CHEM 234, Spring 2019 Final Exam Ian R. Gould

COMPLETE THIS SECTION : Up to TWO POINTS will be removed for incorrect/missing information!

PRINTED **FIRST** NAME *Answer Key* PRINTED **LAST** NAME _____

Person on your **LEFT** (or **Empty** or **Aisle**) _____

Person on your **RIGHT** (or **Empty** or **Aisle**) _____

Class you are REGISTERED FOR (onground or hybrid) _____

The room where most students will take the test for your class, i.e. LS A-191 for onground and PS H-152 for hybrid) _____

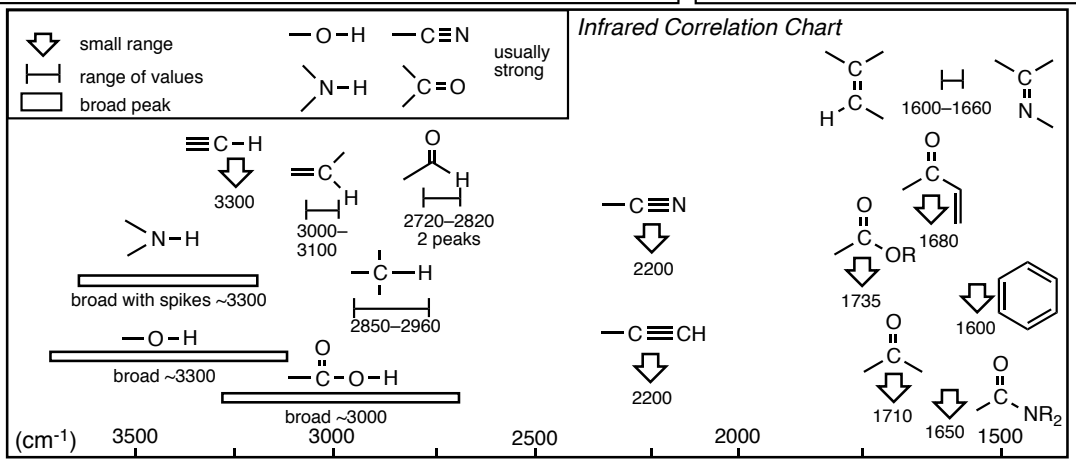
*****YOU ARE NOT ALLOWED TO TAKE SPARE COPIES OF THIS EXAM FROM THE TESTING ROOM*****

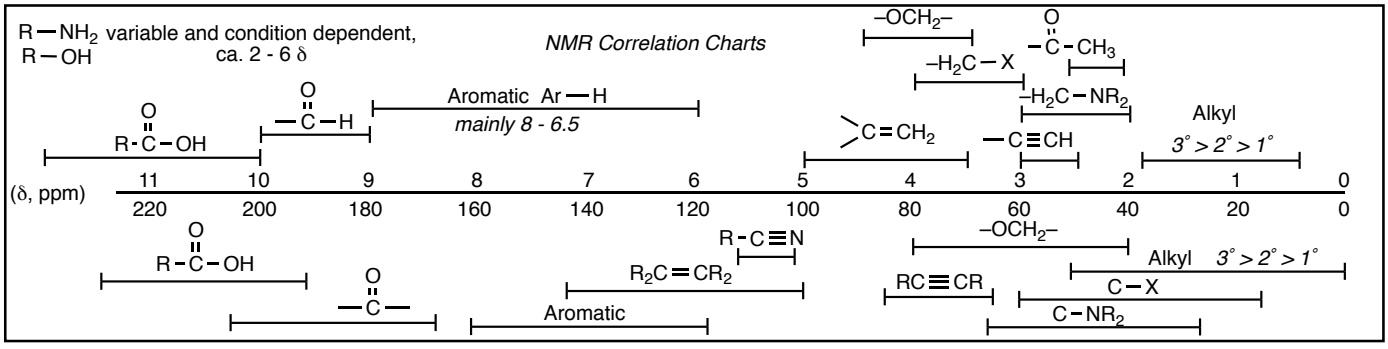
- *PRINT YOUR NAME ON EACH PAGE!*
- *READ THE DIRECTIONS CAREFULLY!*
- *USE BLANK PAGES AS SCRATCH PAPER*
  work on blank pages will not be graded...
- *WRITE CLEARLY!*
- *MOLECULAR MODELS ARE ALLOWED*
- *DO NOT USE RED INK*
- *DON'T CHEAT, USE COMMON SENSE!*

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

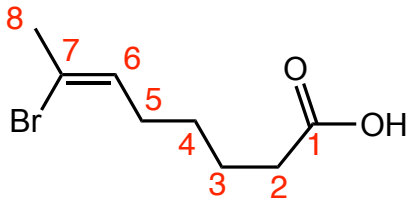
Eclipsing		Gauche	
H/H	~1.0	Me/Me	~0.9
H/Me	~1.4	Et/Me	~0.95
Me/Me	~2.6	i-Pr/Me	~1.1
Et/Et	~3.1	t-Bu/Me	~2.7





Question 1 (14 pts.) Provide a IUPAC name for the following structure, do not forget to use E/Z and R/S as appropriate.

a)

