CHEM 234 | the exam cover sheets look kind of like this | Ian R. Gould

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 EXAM

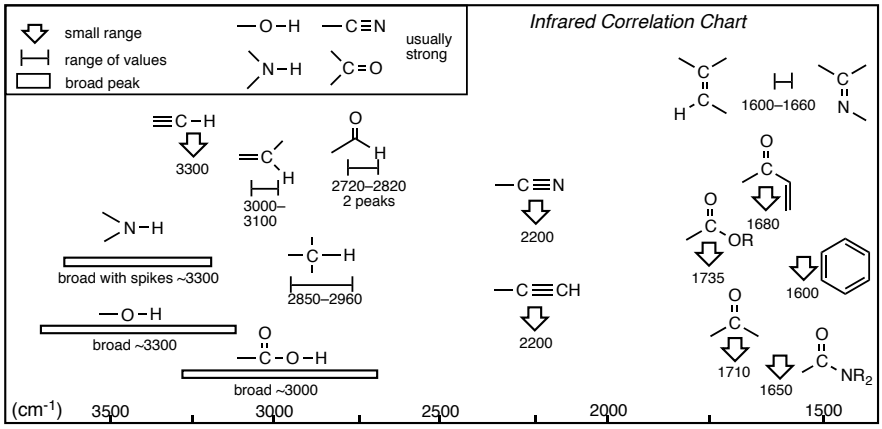
MIDTERM #3
PRACTICE TEST #1

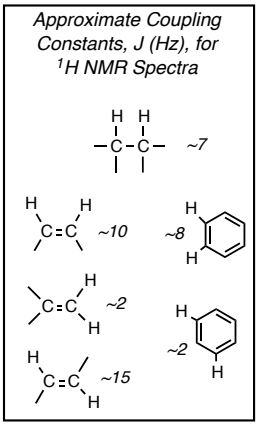
Extra Credit_____/5 **Total (incl Extra)_____/175+5**

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

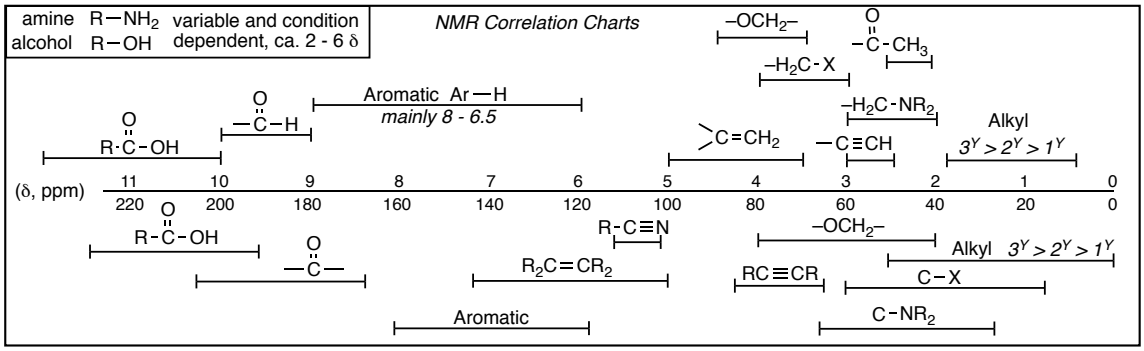
Interaction Energies, kcal/mol

Eclipsing		Gauche	
H/H	~1.0	Me/Me	~0.9
H/Me	~1.4	Et/Me	~0.95
Me/Me	~2.6	i-Pr/Me	~1.1
Me/Et	~2.9	t-Bu/Me	~2.7

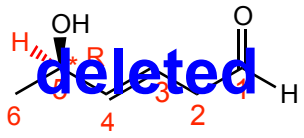




amine R—NH_2 variable and condition dependent, ca. 2 - 6 δ
alcohol R—OH



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



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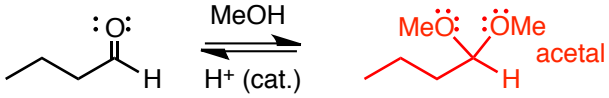
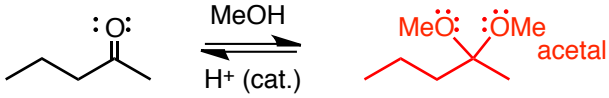
trans-(5R)-hydroxyhex-(3)-enal
OR
(5R)-hydroxyhex-(3E)-enal
aldehyde not numbered, is in position #1 by definition

Question 2 Rank in order of increasing equilibrium constant for formation of an acetal with a brief explanation. Draw the expected acetal for one of the reactions (only), it does not matter which one.

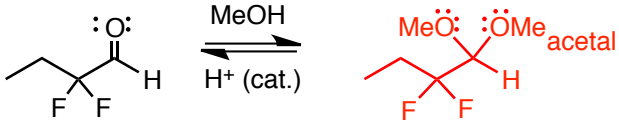
A



B



C



B < A < C
lowest highest

MeOH is a weak L Base, reactivity of carbonyls (C=O) with Lewis bases depends upon substituents effects on the carbonyl carbon, B has two weakly donating alkyl groups attached to the carbon of the C=O and is thus the least reactive and has the smallest equilibrium constant, C has 2 F atoms that inductively withdraw electrons and increase reactivity and equilibrium constant

Question 3 Give the alkyl bromide and the carbonyl compound you would use to synthesize the following alkene in a Wittig synthesis and show all steps and reagents/conditions

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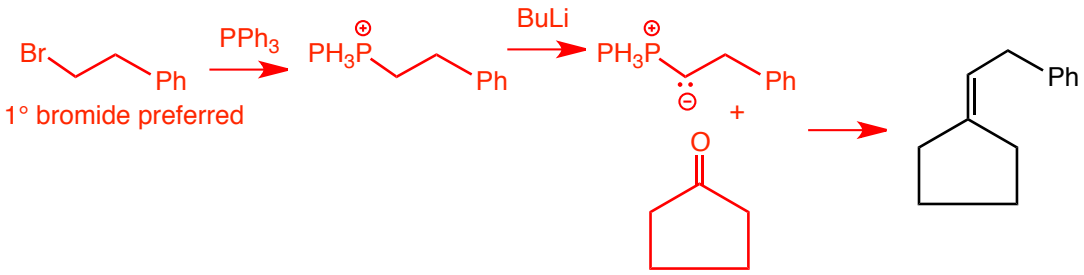
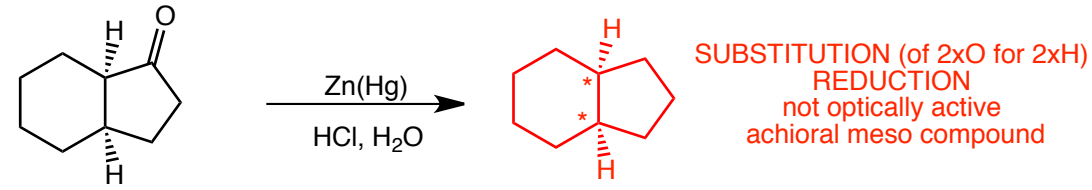


1° bromide preferred

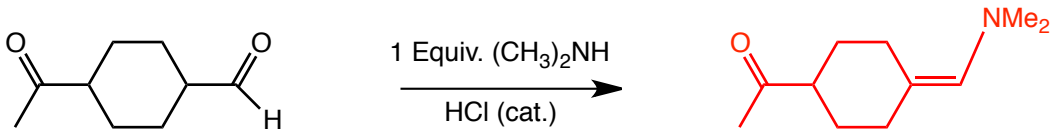
Question 4 For each reaction
a) Provide the missing **reagents/conditions or major organic products as appropriate,** pay attention to stereochemistry including racemic mixtures unless specified
b) Unless otherwise indicated.....
State whether the OVERALL reaction is Addition, Elimination, Substitution or Rearrangement
State whether the reaction is oxidation, reduction or neither
Briefly explain whether the a solution of the product would be optically active or not

a)



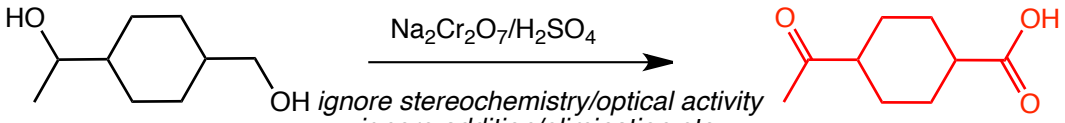
SUBSTITUTION (of 2xO for 2xH)
REDUCTION
not optically active
achioral meso compound

b)



ignore stereochemistry/optical activity
ignore oxidation/reduction
ignore addition/elimination etc

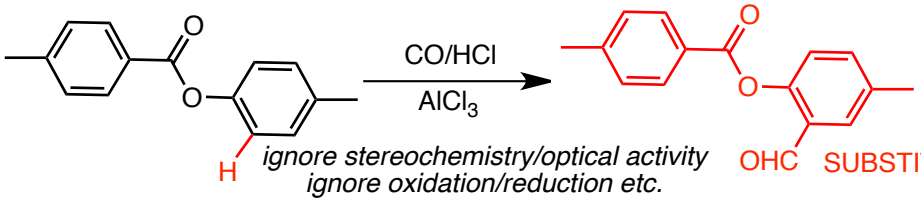
c)



ignore stereochemistry/optical activity
ignore addition/elimination etc.

