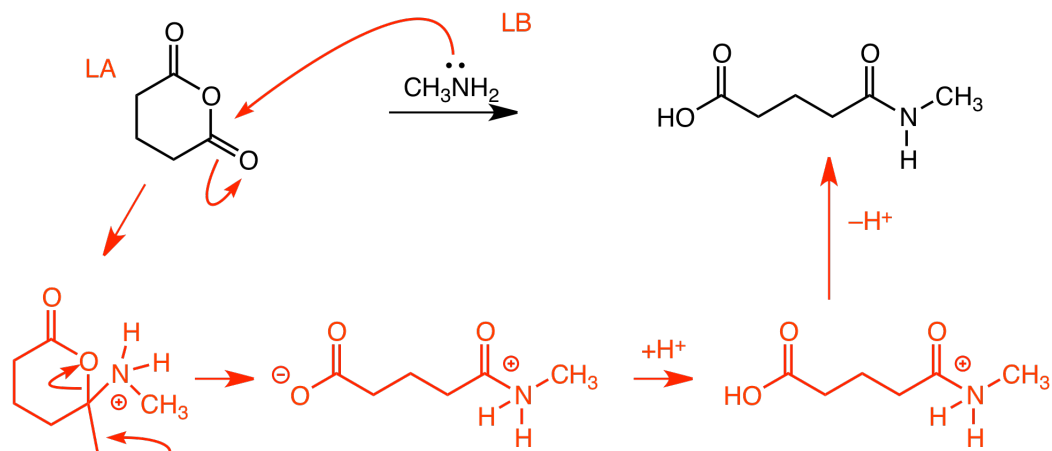
Question 17) Give the major organic product of the following reaction. Remember that deuterium (D) is an isotope of hydrogen that can be used to track what happens to specific hydrogens in a reaction, you can assume that it reacts exactly the same as hydrogen for this problem



Question 18) Give a curved arrow-pushing mechanism for the following reaction, indicate the Lewis and Bronsted acids/bases for each INTERmolecular step, include all important resonance contributors for intermediates, give the number of steps in your mechanism, indicate the Lewis and Bronsted acids/bases for each INTERmolecular step, show where every proton comes from and goes to (no $+H^+/-H^+$), add H atoms and non-bonding electrons as necessary



for the mechanism below you can use the $+H^+/-H^+$ abbreviated notation



the order for these last protonation/deprotonation steps does not matter