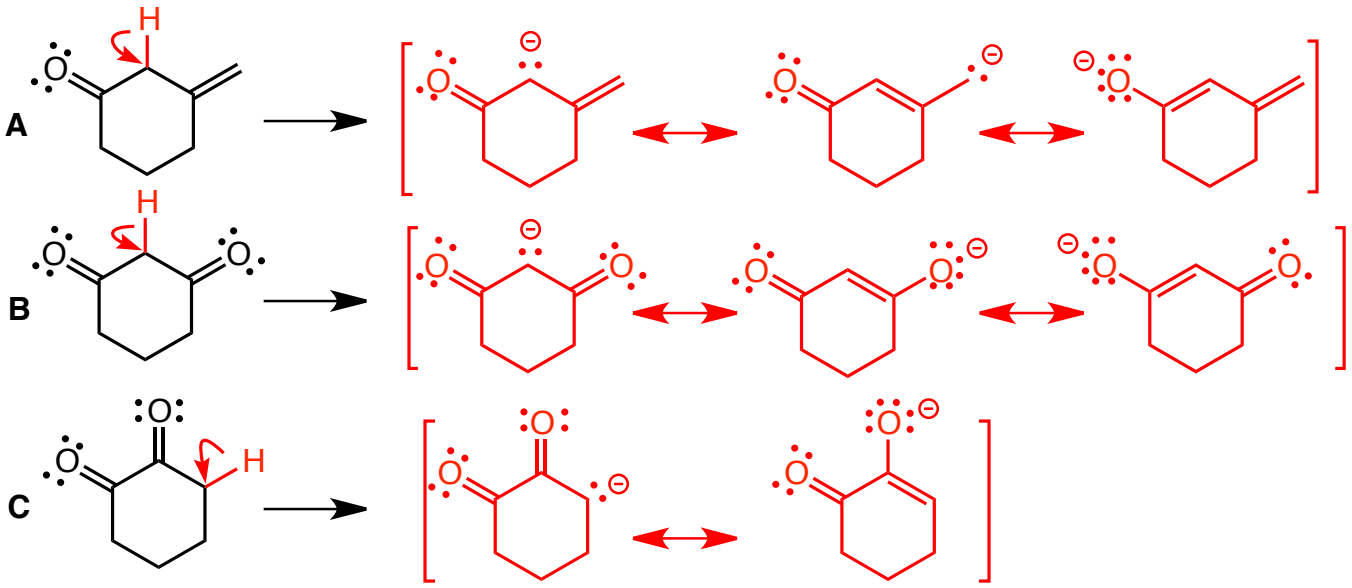


7-bromo-(6Z)-octenoic acid

OR

7-bromooct-(6Z)-enoic acid

Question 2 (24 pts) Rank the following in order of increasing Bronsted acidity, and provide a BRIEF explanation. You MUST draw the structures of ALL OF the conjugate base anions including ALL reasonable resonance contributors



C < A < B

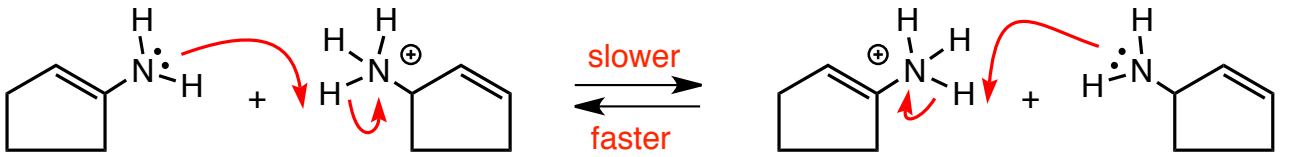
weakest strongest

A and B have 3 resonance contributors to the base anion, these are more stable than the base anion from C, therefore C is the weakest acid. In B the negative charge is delocalized onto 2 negatively charged oxygen atoms compared to an oxygen and a carbon for A, the anion from B is this the most stable, B is thus the strongest acid.

Extra Credit Question (5 pts). What kind of functional group is hydrolyzed to form soap?

carboxylic acid ester amide aldehyde

Question 3 (20 pts.) For the following acid/base equilibrium:
a) draw the curved arrows showing bond making/breaking
b) indicate which is the STRONGER and the WEAKER acid and base on each side
c) Indicate which acid has the larger and which the smaller pKa
d) give a BRIEF explanation for your choice of stronger/weaker that includes the phrase "energy of the electrons"
e) Indicate which reaction (left to right or right to left) is faster and which is slower and indicate on which side the equilibrium lies



weaker base

weaker acid
larger pKa

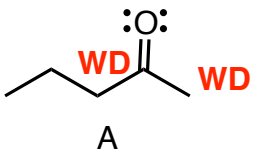
stronger acid
smaller pKa

stronger base

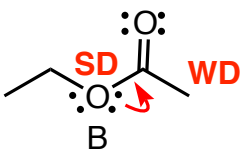
equilibrium lies on THIS side

the weaker base has the lower energy electrons, the non-bonding electrons in A are stabilized by resonance, are this lower in energy

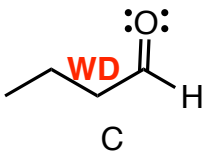
Question 4 (12 pts.) Rank in order of increasing equilibrium constant for formation of a hydrate. Give a BRIEF explanation.



A



B



C

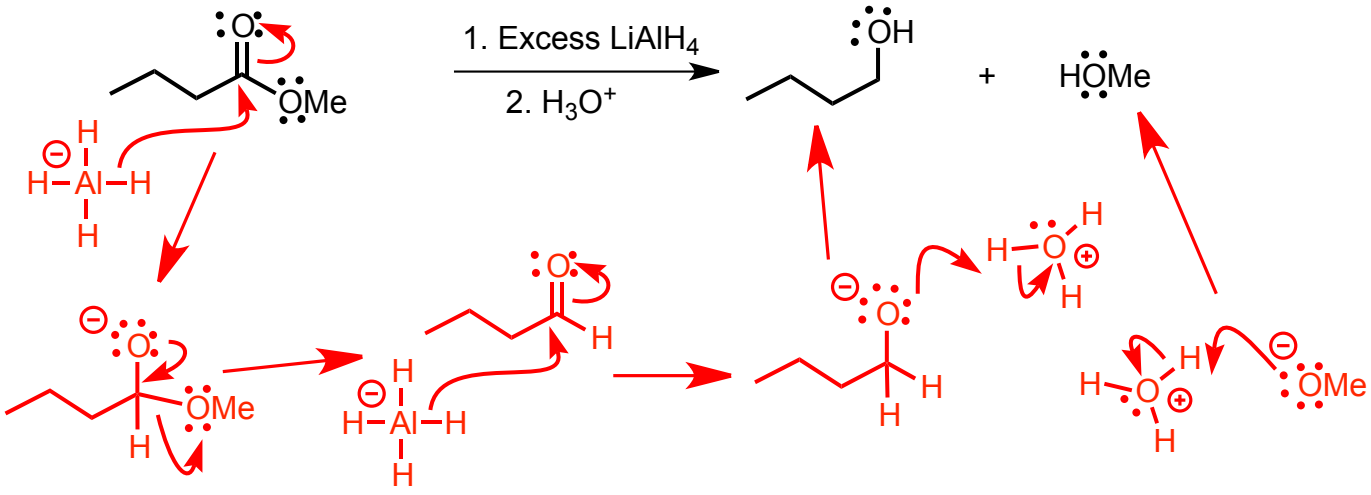
WD = weakly donating
SD = strongly donating

