

**LAST NAME:** \_\_\_\_\_**FIRST NAME:** \_\_\_\_\_**Student number:** \_\_\_\_\_

## **CHM1321 C: ORGANIC CHEMISTRY I**

### **MIDTERM 1A - 2016**

Time allowed: 80 minutes

There are 9 pages in this test. A periodic table is provided at the end. You may GENTLY remove this page and use it to cover your work. Any scratch work should be done on this page. You may keep this page afterwards if you wish.

Molecular model kits (in a clear plastic bag or container) are allowed. Calculators and all other aids are not allowed. You may answer in pen or pencil, and may use different colours.

Please show all work to receive part marks.

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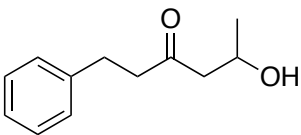
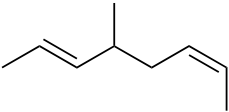
By signing below, you acknowledge that you have read and ensured that you are complying with the above statement.

Signature: \_\_\_\_\_

Part	A	B	C	Total
Points	10 (+2)	20	20	50 (+2)
Mark				
TA				

**Part A – 1 or 2 points per question**

1. (5 pts) Give the line structure or the IUPAC names for the following compounds:

STRUCTURE	NAME
	
	<i>m</i> -diethylbenzene
	

2. (0.5 pt) In valence bond theory, which atomic orbitals overlap to form the  $\sigma_{C-H}$  molecular orbitals of ethane,  $CH_3CH_3$ ?

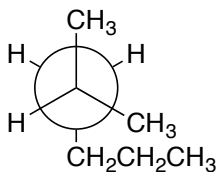
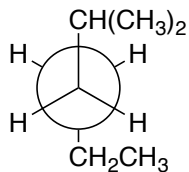
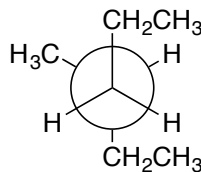
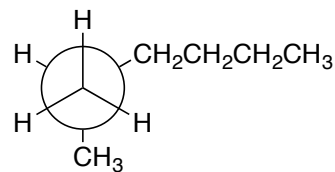
- C  $2p$  + H  $1s$
- C  $2sp$  + H  $1s$
- C  $2sp^2$  + H  $1s$
- C  $2sp^3$  + H  $1s$

3. (0.5 pt) The two chair conformers of *cis*-1,2-dibromocyclohexane are of equal stability.

TRUE

FALSE

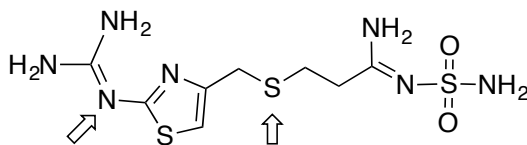
4. (0.5 pt) Which of the following Newman projections represents 3-methylhexane?

**A****B****C****D**

5. (0.5 pt) Which of the following is *not* true regarding the properties of alkanes?

- alkanes are nonpolar
- alkanes burn in air to give  $\text{H}_2\text{O}$  and  $\text{CO}_2$
- alkanes are highly miscible with water
- the strongest intermolecular force between alkane molecules are van der Waals interactions

6. (3 pts) The molecule shown below is known as Pepcid, a drug used to reduce gastric acid production. State the hybridization, geometry, and approximate bond angles of the indicated atoms.

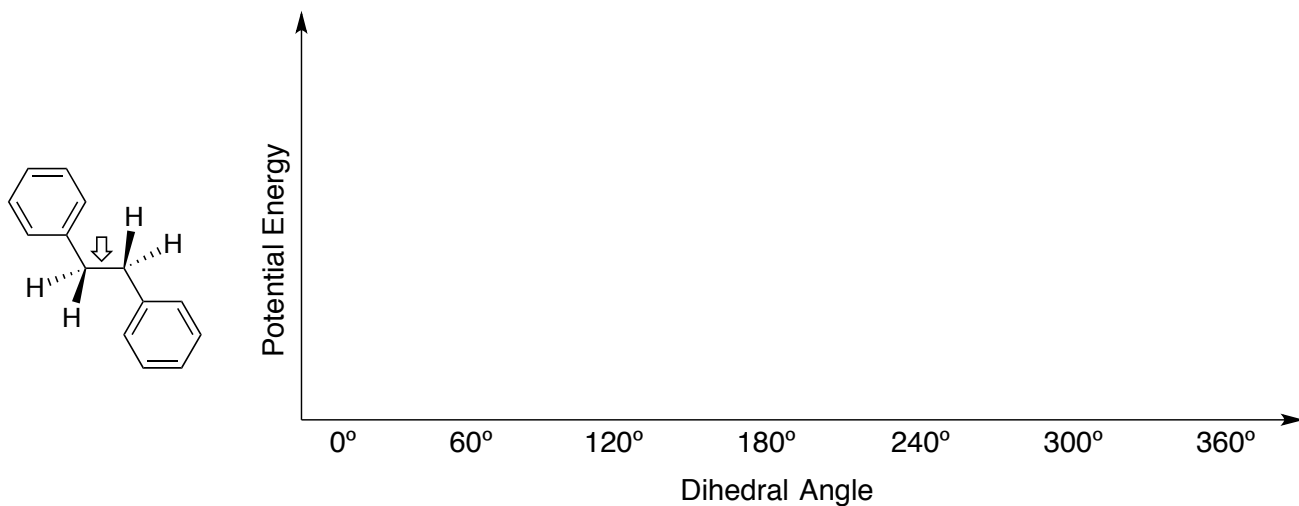


### BONUS (+1.5 pts)

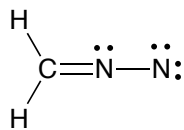
7. Draw line structures of three tertiary alcohols that have the formula  $\text{C}_6\text{H}_{14}\text{O}$ .

**Part B**

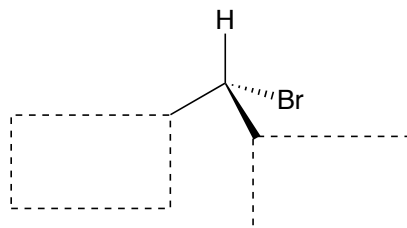
8. (5 pts) Consider the various conformers of following molecule along the indicated bond. On the following axes, sketch the potential energy diagram (as accurately as possible) as the bond is rotated. Draw and name the Newman projections for the highest and lowest energy conformers and label them on your graph.



9. (5 pts) Draw the two other possible resonance structures for the following species, using electron-pushing arrows to show the conversion between resonance forms. Label the most stable resonance form.

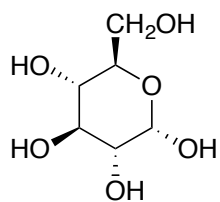


10. (2 pts) Complete the following diagram so that it represents (*R*)-2-bromobutane.



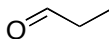
11. (3 pts) Clearly indicate the specific relationship (structural isomers, conformers, enantiomers, etc.) between the following pairs of molecules.


12. (5 pts) The molecule below is glucose, an important carbohydrate. Draw the two chair conformers of this compound and indicate the more stable conformer (if applicable).

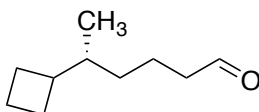


**Part C**

13. (6 pts) Draw the following molecule using the LCAO (hybridization) method. Label all the orbitals ( $p$ ,  $sp$ ,  $sp^2$ , or  $sp^3$ ) and the bonds ( $\sigma$  or  $\pi$ ). Include a legend if you're using different colours.



14. (4 pts) For the following molecule, identify any stereocentres with an asterisk (\*). Give the full name of the molecule (including any relevant stereochemistry). To receive full marks, show all your work.

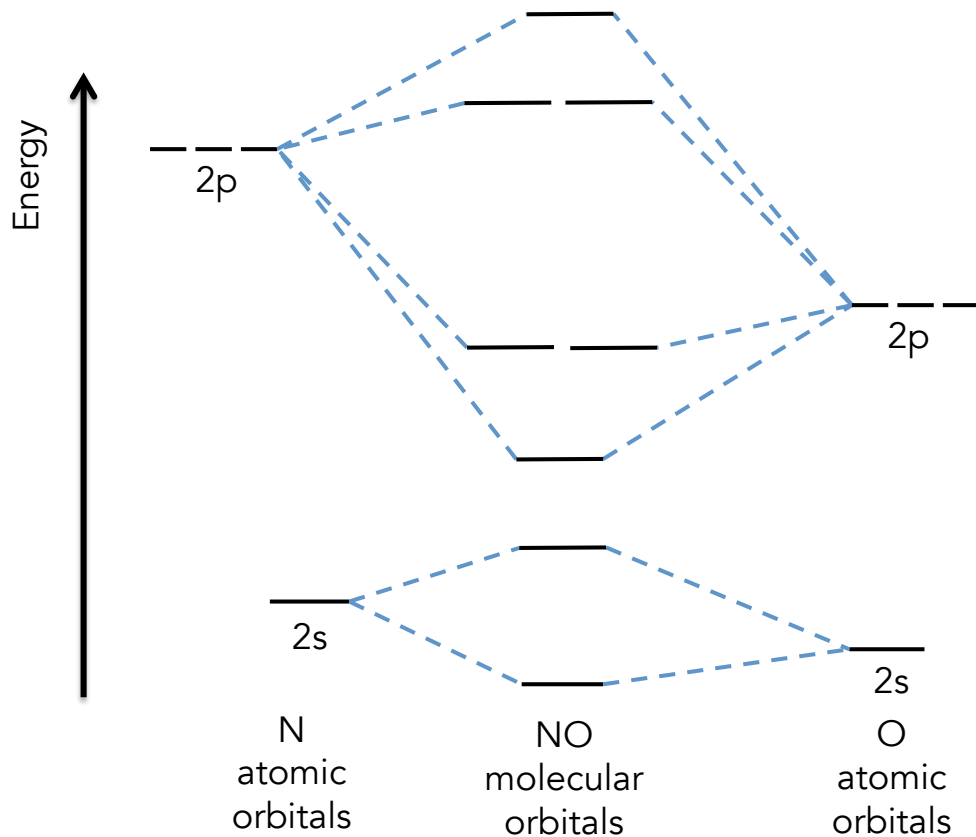


15. (5 pts) You are attempting to separate pentanal and 2-pentanol using TLC. In your first attempt, you use hexane as your mobile phase, and unfortunately obtained the resulting TLC at right (note that I've shown the spots as oval shapes).

- Why did this separation not work? Explain in one or two sentences.
- What modification would you make in your second attempt? Why?
- If you achieved a good separation on your second attempt, which compound would have the larger  $R_f$  value?



16.(5 pts) Using the template below, complete the molecular orbital diagram of NO by adding electrons and completing the appropriate labels. What is the bond order in this species? Why are the atomic orbitals of oxygen shown at a lower energy than nitrogen?



LAST NAME: \_\_\_\_\_

FIRST NAME: \_\_\_\_\_

Student number: \_\_\_\_\_

**CHM1321 C: ORGANIC CHEMISTRY I**  
**MIDTERM 2A - 2016**

Time allowed: 80 minutes

There are 10 pages in this test. A periodic table and pKa table are provided at the end. You may GENTLY remove these pages and use them to cover your work. Any scratch work should be done on these pages. You may keep them afterwards if you wish.

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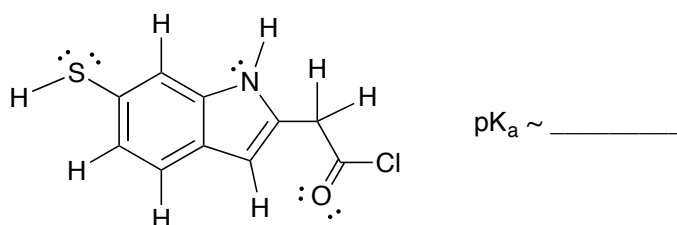
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Signature: \_\_\_\_\_

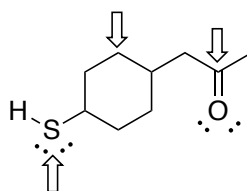
Part	A	B	C	Bonus	Total
Points	10	20	20	3	50
Mark					
TA					

**Part A – 1 or 2 points per question**

1. (2 pts) Circle the most acidic proton in the molecule shown below and give its approximate pKa value.

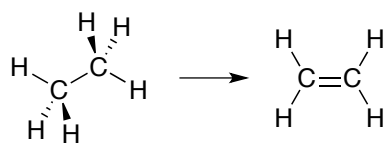


2. (0.5 pt) Reaction yields can be increased by the addition of a catalyst.    TRUE    FALSE
3. (1.5 pts) Label the indicated atoms as electrophilic, nucleophilic, or neither.

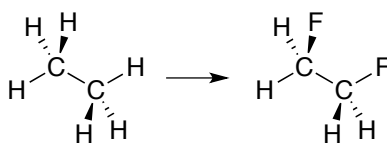


4. (0.5 pt) Circle the bond with the greatest ionic character.    C–Sn    C–Mg    C–Pb    C–Na

5. (1.5 pts) Identify the following transformations as either oxidations or reductions.