OXIDATION

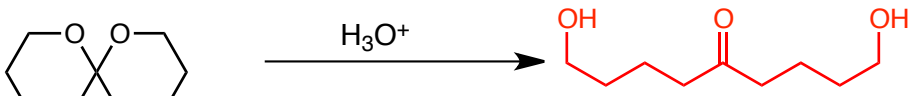
d)



ignore stereochemistry/optical activity
ignore oxidation/reduction etc.

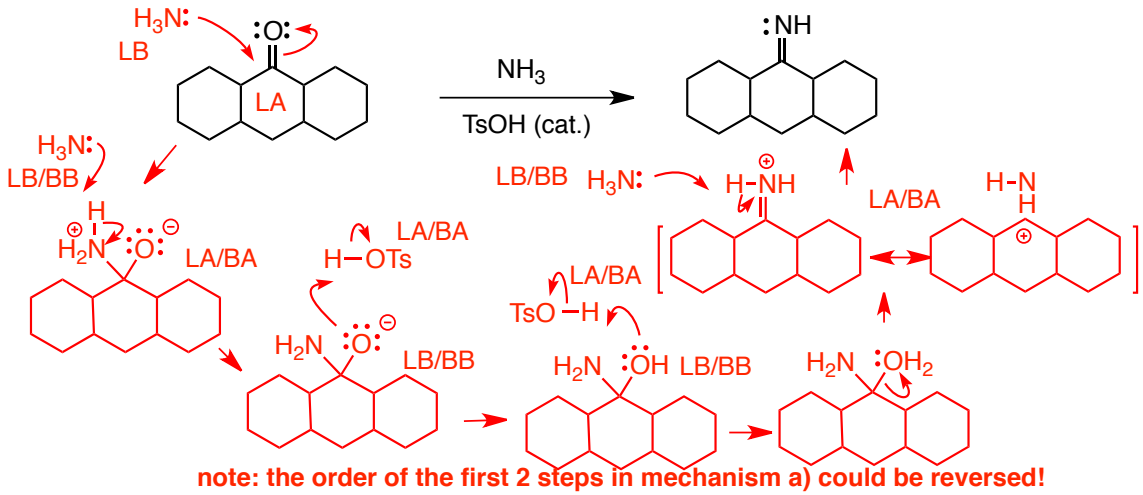
SUBSTITUTION

e)



ignore stereochemistry/optical activity
ignore oxidation/reduction
ignore addition/elimination etc

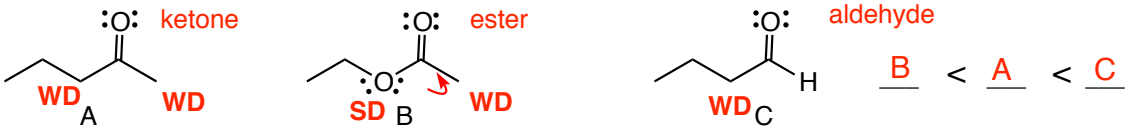
Question 5 Draw the complete arrow pushing mechanism for the following reaction. Indicate the Lewis acid/base at each step, and if they are also Brønsted acids bases. Add non-bonding electrons as necessary. Draw the **ALL important** resonance structure of the intermediates



note: the order of the first 2 steps in mechanism a) could be reversed!

Question 6 Rank the following in terms of increasing rate of reaction with PhMgBr. Give a BRIEF explanation and NAME the three functional groups

WD = weakly donating
SD = strongly donating

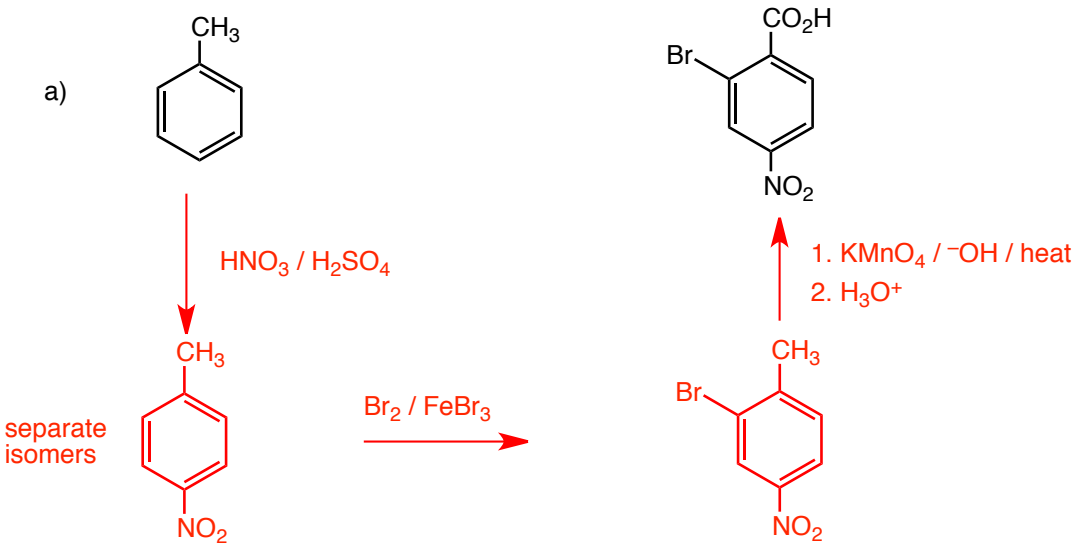


B < A < C

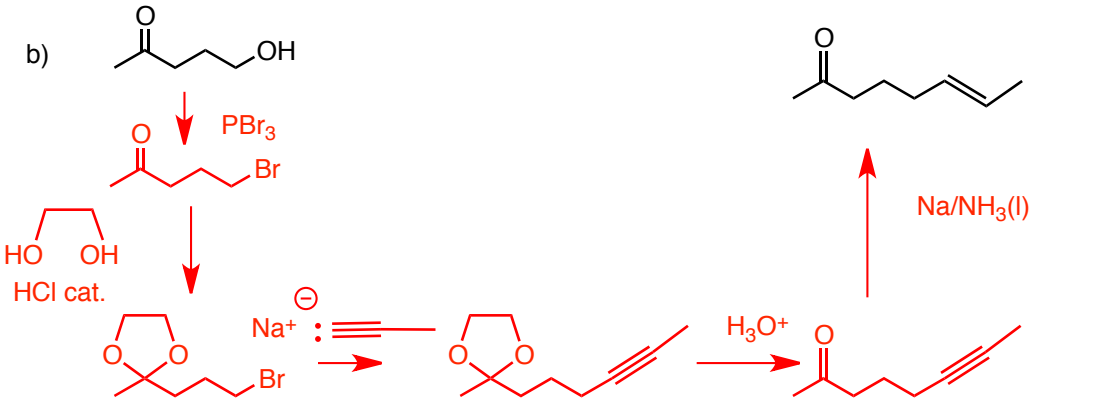
this is reaction of a strong nucleophile/LB with a carbonyl C=O bond, which can be considered to be a small π-system, the carbonyl carbon in the ester **B** has a strong electron donating oxygen substituent on the carbonyl and a weak electrom donating methyl group, which decreases reactivity towards the LB/nucleophile, the ketone **A** has 2 weak alkyl donating substituents on the carbonyl carbon, the aldehyde **C** has only 1 weak alkyl donating group

Question 7 Show how you would make the target molecules from the provided starting structures. Show all intermediate structures, do not show any mechanisms

a)

