

PRINTED  
FIRST NAME \_\_\_\_\_PRINTED  
LAST NAME \_\_\_\_\_ASU ID or  
Posting ID \_\_\_\_\_Person on your **LEFT** (or **Aisle**)Person on your **RIGHT** (or **Aisle**)

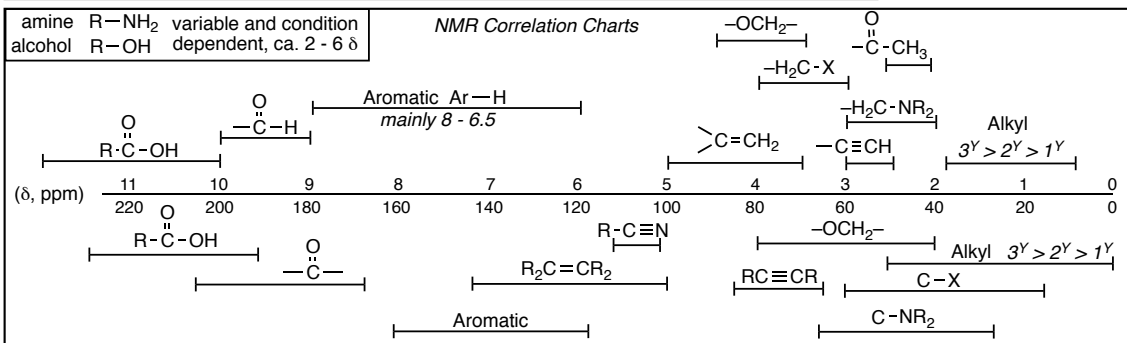
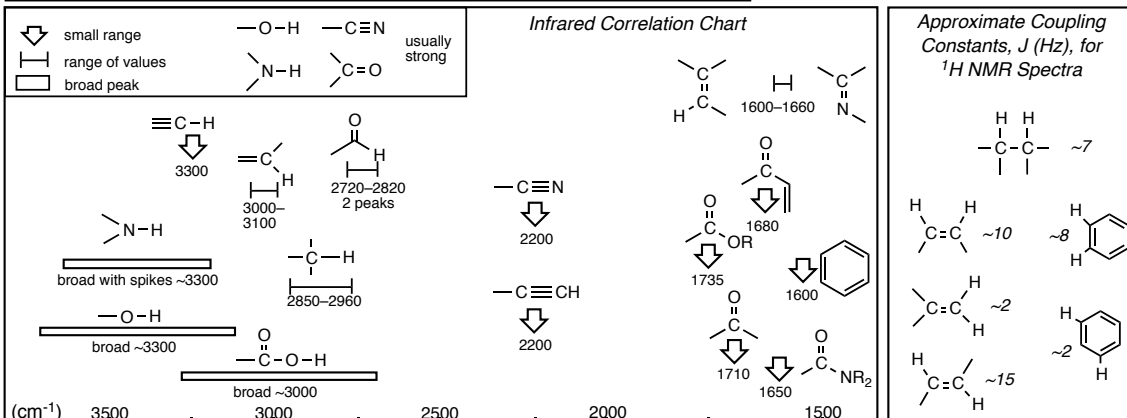
- PRINT YOUR NAME ON EACH PAGE!
- READ THE DIRECTIONS CAREFULLY!
- USE BLANK PAGES AS SCRATCH PAPER  
work on blank pages will not be graded...
- WRITE CLEARLY!
- MOLECULAR MODELS ARE ALLOWED
- DO NOT USE RED INK
- DON'T CHEAT, USE COMMON SENSE!

THIS IS A CHM 234  
PRACTICE EXAMMIDTERM #2  
PRACTICE TEST #1

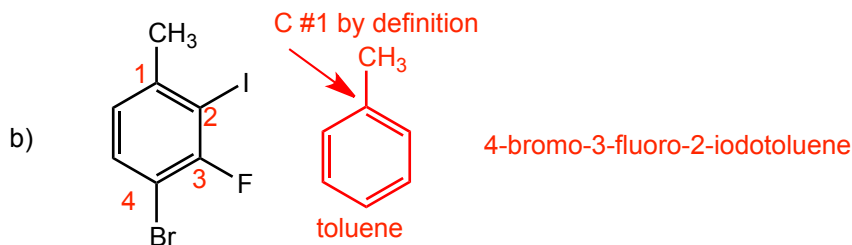
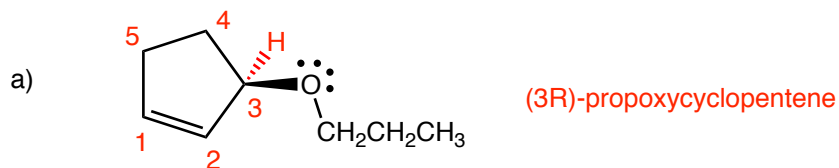
Extra Credit \_\_\_\_\_/5

Total (incl Extra) \_\_\_\_\_/175+5

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

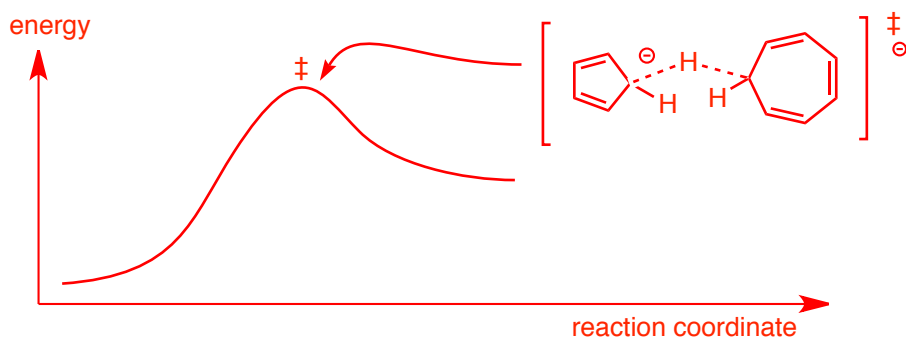
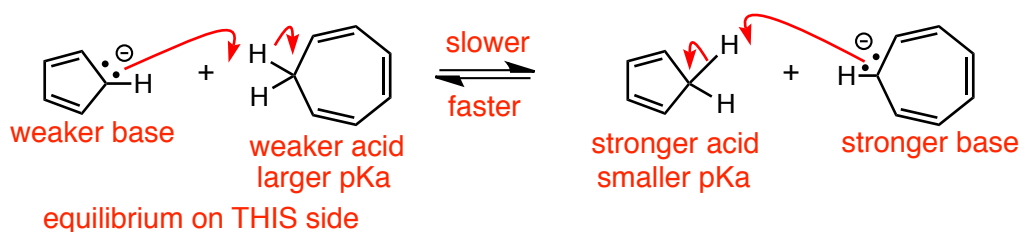


Question 1 Give the IUPAC name for the following compounds. Be sure to use cis/trans, E/Z or R/S where appropriate.



