CHEMISTRY 12A FALL 2019

Answers - Final

FINAL EXAM

DECEMBER 18, 2019

NAME- WRITE BIG _____

STUDENT ID: _____

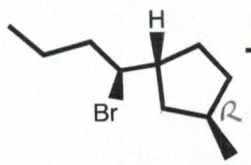
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: _____

- **You will have 3 hours in which to work.**
- **BE NEAT! Non-legible structure drawings will not be graded.**
- **Only answers in the answer boxes will be graded – you can write in other places, but we only grade the answers in the boxes.**
- **All pages of the exam must be turned in.**
- **No calculators**
- **No stencils**
- **Molecular models may be used**

Problem	Points (Maximum)
1	36
2	24
3	15
4	43
5	18
6	24
7	27
8	28
9	21
10	18
11	20
12	26
Total	***300***

1. (36 points) For each reaction, draw the major organic products, **including all stereoisomers**. Write NR if you think there will be no reaction.

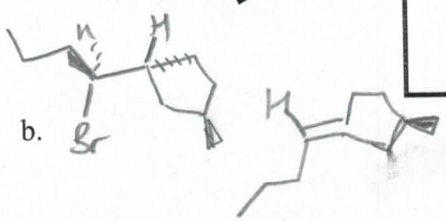
a.



NaOEt

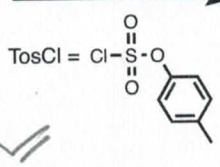
EtOH

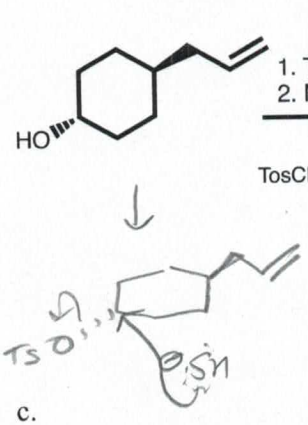
b.



1. TosCl, pyridine
2. NaSH, CH_3CN

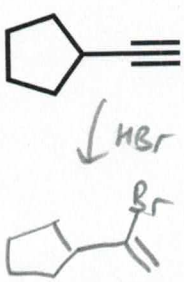
TosCl =



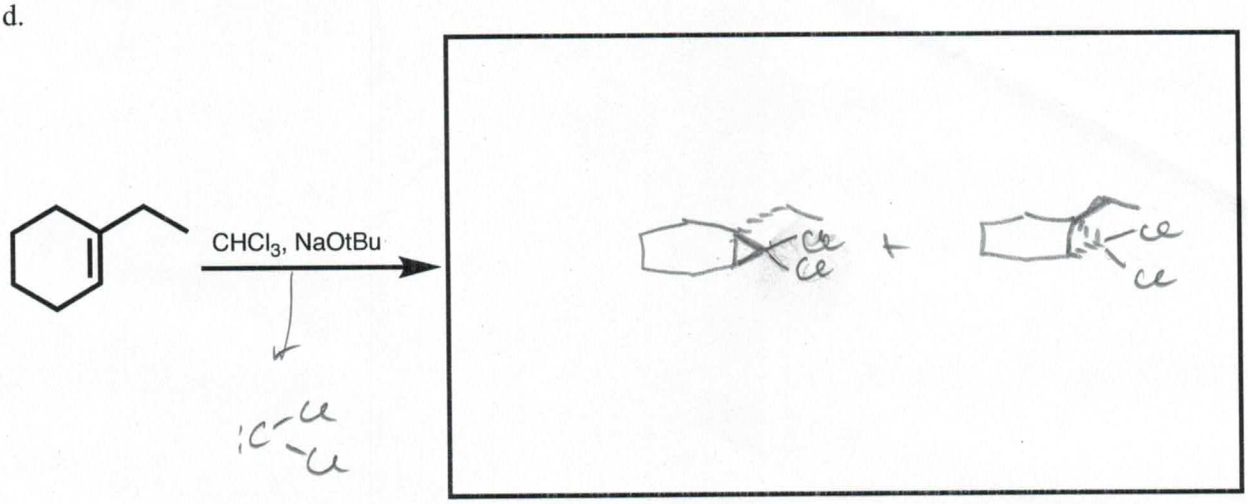


c.