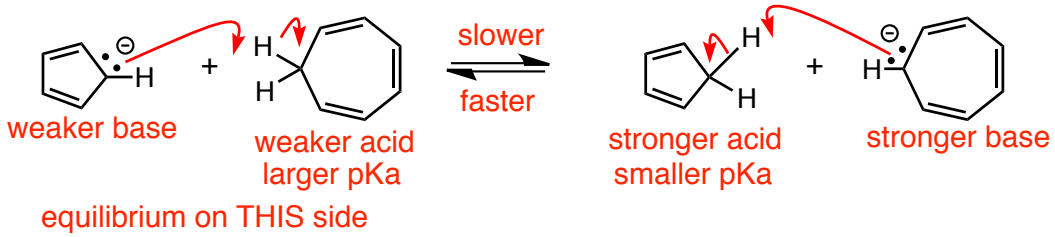


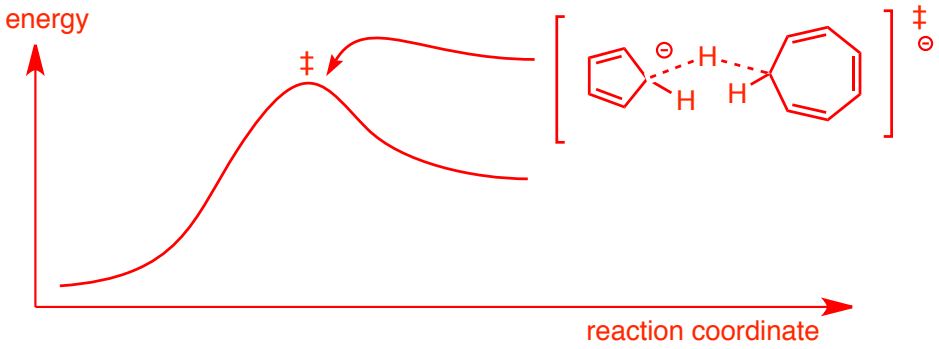
b)



recall, H_3O^+ does not react with alkynes without Hg^{2+} as a catalyst

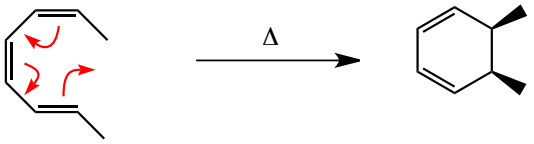
Question 2. For the Bronsted acid/base reaction below:
a) Give the curved arrow-pushing in both directions
b) Draw a reaction energy diagram and include a drawing of the transition state
c) Label the acids/bases and which are stronger and give a brief explanation
d) Indicate which reaction is faster (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 it twists it may become non-aromatic, but will be less stable than the aromatic anion in any geometry

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

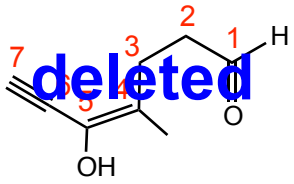


1) draw the arrow-pushing that describes formation of the PROVIDED product
2) How many electrons are involved in the reaction? 6 electrons
3) FOR THE PROVIDED PRODUCT (which may or may not be allowed), would the ring closing be disrotatory or conrotatory? Conrotatory
4) FOR THE PROVIDED PRODUCT (which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

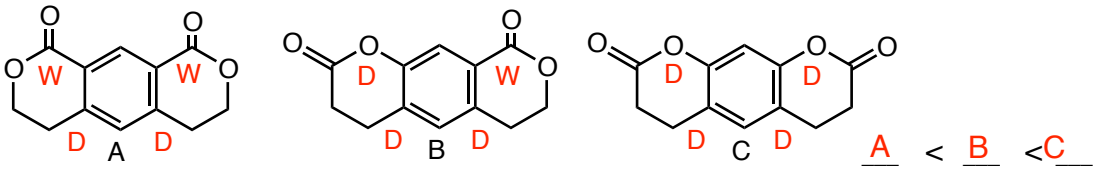
START OF PRACTICE TEST #2

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



5-hydroxy-4-methylhept-(4E)-en-6-ynal

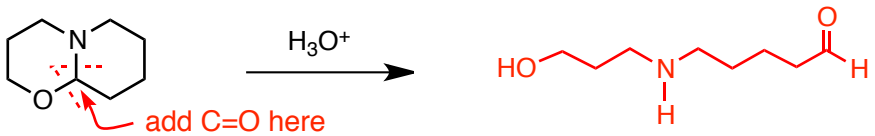
Question 2 Rank the following in terms of increasing rate of electrophilic aromatic substitution, e.g., reaction with HNO_3/H_2SO_4. Give a BRIEF explanation



A < B < C

the reaction is electrophilic aromatic substitution, as far as the central benzene rings are concerned, **A** has 2 D/activating groups and 2 W/deactivating groups, **B** has 3 D/activating groups and 1 W/deactivating group, **C** has 4 D/activating groups, **C** is thus fastest in electrophilic aromatic substitution

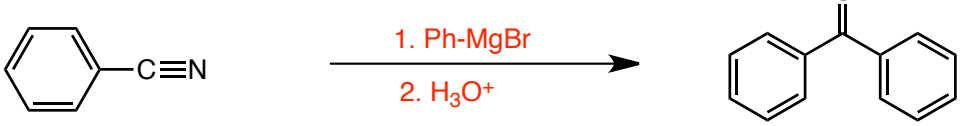
Question 3 Give the product of complet acid catalyzed hydrolysis of the following structure

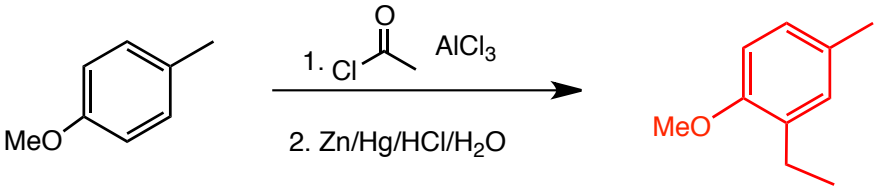


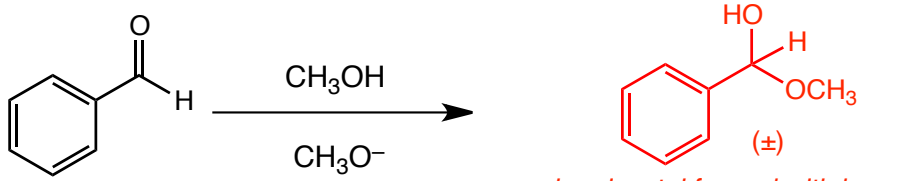
add C=O here

cleave the 2 single bonds indicated by the dashed lines

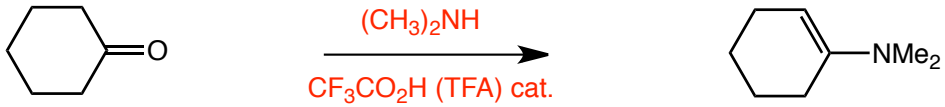
Question 4 For each reaction
a) Provide the missing **reagents/conditions or major organic products as appropriate,** pay attention to stereochemistry including racemic mixtures unless specified

a) 