Question 2. For the Bronsted acid/base reaction below:

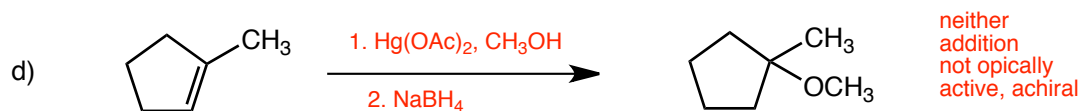
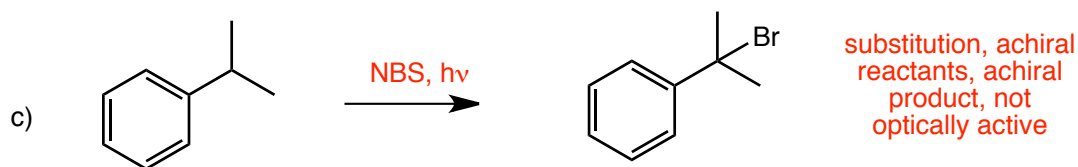
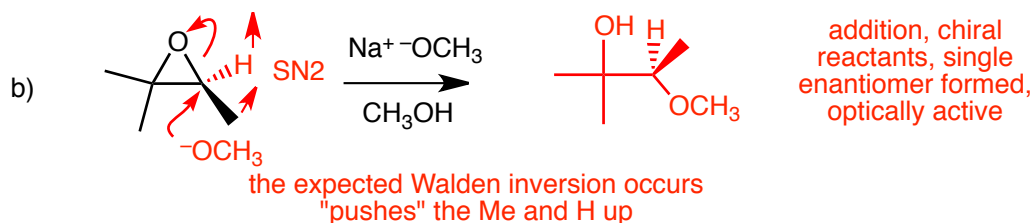
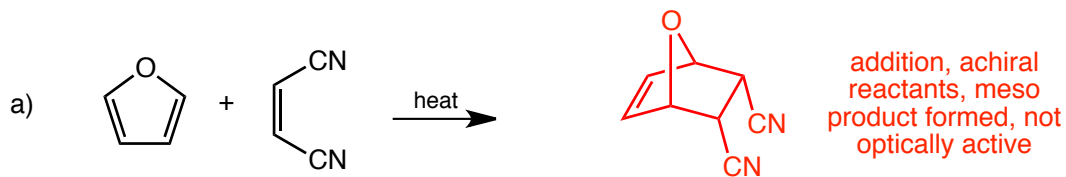
- Give the curved arrow-pushing in both directions
- Draw a reaction energy diagram and include a drawing of the transition state
- Label the acids/bases and which are stronger and give a brief explanation
- Indicate which reaction is faster (left to right or vica versa) and on which side the equilibrium lies and which acid has the smaller and which the larger pKa



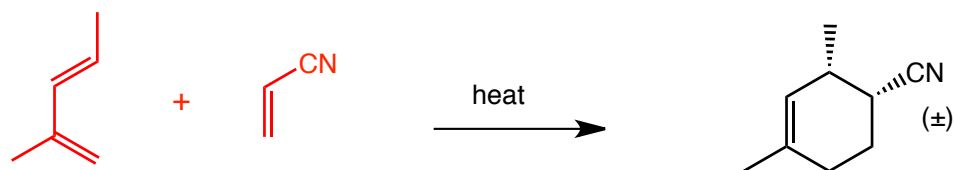
the weaker base has lower energy electrons because the ion is aromatic, the stronger base is anti-aromatic if flat, or it twists it may become non-aromatic, but will be less stable than the aromatic anion in any geometry

Question 3 For each reaction

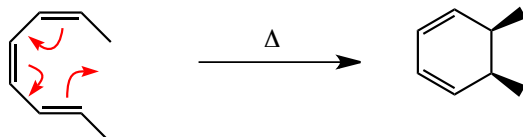
- 1) Provide the missing **reagents/conditions or major organic products as appropriate**
- 2) **State** whether the OVERALL reaction is Addition, Elimination, Substitution or Rearrangement
- 3) **Briefly explain** whether the a solution of the product would be optically active or not
- 4) Pay attention to stereochemistry including racemic mixtures unless specified



Question 4. Provide the missing reactants for the following Diels-Alder reaction.



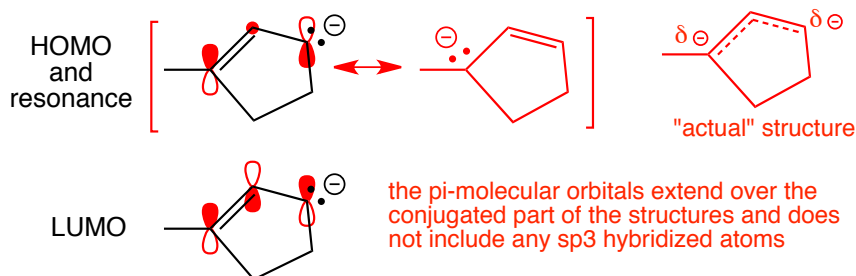
Question 5. The purpose of this question is to determine whether the provided product is allowed or forbidden



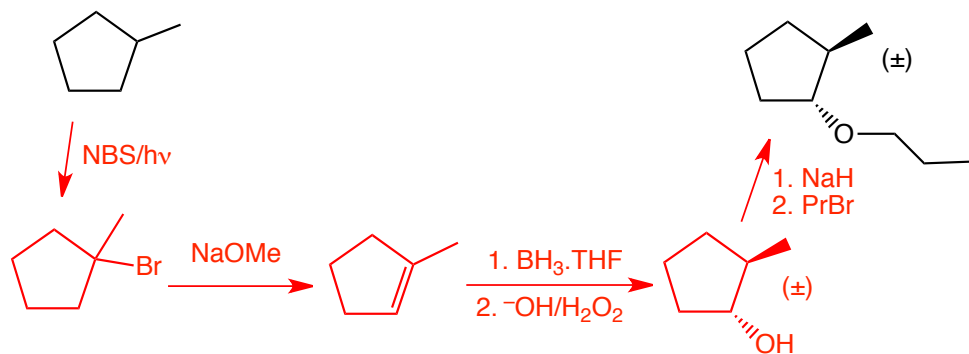
- 1) draw the arrow-pushing that describes formation of the PROVIDED product
- 2) How many electrons are involved in the reaction? **6 electrons**
- 3) FOR THE PROVIDED PRODUCT (which may or may not be allowed), would the ring closing be disrotatory or conrotatory? **Conrotatory**
- 4) FOR THE PROVIDED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

**Forbidden, the allowed product of a 6-electron electrocyclic ring closing reaction would proceed via an aromatic Hückel transition state and would be disrotatory, not Möbius/conrotatory**

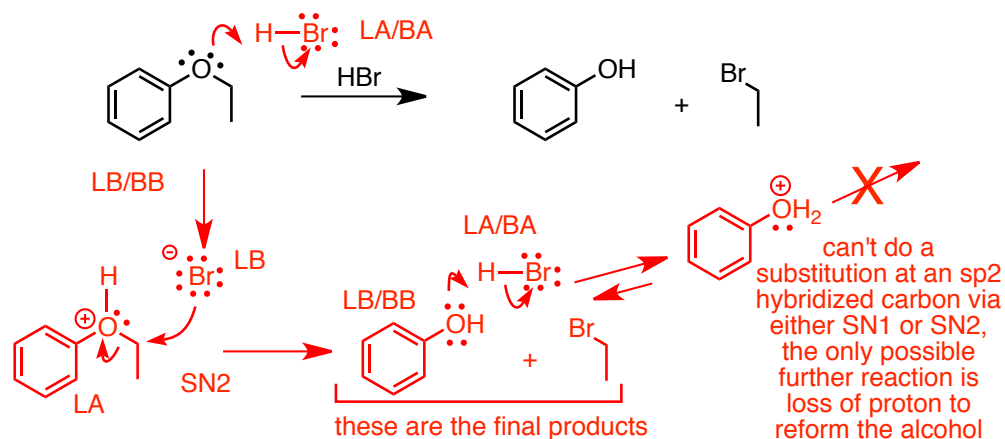
Question 6) For the following ion, draw all reasonable resonance contributors, draw an "actual" structure that includes partial bonds and partial charges (use  $\delta$  to indicate partial charges), and draw the HOMO and LUMOs on TOP of the provided structures



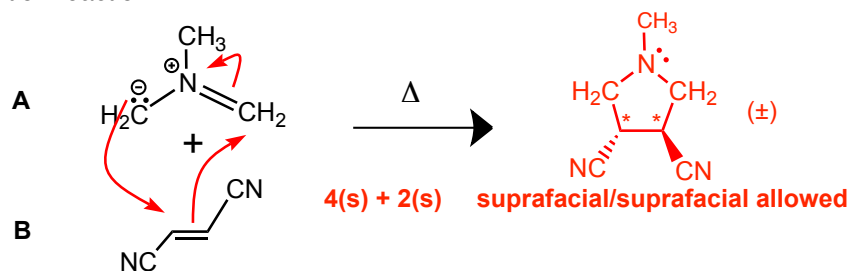
Question 7. Show how you would synthesize the target compound on the right from the starting compound on the left. Show reagents and conditions, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