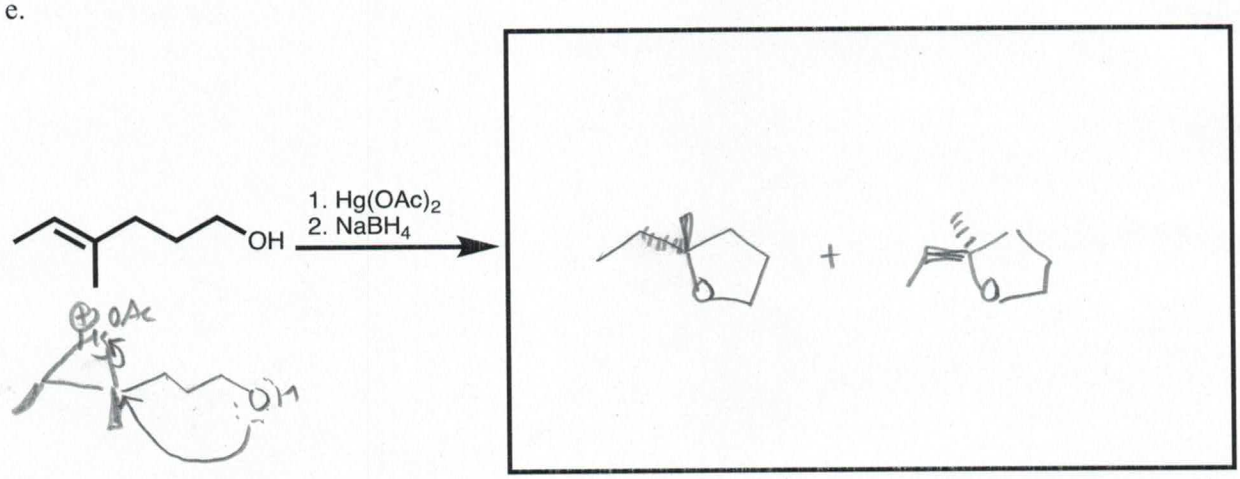
excess HBr



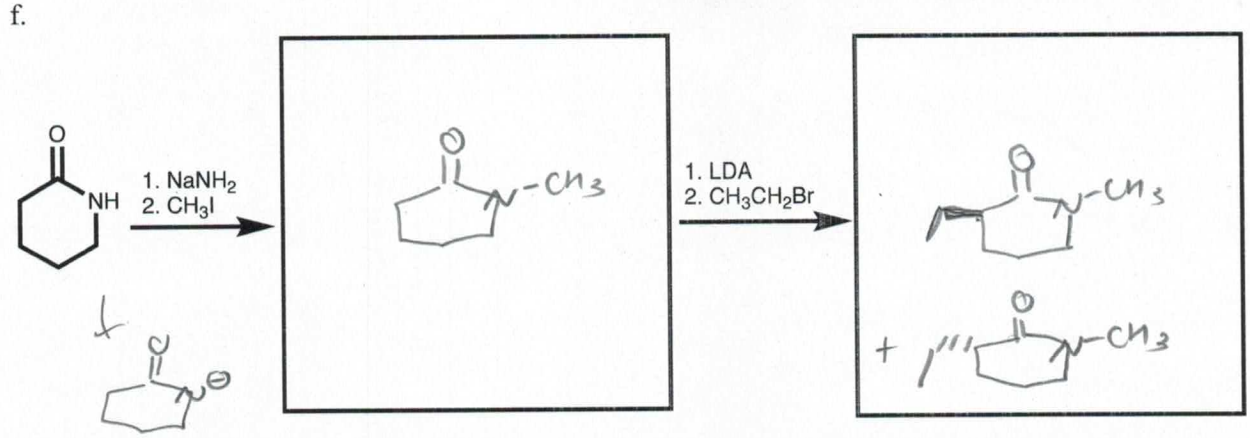
d.


CHCl3, NaOtBu

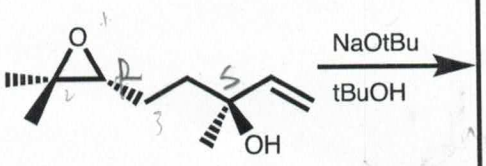
e.


1. Hg(OAc)2
2. NaBH4
OH
OAc

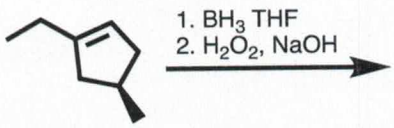
f.


O
NH
1. NaNH2
2. CH3I
1. LDA
2. CH3CH2Br

g.

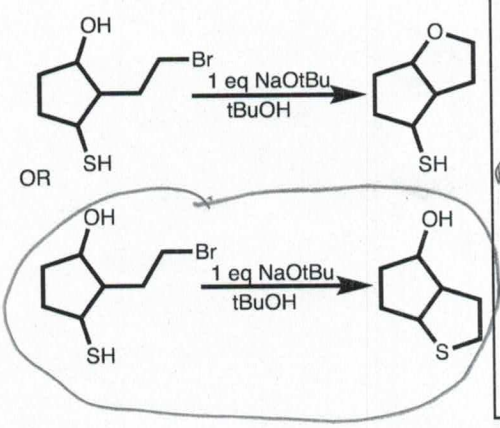


h.



2. (24 points) Circle the reaction in the following pairs of reactions that you would expect to go faster. It is possible that both reactions have the same rate or that one does not occur at a measurable rate. You may disregard any other products besides the ones pictured that may form under the reaction conditions. Give brief explanations in the boxes provided and include relevant structures. Note that only the primary organic products are shown.

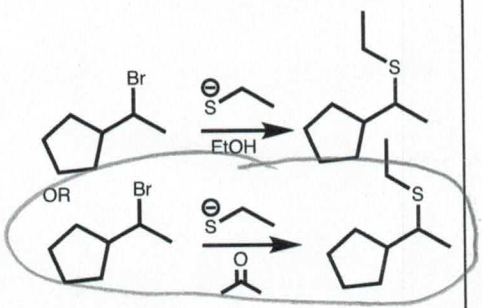
a.



The 1st step is deprotonation. Only one eq of base is added & S-H is more acidic than O-H & therefore, all base will be used up deprotonating R-SH, which will then do an S_N2 on alkyl bromide.

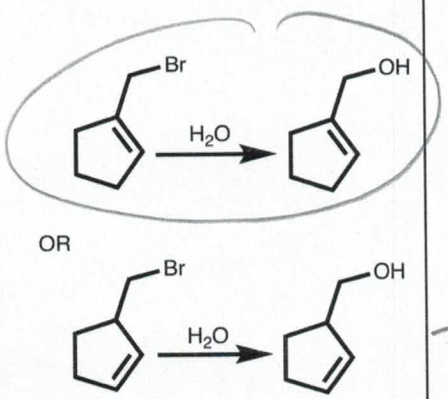
R-SH is more acidic than R-OH because S is one row down in periodic table & larger size stabilizes negative charge in conjugate base.

b.



SN2 rxn w/ negatively charged nucleophile. Reaction should be faster in DMSO than EtOH because DMSO solvates less well. Transition state is less charged & therefore less solvated. As a result ~SO is solvated & stabilized in EtOH while T.S. is not & this slows rxn in EtOH

c.

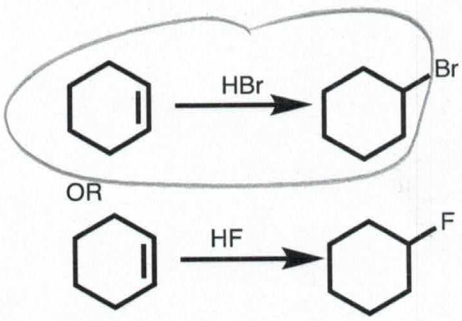


SN1 conditions.