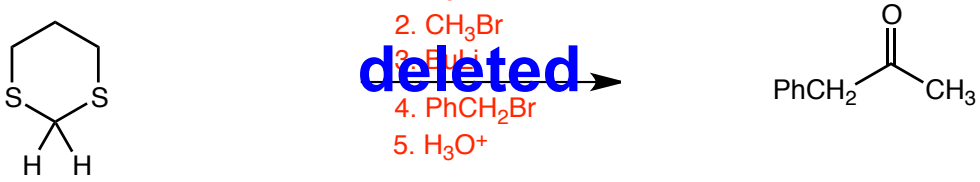
b) 

c) 

hemiacetal formed with base

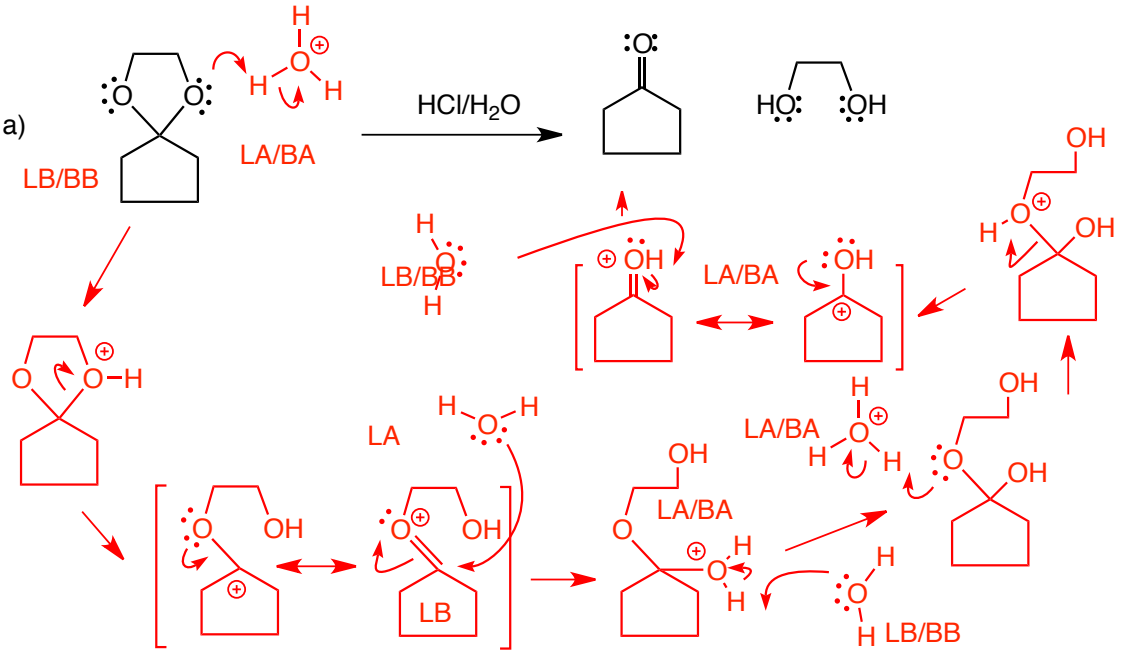
d) 

(or any other organic acid catalyst)

e) 

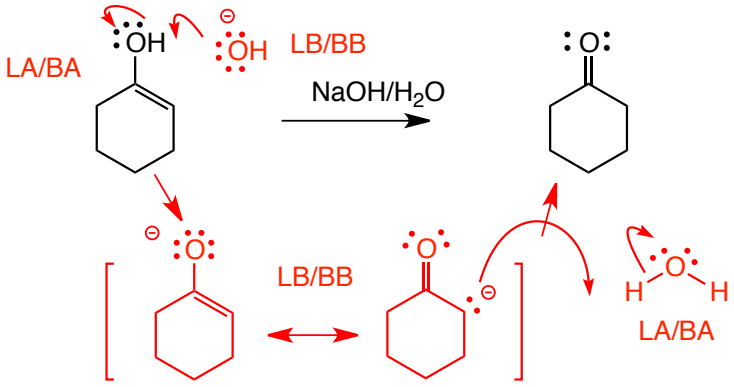
Question 5 Give a full curved arrow-pushing mechanism for the following reactions, show where every proton goes to and comes from (no $+H^+/-H^+$) and indicate the Lewis and Bronsted acids/bases at each intermolecular step, include important resonance contributors for all intermediates, give the number of steps in your mechanism.

a)



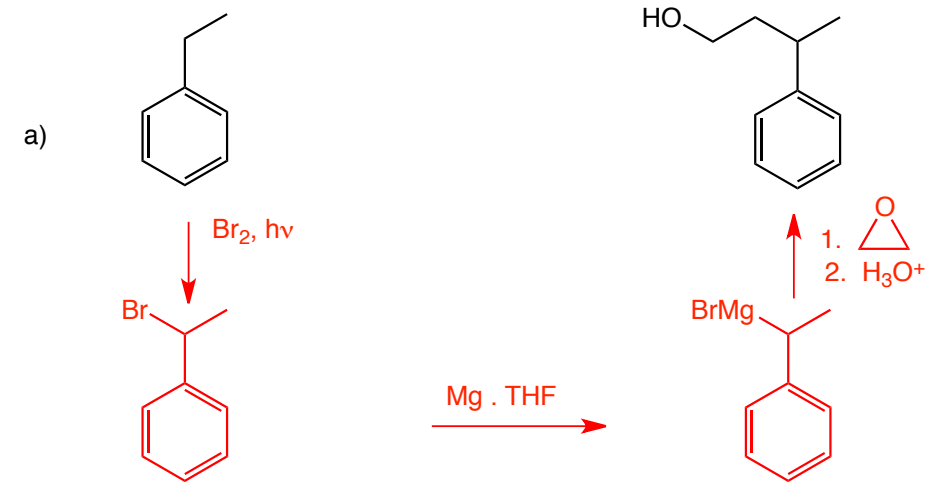
SEVEN steps

b)

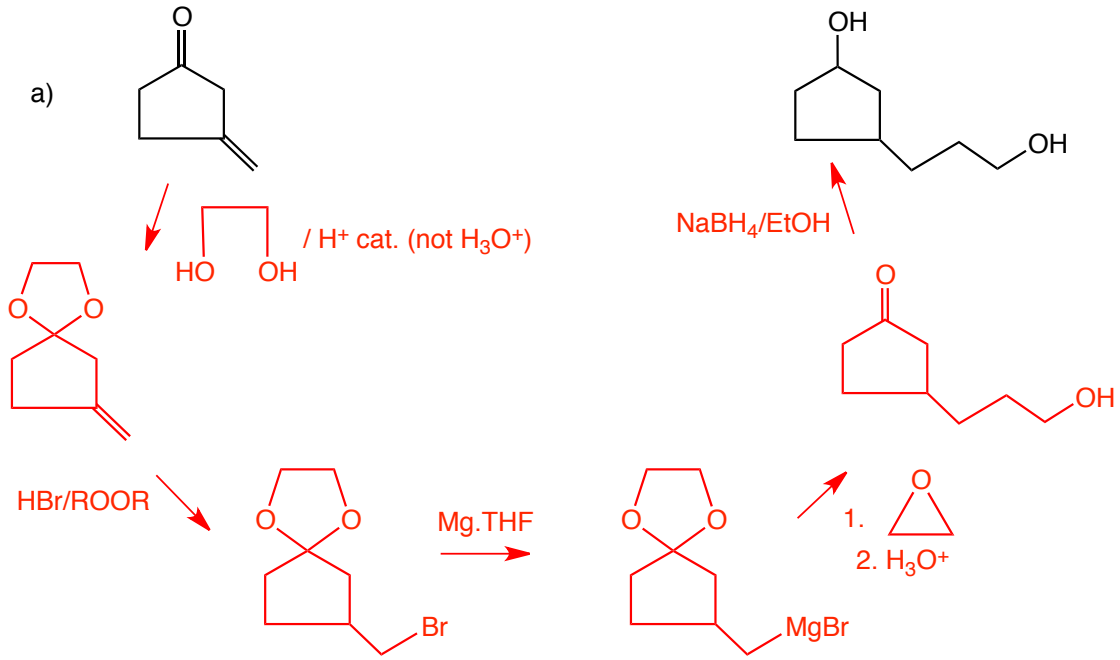


Question 6. Show how you would synthesize the target componds on the right from the starting compounds on the left. Show reagents and conditions, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

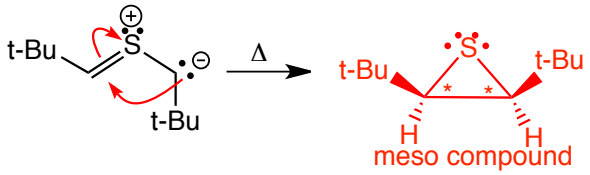
a)



a)



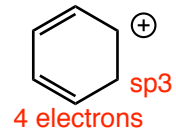
Question 6) The ylide below undergoes an electrocyclic ring closure reaction



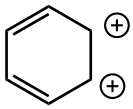
a) give the curved arrow-pushing that accounts for product formation
b) draw the product, paying special attention to relative stereochemistry of any substituents
c) indicate the locations of any chiral (asymmetric) carbons atoms with the * symbol, and state whether it is racemic, a meso compound or achiral
d) give the NUMBER of electrons involved in the reaction 4
e) state whether the allowed reaction proceeds via a Huckel or a Mobius transition state Mobius
f) state whether the allowed reaction proceeds via a conrotatory or a disrotatory ring closing conrotatory

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)

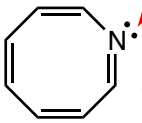
Question 9) Classify the following structures as aromatic, non-aromatic or anti-aromatic, assume all structures are as flat as possible, AND give the number of electrons involved in the conjugated system



4 electrons
non-aromatic



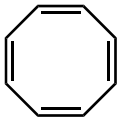
4 electrons
anti-aromatic



these electrons are in sp2 hybrid A.O.