B < A < C

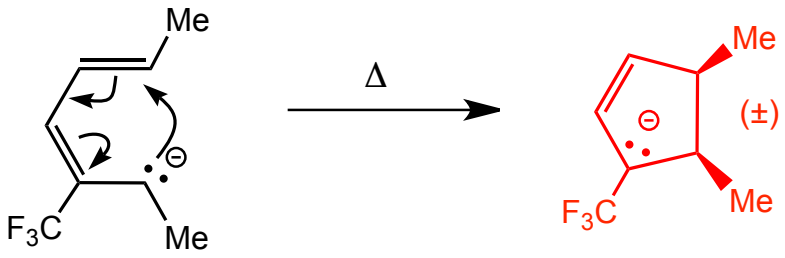
smallest largest

this is addition of a weak nucleophile/LB, water, to 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 5. (20 pts.) Give a curved arrow-pushing mechanism for the reduction of the provided ester to butanol and methanol. You must draw the Lewis structure of the $^{-}AlH_4$ anion and you MUST show exactly where each proton comes from and goes to here, no +H+ and -H+ notation, and you must also show how the methanol is formed.



Question 6 (24 pts) For the electrocyclic ring closure reaction below, and using the curved arrow-pushing provided:
a) Give the ALLOWED product



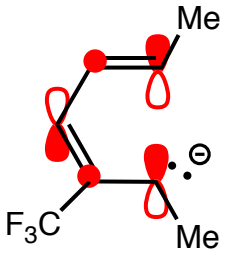
c) How many electrons are involved in this reaction 6

d) Does the ALLOWED reaction proceed via a disrotatory or a conrotatory ring closure
disrotatory

e) Does the allowed reaction proced via a Huckel or a Mobius transition state? Give a BRIEF explanation

Huckel, because 6 electrons in a cyclic loop Huckel transition state are aromatic and lower in energy than a Mobius transition state

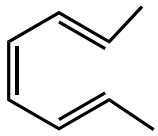
f) Draw the HOMO of the reactant anion ON TOP of the structure to the right



HOMO

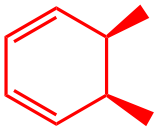
Question 7 (63 pts) Provide the missing major organic products or reagents/conditions for the following reactions. **Do not forget to include stereochemistry as appropriate** and INDICATE ANY RACEMIC MIXTURES.

a)

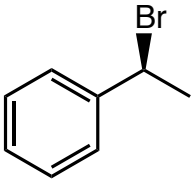


heat

(electrocyclic ring closure reaction)

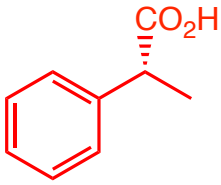


b)

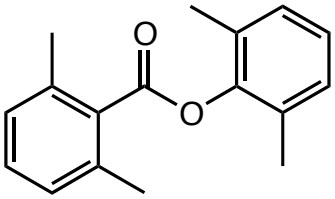


1. NaCN

2. H_3O^+ (heat)

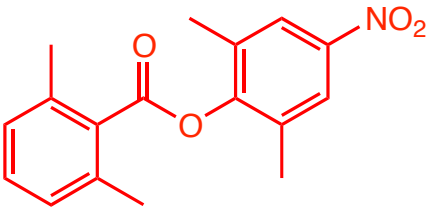


c)

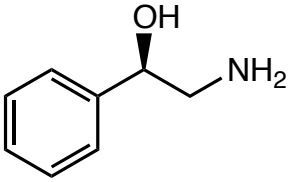


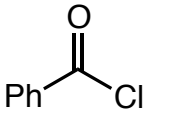
HNO_3

H_2SO_4

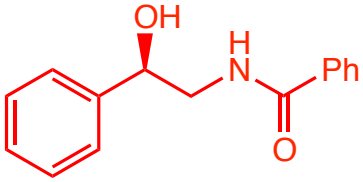


d)

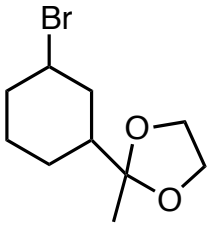




1 equivalent



e)

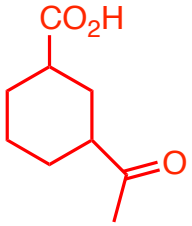


1. Mg . THF

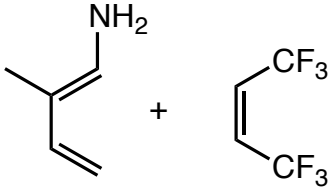
2. CO_2

3. H_3O^+

(ignore stereochemistry for this problem)

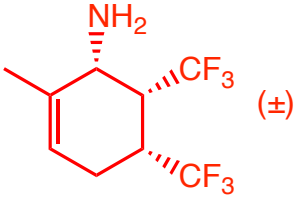


f)