\_\_\_\_\_

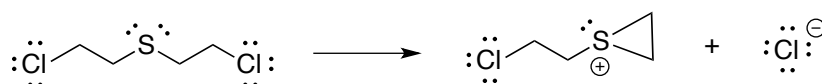


\_\_\_\_\_

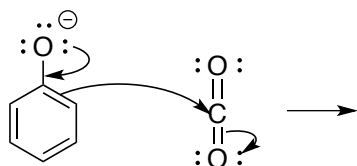


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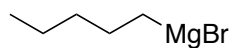
6. (1 pt) Add electron-pushing arrows to complete the mechanism of the following reaction.



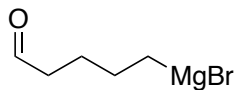
7. (1.5 pts) Using the electron-pushing arrows as a guide, draw the structure of the expected product.



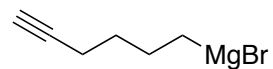
8. (1.5 pts) Label the following compounds as *feasible* or *unfeasible* Grignard reagents.



\_\_\_\_\_



\_\_\_\_\_

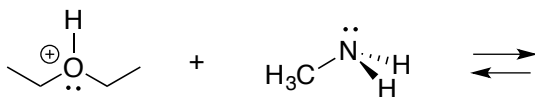


\_\_\_\_\_

**Part B**

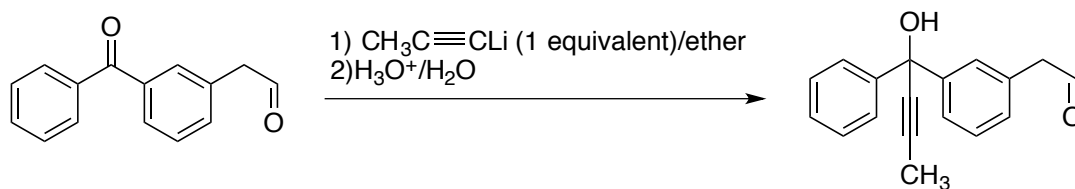
9. (4 pts) For the *acid-base* reaction below:

- Draw a mechanism and the expected products.
- Identify the acid, base, conjugate acid, and conjugate base.
- Does the equilibrium favour the starting materials or products? Justify your answer.

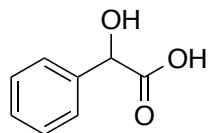


10. The reaction below shows an incorrect final product.

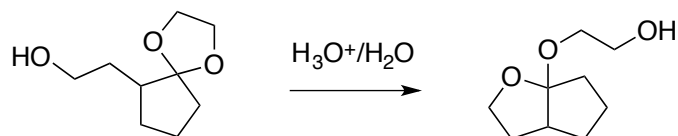
- (2 pts) Why is this the wrong product? Explain in one or two sentences.
- (4 pts) Draw the mechanism for the reaction, showing the formation of the correct final product.



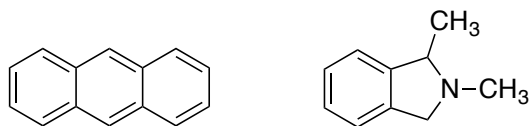
11. (3 pts) Create a retrosynthesis for the following product, starting from benzaldehyde.



12. (4 pts) Draw a mechanism to explain the following reaction.

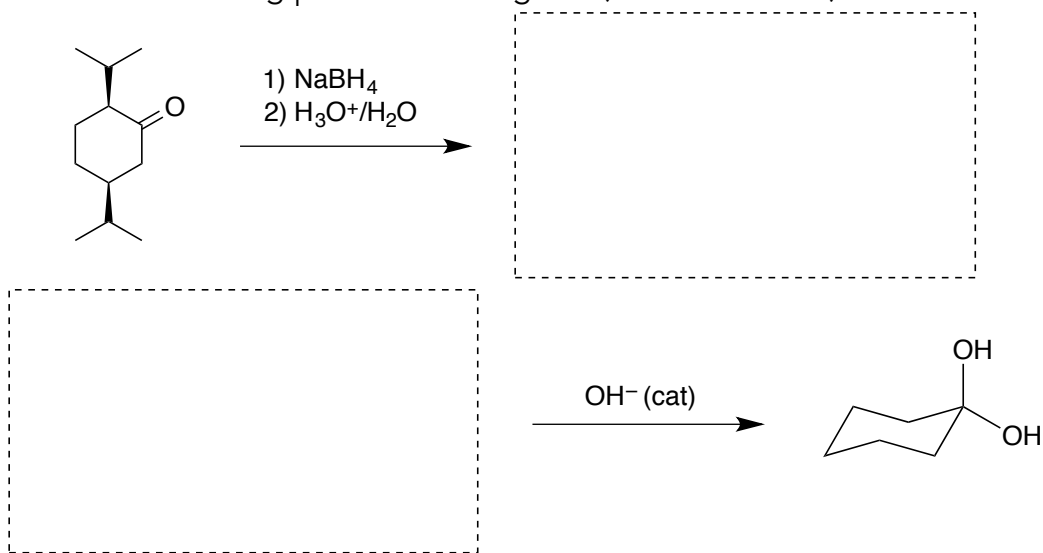


13. (3 pts) Describe how you would separate a mixture of the following two compounds. Both compounds are insoluble in water and soluble in ether. You may use chemical equations to support your answer.



### Part C

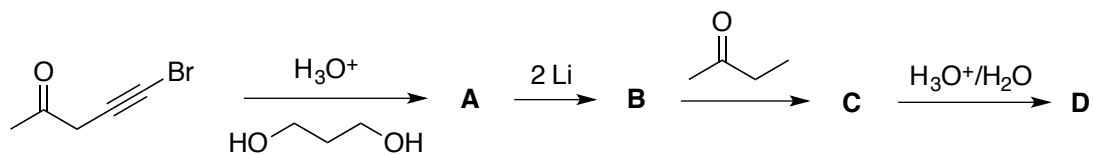
14. (3 pts) Provide the missing products or reagents (no mechanisms).



15. When propanoic acid reacts with sodium borohydride, 1-propanol is not obtained. However, bubbling is still observed and heat is produced.

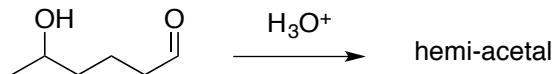
- (3 pts) Why is 1-propanol not obtained? Explain, using a reaction mechanism.
- (1 pt) What is the actual product of this reaction?

16. (4 pts) Provide the structures of the compounds **A** to **D** below.



<b>A</b>	<b>B</b>
<b>C</b>	<b>D</b>

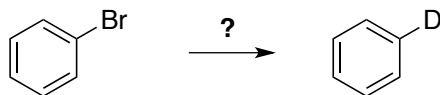
17. 5-hydroxyhexanal forms a hemi-acetal in acidic solution.



- (4 pts) Draw the mechanism of the reaction.
- (1 pt) How many stereoisomers are possible for 5-hydroxyhexanal?
- (4 pts) How many stereoisomers are possible for the hemi-acetal? Draw their structures unambiguously, and indicate which pairs are enantiomers.

**BONUS (+3 pts)**

Propose a synthesis (no mechanisms, just the steps) for the following transformation.



LAST NAME: \_\_\_\_\_ FIRST NAME: \_\_\_\_\_

Student number: \_\_\_\_\_ Seat Number: \_\_\_\_\_

**CHM1321 C: ORGANIC CHEMISTRY I**  
**FINAL EXAM – APRIL 2016**

Professor: Dr. K.-S. Focsaneanu (Fox)

Time allowed: 3 hours

Part	A	B	C	Lab	Bonus	Total
Points	20	40	25	15	+3	100 (+ 3)
Mark						
TA						

There are 16 pages in this exam. A periodic table and pKa table are provided at the end. You may GENTLY remove these pages and use them to cover your work. Any scratch work should be done on these pages or on the supplied scrap paper. You may keep them afterwards if you wish.

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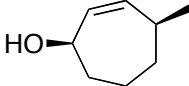
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Signature: \_\_\_\_\_

*I loved being your instructor this semester. Good luck on this exam and in your future studies!*

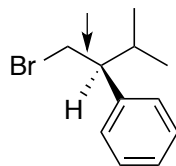
**Part A**

1. (2.5 pts) In the following table, provide the missing IUPAC name or line structure.

Name	Structure
	 <p>The structure shows a seven-membered ring with a double bond between the top and top-right carbons. A hydroxyl group (HO) is attached to the left carbon of the ring. A methyl group is attached to the top-right carbon of the ring, pointing upwards and to the right.</p>
3- <i>tert</i> -butyldecanal	

2. (0.5 pt) The awesome German word used to indicate a switch in polarity at a carbon atom (from positive to negative, or visa versa) is \_\_\_\_\_.
3. (5 pts) In the space below, sketch the  $\pi$  and  $\pi^*$  molecular orbitals of a C=C bond and a C=O bond. Why are they shaped slightly differently?

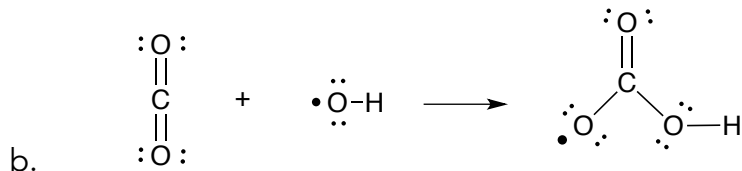
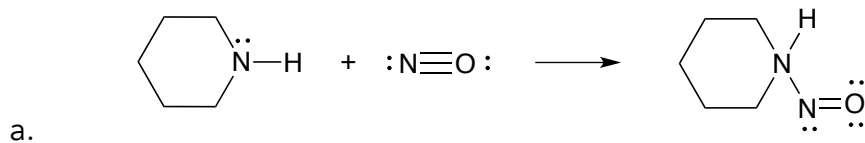
4. (2 pts) Draw and name the Newman projection for the most stable conformer of the molecule below along the C1–C2 bond (indicated with an arrow).



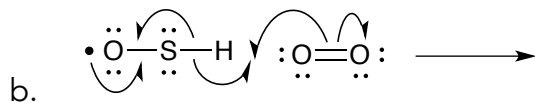
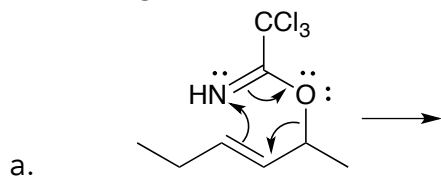
5. (3 pts) From the following molecules, circle the aromatic compound. In the space below, draw the LCAO orbital diagram of the  $\pi$  system of the molecule you've chosen.



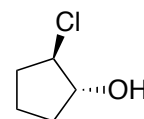
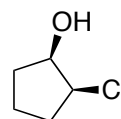
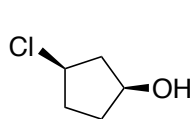
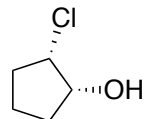
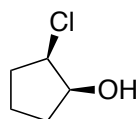
6. (2.5 pts) Add formal charges and electron-pushing arrows as needed to complete the following reactions:



7. (2.5 pts) Using the electron-pushing arrows as a guide, draw the expected product of the following reactions.



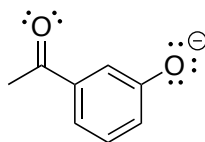
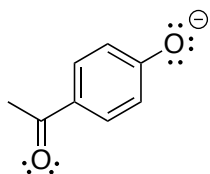
8. (2 pts) Clearly indicate the specific relationship (structural isomers, conformers, enantiomers, diastereoisomers, etc.) between molecule **A** and structures **B** through **E**.



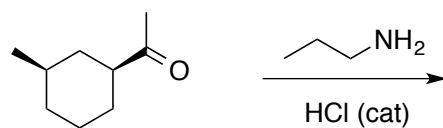
A and B are:	A and C are:
A and D are:	A and E are:

**Part B**

9. (6 pts) Which ion is more stable? Use resonance structures to find your answer. Label each resonance structure as either a MAJOR or MINOR contributor to the overall hybrid.



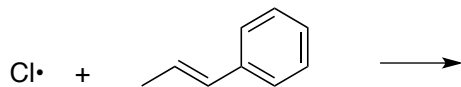
10. Consider the following reaction:



a. (5 pts) Draw the full mechanism and show the final product of the following reaction. Clearly indicate any stereochemistry, if necessary.

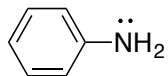
b. (3 pts) Draw the two chair conformers of your product and indicate which chair is the more stable conformer.

11. Consider the following elementary step, which is part of a free radical chain reaction:



- (3 pts) Draw the mechanism and product of this step.
- (1 pt) What is the name of this type of reaction? \_\_\_\_\_
- (4 pts) Give two reasons to explain the regioselectivity of your product. In your answer, include all the relevant resonance structures.