Top reaction forms stable allylic carbocation.

Bottom forms an unstable primary carbocation. The transition state resembles carbocation intermediate & rxn that forms more stable carbocation goes faster.

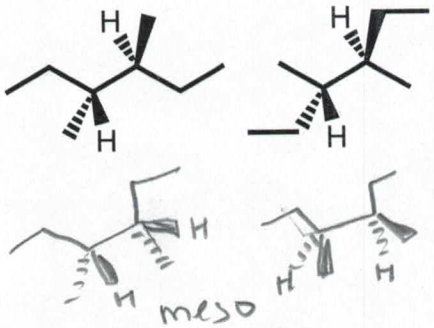
d.



Rate of reaction depends on strength of electrophile. H-Br is much more acidic than H F & therefore, a stronger electrophile. Transition state includes a partially broken H-x bond & more acidic H-x will be more stable in T.S, & rxn will go faster.

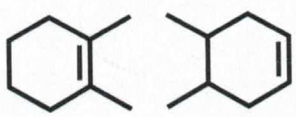
3. (15 points) Identify the following pairs of molecules as enantiomers, diastereomers, constitutional isomers, identical, or different molecules.

a.



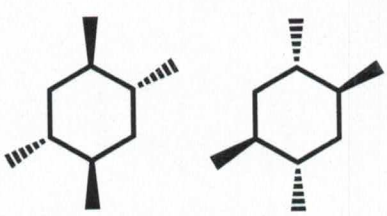
identical

b.



constitutional isomers

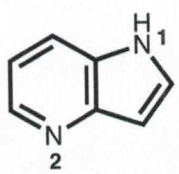
c.



enantiomers

4. (43 points) Consider the molecules below.

a.



	Hybridization	Orbital of lone pair
N1	sp^2	p
N2	sp^2	sp^2

i. Fill in the table next to the molecule.

ii. Is this molecule aromatic? Explain your answer.

Yes. $2n+2$ e⁻ $n=4$ $10\pi e^-$

cyclic, planar, fully conjugated

iii. Which nitrogen atom in this molecule is **most** basic? Explain your answer.

N2 is most basic, lone pair is sp^2 & not involved in resonance making it less stable & more basic

N1 lone pair is part of aromatic system & is less basic

b. Consider the molecule below.

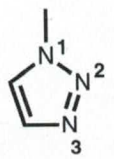
	Hybridization	Orbital of lone pair
N	sp^2	sp^2

i. Fill in the table next to the molecule.

ii. Is this molecule aromatic? Explain your answer.

No. Not fully conjugated

c. Consider the molecule below.



	Hybridization	Orbital of lone pair
N1	sp^2	p
N2	sp^2	sp^2
N3	sp^2	sp^2

i. Fill in the table next to the molecule.

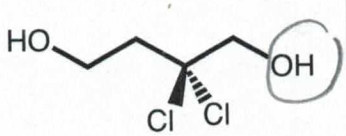
ii. Is this molecule aromatic? Explain your answer.

yes $6\pi e^-$, fully conjugated, cyclic, planar

iii. Which nitrogen atom in this molecule is **least** basic? Explain your answer.

N1 is least basic because it is part of aromatic system. Protonating at N1 would break aromaticity. Protonating at N2 & N3 would not effect aromaticity

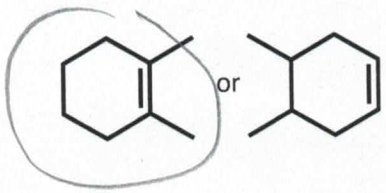
d. Which is the most acidic proton in the molecule below? Explain your selection.



This OH is closest to the electron-withdrawing Cl groups. These stabilize conjugate base by induction.

5. (18 points) Circle the molecule that is most stable in the following pairs. Explain your choice.

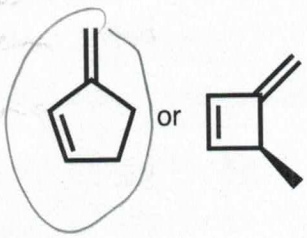
a.



more substituted double bond is more stable.

This is due to hyperconjugation with C-H or C-C bonds of alkyl groups

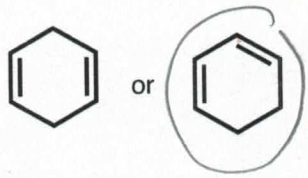
b.



less ring strain.

In particular bond angle strain is greater in 4-membered ring which has 90° angles while sp^2 hybridization prefers 120° angles. In contrast 5 membered ring has 108° angles

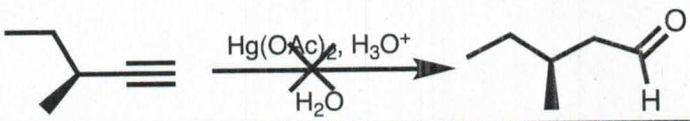
c.

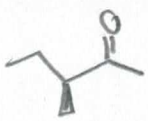
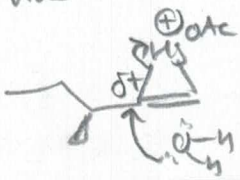
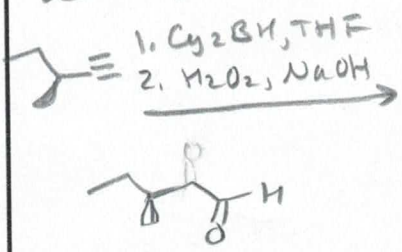


Conjugation of double bonds gives stable 1,3-diene orbitals.

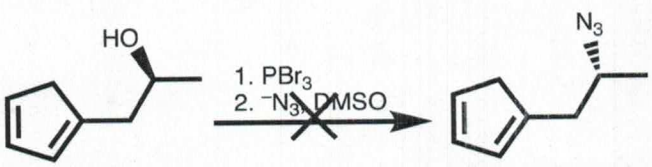
6. (24 points) The following reactions would not occur as written. i. What product would actually be made? ii. Why was the desired product not formed? iii. How could you change either the substrates or reaction conditions to give the desired products in as few steps as possible?