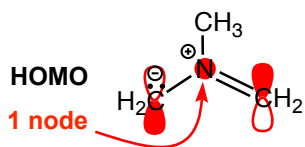
Question 8) Explain why the products of the following reaction are an alcohol and a bromide, rather than two bromides, Draw a mechanism to support your reasoning



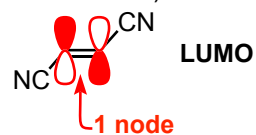
Question 9). Give the curved arrow-pushing and the ALLOWED product of the following cycloaddition reaction



b) Give a pictorial representation of the wavefunction of the HOMO ON TOP OF THE STRUCTURE below for A, indicate the number and positions of any vertical nodes (ignore horizontal nodes)



c) Give a pictorial representation of the wavefunction of the LUMO ON TOP OF THE STRUCTURE below for B, indicate the number and positions of any vertical nodes (ignore horizontal nodes)

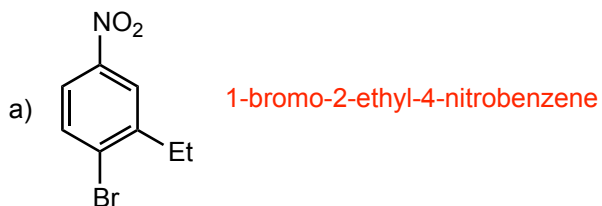


d) Give a brief justification for the stereochemistry in your allowed product, you must include the following terms in your justification: suprafacial and/or antarafacial, HOMO, LUMO, bonding and/or anti-bonding

the ALLOWED product of the reaction must have two bonding interactions in the transition state, consideration of the wavefunctions of the HOMO and the LUMO indicates that suprafacial/suprafacial reaction is allowed, thus the 2 -CN groups start trans- and are also trans- in the product

**START OF PRACTICE TEST #2**

Question 1 Give the IUPAC name for the following compound. Be sure to use cis/trans, E/Z or R/S where appropriate.



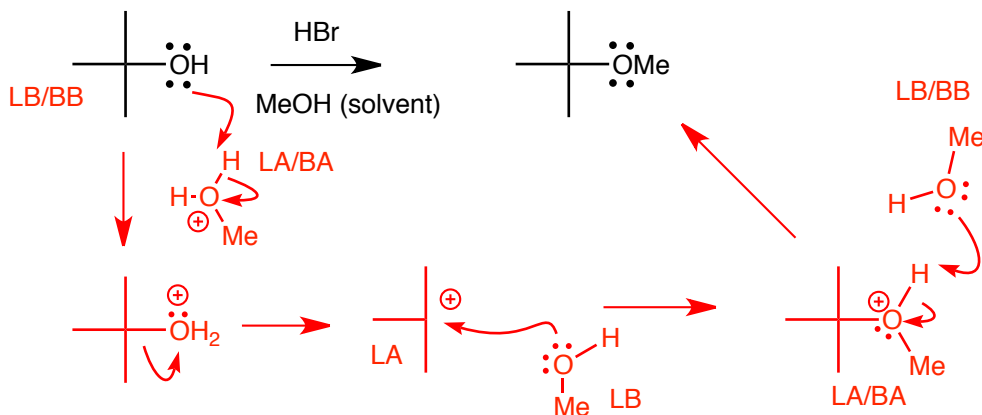
ethers are always just "alkoxy" substituents

(alcohol highest priority functional group, determines numbering)

Question 2. Give a complete curved arrow pushing mechanism, and...

1) Indicate the Lewis acid/Lewis base (LA, LB) at each step as appropriate, and whether they are also Brønsted acids/bases (LA/BA, LB, BB)

2) GIVE THE NUMBER OF STEPS IN YOUR MECHANISM

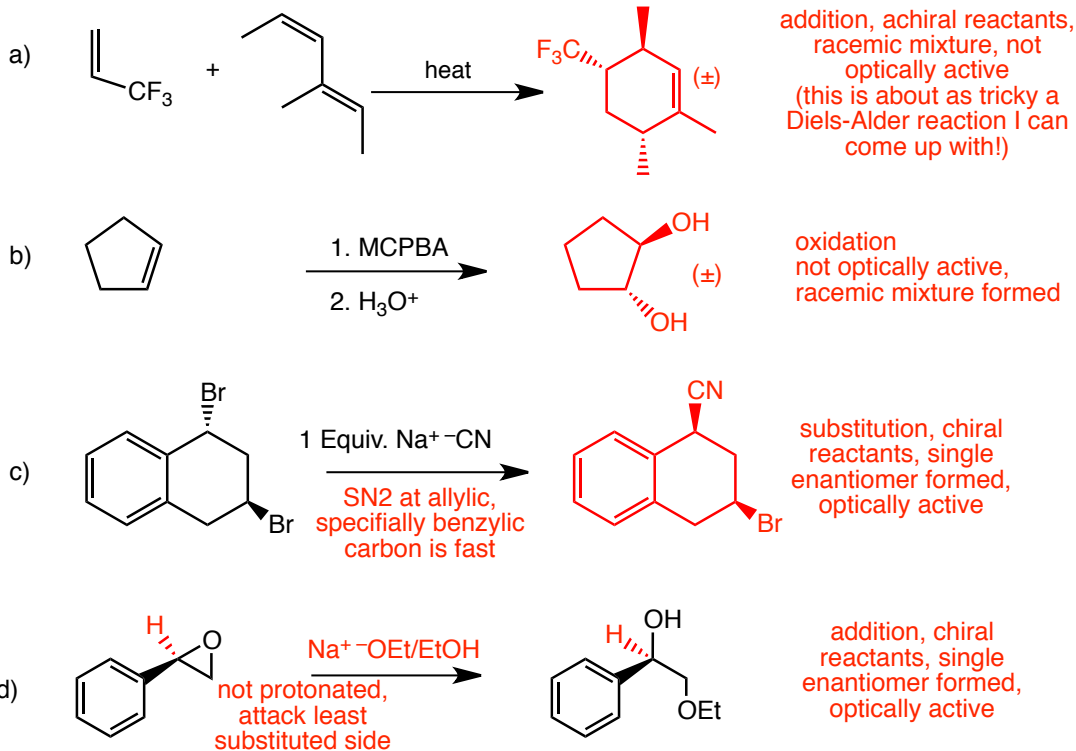


when dissolved in MeOH, HBr is essentially completely dissociated, just the same as it is in H<sub>2</sub>O

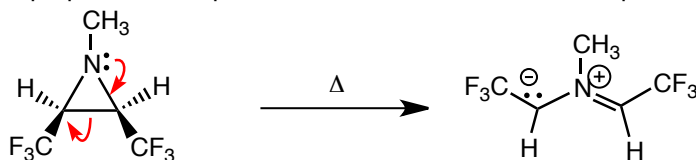
**4 steps**

Question 3 For each reaction

- 1) Provide the missing **reagents/conditions or major organic products as appropriate**
- 2) **State** whether the OVERALL reaction is Addition, Elimination, Substitution or Rearrangement
- 3) **Briefly explain** whether the a solution of the product would be optically active or not
- 4) Pay attention to stereochemistry including racemic mixtures unless specified



Question 4) 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? **4 electrons**
- 3) FOR THE PROVIDED PRODUCT (which may or may not be allowed), would the ring opening be disrotatory or conrotatory? **Disrotatory**
- 4) FOR THE PROVIDED PRODUCT (which may or may not be allowed), would the transition state be Hückel or Möbius? **Hückel**
- 5) Is THE REACTION SHOWN allowed or forbidden, and why?