8 electrons

anti-aromatic

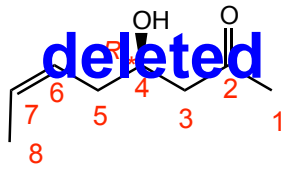


8 electrons

anti-aromatic

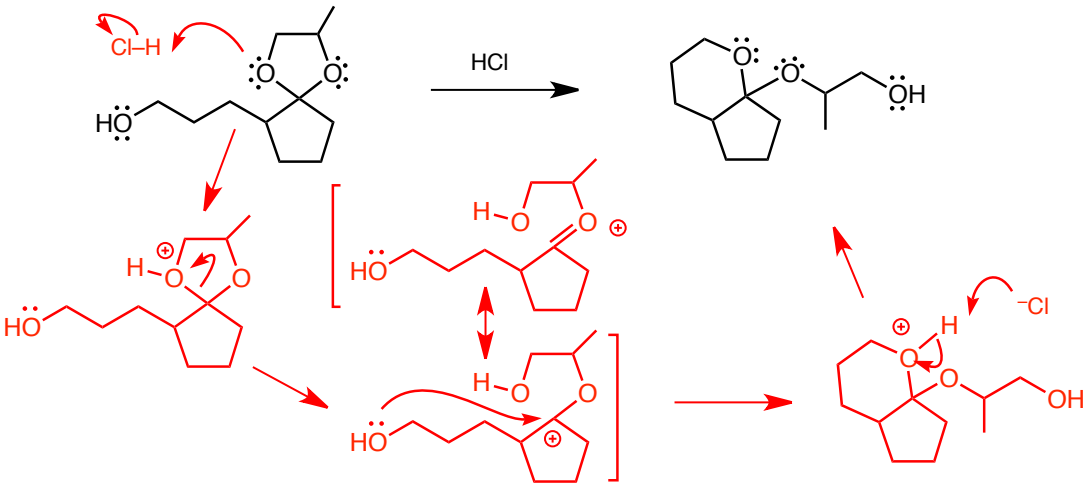
START OF PRACTICE TEST #3

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



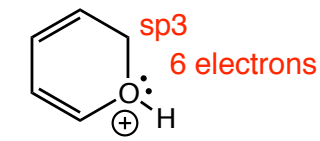
(4R)-hydroxyoct-(6Z)-en-2-one

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), show where every proton comes from and goes to (no $+H^+/-H^+$)
2) GIVE THE NUMBER OF STEPS IN YOUR MECHANISM

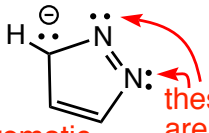


FOUR steps

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

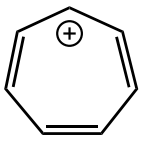


non-aromatic



aromatic
6 electrons

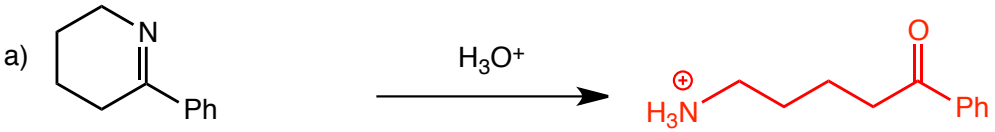
these electrons are in sp2 hybrid A.O.s



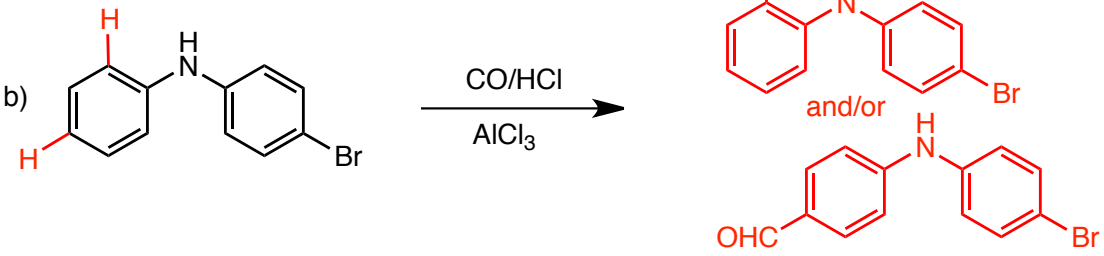
aromatic
6 electrons

Question 3 For each reaction
1) Provide the missing **reagents/conditions or major organic products as appropriate**

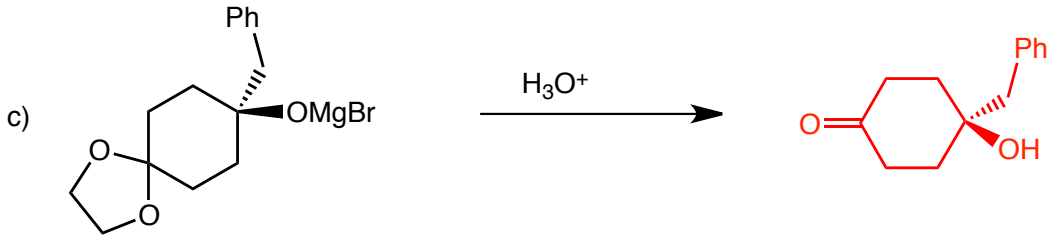
a)



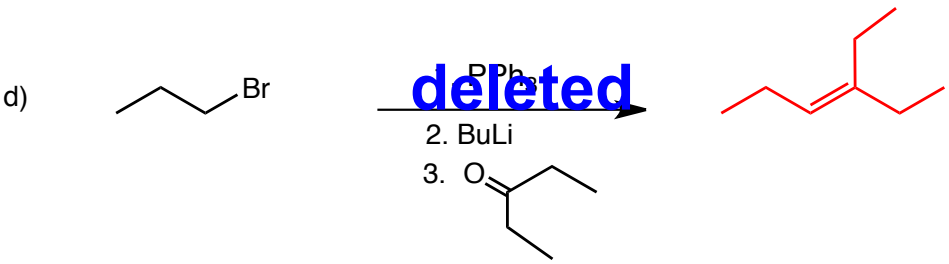
b)



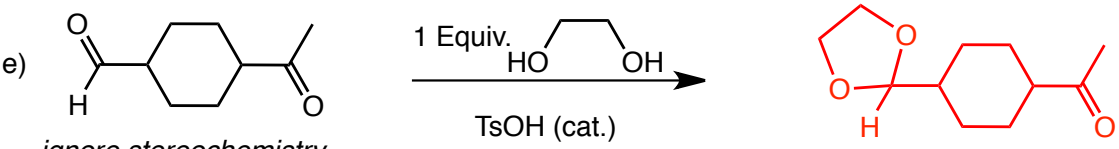
c)



d)



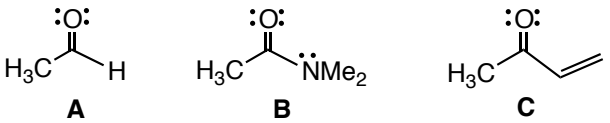
e)



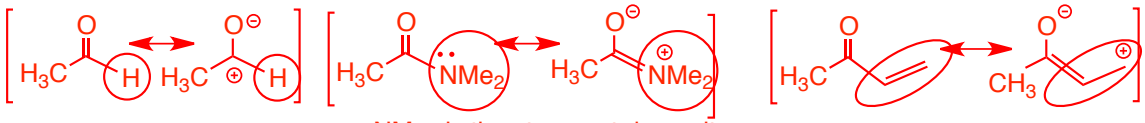
ignore stereochemistry

Question 4 Rank the following in terms of increasing frequency of carbonyl stretching vibration in an IR spectrum. To solve this problem you will ened to draw minor resonance contributors and remember that stronger bonds vibrate with higher frequency)

the more the minor resonance structure contributes to the overall structure, the more the C=O bond has single bond character, the lower the vibrational frequency....