+

heat



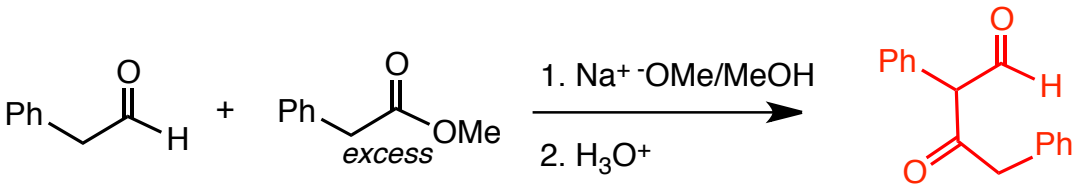
(±)

Question 7, Contd... Provide the missing major organic products for the following reactions. **Do not forget to include stereochemistry as appropriate** and INDICATE ANY RACEMIC MIXTURES.

h)

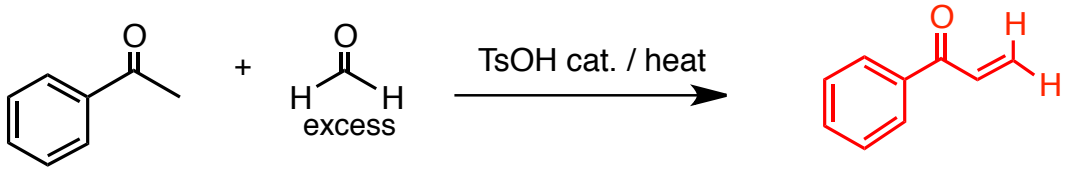
(ignore stereochemistry for this problem)

i)

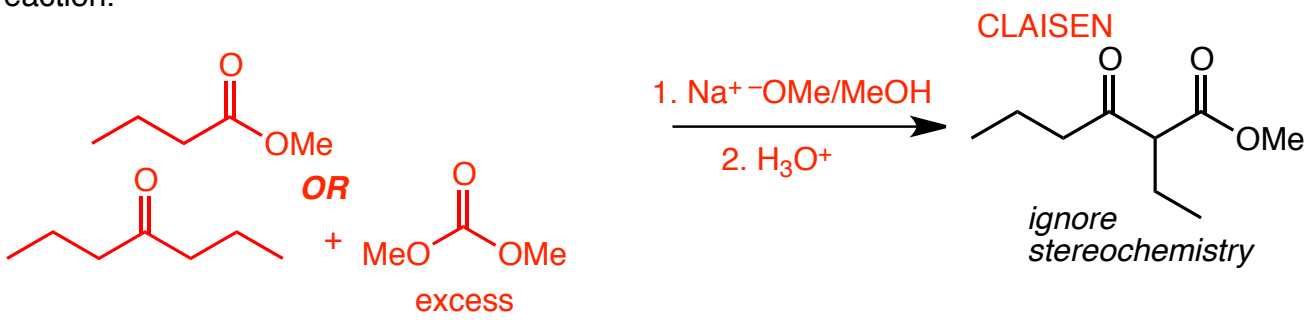


(ignore stereochemistry for this problem)

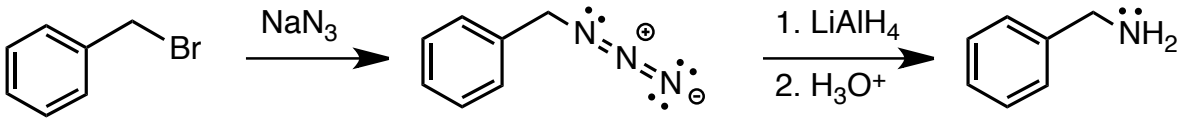
j)

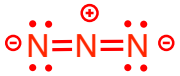


Question 8 (10 pts) Give all reactants/reagents and conditions that would be used to give the provided structure below. Indicate whether the reaction is a Aldol reaction or a Claisen reaction.



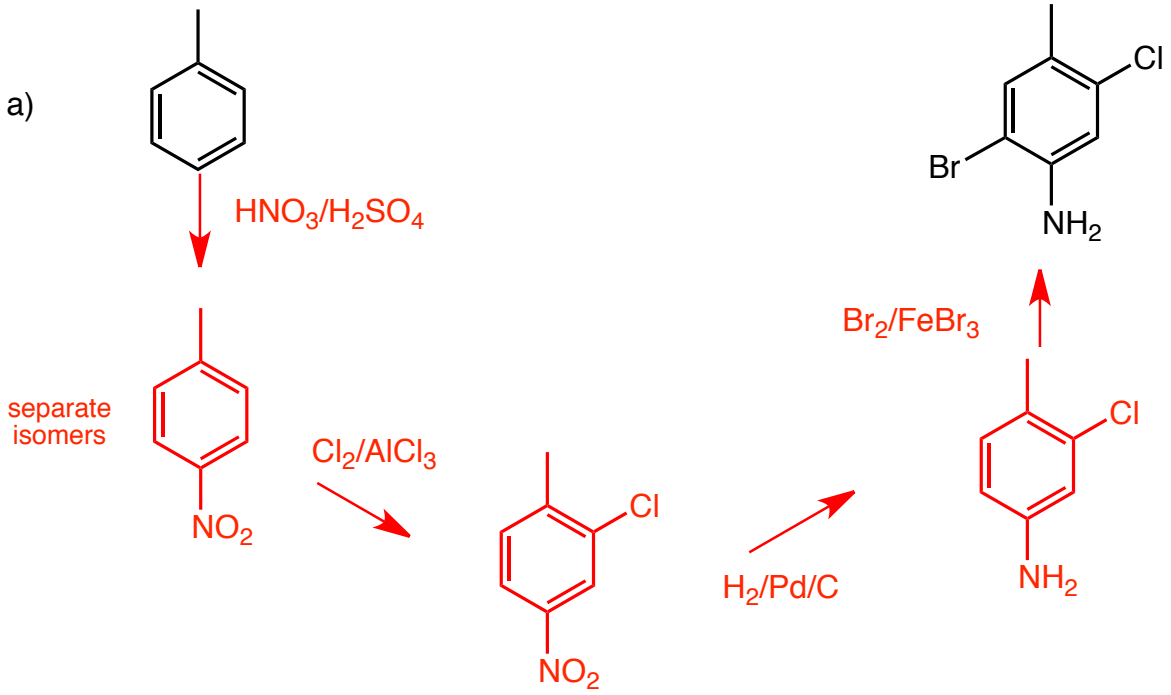
Question 9 (8 pts.) One method of synthesizing a primary amine is to convert a bromide into an azide by doing an SN2 reaction with sodium azide (NaN_3), and then reducing with lithium aluminum hydride. In the provided box, draw a complete Lewis structure of the azide anion, including all non-bonding electrons and formal charges. This is not a reagent memorization problem, it is working out how to do an SN2 reaction problem.