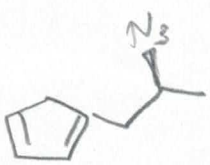
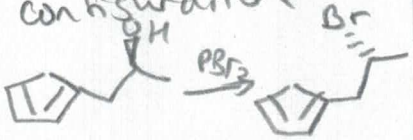
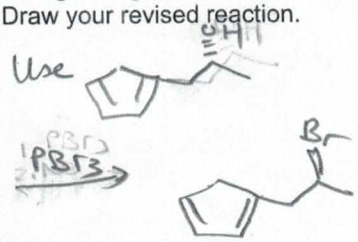
a.



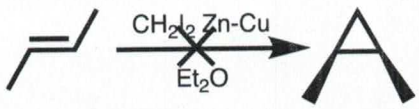
What product(s) is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Include **drawings** of any relevant structures)	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
	In oxymercuration water adds to more substituted carbon because it has more δ+ 	Use hydroboration which gives anti-Markovnikov addition 

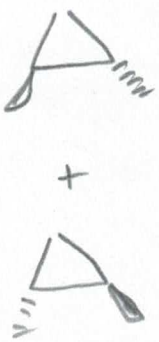
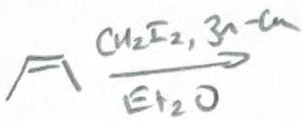
b.



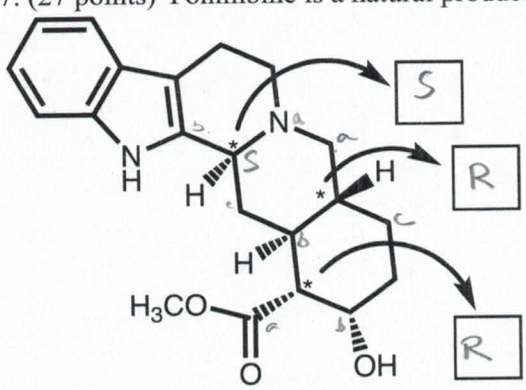
What product(s) is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Include **drawings** of any relevant structures)	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
	PBr_3 involves S_N2 w/ inversion of config Followed by S_N2 w/ N_3 retains orginal configuration 	Use 

c.



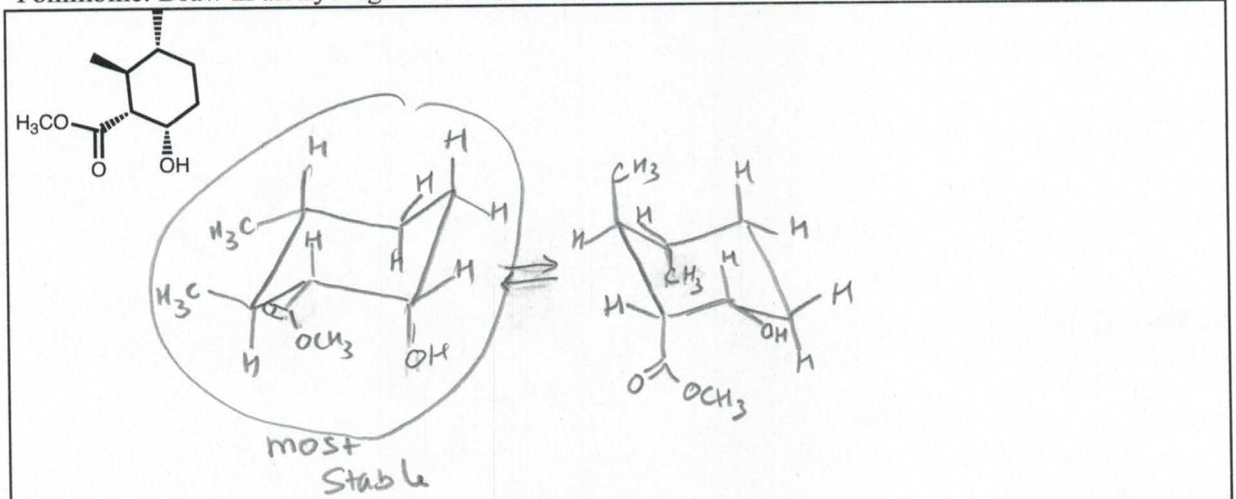
What product(s) is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Include **drawings** of any relevant structures)	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
	Because bonds formation is concerted 	Use  as S.M.  

7. (27 points) Yohimbine is a natural product used as a veterinary drug to reverse sedation.

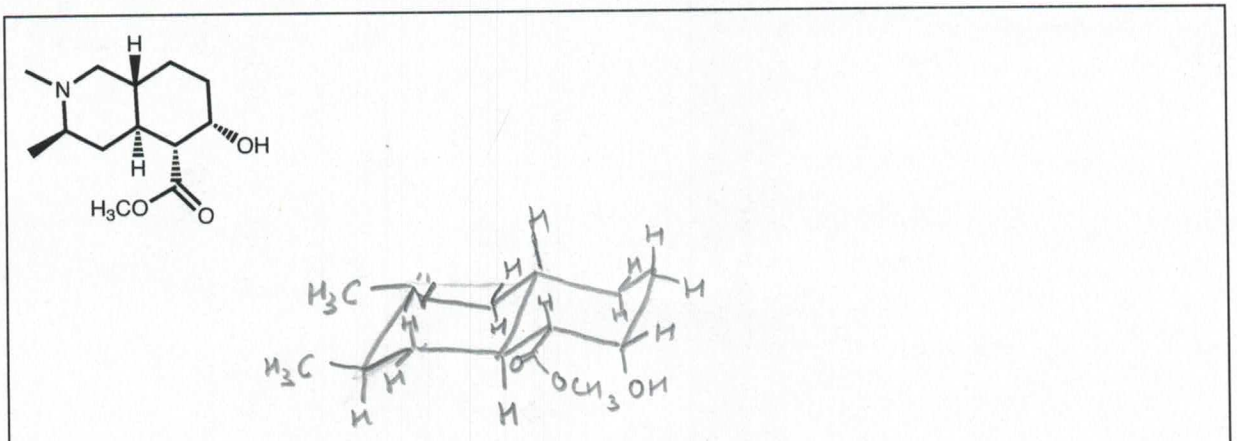


a. Assign the indicated stereocenters as *R* or *S* in the small boxes above.

b. Draw both chair conformations of the molecule below, which is similar to the ring on the far right of Yohimbine. Draw in all hydrogens and circle the most stable conformation.