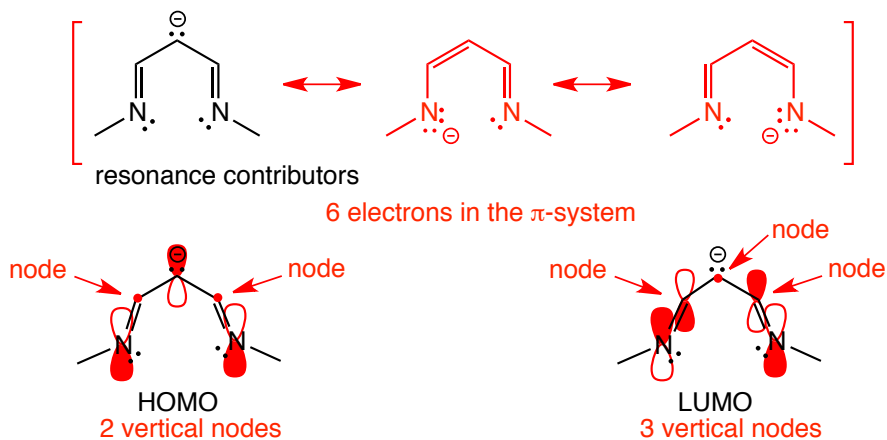
Forbidden, the allowed product of a 4-electron electrocyclic ring opening reaction would proceed via a Möbius transition state and would be conrotatory, not Hückel and disrotatory

Question 4. Provide the missing reactants for the following Diels-Alder reaction.

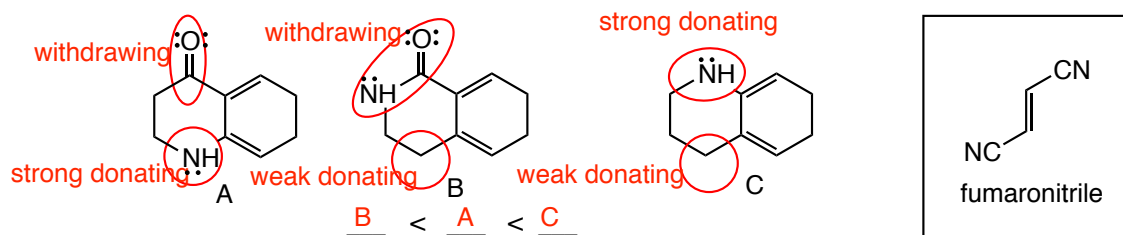


Question 5. For the following structure:

- Draw all additional reasonable resonance contributors
- Draw on TOP of the structure a pictorial representation of the wavefunction of both the HOMO and the LUMO, give the number of vertical node (only) and indicate their positions.



Question 6. Rank the following structures in order of increasing rate of reaction in a Diels-Alder reaction with fumaronitrile (shown), and give a brief explanation that includes the terms "donating group", "withdrawing group", "energy of the electrons", "HOMO".



the dienes differ by the substituents that are circled, the energy of the electrons in the diene, specifically those in the HOMO, are raised by donating groups and lowered by withdrawing groups, raising the energy of the electrons in the HOMO decreases the HOMO/LUMO gap (the LUMO on the fumaronitrile), which decreases the reaction activation energy and increases the rate

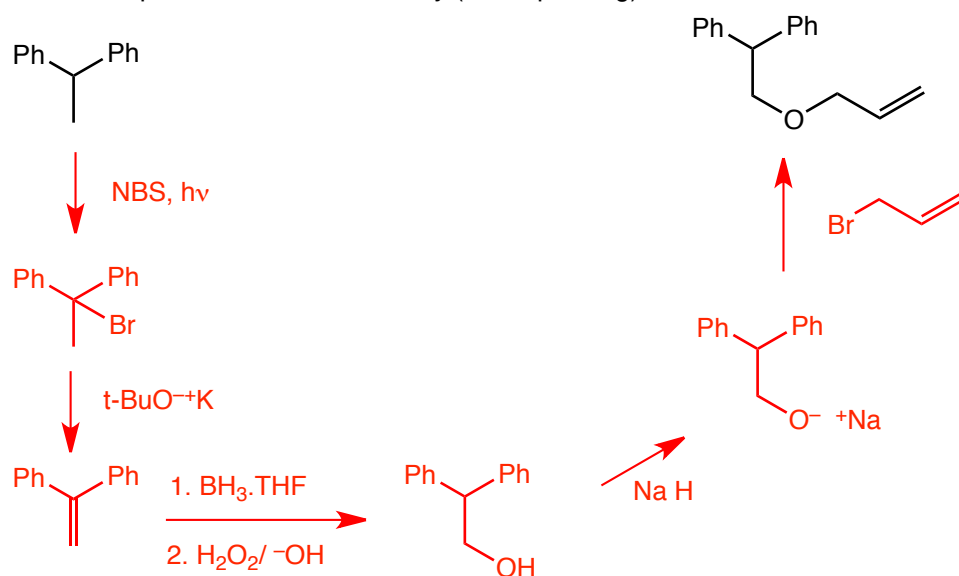
C has a strong donating group (non-bonding electrons on N) and a weak donating group (the alkyl chain), it reacts fastest

A has a withdrawing and a strong donating group (non-bonding electron on the nitrogen), it is intermediate

B has a withdrawing and only a weak donating group (the alkyl chain), it is slowest

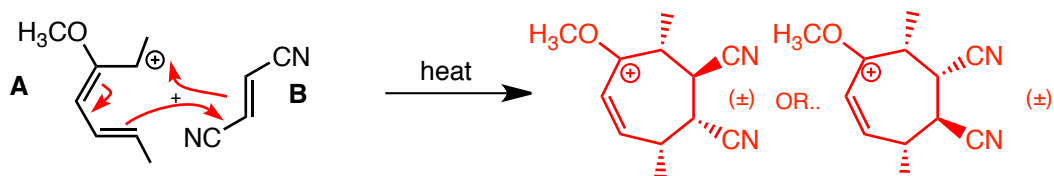


Question 7. Show how you would synthesize the target compounds on the right from the starting compounds on the left. Show reagents and conditions, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



Question 7 (20 pts.)

a) Give the curved arrow-pushing and the ALLOWED product of the following cycloaddition. State whether the product is achiral, a meso compound, a pure enantiomer or a racemic mixture



b) Draw the HOMO for reactant **A** and the LUMO for reactant **B** on top of the structures below, understanding that it may not be possible to get the geometry of the orbitals with respect to the structures exactly correct because the structures have to be drawn flat on the paper

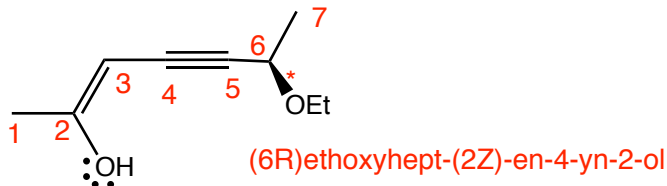


c) does the allowed reaction proceed suprafacial/suprafacial or suprafacial/antarafacial?

suprafacial/suprafacial

**START OF PRACTICE TEST #3**

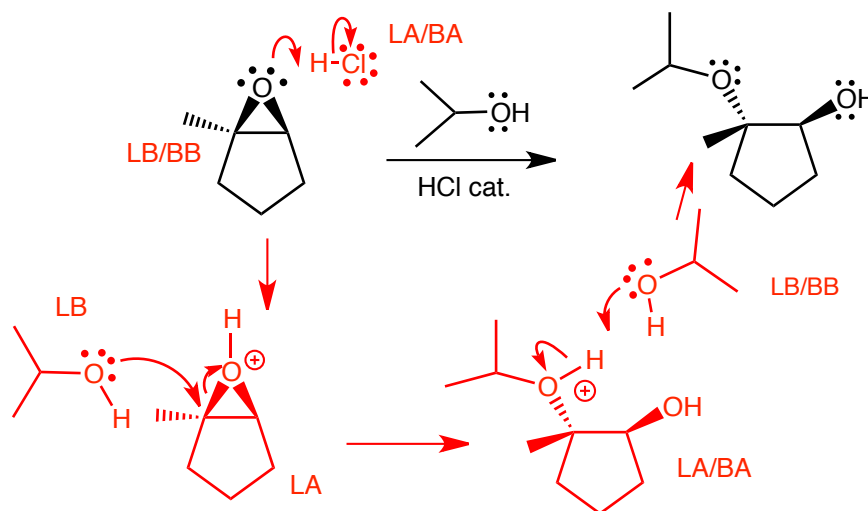
Question 1 Give the IUPAC name for the following compound. Be sure to use cis/trans, E/Z or R/S where appropriate.