Lewis structure of the azide anion	

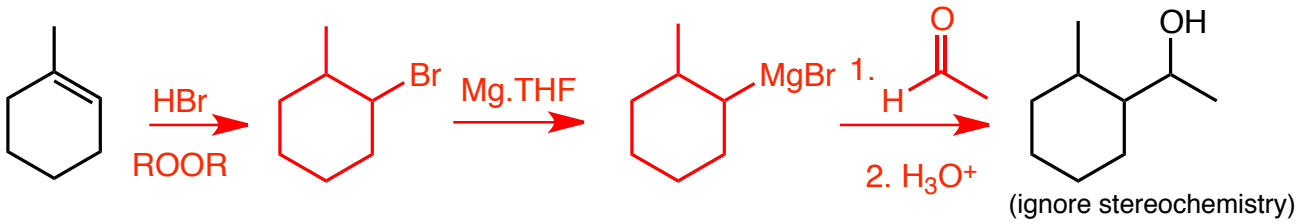
Question 10 (40 pts.) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers**

a)



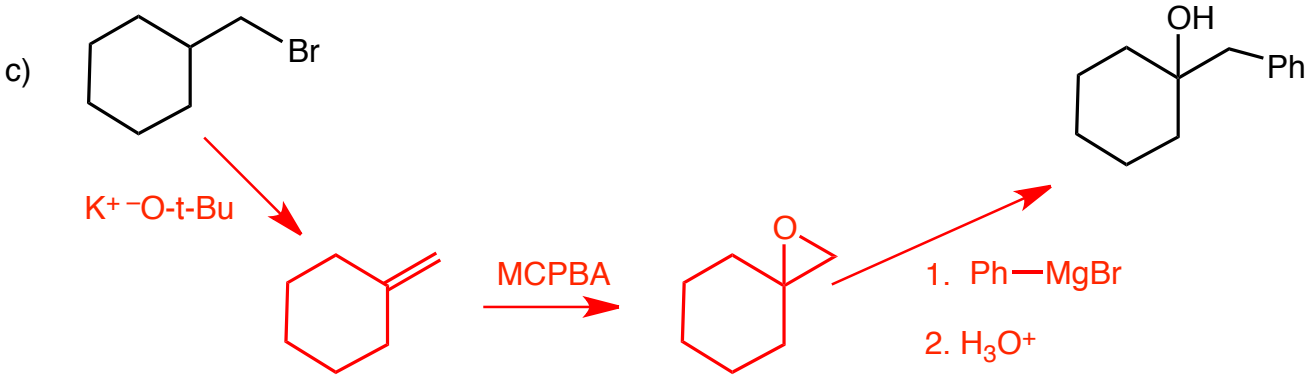
These questions use only reactions from the "minimal" sets that were provided on the class website

b)



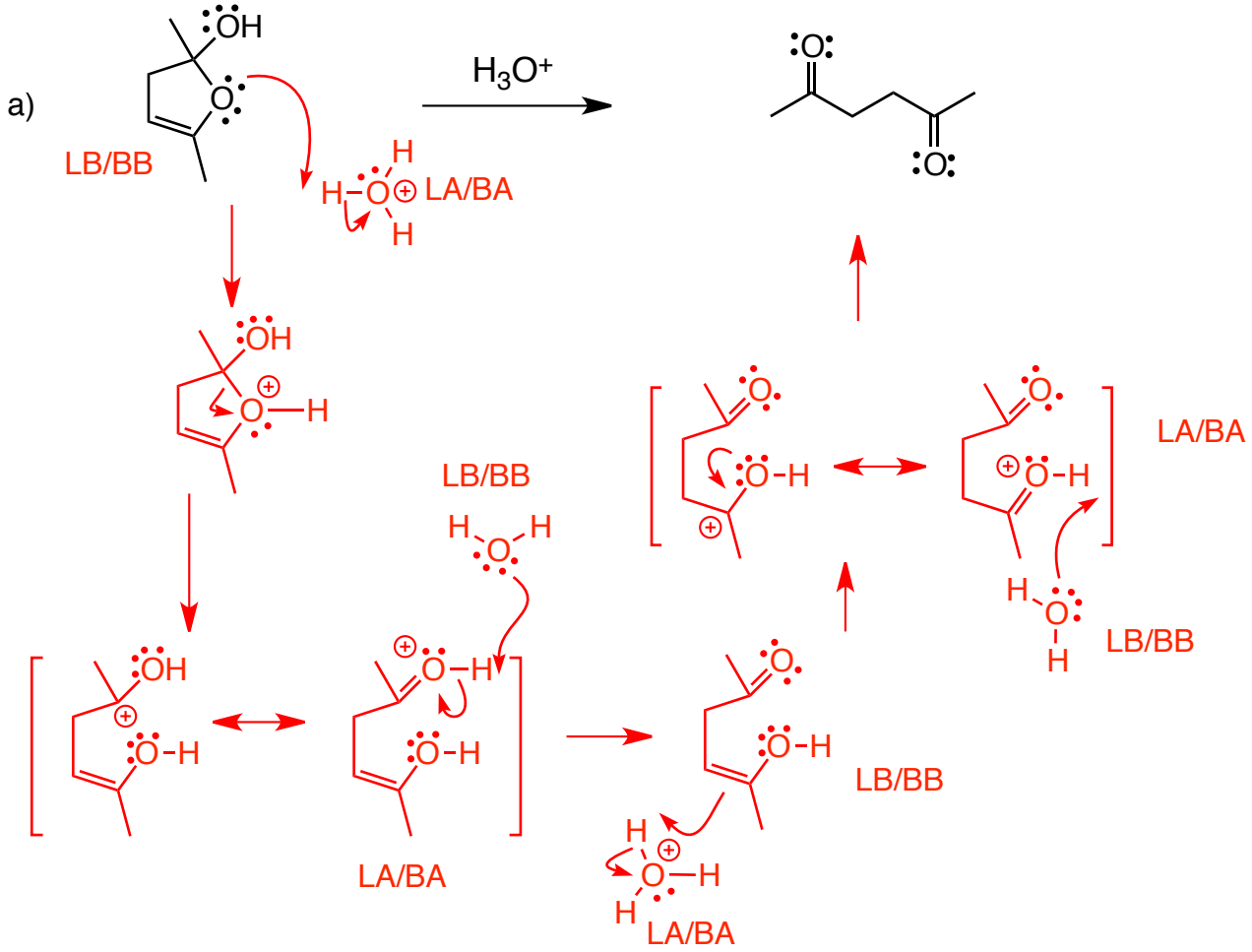
(ignore stereochemistry)