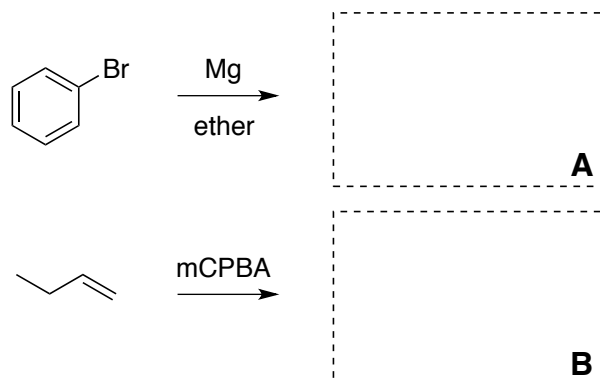
12. For the following molecule:



- (3 pts) Draw the mechanism and products of the acid-base reaction of this molecule with  $\text{H}_3\text{O}^+$ .
- (2 pts) Are the reactants or products favoured? Justify your answer.

13. The following is synthesis for the formation of a fragrance from bromobenzene.

a. (2 pts) First, draw the structures of the products of these reactions.

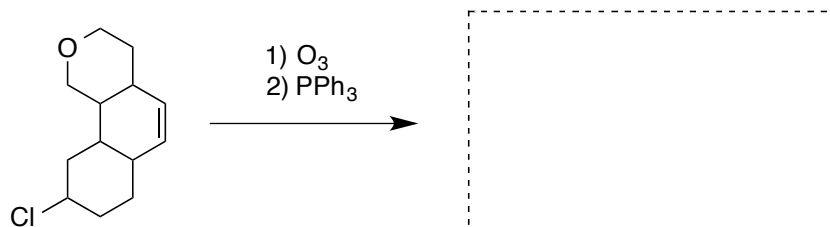


b. (3 pts) Now, draw the mechanism for the reaction of A and B together, followed by aqueous acid workup:

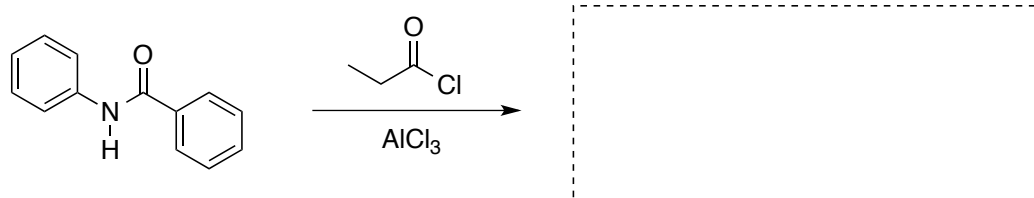
c. (3 pts) How many stereoisomers are possible for the final product? Draw their structures unambiguously, and label any stereocentres as *R* or *S*.

14. (5 pts) Complete the following by providing the missing product or reagents (no mechanisms). Show stereochemistry, when necessary.

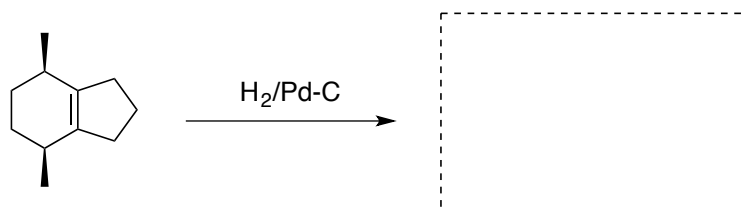
a.



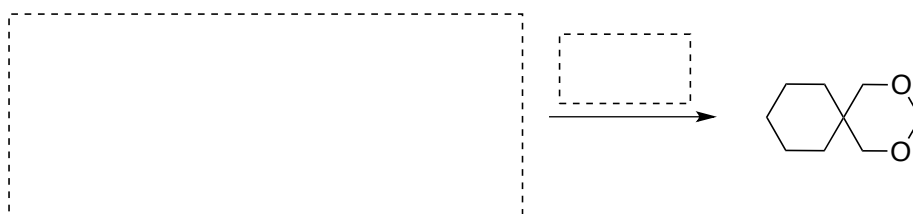
b.



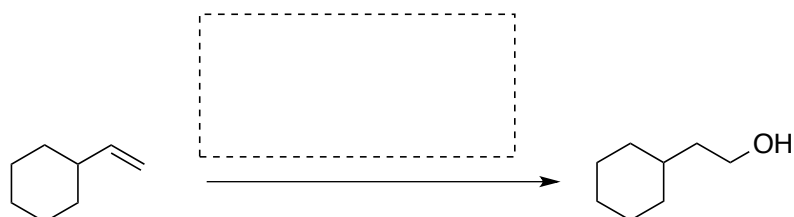
c.



d.

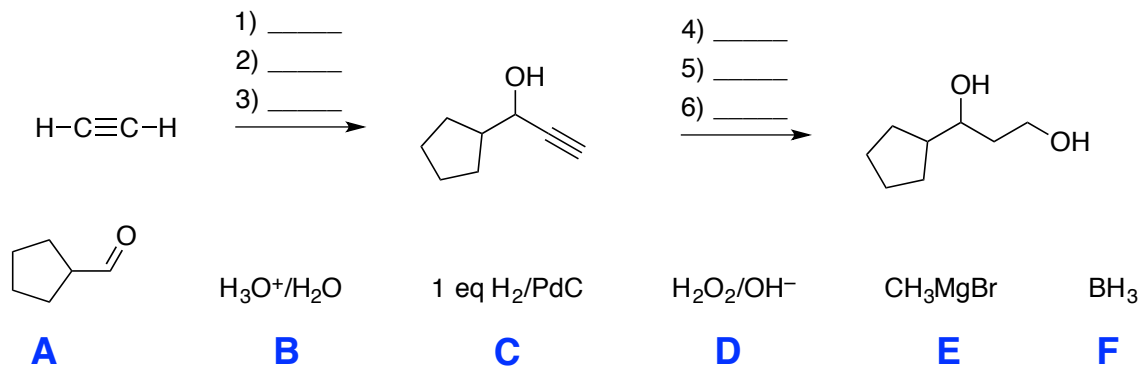


e.





16. (6 pts) Place the following reagents in the correct order to complete the synthesis below. Each reagent is used only once.

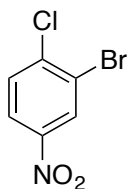


17. These two products, **A** and **B**, come from the same original starting material, but are synthesized via two different routes.

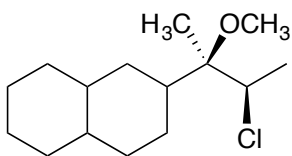


- (1 pt) What is the original starting material? Draw its structure.
- (3 pts) Show the two different routes to **A** and **B** (no mechanisms). Label the products as either *SYN* or *ANTI*.

18. (3 pts) Create a complete retrosynthesis for the following compound, starting from benzene.



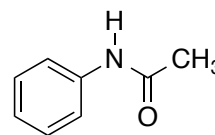
19. (3 pts) Propose a synthesis of the compound below starting from an alkene and using any other reagents that you require. Make sure that the compound below is the major product in your synthesis.



## Laboratory Section

20. Consider the following experimental procedure from the nitration of acetanilide:

“Place 1.00 g of acetanilide in a 25 mL round bottom flask. Add 3 mL of  $\text{H}_2\text{SO}_4$  to dissolve the solid and cool the solution in an ice bath. In a 50 mL Erlenmeyer flask, carefully combine 0.80 mL  $\text{HNO}_3$  and 1.4 mL sulfuric acid, and add slowly to the round-bottom flask . Allow to react for 10 min, with stirring.”



- (3 pts) What is the function of the sulfuric acid? Explain, using a sentence and a chemical reaction.
- (3 pts) Draw the structures of the two expected products, and indicate which is the major product and which is the minor product. Why are they not formed in equal amounts?
- (5 pts) Is nitration of acetanilide kinetically faster or slower than nitration of plain benzene? Draw reaction intermediates and a reaction energy profile to support your answer.

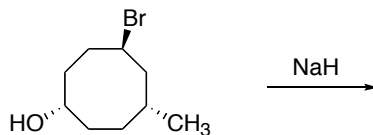
21. (4 pts) From the list below, circle the strongest intermolecular force found in acetone.

DIPOLE–DIPOLE      HYDROGEN–BONDING      ION-DIPOLE  
DIPOLE–INDUCED DIPOLE      INDUCED DIPOLE–INDUCED DIPOLE

In the space below, draw a representation of the force you have selected occurring between at least 3 acetone molecules.

### Bonus

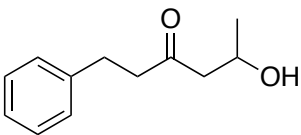
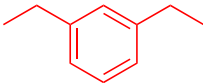
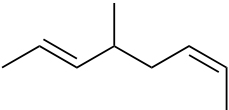
What is the expected product of the following reaction? Draw a mechanism to show how it is formed.



Part	A	B	C	Total
Points	10 (+2)	20	20	50 (+2)
Mark				
TA				

### Part A – 1 or 2 points per question

1. (5 pts) Give the line structure or the IUPAC names for the following compounds:

STRUCTURE	NAME
	5-hydroxy-1-phenyl-3-hexanone
	m-diethylbenzene
	(2E,6Z)-4-methyl-2,6-octadiene

2. (0.5 pt) In valence bond theory, which atomic orbitals overlap to form the  $\sigma_{C-H}$  molecular orbitals of ethane,  $CH_3CH_3$ ?

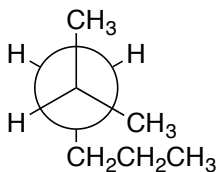
- C 2p + H 1s
- C 2sp + H 1s
- C 2sp<sup>2</sup> + H 1s
- C 2sp<sup>3</sup> + H 1s

3. (0.5 pt) The two chair conformers of *cis*-1,2-dibromocyclohexane are of equal stability.

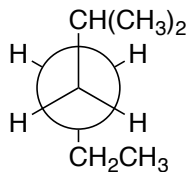
TRUE

FALSE

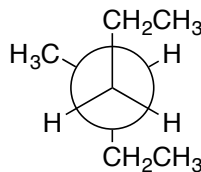
4. (0.5 pt) Which of the following Newman projections represents 3-methylhexane?



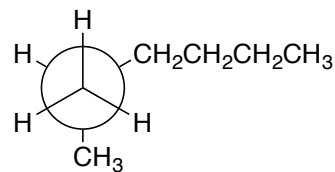
A



B



C

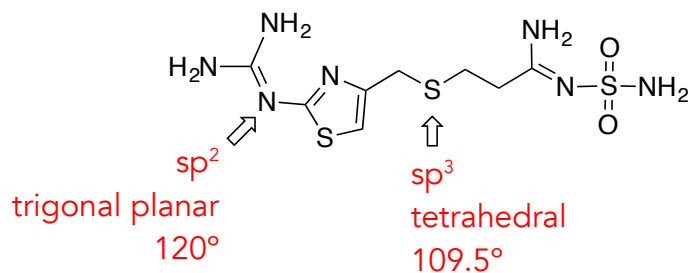


D

5. (0.5 pt) Which of the following is *not* true regarding the properties of alkanes?

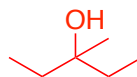
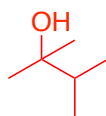
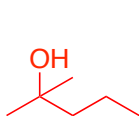
- alkanes are nonpolar
- alkanes burn in air to give  $\text{H}_2\text{O}$  and  $\text{CO}_2$
- alkanes are highly miscible with water
- the strongest intermolecular force between alkane molecules are van der Waals interactions

6. (3 pts) The molecule shown below is known as Pepcid, a drug used to reduce gastric acid production. State the hybridization, geometry, and approximate bond angles of the indicated atoms.



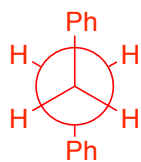
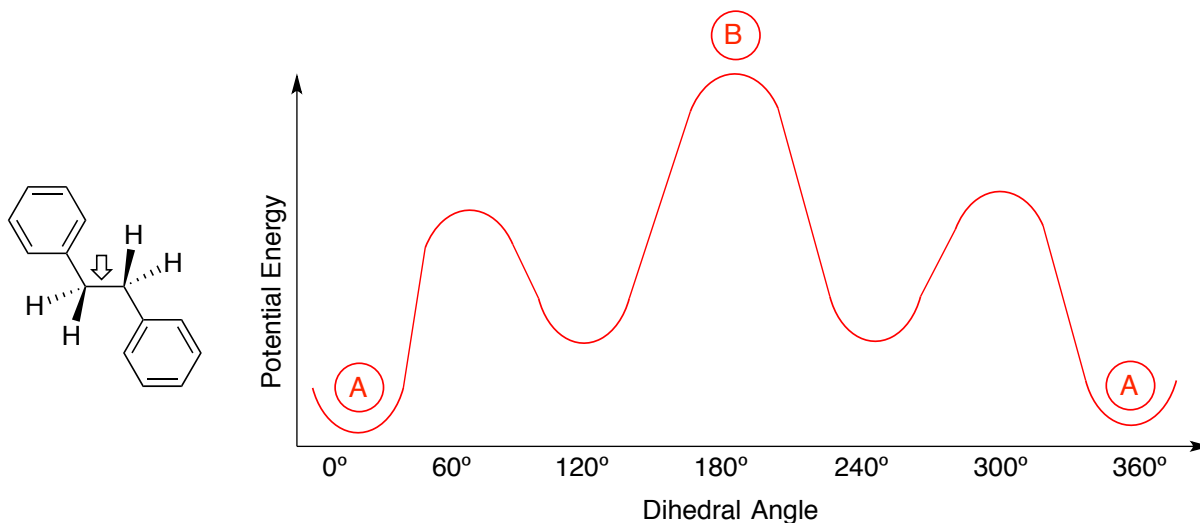
**BONUS (+1.5 pts)**

7. Draw line structures of three tertiary alcohols that have the formula  $\text{C}_6\text{H}_{14}\text{O}$ .



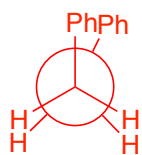
## Part B

8. (5 pts) Consider the various conformers of following molecule along the indicated bond. On the following axes, sketch the potential energy diagram (as accurately as possible) as the bond is rotated. Draw and name the Newman projections for the highest and lowest energy conformers and label them on your graph.