B < C < A

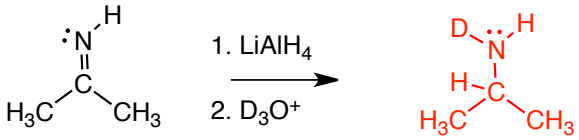


H is not a donor, does not stabilize the minor resonance structure which is thus a small contributor to the structure

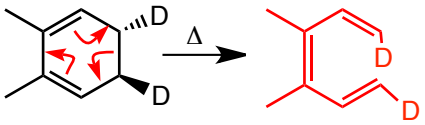
-NMe_2 is the strongest donor, it stabilizes the minor structure resulting in a largest contribution to the structure of these three

-$CH=CH_2$ is a weak donor, it is in the middle

Question 5 Give the product of the following reaction. Remember that D represents deuterium, an isotope of hydrogen, that is used to keep track of where hydrogen atoms go in chemical reactions. We did not cover this reaction class, but you should be able to work it out based on what you know about the mechanisms of these reduction reactions



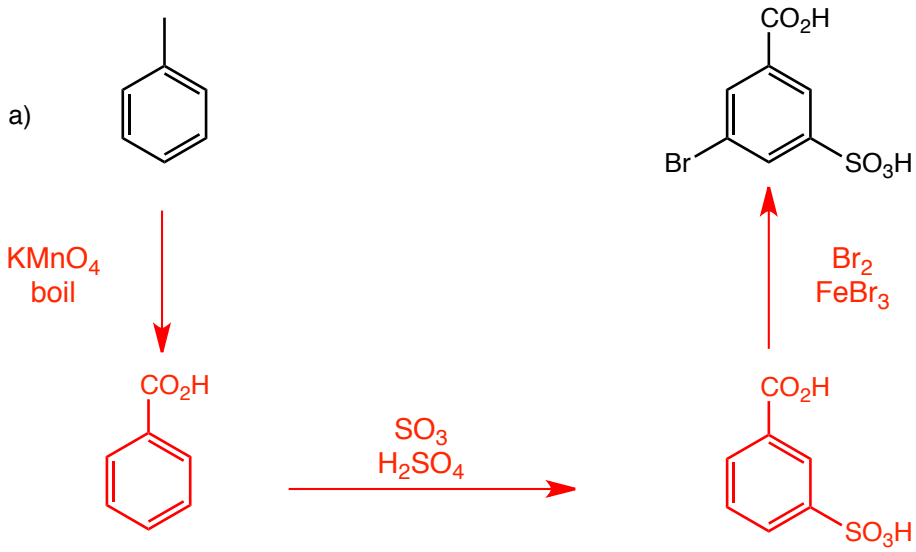
Question 9) The structure below undergoes an electrocyclic ring opening reaction (remember, D means deuterium, an isotope of hydrogen that is often used as a labelled hydrogen atom)



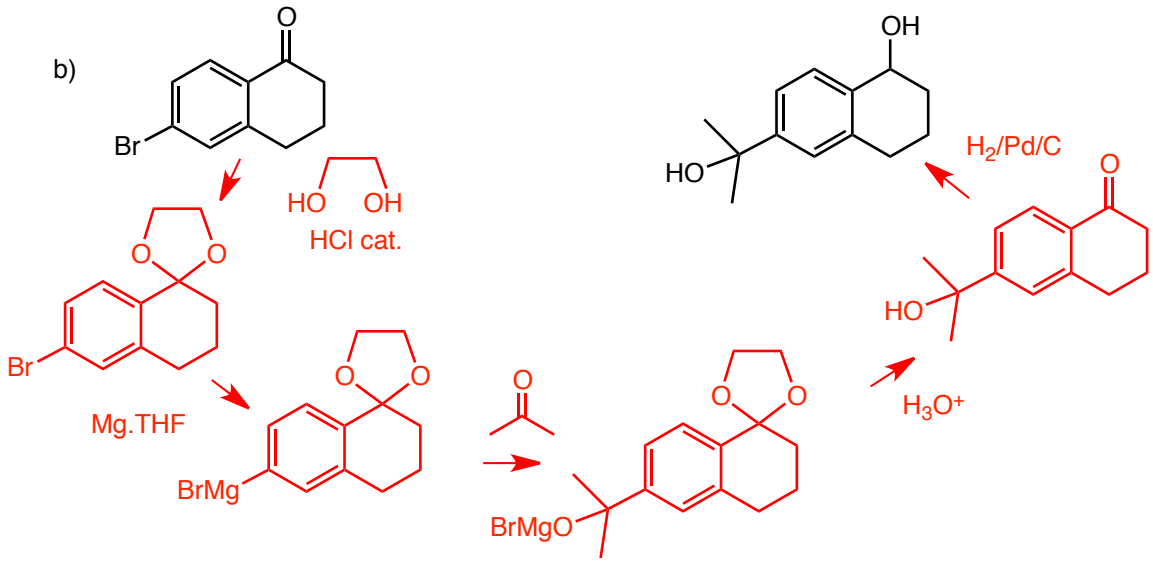
a) give the curved arrow-pushing that accounts for product formation
b) draw the product, paying special attention to relative stereochemistry of any substituents
c) give the NUMBER of electrons involved in the reaction 6
d) state whether the allowed reaction proceeds via a Huckel or a Mobius transition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

Question 6. 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.

a)

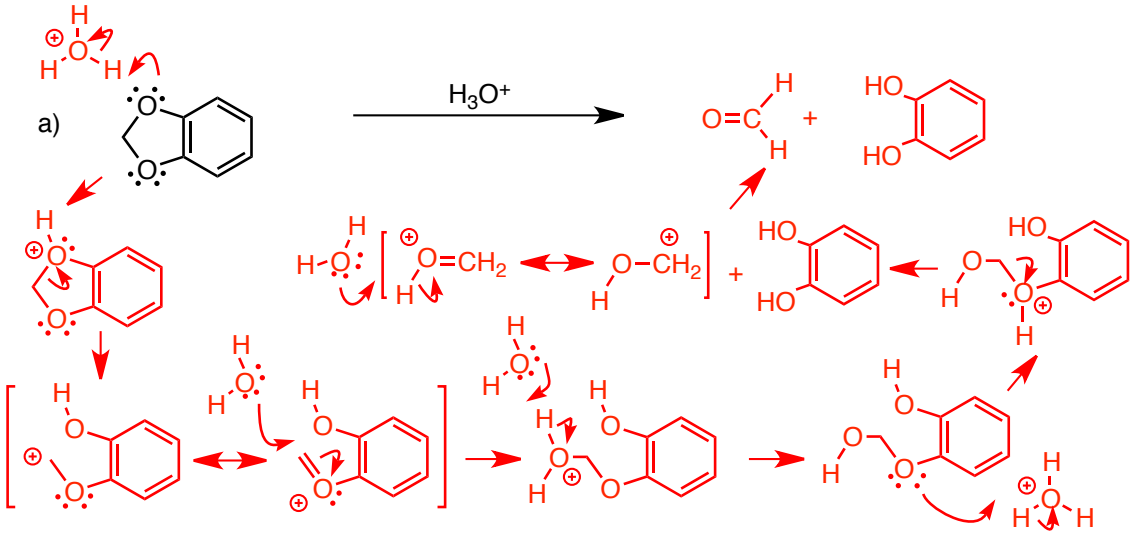


b)