c)

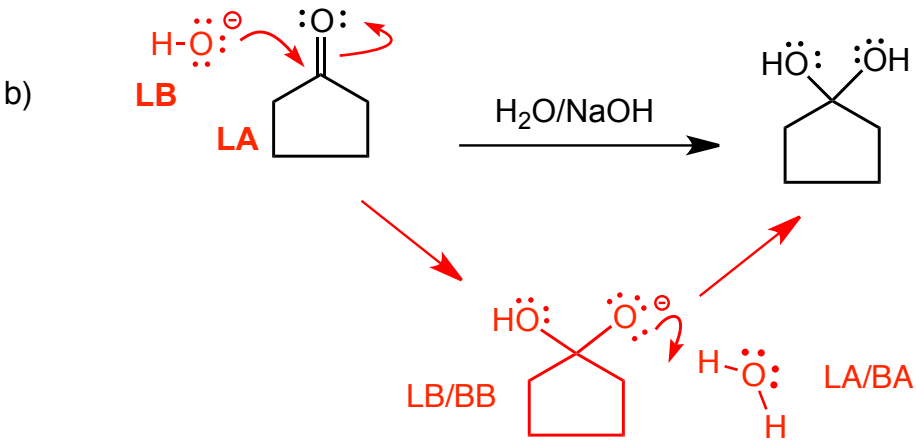


Question 11 (30 pts.) Give a curved arrow-pushing mechanism for the following reaction
Show where all protons come from and go to (no $+H^+/-H^+$)
Show all resonance contributors to the intermediate structures
Label the Lewis acid/base and and Bronsted acids/bases as appropriate

a)

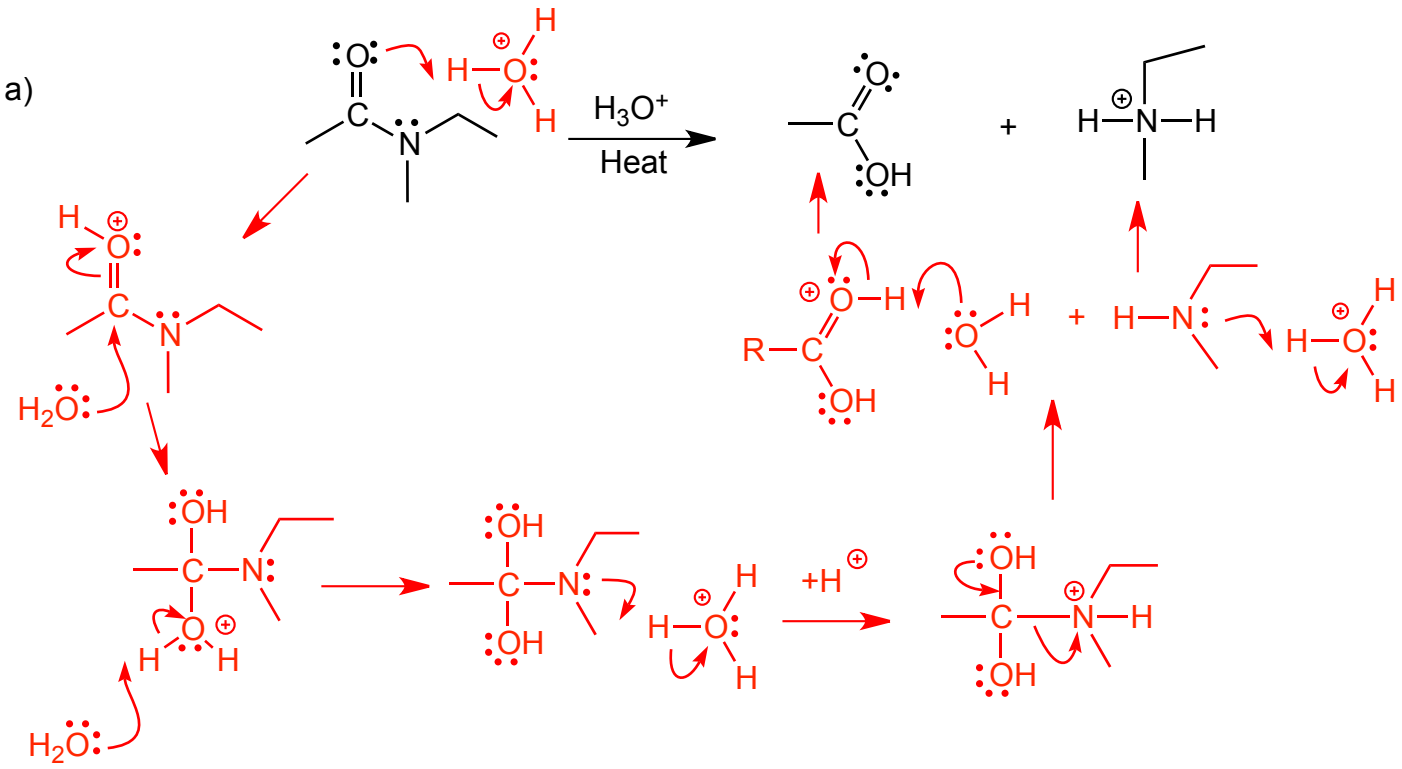


b)