(A)

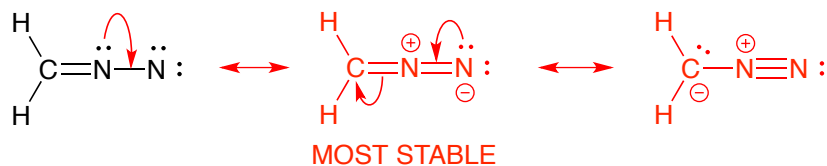
LOWEST ENERGY  
ANTI-STAGGERED



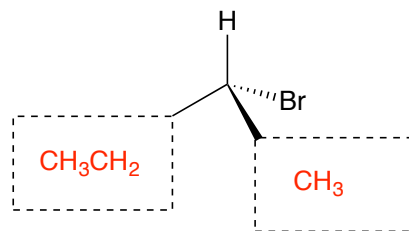
(B)

HIGHEST ENERGY  
ECLIPSED

9. (5 pts) Draw the two other possible resonance structures for the following species, using electron-pushing arrows to show the conversion between resonance forms. Label the most stable resonance form.



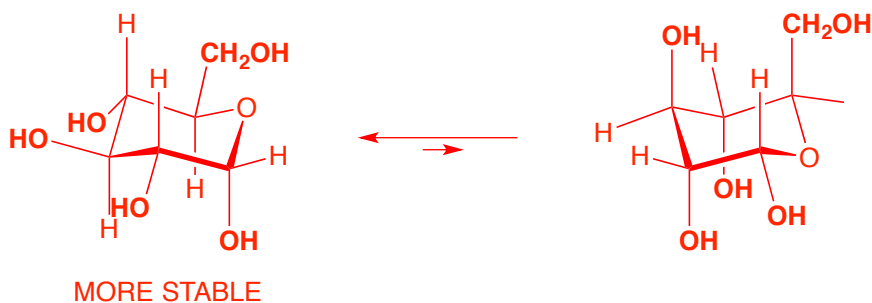
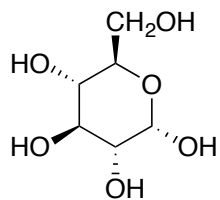
10. (2 pts) Complete the following diagram so that it represents (*R*)-2-bromobutane.



11. (3 pts) Clearly indicate the specific relationship (structural isomers, conformers, enantiomers, etc.) between the following pairs of molecules.

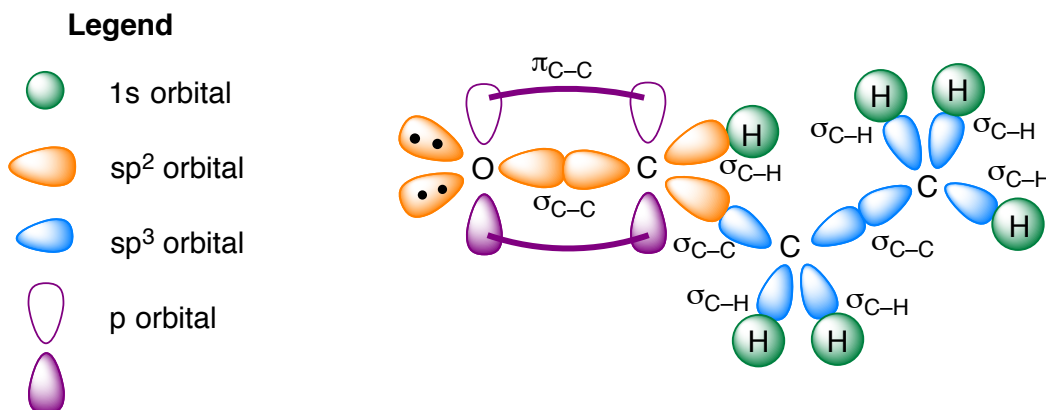
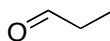
	<b>DIASTEREOMERS</b>
	<b>STRUCTURAL ISOMERS</b>
	<b>CONFORMERS</b>

12. (5 pts) The molecule below is glucose, an important carbohydrate. Draw the two chair conformers of this compound and indicate the more stable conformer (if applicable).

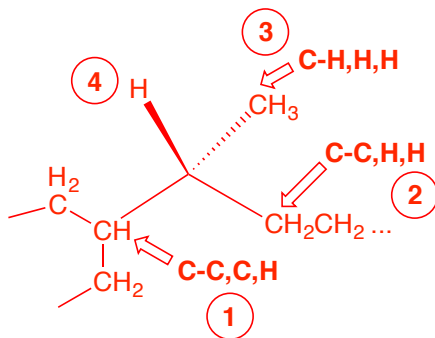
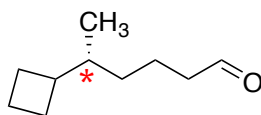


## Part C

13. (6 pts) Draw the following molecule using the LCAO (hybridization) method. Label all the orbitals ( $p$ ,  $sp$ ,  $sp^2$ , or  $sp^3$ ) and the bonds ( $\sigma$  or  $\pi$ ). Include a legend if you're using different colours.



14. (4 pts) For the following molecule, identify any stereocentres with an asterisk (\*). Give the full name of the molecule (including any relevant stereochemistry). To receive full marks, show all your work.



R-5-cyclobutylhexanal

15. (5 pts) You are attempting to separate pentanal and 2-pentanol using TLC. In your first attempt, you use hexane as your mobile phase, and unfortunately obtained the resulting TLC at right (note that I've shown the spots as oval shapes).

- Why did this separation not work? Explain in one or two sentences.
- What modification would you make in your second attempt? Why?
- If you achieved a good separation on your second attempt, which compound would have the larger  $R_f$  value?

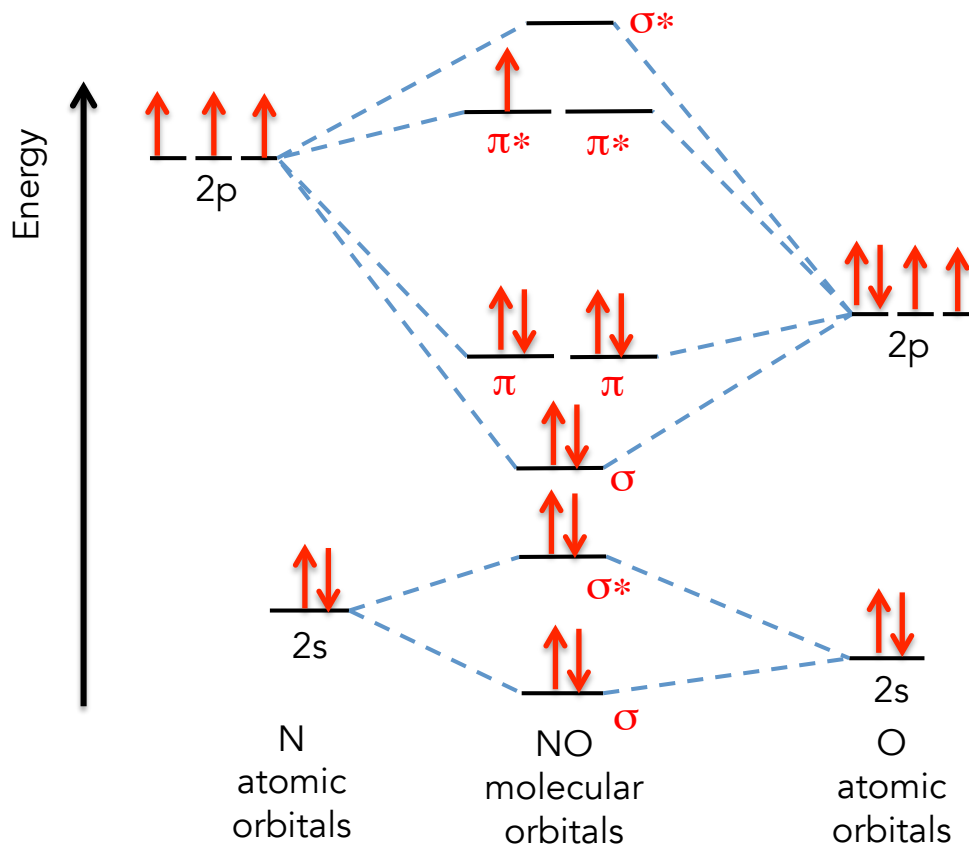


a). Hexane is too non-polar a solvent to use as a mobile phase: the solutes (an aldehyde and an alcohol, both polar substances) instead have strong intermolecular forces with the very polar stationary phase, and thus do not migrate appreciably.

b). I'd try increasing the polarity of the mobile phase, perhaps by mixing hexane with something like ethyl acetate (ideally, a range of mixtures, of increasing polarity, might be needed to find the best possible separation).

c). larger  $R_f$  = PENTANAL

16.(5 pts) Using the template below, complete the molecular orbital diagram of NO by adding electrons and completing the appropriate labels. What is the bond order in this species? Why are the atomic orbitals of oxygen shown at a lower energy than nitrogen?



Bond Order =  $(8 - 3)/2 = 2.5$

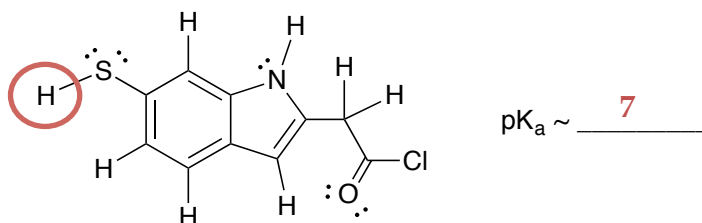
Oxygen's atomic orbitals appear at a lower energy (relative to nitrogen) due to the higher electronegativity of the atom.

Part	A	B	C	Bonus	Total
Points	10	20	20	3	50
Mark					
TA					

### Part A – 1 or 2 points per question

1. (2 pts) Circle the most acidic proton in the molecule shown below and give its approximate pKa value.

From: Exam 2015

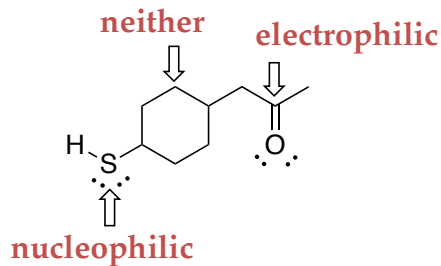


2. (0.5 pt) Reaction yields can be increased by the addition of a catalyst. TRUE **FALSE**

From: Midterm 2 2014

3. (1.5 pts) Label the indicated atoms as electrophilic, nucleophilic, or neither.

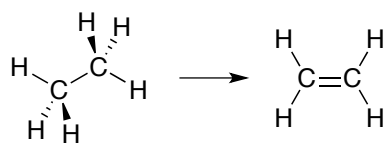
From: Sapling Assignment 5



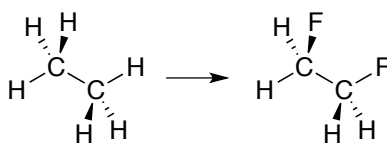
4. (0.5 pt) Circle the bond with the greatest ionic character. C-Sn C-Mg C-Pb **C-Na**

From: Midterm 2 2014

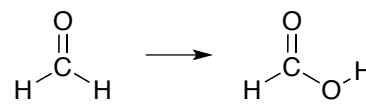
5. (1.5 pts) Identify the following transformations as either oxidations or reductions.