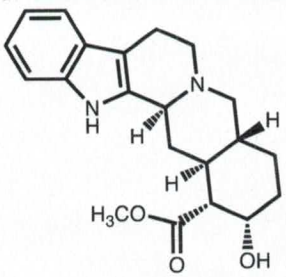


c. Draw a chair structure of the molecule below, which is comprised of two of the rings from Yohimbine. Can this molecule undergo ring flip? Why or why not?

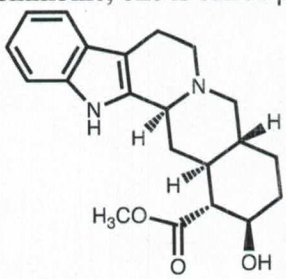


This cannot ring flip. Trans-decalin structures cannot flip because the rings are not long enough to stretch to a diaxial conformation

d. There are several isomers of Yohimbine, one is called β-yohimbine and is shown below.



Yohimbine



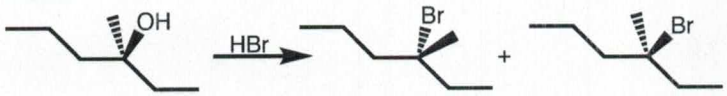
β-Yohimbine

Which is more stable, β-Yohimbine or Yohimbine? Explain your answer.

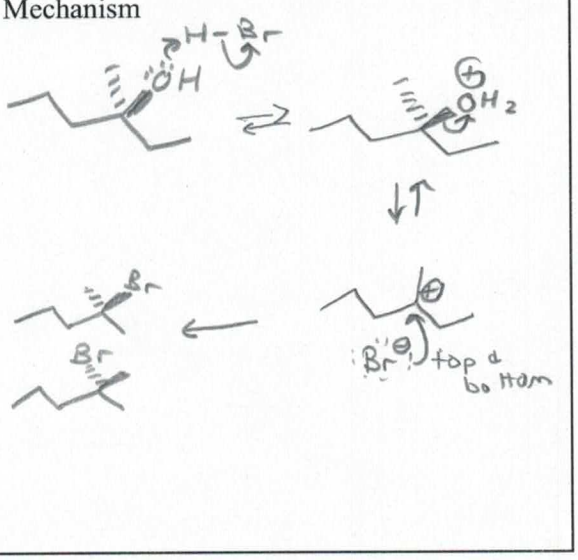
β-yohimbine because the ester & hydroxyl groups are equatorial, In yohimbine the hydroxyl group is axial

8. (28 points) The two reactions below produce different products. For each reaction, in box on the left, draw a mechanism of the reaction using arrows to show the flow of electrons. In the box on the right, draw a reaction coordinate diagram. Use the protonated alcohol as your starting material in the reaction coordinate diagram. In the diagram, label ΔG° for the reaction and $\Delta G^\ddagger$ for the rate determining step.

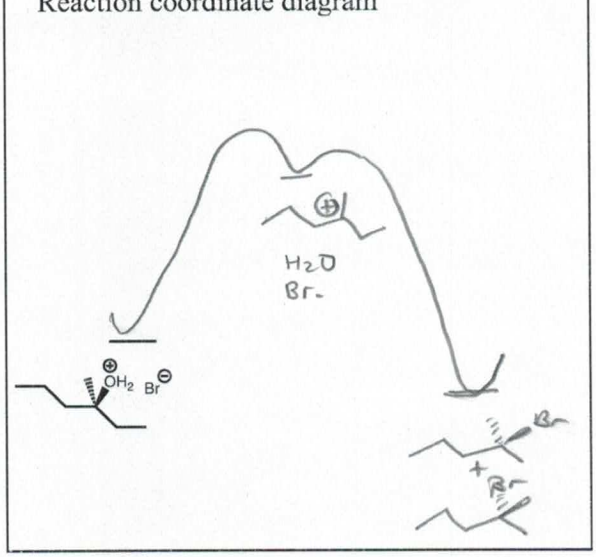
Reaction 1:



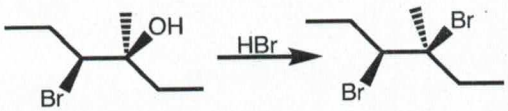
Mechanism



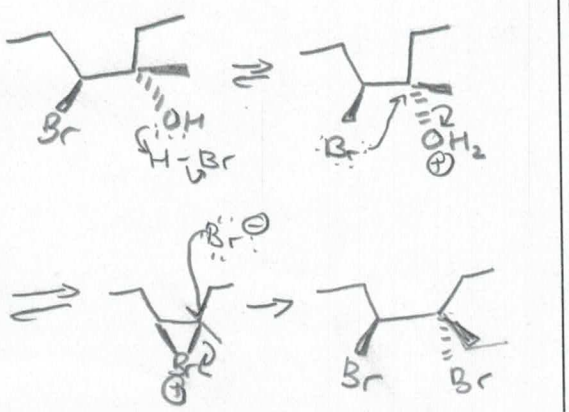
Reaction coordinate diagram



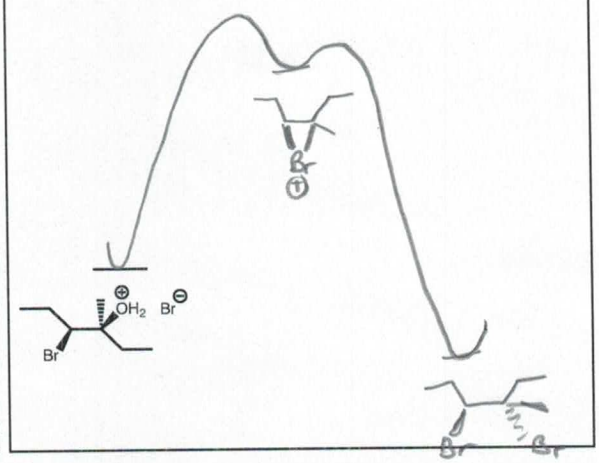
Reaction 2:



Mechanism



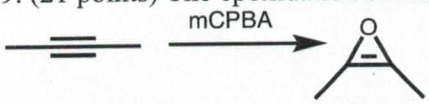
Reaction Coordinate Diagram



b. Which reaction do you expect to be faster? Explain your answer.