Question 2. Give a complete curved arrow pushing mechanism, and...

1) Indicate the Lewis acid/Lewis base (LA, LB) at each step as appropriate, and whether they are also Brønsted acids/bases (LA/BA, LB, BB)

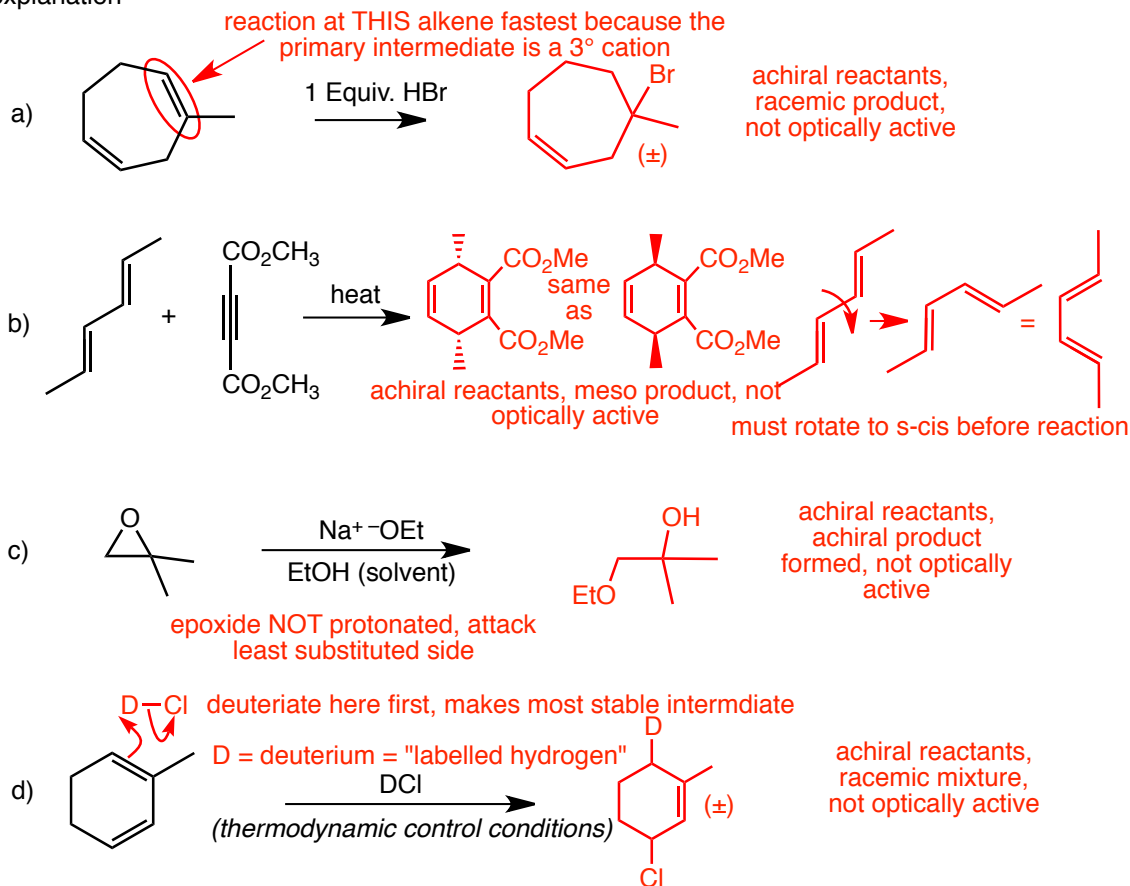
2) GIVE THE NUMBER OF STEPS IN YOUR MECHANISM



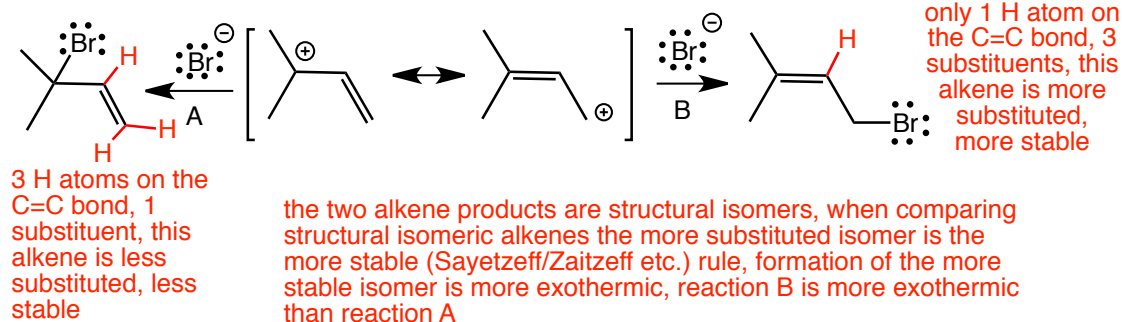
when dissolved in *i*-PrOH, HCl will be partially dissociated, and so it is not obvious which acid species, HCl itself or protonated alcohol will be responsible for protonation of the epoxide, you can use either, however, the *i*-PrOH solvent will be present at MUCH higher concentrations than the conjugate base anion from HCl, and therefore deprotonation occurs to *i*-PrOH (even if the proton eventually gets returned to form HCl)

Question 4 For each reaction

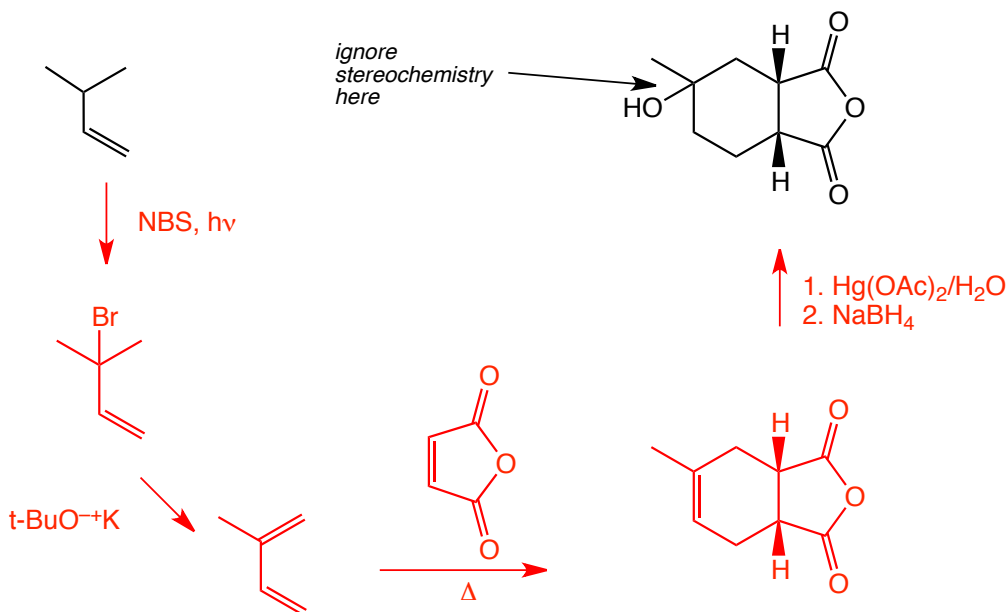
- 1) Provide the missing **reagents/conditions or major organic products as appropriate**
- 2) Pay attention to stereochemistry including racemic mixtures unless specified
- 3) State whether a solution of the product(s) would be optically active or not and give a brief explanation



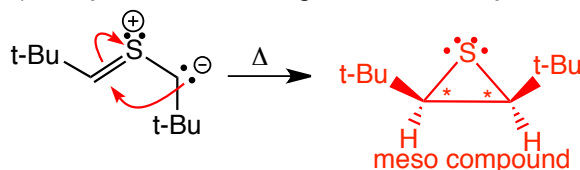
Question 5) Indicate which reaction is more exothermic, give an explanation