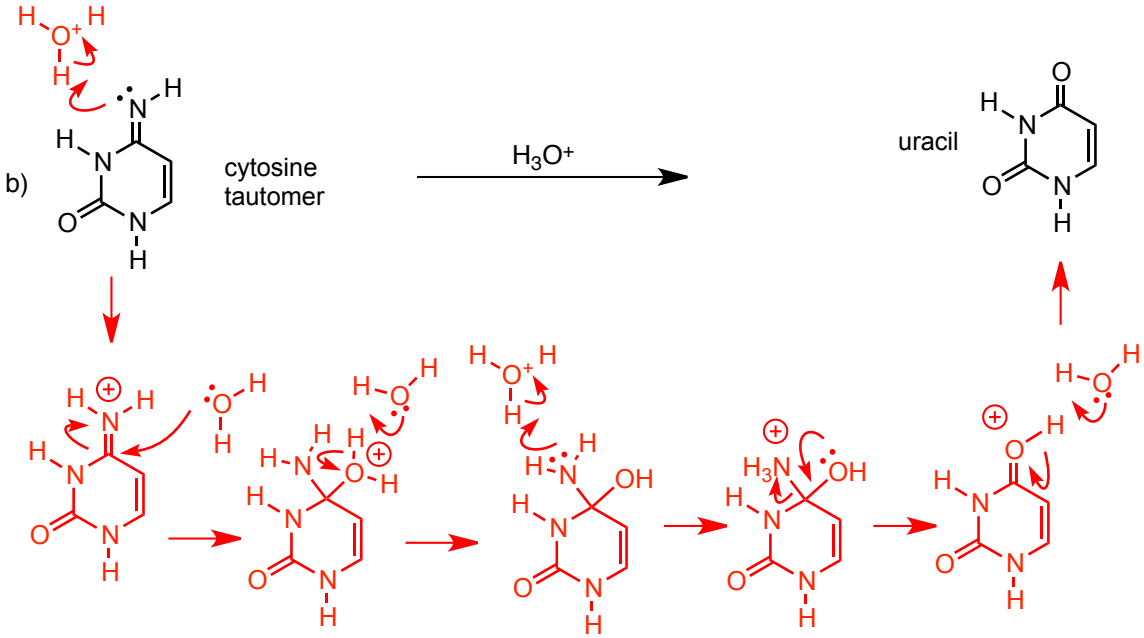
Question 7 Give a full curved arrow-pushing mechanism for the following reactions, show where every proton goes to and comes from (no $+H^+/-H^+$) and indicate the Lewis and Bronsted acids/bases at each intermolecular step, include important resonance contributors for all intermediates, give the number of steps in your mechanism.

a)



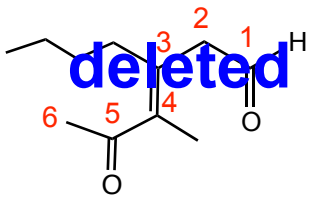
cytosine is one of the pyrimidine bases in DNA, it can be converted into uracil. if this happens this can be a damage mechanism that could lead to mutation. Assume that this reaction occurs via the usual acid catalyzed mechanisms that we study in class, give a mechanism for formation of uracil from teh provided tautomer of cytosine

b)



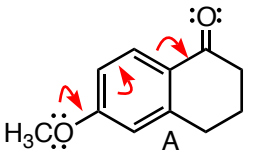
START OF PRACTICE TEST #4

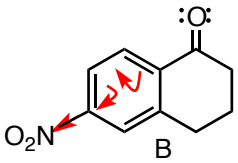
Question 1 Give the IUPAC name for the following compound. Be sure to use cis/trans, E/Z or R/S where appropriate.

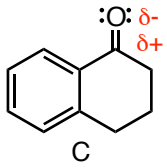


3-butyl-4-methyl-5-oxo-hex-(3E)-enal

Question 2 Rank the following in order of increasing equilibrium constant for formation of a hydrate. Give a BRIEF explanation



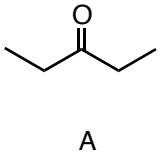


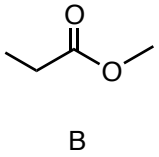


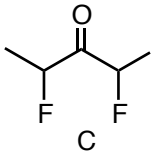
A < C < B

the reaction is addition of a weak nucleophile to the C=O group, A is least reactive since it has a strong donating group that can stabilize the carbonyl carbon via resonance, B has a withdrawing group that destabilizes the carbonyl carbon

Question 3. Rank in order of increasing rate of reaction with $^{-}$CN, give a BRIEF explanation





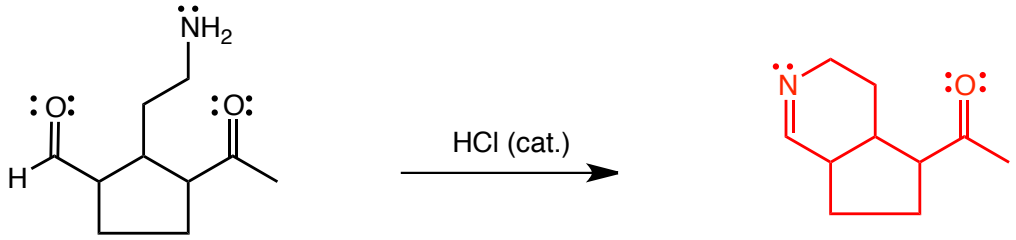


(fastest) C < A < B (slowest)

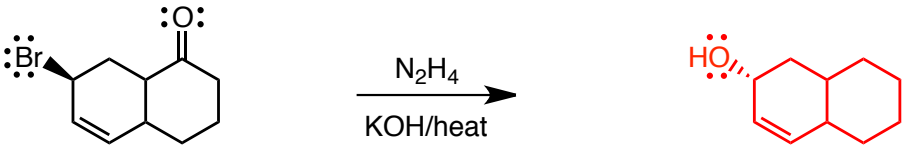
B has donating group (oxygen) adjacent to the C=O, decreases reactivity towards nucleophilic attack, C has two electronegative groups adjacent to the C=O, inceasing reactivity towards nucleophilic attack

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

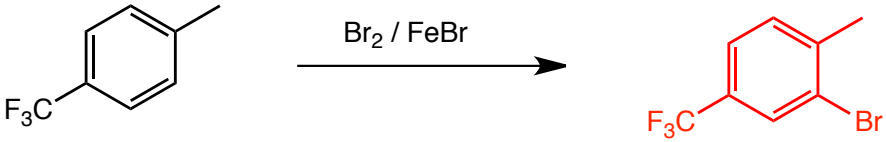
a)



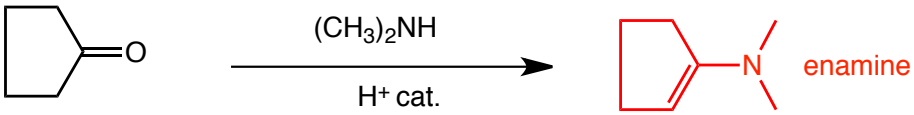
b)



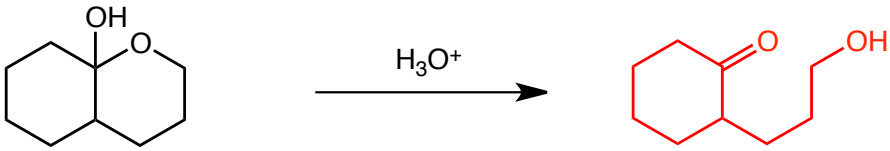
c)



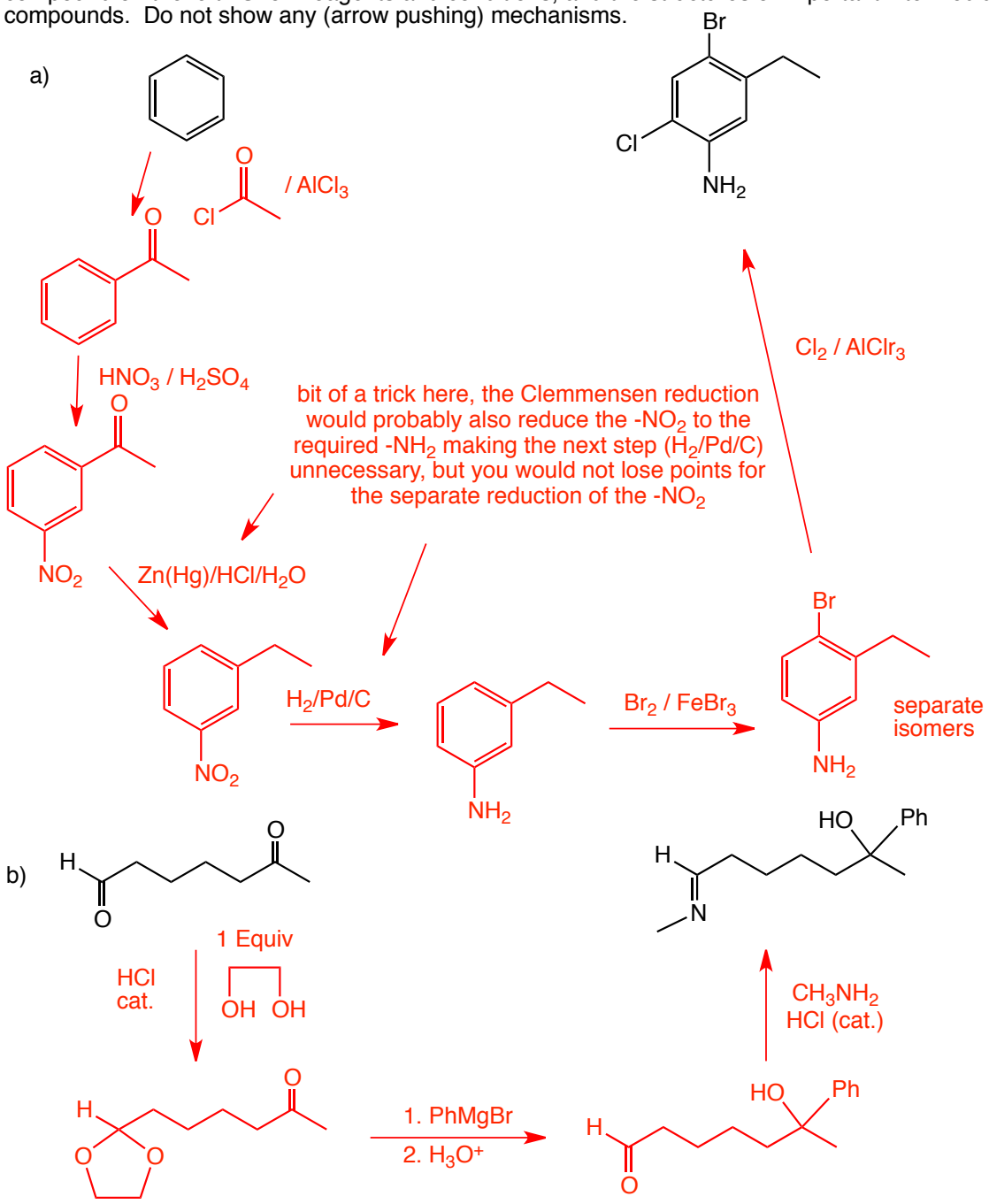
d)