**oxidation**



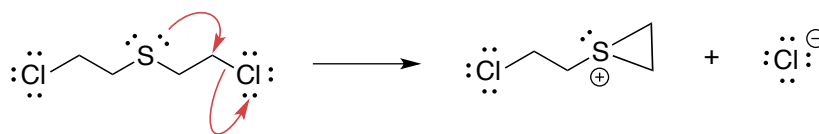
**oxidation**



**oxidation**

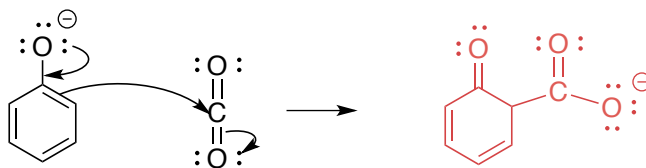
Similar to: Midterm 2 2015

6. (1 pt) Add electron-pushing arrows to complete the mechanism of the following reaction.



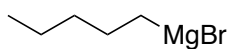
Similar to: past Midterms, Exams and Sapling Q's

7. (1.5 pts) Using the electron-pushing arrows as a guide, draw the structure of the expected product.

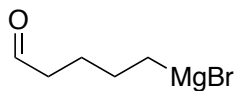


Similar to: past Midterms, Exams and Sapling Q's

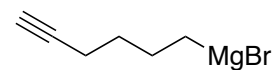
8. (1.5 pts) Label the following compounds as *feasible* or *unfeasible* Grignard reagents.



**feasible**



**unfeasible**



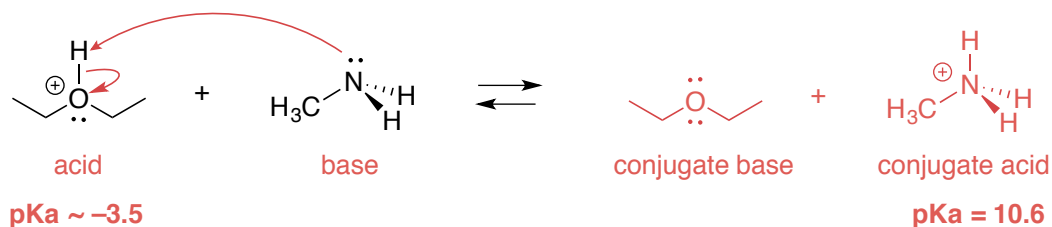
**unfeasible**

From: Sapling Practice Quiz 2

**Part B**

9. (4 pts) For the acid-base reaction below:

- Draw a mechanism and the expected products.
- Identify the acid, base, conjugate acid, and conjugate base.
- Does the equilibrium favour the starting materials or products? Justify your answer.

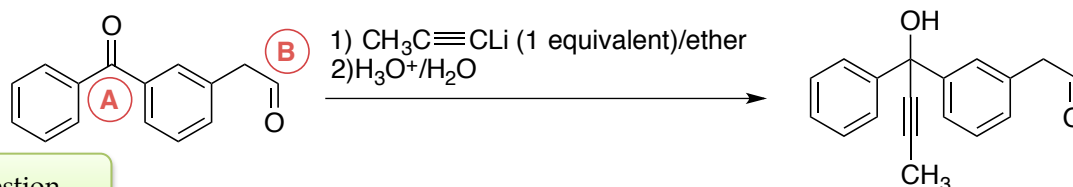


The reaction goes towards products, because the protonated ether is a stronger acid than the methylammonium ion (the preferred reaction direction is always from stronger acid to weaker acid).

Similar to: past Midterms (same question, different reaction)

10. The reaction below shows an incorrect final product.

- (2 pts) Why is this the wrong product? Explain in one or two sentences.
- (4 pts) Draw the mechanism for the reaction, showing the formation of the correct final product.

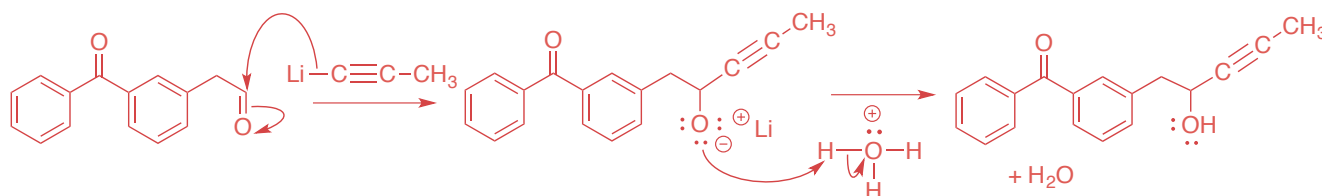


New question

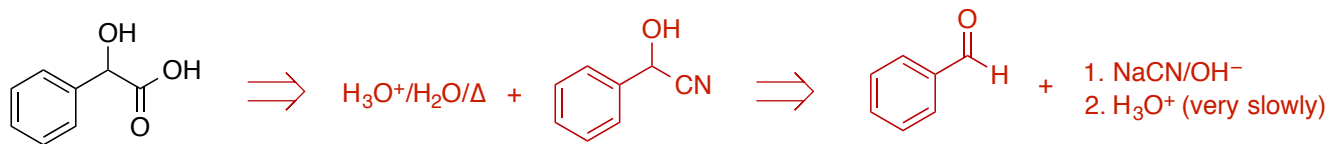
The nucleophile adds to the **WRONG CARBONYL**. Comparing the two electrophiles, labeled A and B above:

- A is a **KETONE**: the partial positive charge on the C atom is **REDUCED** due to hyperconjugation **AND** resonance effects. Additionally, the two phenyl groups reduce accessibility at the C atom.
- B is an **ALDEHYDE**: this carbonyl has greater ease of access (less steric repulsion) and a larger partial positive charge on the C atom (hyperconjugation only on one side, no resonance effects).

Therefore, B is the **STRONGER ELECTROPHILE** and will thus **REACT FASTER**, leading to the major product:



11. (3 pts) Create a retrosynthesis for the following product, starting from benzaldehyde.

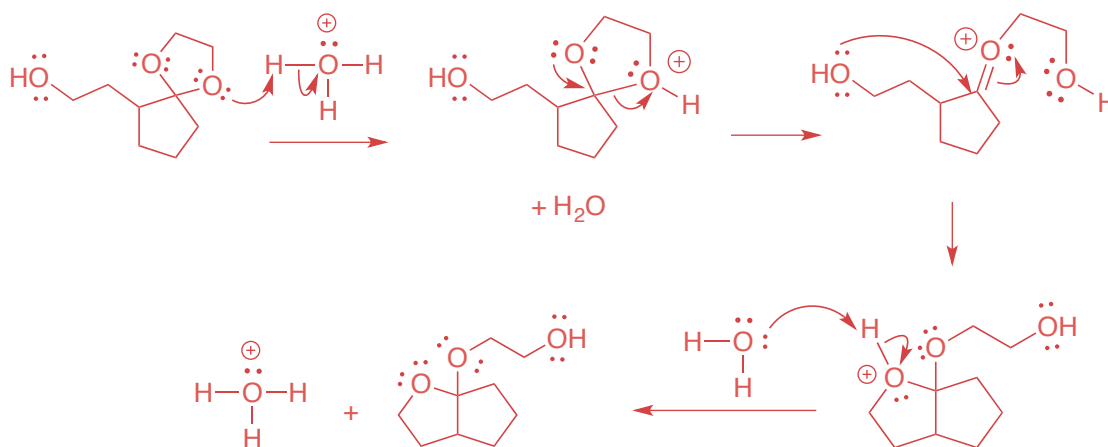
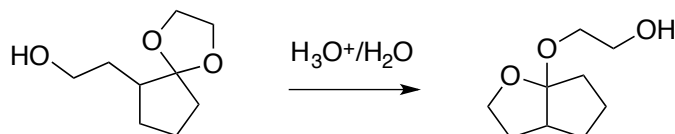


(formation of the cyanohydrin can be shown in one step or two, both are acceptable)

From: Exam 2015

12. (4 pts) Draw a mechanism to explain the following reaction.

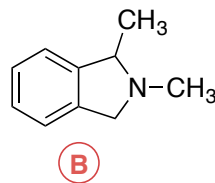
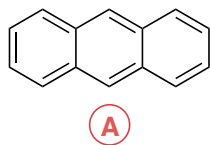
From: Problem Set #7



(a mechanism using a carbocation intermediate instead of the oxonium ion is also acceptable)

13. (3 pts) Describe how you would separate a mixture of the following two compounds. Both compounds are insoluble in water and soluble in ether. You may use chemical equations to support your answer.

From: Lab Manual,  
Expt #3 Q's



A is a completely non-polar hydrocarbon, whereas B is a tertiary amine. Tertiary amines are decent bases, so they can be easily protonated with a reasonably strong acid (say, 10% aqueous HCl).

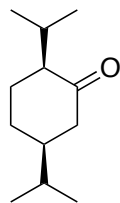
A general scheme for separation could thus be:

1. Dissolve the solid mixture in ether (both are soluble), creating a homogeneous solution.
2. Wash the ether with 10% aqueous acid solution and allow the two phases to separate: the now protonated amine ( $R_3NH^+$ ) will partition into the aqueous phase, leaving A in the organic phase.
3. Separate the two layers with a separatory funnel.
4. Wash the aqueous layer with excess base (e.g. 10% aqueous NaOH). This will deprotonate  $R_3NH^+$ , yielding back the original tertiary amine. Since this compound is insoluble in water, it will precipitate out of solution.

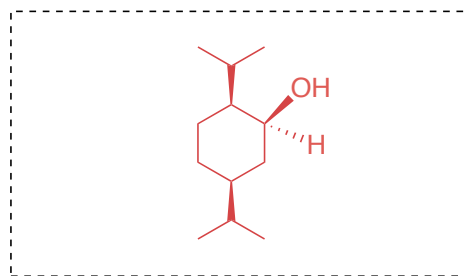
### Part C

5. (3 pts) Provide the missing products or reagents (no mechanisms).

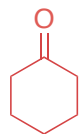
Similar to: Q's  
from Midterm 2  
2014 and 2015



1)  $NaBH_4$   
2)  $H_3O^+/H_2O$

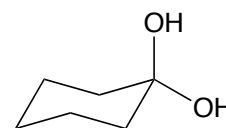


New question



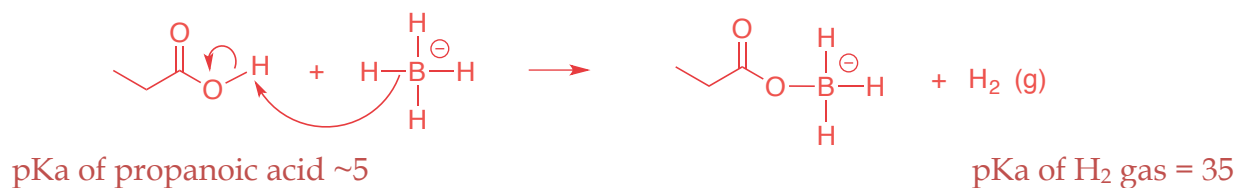
+  $H_2O$

$OH^-$  (cat)



6. When propanoic acid reacts with sodium borohydride, 1-propanol is not obtained. However, bubbling is still observed and heat is produced.
- (3 pts) Why is 1-propanol not obtained? Explain, using a reaction mechanism.
  - (1 pt) What is the actual product of this reaction?

Propanoic acid is an ACID, meaning it will undergo an acid-base reaction with the nucleophile (hydride) rather than undergo reduction. The observed bubbling is caused by the formation of hydrogen gas:



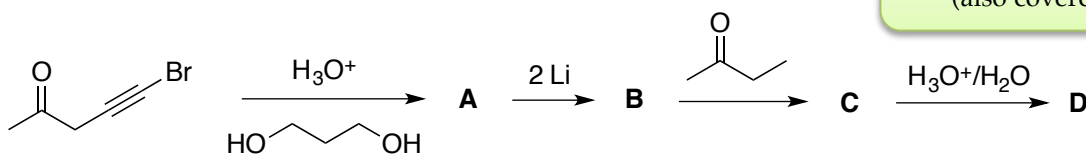
Therefore, this acid-base reaction is STRONGLY product favoured.

(If you showed this reaction occurring 3 more times to get the tetra-boroate ester, that's also acceptable – the main point is that you make hydrogen gas!)

From: Lab Manual,  
Expt #4 Q's

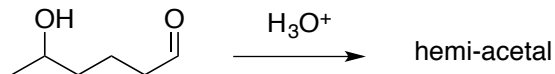
7. (4 pts) Provide the structures of the compounds **A** to **D** below.

Similar to: Q's from Midterm 2  
2014 and 2015  
(also covered in the DGD)



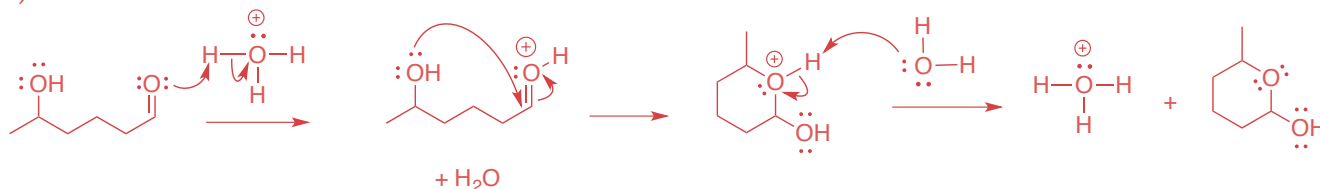
<p><b>A</b></p>	<p><b>B</b></p> <p>(the other Li forms LiBr)</p>
<p><b>C</b></p>	<p><b>D</b></p> <p>(+ HO(CH<sub>2</sub>)<sub>3</sub>OH)</p>

8. 5-hydroxyhexanal forms a hemi-acetal in acidic solution.