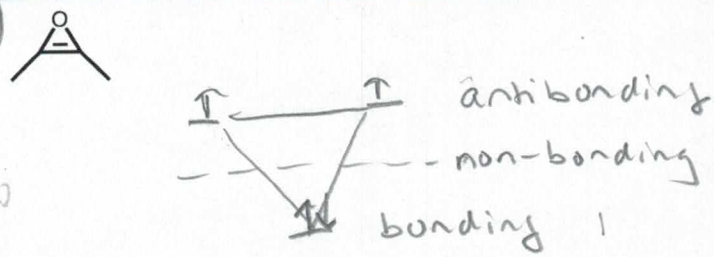
Reaction 2 will be faster.
The bromonium intermediate is much more stable than the carbocation because the bromonium has all octets. The transition state resembles the intermediate for both reaction so Reaction 2 is faster.

9. (21 points) The epoxidation of alkynes does not proceed readily because the product is very unstable.



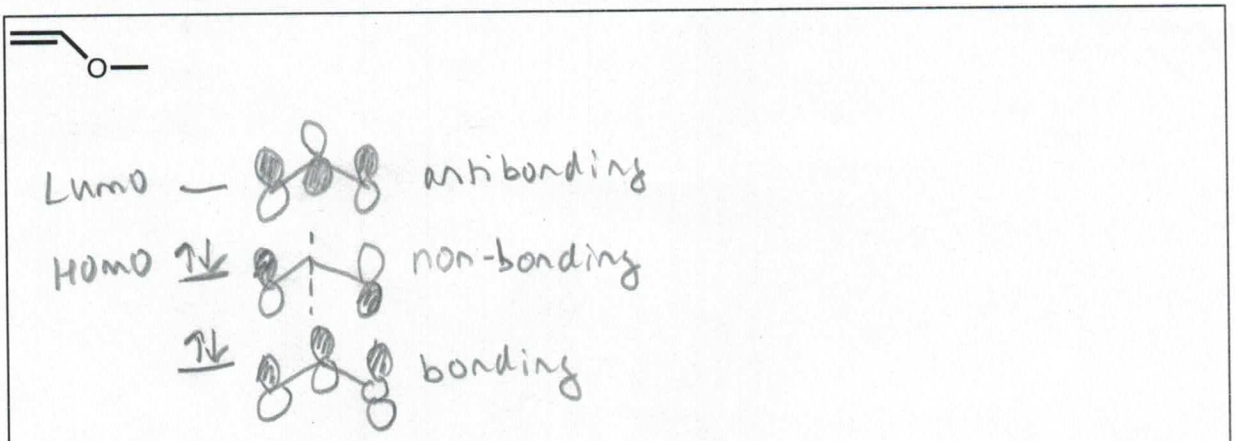
a. Using the Frost method, draw the energy levels for the product and explain why this product is unstable. Label i. the ~~HOMO, LUMO~~, ~~ii. all nodes~~, iii. bonding, antibonding, and non bonding orbitals and iv. Fill the orbitals with electrons. You do not need to sketch the orbitals.

Assume O sp^2 hybridized & planar



Unstable because when O is sp^2 hybridized molecule is antiaromatic w/ two half filled antibonding orbitals.

b. The related linear molecule below is relatively stable. Sketch the molecular orbitals for this molecule and fill the orbitals with electrons. Label i. the HOMO, LUMO, ii. all nodes, iii. bonding, antibonding, and non bonding orbitals and iv. Fill the orbitals with electrons.

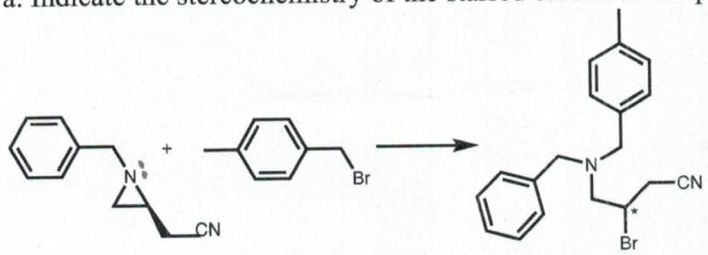


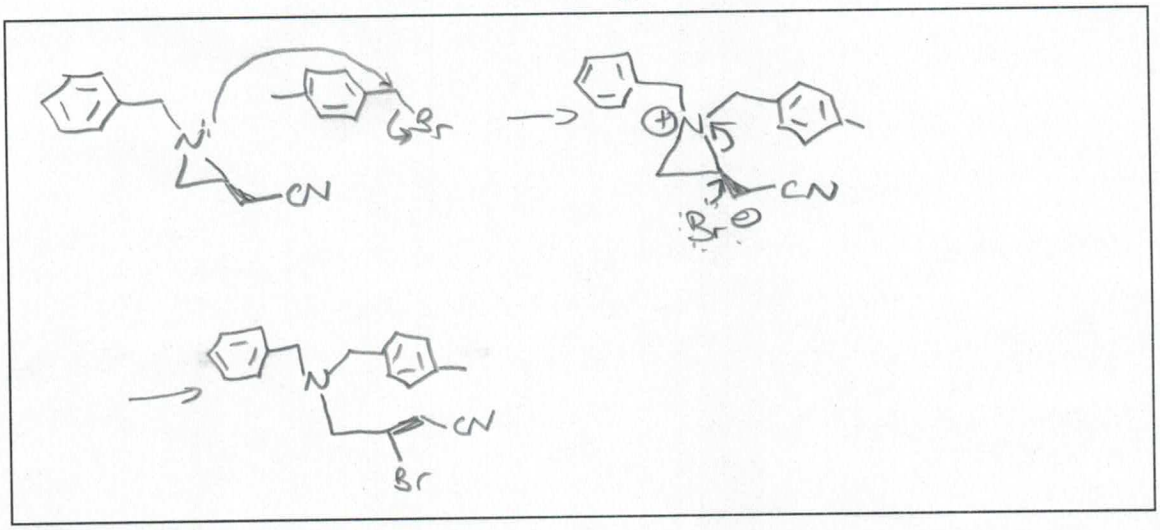
c. Explain why the linear molecule in part b is stable relative to the cyclic molecule in part a.