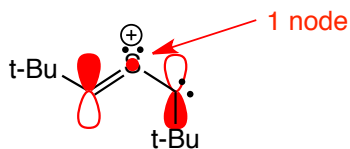
Question 5. Show how you would synthesize the target compounds on the right from the starting compounds on the left. Show reagents and conditions, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



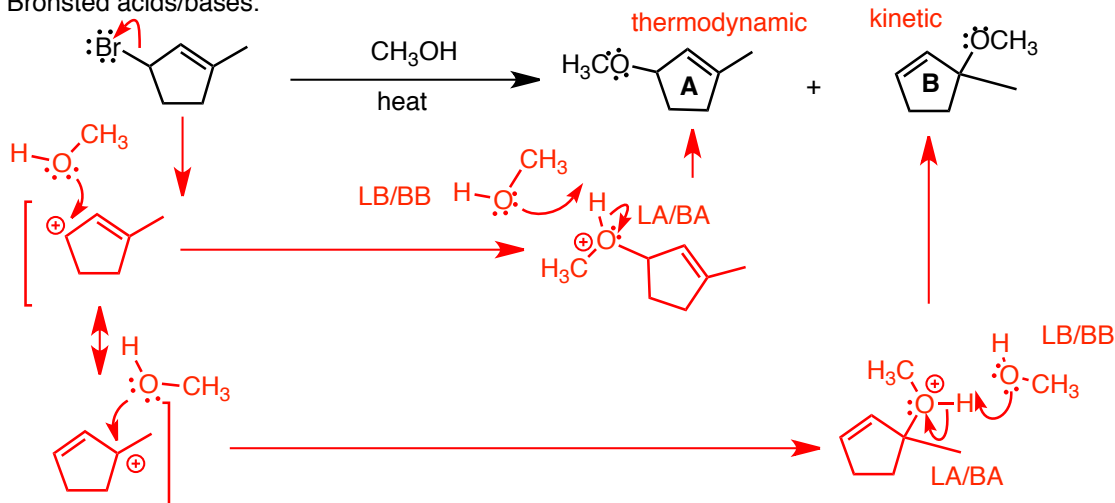
Question 6) The glide below undergoes an electrocyclic ring closure reaction



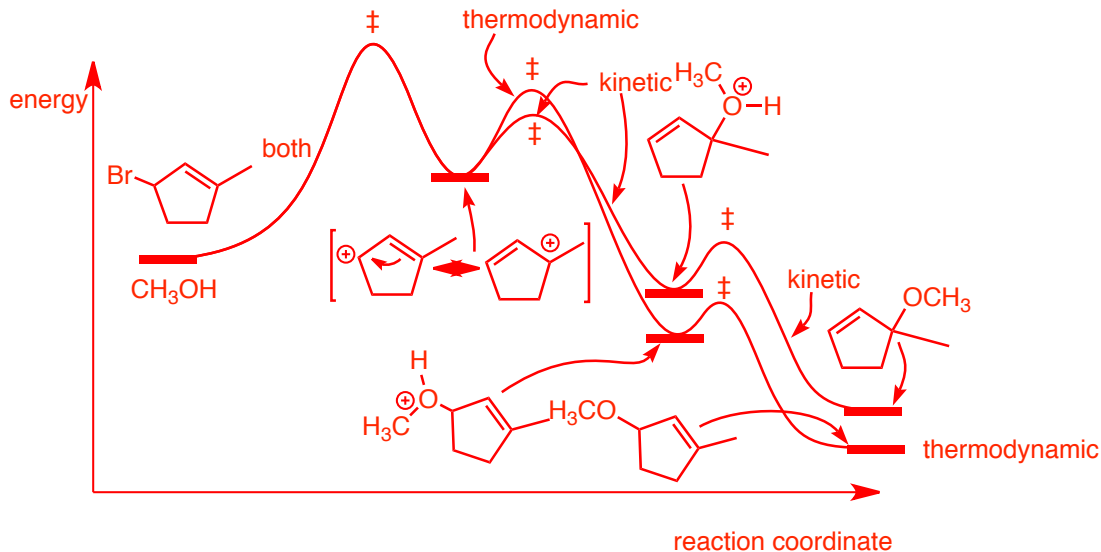
- give the curved arrow-pushing that accounts for product formation
- draw the product, paying special attention to relative stereochemistry of any substituents
- indicate the locations of any chiral (asymmetric) carbon atoms with the  $*$  symbol, and state whether it is racemic, a meso compound or achiral
- give the NUMBER of electrons involved in the reaction
- state whether the allowed reaction proceeds via a Hückel or a Möbius transition state
- state whether the allowed reaction proceeds via a conrotatory or a disrotatory ring closing
- Draw a pictorial representation of the HOMO on top of the structure below, give the number of vertical nodes (only) and indicate their positions



Question 7. a) Give a full curved-arrow pushing mechanism for formation of both products of the provided reaction. One of these products would be formed preferentially under conditions of kinetic control, the other preferentially under conditions of thermodynamic control, indicate which is which. Indicate the Lewis acid and base at each step and whether they are also Bronsted acids/bases.



b) Give a reaction energy diagram for both reactions in the SAME DIAGRAM



c) Give a brief explanation of how temperature is related to kinetic and thermodynamic control

at all temperatures the kinetic product is formed faster, at lower temperatures the reactions will be more IRREVERSIBLE, the kinetic product product will predominate, at higher temperatures the reactions will become more REVERSIBLE and the lower energy thermodynamic product can be formed and will start to accumulate

Question 8. The purpose of this question is to determine whether the provided product of the cycloaddition reaction given below is allowed or forbidden (there are several possible products of this reaction, we will focus our attention on this one to see if it is allowed)

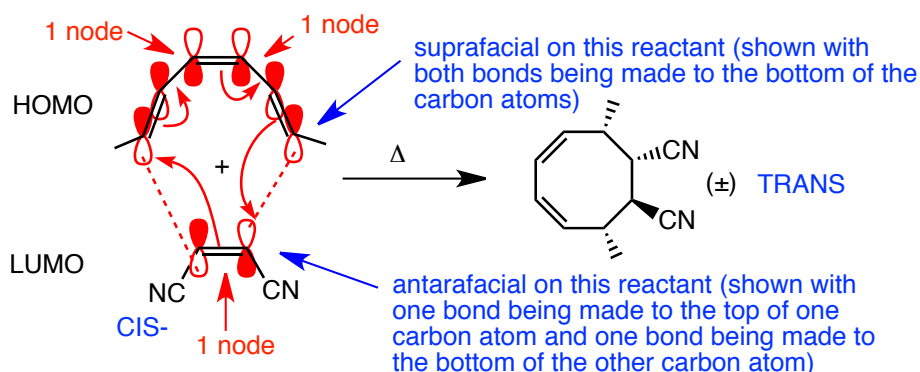
- a) give the curved arrow-pushing that accounts for product formation  
 b) draw the HOMO and LUMO ON TOP OF THE structures as indicated above, and give the number of vertical nodes and clearly indicate their positions  
 c) IGNORING THE PROVIDED product for now, use the information from the F.M.O.s to decide whether the ALLOWED reaction would be suprafacial/suprafacial or suprafacial/antarafacial

your answer suprafacial/antarafacial

- d) Using the stereochemistry of the PROVIDED PRODUCT, decide state whether the it was formed via suprafacial/suprafacial or suprafacial/antarafacial cycloaddition

your answer suprafacial/antarafacial

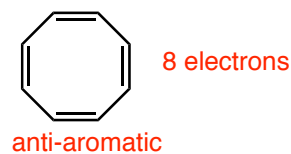
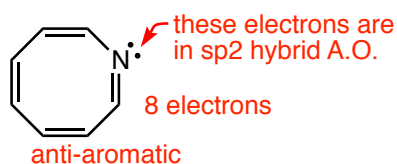
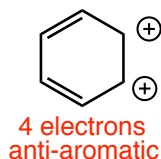
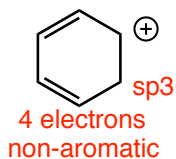
- d) state whether the PROVIDED PRODUCT is allowed or forbidden, and give a BRIEF explanation that mentions the frontier molecular orbitals.