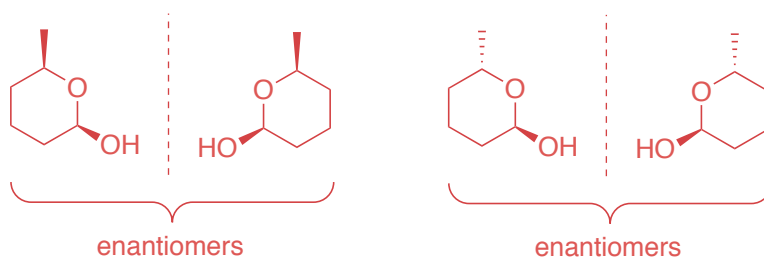
- (4 pts) Draw the mechanism of the reaction.
- (1 pt) How many stereoisomers are possible for 5-hydroxyhexanal?
- (4 pts) How many stereoisomers are possible for the hemi-acetal? Draw their structures unambiguously, and indicate which pairs are enantiomers.

a)



b) 2 (one stereocentre)

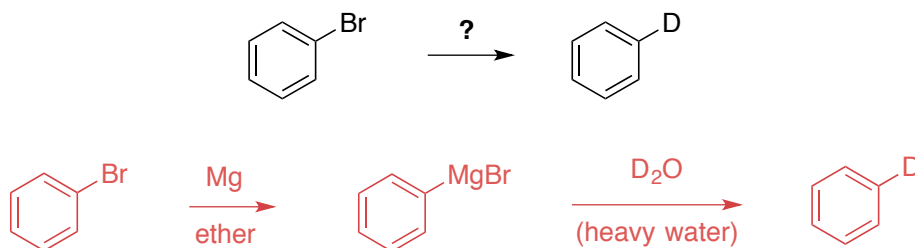
c) 4 (two stereocentres)



This Brown Suggested  
Problem #16.29

### BONUS (+3 pts)

Propose a synthesis (no mechanisms, just the steps) for the following transformation.

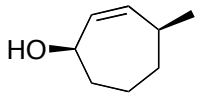
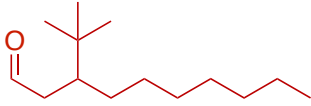


Covered in the DGD

**Part A**

1. (2.5 pts) In the following table, provide the missing IUPAC name or line structure.

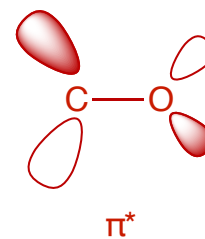
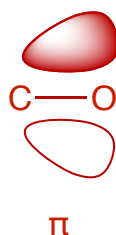
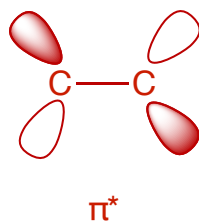
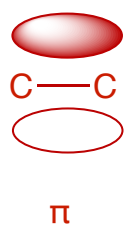
Both are from Problem set #1

Name	Structure
<i>cis</i> -4-methylcyclohept-2-enol	
3- <i>tert</i> -butyldecanal	

2. (0.5 pt) The awesome German word used to indicate a switch in polarity at a carbon atom (from positive to negative, or visa versa) is UMPOLUNG.
3. (5 pts) In the space below, sketch the  $\pi$  and  $\pi^*$  molecular orbitals of a C=C bond and a C=O bond. Why are they shaped slightly differently?

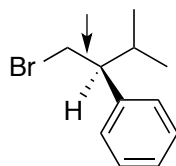
Midterm 2 2015

New Question



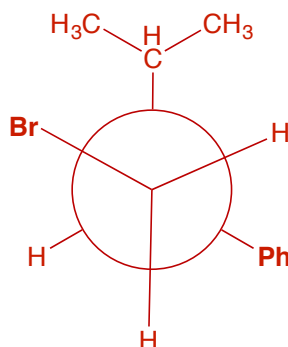
The C=C bond is perfectly covalent: both atoms have equivalent electronegativities and thus contribute equally to the molecular orbitals. The C=O bond is polarized: O is more electronegative than C, and so the differing energies lead to lop-sided molecular orbitals.

4. (2 pts) Draw and name the Newman projection for the most stable conformer of the molecule below along the C1–C2 bond (indicated with an arrow).



Similar to Midterm 1 2016

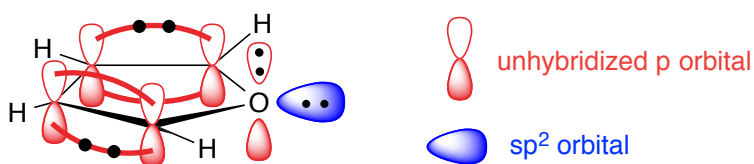
Bromine and the phenyl group are the largest groups on this molecule, so it must be rotated so that they are in an ANTI-STAGGERED configuration:



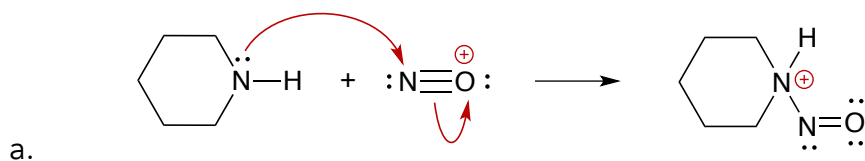
5. (3 pts) From the following molecules, circle the aromatic compound. In the space below, draw the LCAO orbital diagram of the  $\pi$  system of the molecule you've chosen.



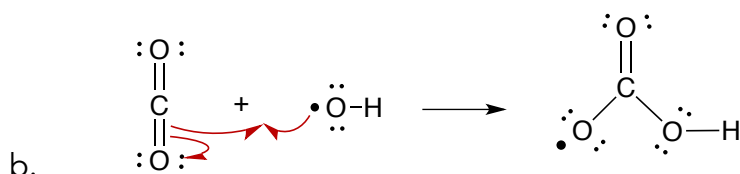
Final Exam 2014



6. (2.5 pts) Add formal charges and electron-pushing arrows as needed to complete the following reactions:

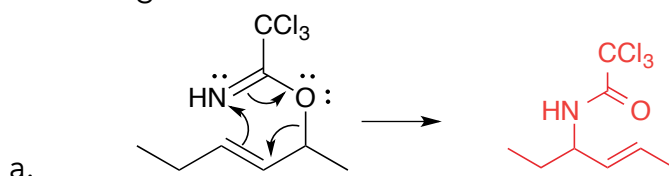


New version

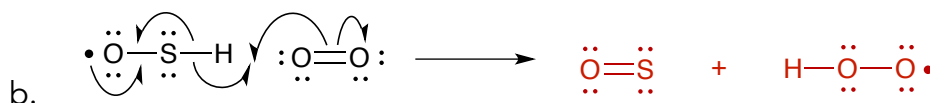


New version

7. (2.5 pts) Using the electron-pushing arrows as a guide, draw the expected product of the following reactions.

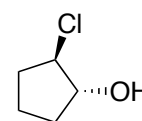
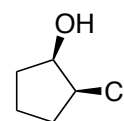
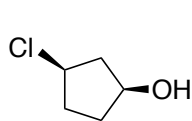
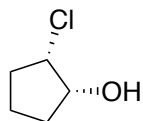
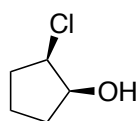


Final Exam 2014



New version

8. (2 pts) Clearly indicate the specific relationship (structural isomers, conformers, enantiomers, diastereoisomers, etc.) between molecule **A** and structures **B** through **E**.

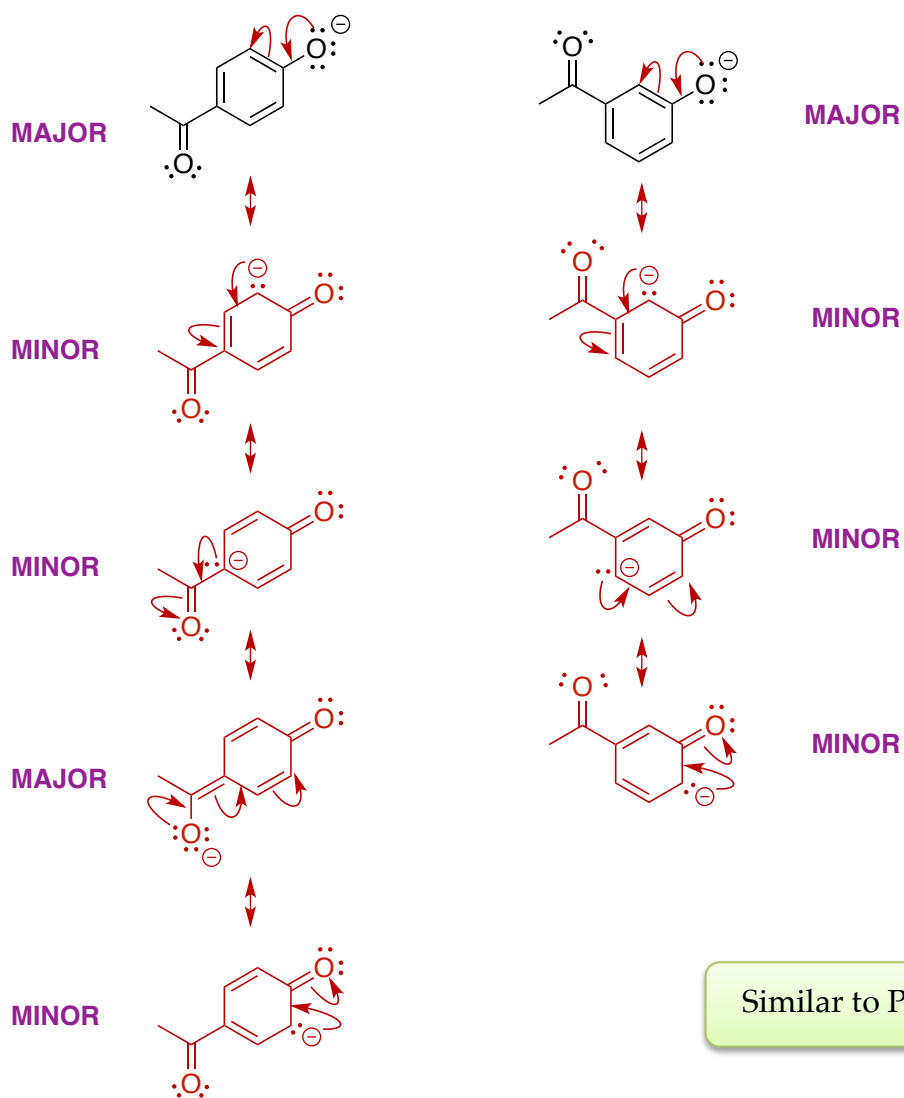


A and B are: <b>ENANTIOMERS</b>	A and C are: <b>STRUCTURAL ISOMERS</b>
A and D are: <b>ENANTIOMERS</b>	A and E are: <b>DIASTEREOISOMERS</b>

Similar to Final Exam 2015

**Part B**

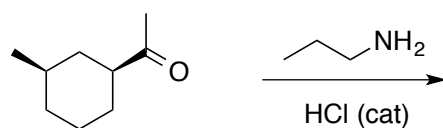
9. (6 pts) Which ion is more stable? Use resonance structures to find your answer. Label each resonance structure as either a MAJOR or MINOR contributor to the overall hybrid.