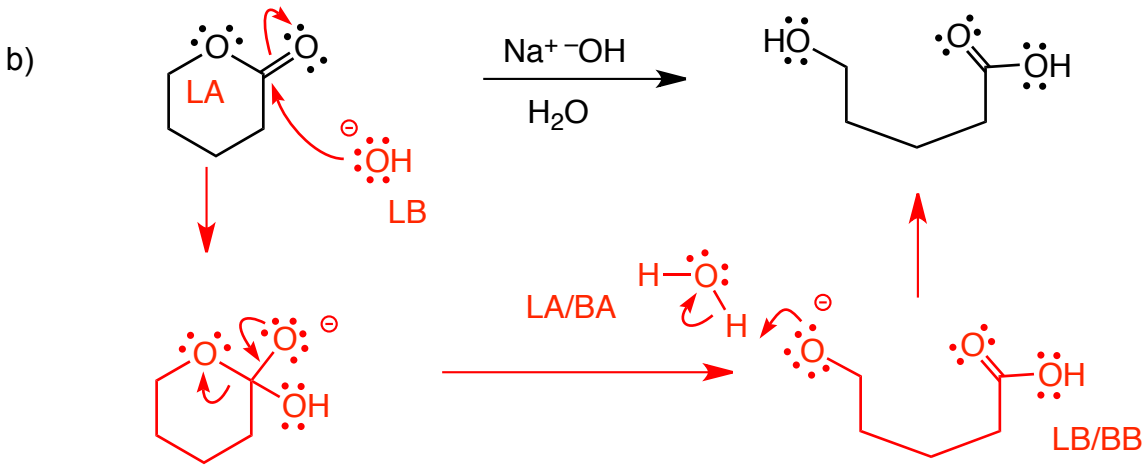


Question 12 (36 pts). Give a curved arrow pushing mechanisms for the following two reactions.
1) Add non-bonding electrons and C-H bonds to the line-angle structures as required.
2) Indicate the Lewis acid/Lewis base (LA, LB) at each INTERMOLECULAR step as appropriate, and whether they are also Brønsted acids/bases (LA/BA, LB,BB)
3) **YOU DO NOT HAVE TO DRAW RESONANCE CONTRIBUTORS for intermediates**
4) GIVE THE NUMBER OF STEPS IN YOUR MECHANISMS
5) Show where ALL protons come form and go to, no abbreviated $+H^+/-H^+$ notation

a)

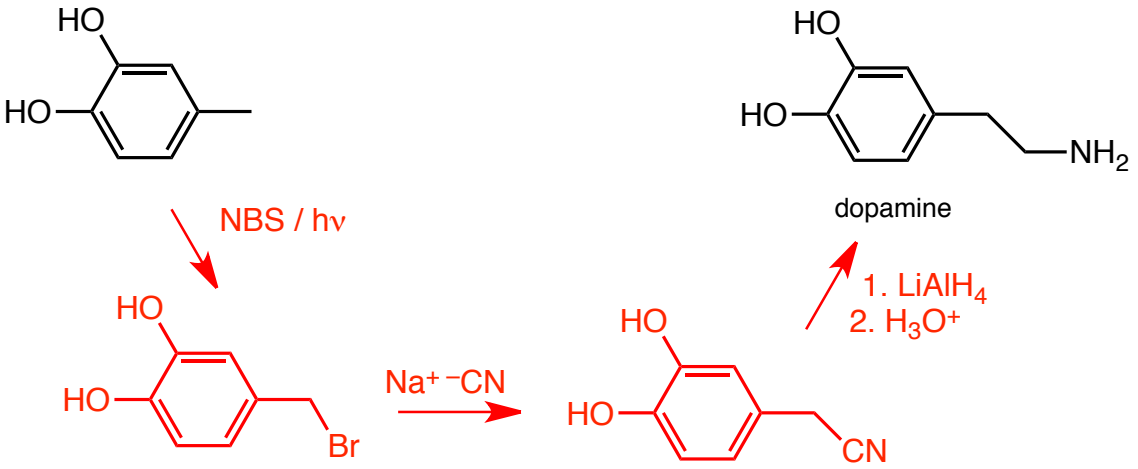


b)