The provided product is ALLOWED, it is formed in suprafacial/antarafacial reaction and the phases of the HOMO and LUMO at the relevant carbons result in two bonding interactions for such a reaction

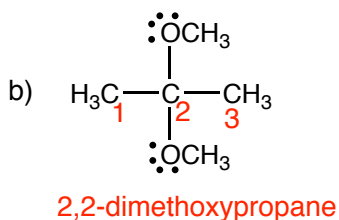
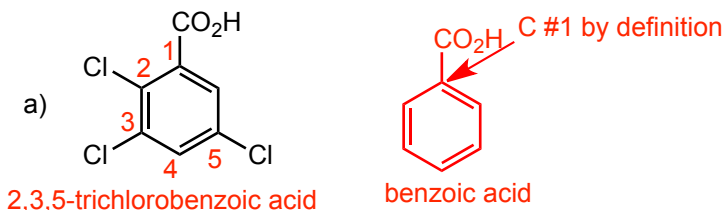
the reaction is antarafacial on the lower reactant because the cis-stereochemistry of the substituents becomes trans- in the product (this would not be included as part of the answer)

Question 9) Classify the following structures as aromatic, non-aromatic or anti-aromatic, assume all structures are as flat as possible, AND give the number of electrons involved in the conjugated system

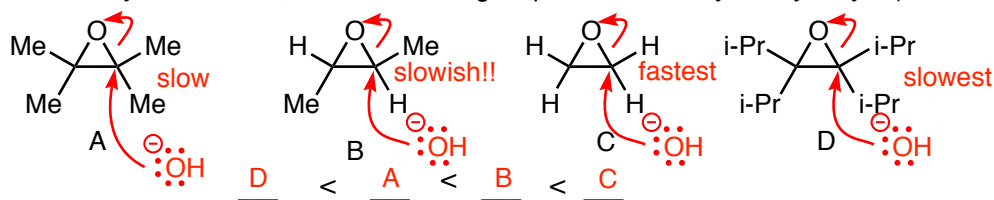


## START OF PRACTICE TEST #4

Question 1 Give the IUPAC name for the following compound. Be sure to use cis/trans, E/Z or R/S where appropriate.

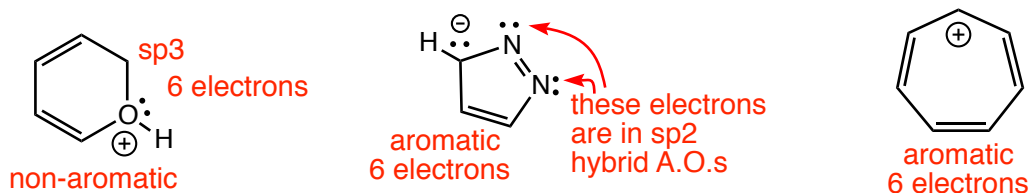


Question 2) Rank the following in order of increasing rate of reaction in a base catalyzed hydrolysis reaction (addition of water in the presence of hydroxide) and give a brief explanation (hint, think about the slowest, rate determining step for base catalyzed hydrolysis)



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

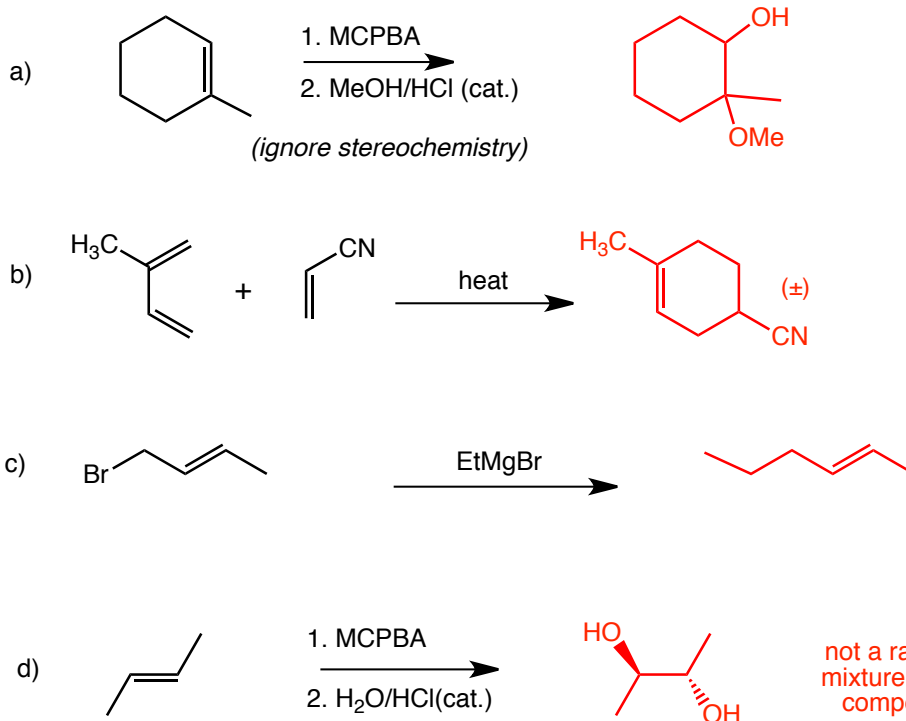
Question 3) Classify the following structures as aromatic, non-aromatic or anti-aromatic, assume all structures are as flat as possible, AND give the number of electrons involved in the conjugated system



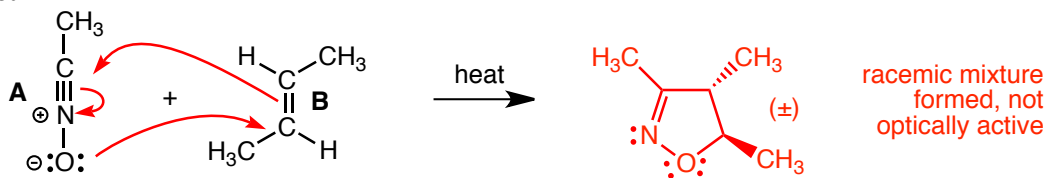
Question 4. For each reaction.

1) Provide the missing **reagents/conditions** or **major organic products** as appropriate

2) Pay attention to stereochemistry including racemic mixtures unless specified



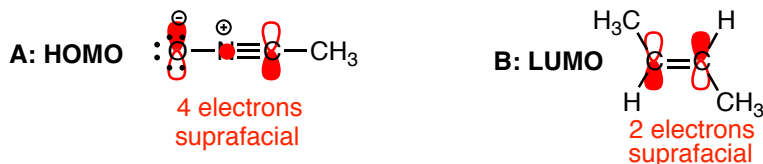
Question 5) a) Give the curved arrow pushing and the product of the following reaction. Pay attention to stereochemistry and state whether a solution of the product(s) would be optically active or not.

For BOTH of the reactants **A** and **B**:

b) Give a pictorial representation of the requested frontier molecular orbital as requested on top of the provided structure

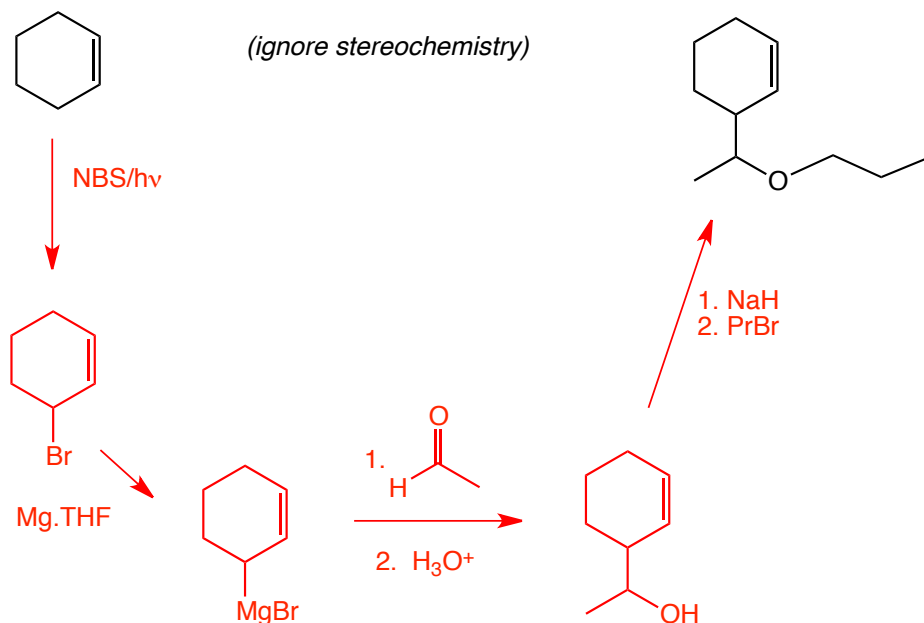
c) Give the number of electrons in the conjugated system that are relevant to the reaction