In the linear molecule the non-bonding orbitals has electrons but antibonding is empty
In contrast,  has two-half filled antibond orbitals & no net bond.

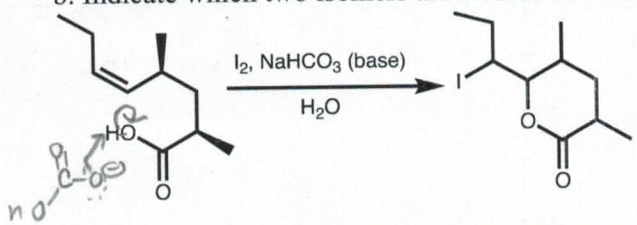
10. (18 points) Draw the mechanisms of the following reactions using arrows to indicate the flow of electrons.

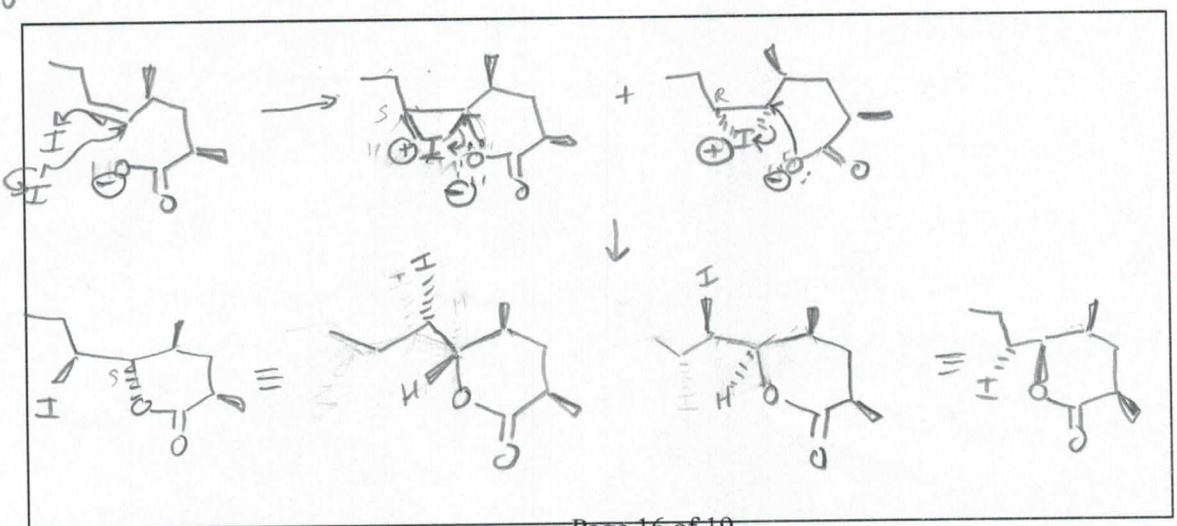
a. Indicate the stereochemistry of the starred carbon in the product.



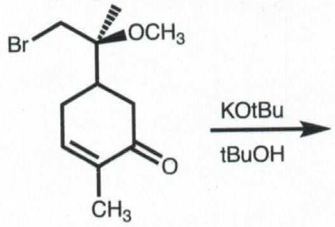


b. Indicate which two isomers are formed in this reaction.

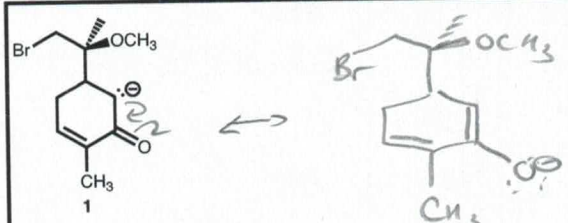


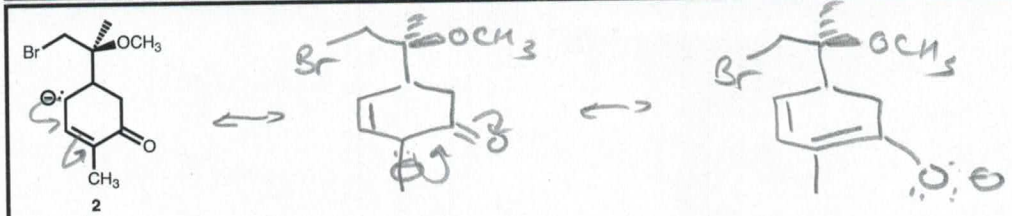


11. (20 points) You decide to perform the following reaction.



a. You expect one of two anions to form. Draw the resonance structures of each in the boxes below.