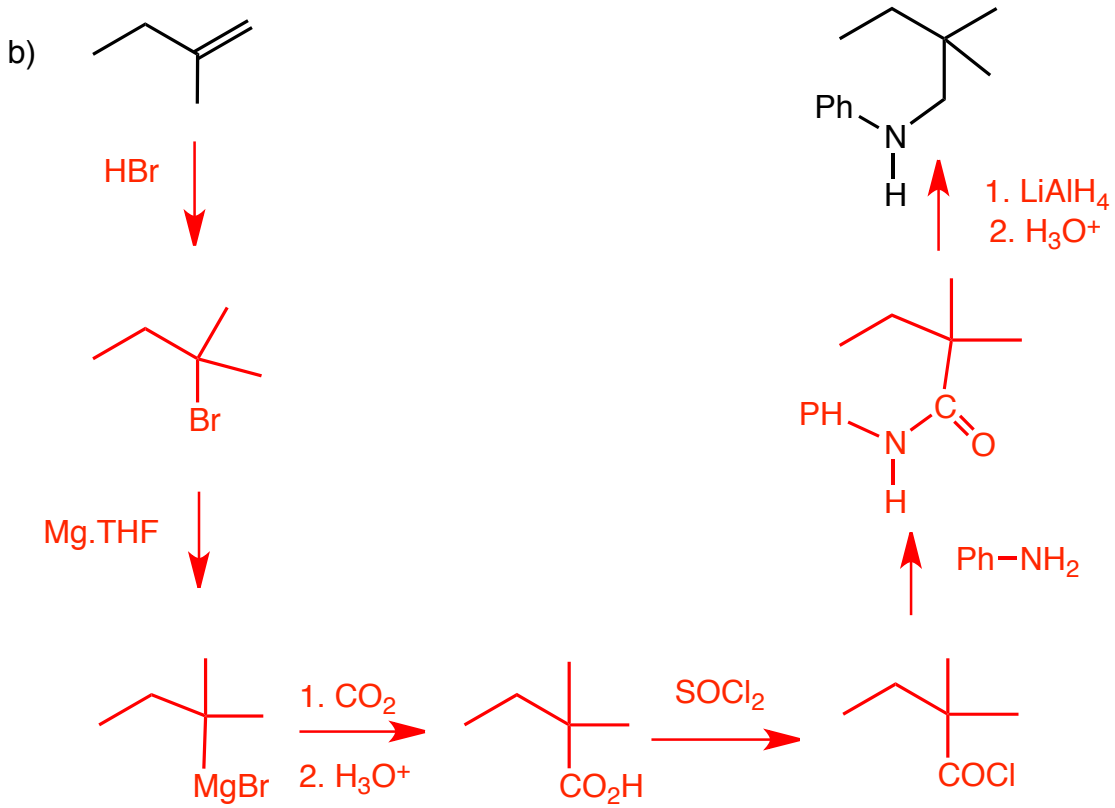


Question 13 (40 pts.) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

a)

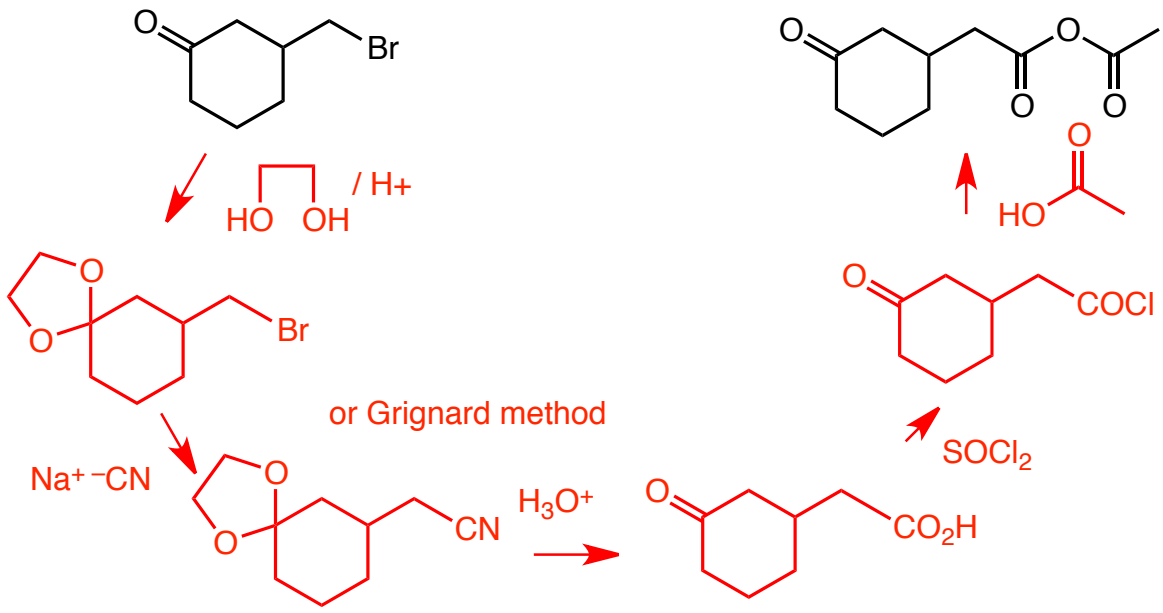


b)

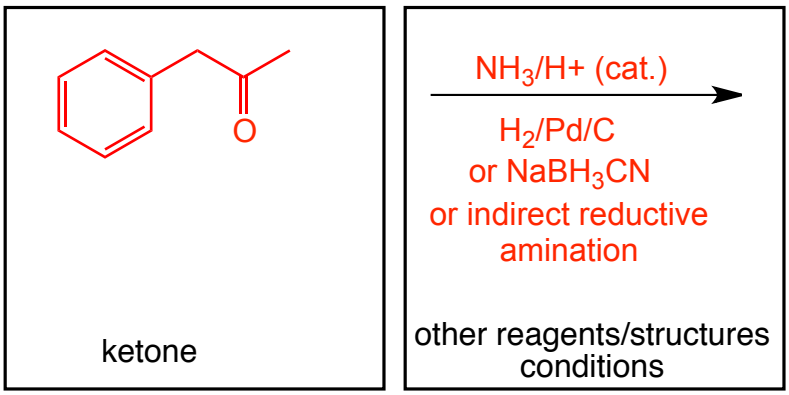


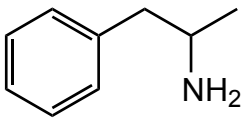
Question 14 (20 pts.) Synthesize the (target) molecule on the right from the starting molecule the left. this can not be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates. *Ignore stereochemistry!*

a)



Question 15 (14 pts.) Give the structure of the ketone (in the provided box) and ALL OTHER reagents/conditions (on the reaction arrow) you would use to synthesize amphetamine via a reductive amination





amphetamine