e)

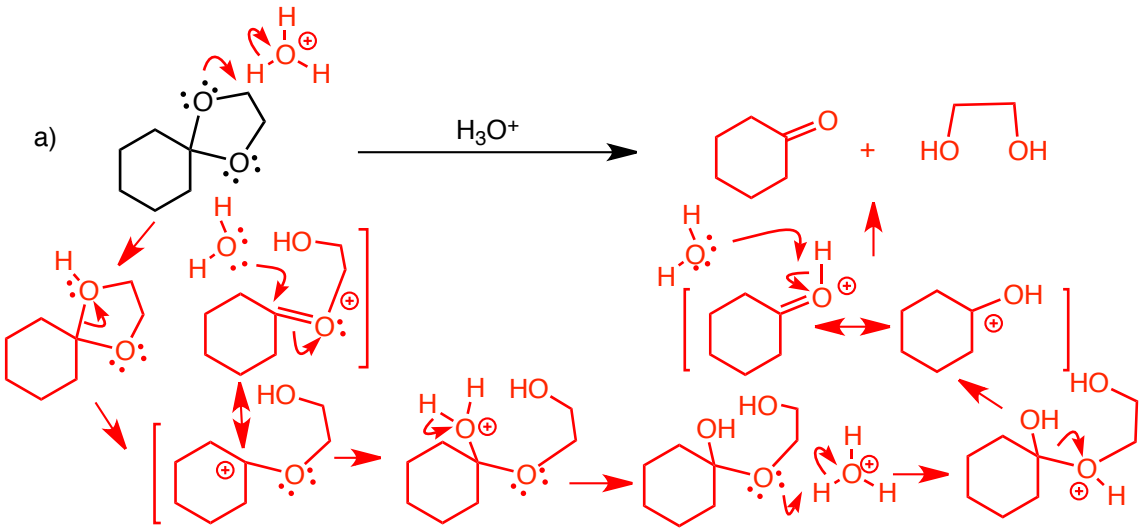


Question 5. Show how you would synthesize the target compound on the right from the starting compound on the left. Show reagents and conditions, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

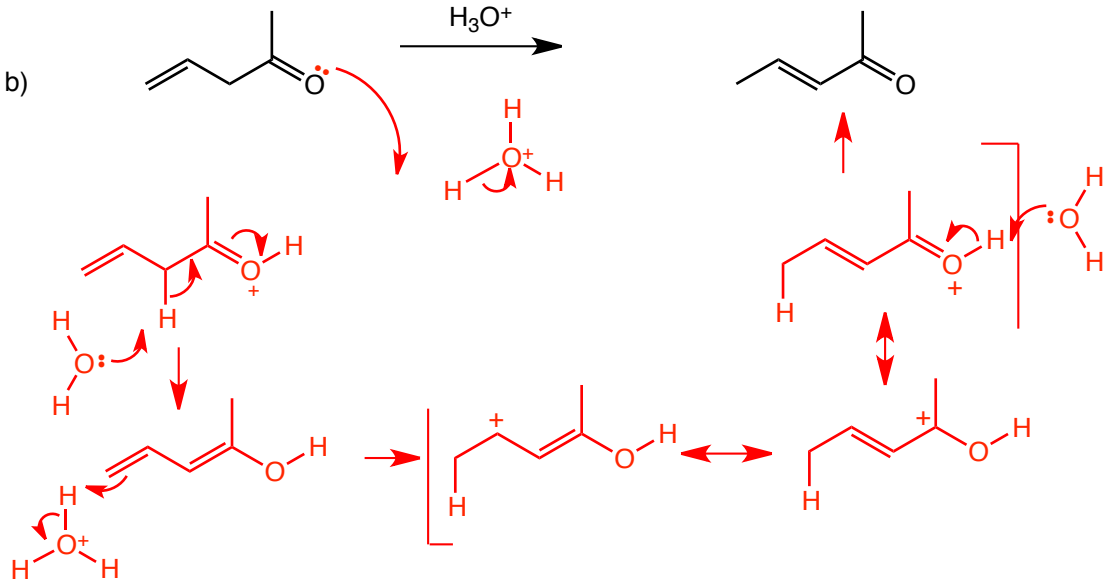


Question 6 Give a full curved arrow-pushing mechanism for the following reactions, show where every proton goes to and comes from (no $+H^+/-H^+$) and indicate the Lewis and Bronsted acids/bases at each intermolecular step, include important resonance contributors for all intermediates, give the number of steps in your mechanism.

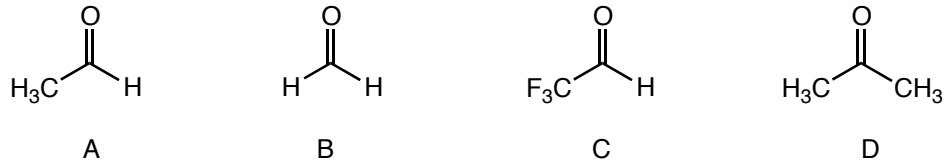
a)



b)



Question 7 Rank in order of increasing rate of reaction with a Grignard reagent, giove a brief explanation in terms of nucleophiles and electrophile stregth and tthe factors that control these in this context.



A B C D

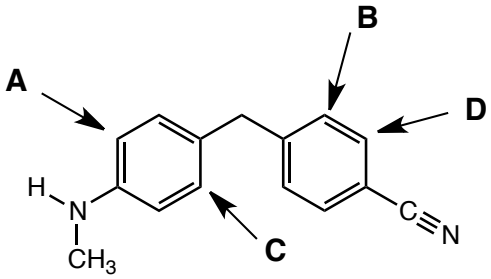
D < A < B < C

In these reactions the Grignard is the Lewis base and the carbonyls are the Lewis acid, the stronger the Lewis acid the faster the reaction

the carbonyl carbon in D has two weak donating -CH3 groups attached, which decerases the electrophilicity, this reaction is slower than A (one donating group) which is slower than B (zero donating groups)

C is fastest of all, the -CF3 is electron withdrawing, which incerases the electrophilicity of the carbonyl carbon

Question 8. Rank in order of increasing rate of electrophilic aromatic substitution at the carbons indicated by the arrows. Give a BRIEF explanation.



D < B < C < A

slowest fastest

Reaction at both A and C is faster than at B and D, because both are activated by strong (amine) and weak (aryl) donating groups on the ring. Reaction at A is activated more than at C because the strongest donating group activates more. Reaction at B and D is deactivated by the by strongly withdrawing nitrile group, but D is deactivated more than at C.