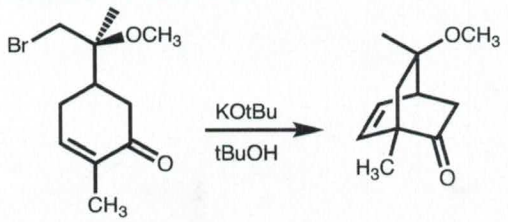


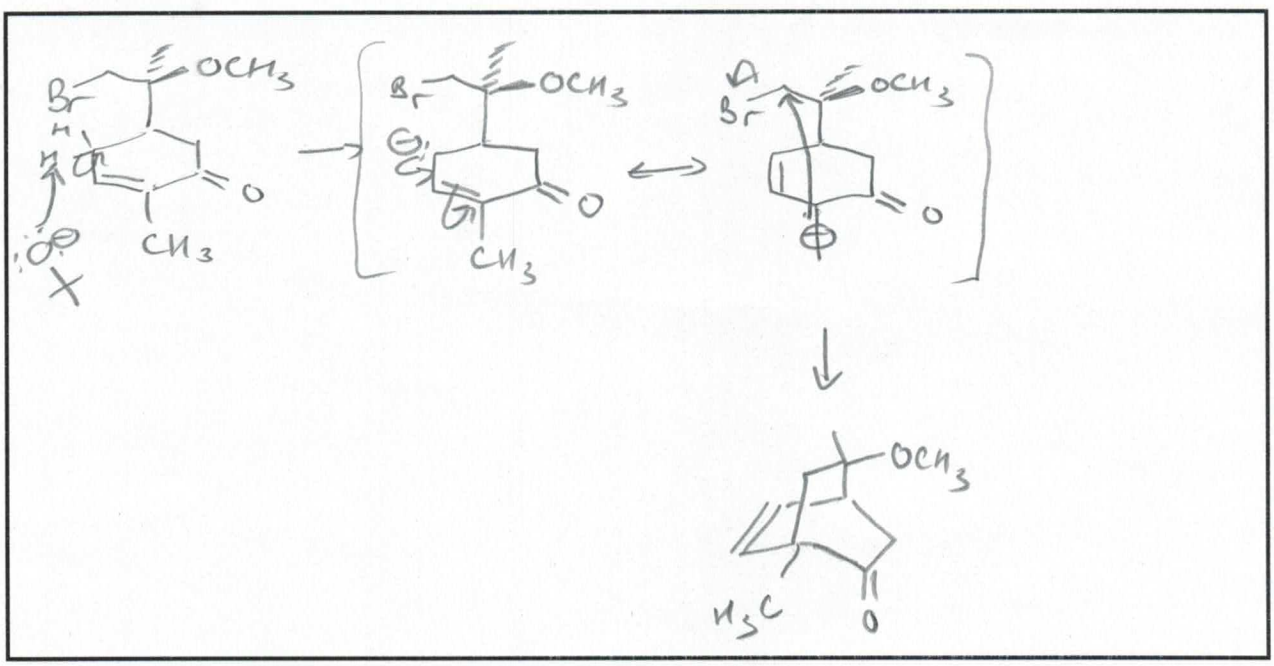


b. Which anion is more stable? Explain your answer.

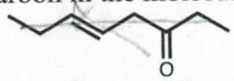
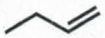
2 is more stable because charge is spread out over more atoms in more resonance structures

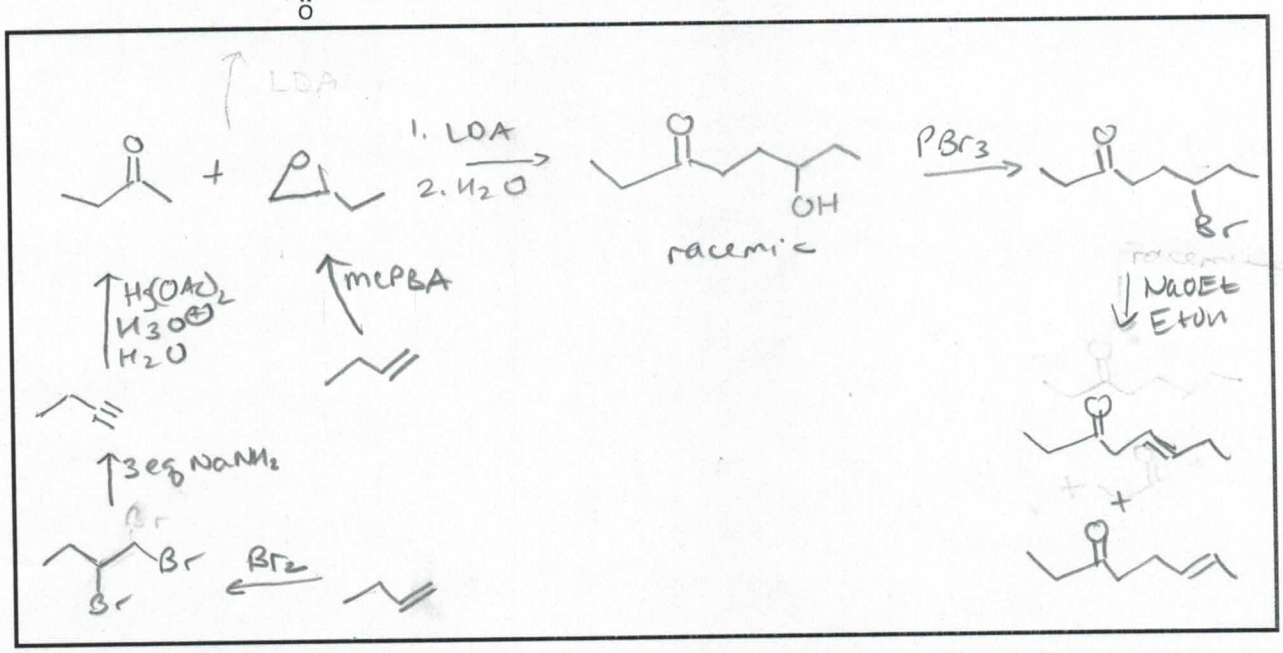
c. The product of the reaction is shown below. Draw a mechanism of this reaction using arrows to show the flow of electrons.



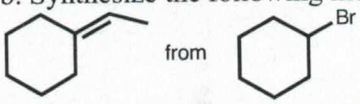


12. (26 points) a. Synthesize the following molecule using the indicated starting material as the only source of carbon in the molecule. You may use any other reagents.

Synthesize  from 



b. Synthesize the following molecule using the indicated starting material and any other reagents.

 from