d) State whether the allowed reaction is suprafacial or antarafacial

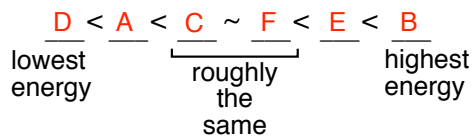
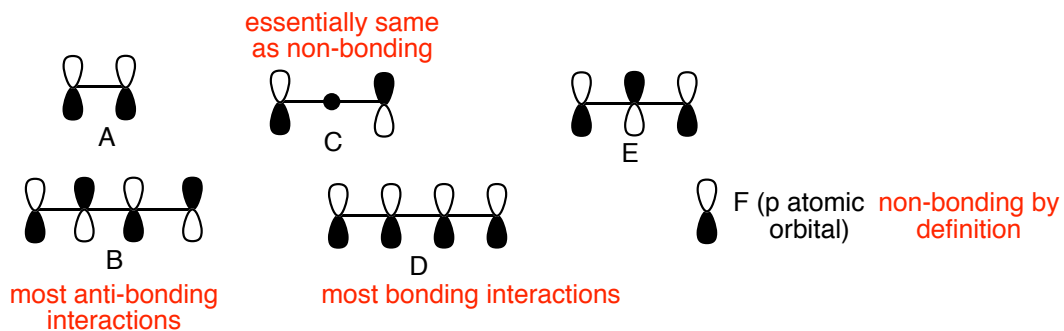




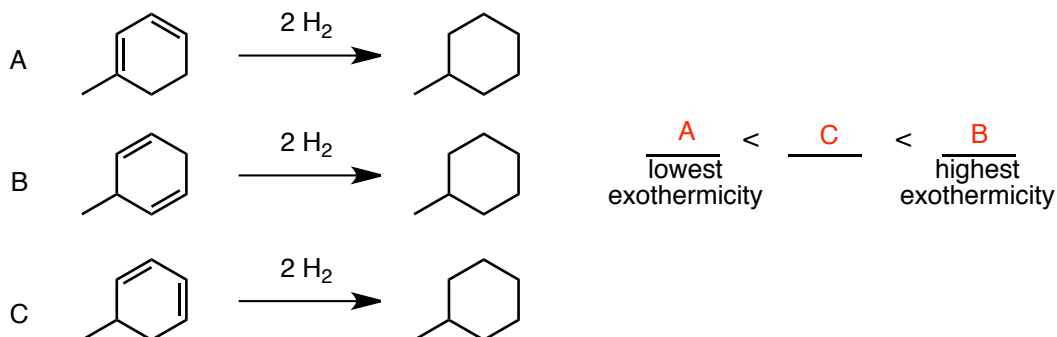
Question 6. Show how you would synthesize the target compound on the right from the starting compound on the left. Show reagents and conditions, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



Question 7. Consider the energy of an electron in each of the following  $\pi$ -molecular orbitals AND a p atomic orbital on a carbon atom and rank them in order of increasing energy. Two of the energies will be essentially equal, as indicated below

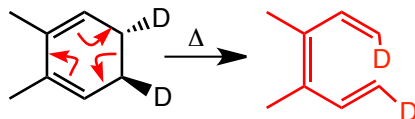


Question 8) Rank the following reactions, A, B and C, in order of INCREASING exothermicity. Give a BRIEF explanation



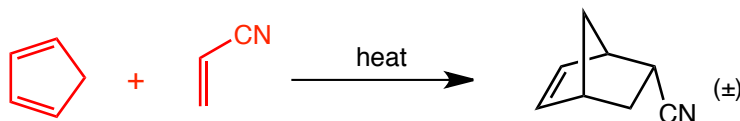
the products are all the same, the energies at the end of all reactions is thus the same, the difference is in the reactants. A and C are conjugated, electrons are lower in energy, the reactants in A and C start lower in energy, thus less exothermic than B, the diene is more substituted in A compared to C, diene A is thus more stable, lower in energy, reaction A is least exothermic

Question 9) The structure below undergoes an electrocyclic ring opening reaction (remember, D means deuterium, an isotope of hydrogen that is often used as a labelled hydrogen atom)

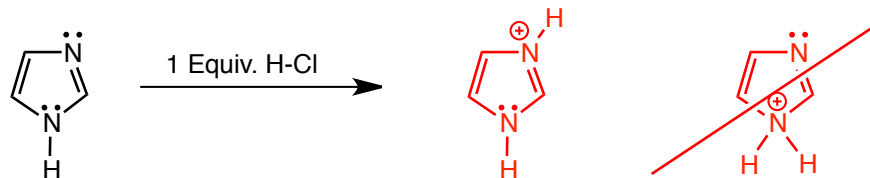


- give the curved arrow-pushing that accounts for product formation
- draw the product, paying special attention to relative stereochemistry of any substituents
- give the NUMBER of electrons involved in the reaction **6**
- state whether the allowed reaction proceeds via a Huckel or a Mobius transition state **Huckel**
- state whether the allowed reaction proceeds via a conrotatory or a disrotatory ring closing **disrotatory**

Question 10. Provide the missing reactants for the following Diels-Alder reaction.

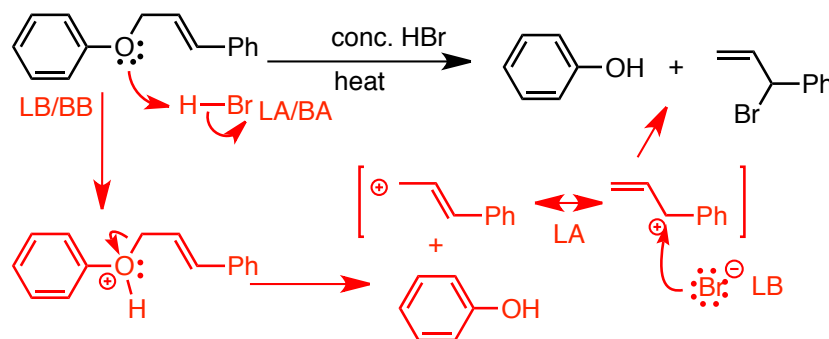


Question 11. One equivalent of H-Cl will preferentially protonate one of the nitrogens in imidazole (shown below) and not the other. Give the major product of the reaction shown below and give a brief explanation for your choice of product



imidazole is aromatic, protonation of the upper nitrogen generates a product that is still aromatic, whereas protonation of the lower nitrogen generates a product that is no longer aromatic and has higher energy electrons

Question 12) Provide a detailed (arrow pushing) mechanisms for the following transformations. draw all important resonance structures. For each intermolecular step, identify the Lewis acid and base (LA/LB) as appropriate, and whether they are also Bronsted acids/bases (BA/BB), give the number of steps in your mechanism (hint BOTH SN1 and SN2 can occur at allylic carbon atoms)



this problem is slightly tricky, substitution here is SN1, the choice between SN1 and SN2 in simpler cases is the usual one, you can't do SN2 on a tertiary carbon and you can't do SN1 on a primary carbon, secondary is always a bit ambiguous, as is allylic, because both SN2 and SN1 are favored at this positions, HOWEVER, this is a mechanism problem, and in this case I gave you the product and you can see that the substitution can't have been Sn2 because the -Br is not on the original carbon that had the leaving group, so in this case it had to be SN1

Question 13. Show how you would synthesize the target compound on the right from the starting compound on the left. Show reagents and conditions, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