Similar to Problem Set #10

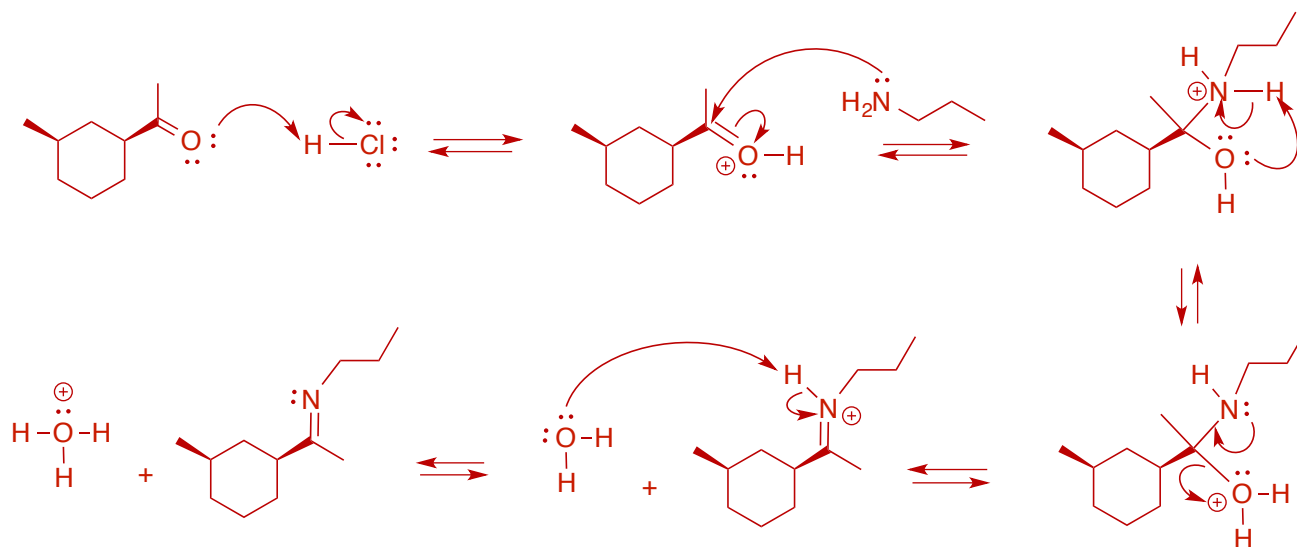
The left-hand anion is more stable, as it is possible to draw an extra major resonance structure placing the negative charge on the carbonyl oxygen atom.

10. Consider the following reaction:

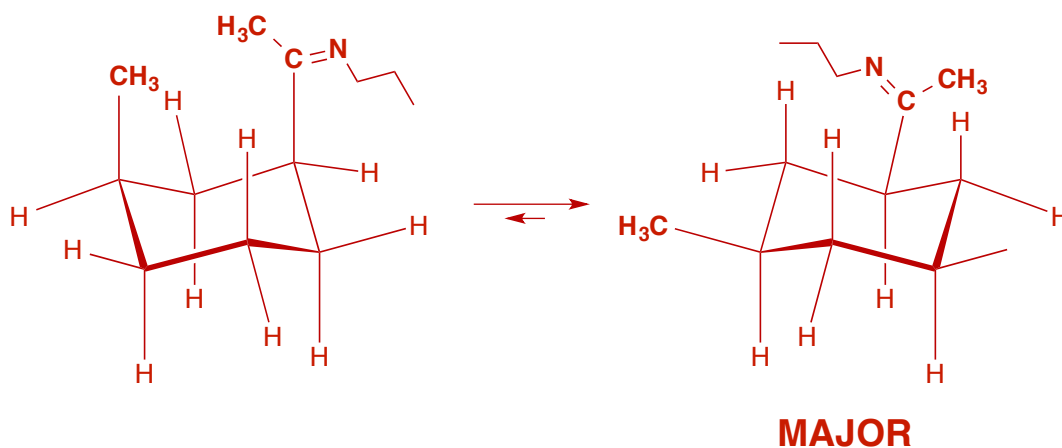


Final Exam 2015

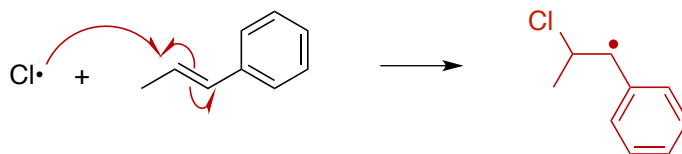
- a. (5 pts) Draw the full mechanism and show the final product of the following reaction. Clearly indicate any stereochemistry, if necessary.



- b. (3 pts) Draw the two chair conformers of your product and indicate which chair is the more stable conformer.



11. Consider the following elementary step, which is part of a free radical chain reaction:

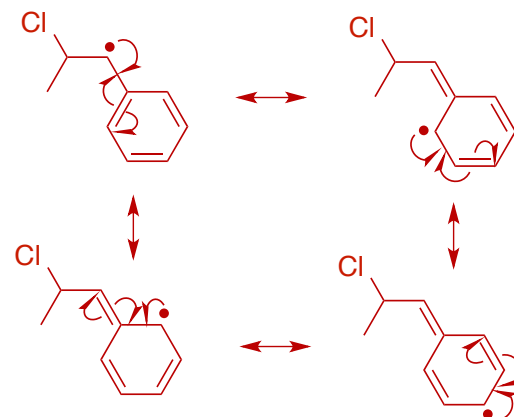


Final Exam 2015

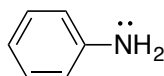
- (3 pts) Draw the mechanism and product of this step.
- (1 pt) What is the name of this type of reaction? π-addition
- (4 pts) Give two reasons to explain the regioselectivity of your product. In your answer, include all the relevant resonance structures.

1. **STERICS:** the chlorine atom attacks the less hindered carbon of the double bond because it is less sterically hindered (greater ease of access for a methyl group versus a phenyl group).

2. **RESONANCE:** the resulting free radical product is the more stable secondary carbon-centred radical. It is stabilized via resonance through the aromatic ring.



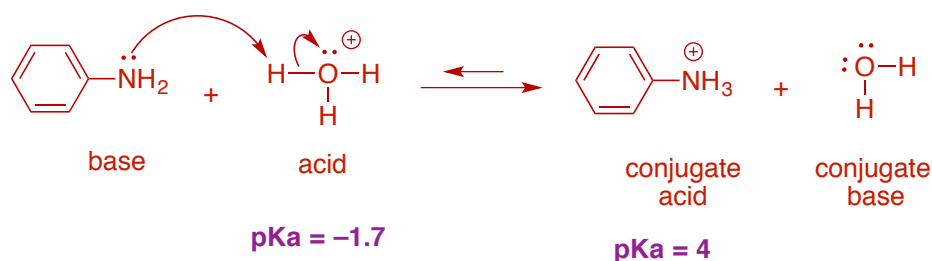
12. For the following molecule:



Common question!

- (3 pts) Draw the mechanism and products of the acid-base reaction of this molecule with  $\text{H}_3\text{O}^+$ .
- (2 pts) Are the reactants or products favoured? Justify your answer.

a.

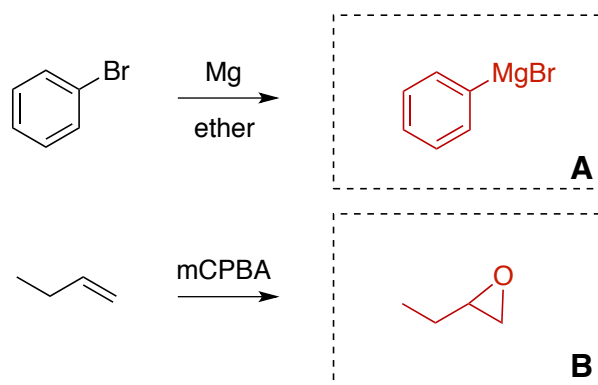


b. Using the pKa's we can see that the hydronium ion is the stronger acid. Therefore, the reaction is product-favoured.

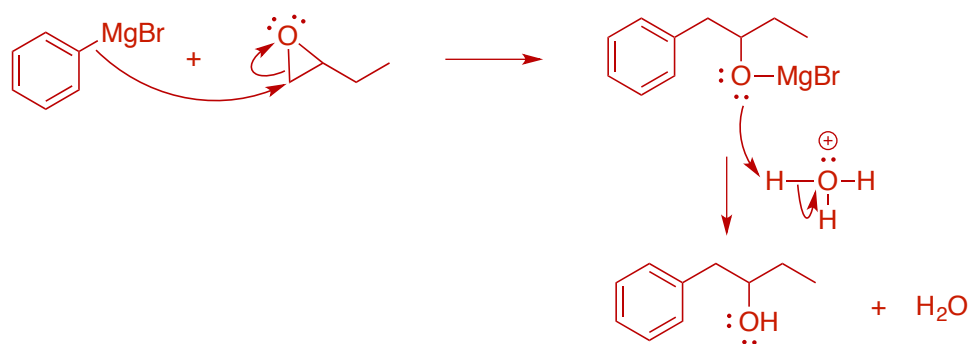
13. The following is synthesis for the formation of a fragrance from bromobenzene.

a. (2 pts) First, draw the structures of the products of these reactions.

This whole question is a broken-down version of Brown 16.21



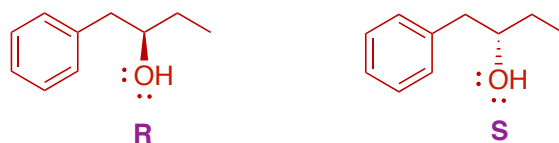
b. (3 pts) Now, draw the mechanism for the reaction of A and B together, followed by aqueous acid workup:



Note: Nucleophilic conditions, therefore the nucleophile attacks the less substituted carbon of the epoxide ring.

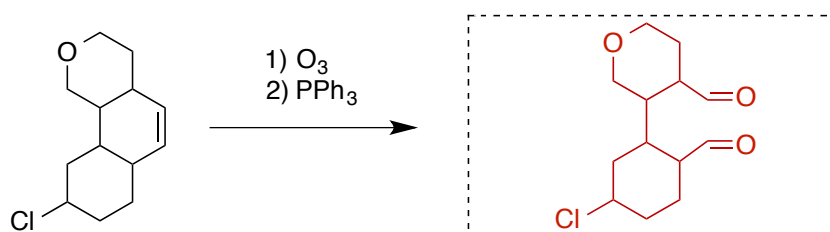
c. (3 pts) How many stereoisomers are possible for the final product? Draw their structures unambiguously, and label any stereocentres as *R* or *S*.

There are two stereoisomers:



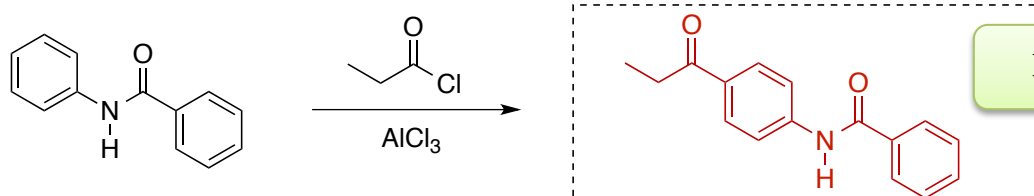
14. (5 pts) Complete the following by providing the missing product or reagents (no mechanisms). Show stereochemistry, when necessary.

a.



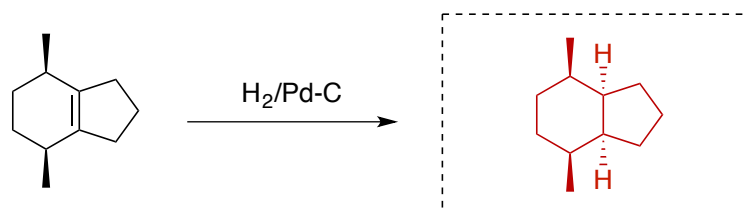
Final Exam 2015

b.



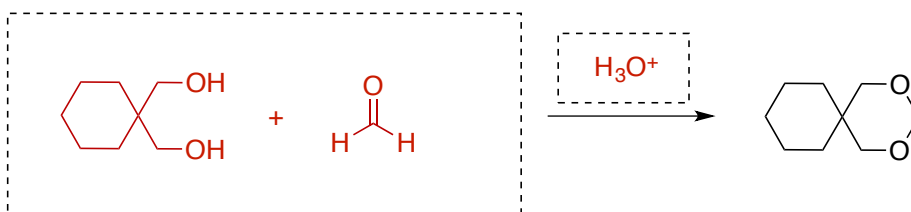
In-class question

c.



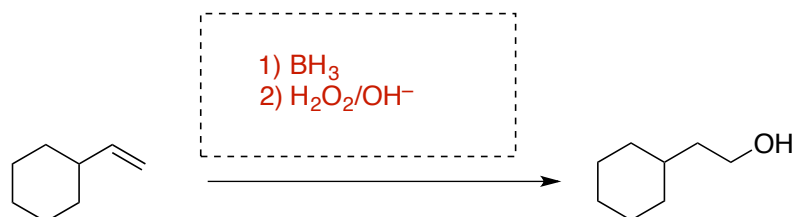
New question

d.



Sapling Assignment #7

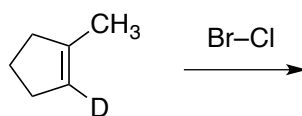
e.



Covered in the DGD

**Part C**

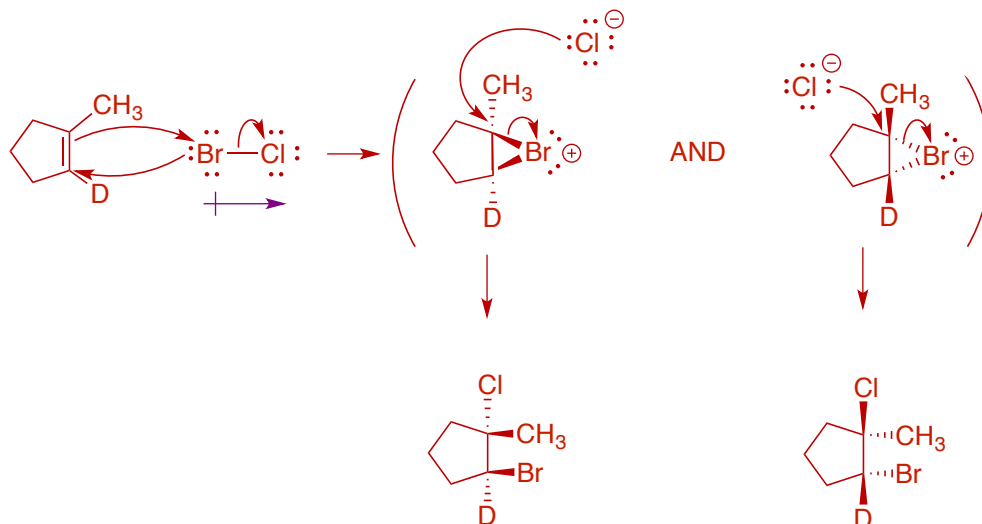
15. Consider the following reaction:



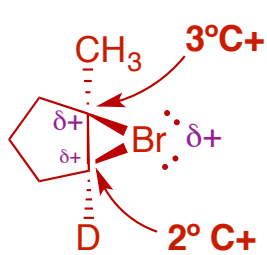
Similar to previous exam questions

a. (4 pts) Draw a detailed mechanism for the reaction, including all final products.

Note that the halogen is already polar (Cl is more electronegative than Br), and so an induced dipole is not necessary here – the bromine atom is the electrophile and adds first.

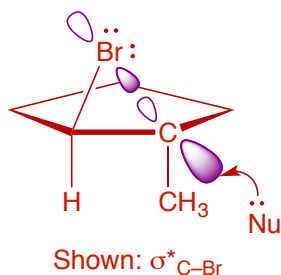


b. (3 pts) Provide a brief explanation for the relative locations of the halogens in the final product (*i.e.* their *regiochemistry*). Support your answer by drawing a structure or scheme.



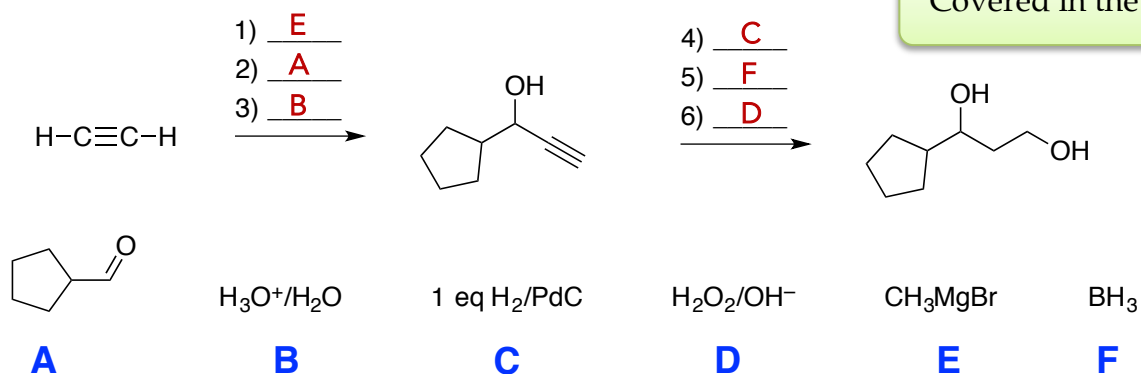
First, the bromine adds to the alkene for the reason explained above. Next, the nucleophile (chloride anion) attacks the bromonium ion. Since it is UNSYMMETRIC, there are two possible carbocation intermediates: a secondary carbocation ( $2^\circ \text{C}^+$ ) and a tertiary carbocation ( $3^\circ \text{C}^+$ ). Since the  $3^\circ \text{C}^+$  is more stable, the nucleophile attacks this electrophilic site, yielding the 1,2-product.

c. (2 pts) Briefly account for the *stereochemistry* of the final product. Support your answer by drawing a structure or scheme.

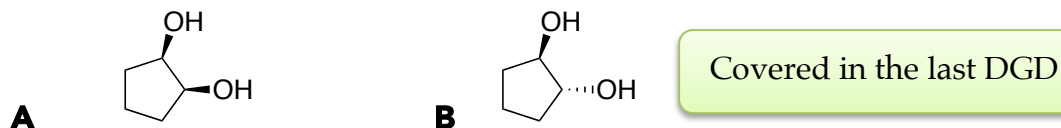


Incoming nucleophiles must add to the  $\sigma^*_{\text{C-Br}}$  orbital in order to break the C-Br bond. The major lobe of this orbital is located ANTIPERIPLANAR to the C-Br bond  $\rightarrow$  this is why the chloride ion attacks from the opposite side to yield the ANTI product.

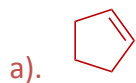
16. (6 pts) Place the following reagents in the correct order to complete the synthesis below. Each reagent is used only once.



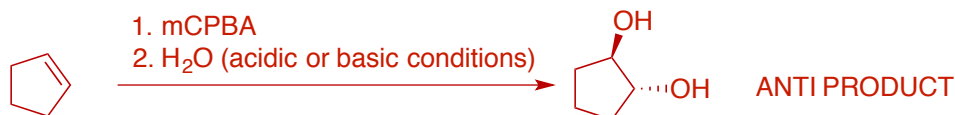
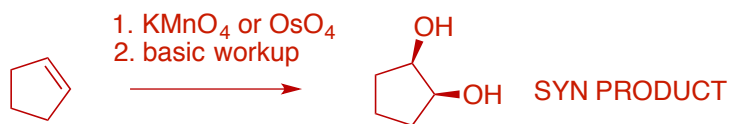
17. These two products, **A** and **B**, come from the same original starting material, but are synthesized via two different routes.



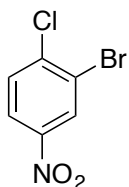
- a. (1 pt) What is the original starting material? Draw its structure.
- b. (3 pts) Show the two different routes to **A** and **B** (no mechanisms). Label the products as either *SYN* or *ANTI*.



b).

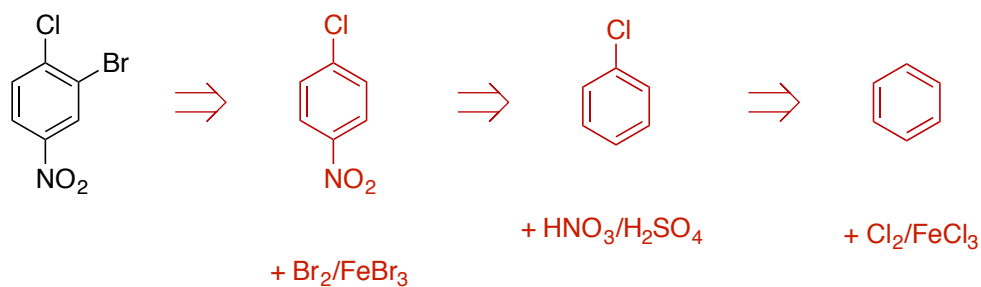


18. (3 pts) Create a complete retrosynthesis for the following compound, starting from benzene.

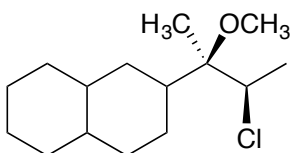


Similar to an example covered in class

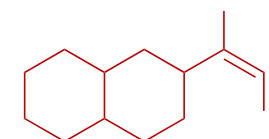
This is the BEST route (most effective):



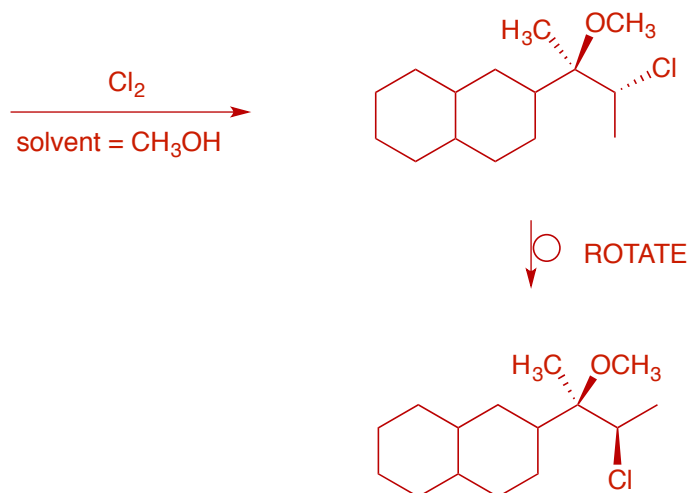
19. (3 pts) Propose a synthesis of the compound below starting from an alkene and using any other reagents that you require. Make sure that the compound below is the major product in your synthesis.



Covered in the DGD



Double bond must be *E*

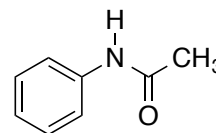


## Laboratory Section

Similar to Final Exam 2014

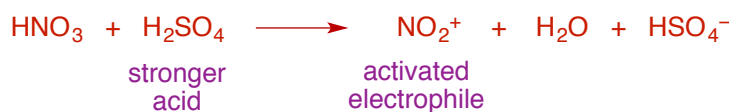
20. Consider the following experimental procedure from the nitration of acetanilide:

“Place 1.00 g of acetanilide in a 25 mL round bottom flask. Add 3 mL of  $\text{H}_2\text{SO}_4$  to dissolve the solid and cool the solution in an ice bath. In a 50 mL Erlenmeyer flask, carefully combine 0.80 mL  $\text{HNO}_3$  and 1.4 mL sulfuric acid, and add slowly to the round-bottom flask. Allow to react for 10 min, with stirring.”



- (3 pts) What is the function of the sulfuric acid? Explain, using a sentence and a chemical reaction.
- (3 pts) Draw the structures of the two expected products, and indicate which is the major product and which is the minor product. Why are they not formed in equal amounts?
- (5 pts) Is nitration of acetanilide kinetically faster or slower than nitration of plain benzene? Draw reaction intermediates and a reaction energy profile to support your answer.

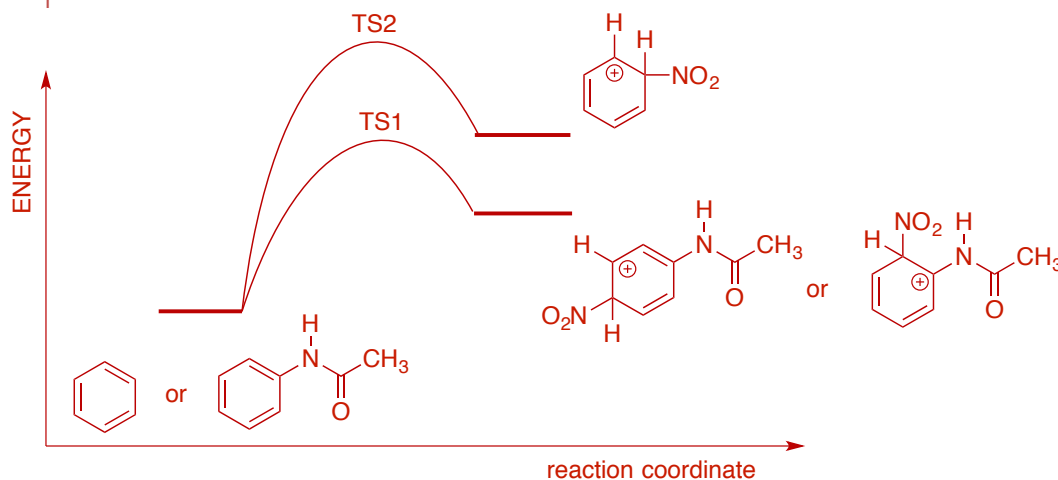
a) The sulfuric acid is a BRONSTED ACID; its function is to ACTIVATE THE ELECTROPHILE:



b) The PARA product is formed in major amounts due to the large steric hindrance associated with ORTHO addition.



c) The key to the reaction rate is the energy of the transition state: by lowering  $E_a$ , the rate increases. So, any factor which stabilizes the TS will accelerate the reaction. In the case of acetanilide, the nitrogen atom group is a strong activating group (SAG). It is an electron-donating group (via its lone pair) and stabilizes the arenium ion intermediate via resonance following ortho or para addition.

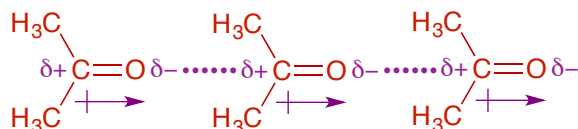


21. (4 pts) From the list below, circle the strongest intermolecular force found in acetone.

- DIPOLE-DIPOLE**      HYDROGEN-BONDING      ION-DIPOLE  
 DIPOLE-INDUCED DIPOLE      INDUCED DIPOLE-INDUCED DIPOLE

In the space below, draw a representation of the force you have selected occurring between at least 3 acetone molecules.

New Question



## Bonus

What is the expected product of the following reaction? Draw a mechanism to show how it is formed.

