

NAME (Print): \_\_\_\_\_

Chemistry 310N  
Dr. Brent Iverson  
Final  
May 8, 2008

SIGNATURE: \_\_\_\_\_

Please print the  
first three letters  
of your last name  
in the three boxes

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**Please Note:** This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

*For synthesis problems GO FOR PARTIAL CREDIT EVEN IF YOU DO NOT KNOW THE ENTIRE ANSWER!!!WRITE DOWN WHAT YOU DO KNOW IN THE REACTION SEQUENCE SOMEWHERE. YOU WILL GET PARTIAL CREDIT IF IT IS CORRECT*

**Note: You must have your answers written in pen if you want a regrade!!!!**

## Honor Code

The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

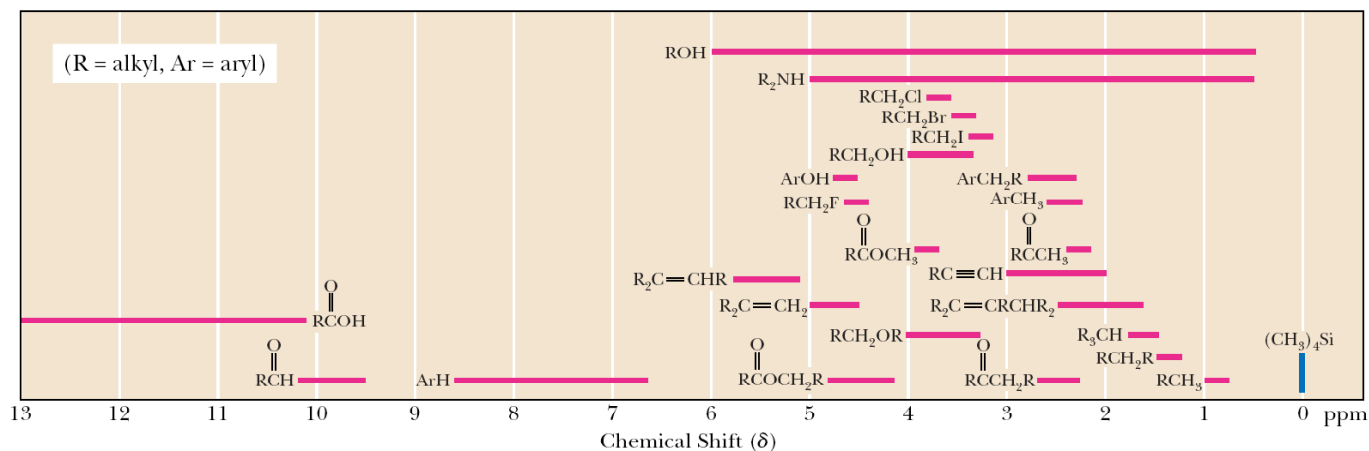
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(Your signature)

Compound		pK <sub>a</sub>
Hydrochloric acid	$\text{H-Cl}$	-7
Protonated alcohol	$\text{RCH}_2\text{O}^+\text{H}_2$	-2
Hydronium ion	$\text{H}_3\text{O}^+$	-1.7
Protonated Amide	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}^+\text{H}_3$	-0.5
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$	3-5
Ammonium ion	$\text{H}_4\text{N}^+$	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	10
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	13
Water	$\text{HOH}$	15.7
Alcohols	$\text{RCH}_2\text{OH}$	15-19
Acid chlorides	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	18-20
Esters	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift ( $\delta$ )*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift ( $\delta$ )*
$R_2NH$	0.5-5.0	$RCH_2OH$	3.4-4.0
$ROH$	0.5-6.0	$RCH_2Br$	3.4-3.6
$RCH_3$	0.8-1.0	$RCH_2Cl$	3.6-3.8
$RCH_2R$	1.2-1.4	$\begin{array}{c} O \\    \\ RCOCH_3 \end{array}$	3.7-3.9
$R_3CH$	1.4-1.7	$\begin{array}{c} O \\    \\ RCOCH_2R \end{array}$	4.1-4.7
$R_2C=CRCHR_2$	1.6-2.6	$RCH_2F$	4.4-4.5
$RC\equiv CH$	2.0-3.0	$ArOH$	4.5-4.7
$\begin{array}{c} O \\    \\ RCCH_3 \end{array}$	2.1-2.3	$R_2C=CH_2$	4.6-5.0
$\begin{array}{c} O \\    \\ RCCH_2R \end{array}$	2.2-2.6	$R_2C=CHR$	5.0-5.7
$ArCH_3$	2.2-2.5	$\begin{array}{c} O \\ / \backslash \\ H_2C \quad CH_2 \end{array}$	3.3-4.0
$RCH_2NR_2$	2.3-2.8	$\begin{array}{c} O \\    \\ RCH \end{array}$	9.5-10.1
$RCH_2I$	3.1-3.3	$\begin{array}{c} O \\    \\ RCOH \end{array}$	10-13
$RCH_2OR$	3.3-4.0		

\* Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.



1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

2. (1 pt each) Fill in each blank with the word that best completes the following sentences about NMR.

For organic chemistry, NMR is primarily concerned with atoms having a spin quantum number of \_\_\_\_\_. The two most important isotopes for organic chemistry structure determination by NMR are \_\_\_\_\_ and \_\_\_\_\_. Of these two, \_\_\_\_\_ is a common isotope and the predominant isotope found in molecules, while \_\_\_\_\_ is very rare.

The key to the NMR experiment is that in a strong external \_\_\_\_\_ field, the difference in energy between nuclear spin states is \_\_\_\_\_ to that field. For  $^1\text{H}$  atoms, the two nuclear spin states are referred to as +\_\_\_\_\_ and -\_\_\_\_\_.

When irradiated with electromagnetic radiation of a wavelength that corresponds to the exact energy difference between nuclear spin states, the energy is absorbed, a process referred to as \_\_\_\_\_. The wavelength used for irradiation is in the \_\_\_\_\_ range of the electromagnetic spectrum.

Electron density is induced to move in a strong external magnetic field, and this movement induces a \_\_\_\_\_ field that is \_\_\_\_\_ to the external magnetic field. This has the effect of \_\_\_\_\_ the underlying nuclei from the external magnetic field. The signal for an H atom with greater electron density around it will come at \_\_\_\_\_ ppm in an NMR spectrum compared to a similar H atom with less electron density.

3. (21 pts) Fill in each blank with the word that best completes the following sentences.

Think of electron density as \_\_\_\_\_, in which you can get extra stability when they add constructively, and you lose stability when they cancel each other (add destructively).

You generate as many new molecular orbitals as \_\_\_\_\_ orbitals used to create them. Approximately half are \_\_\_\_\_ molecular orbitals (waves add constructively) and are filled with electron density, and half are \_\_\_\_\_ molecular orbitals (waves add destructively) and are not filled with electron density.

Adjacent 2p orbitals overlap, allowing the \_\_\_\_\_ electron density to delocalize into all the adjacent 2p orbitals, their wave functions adding constructively to provide stability.

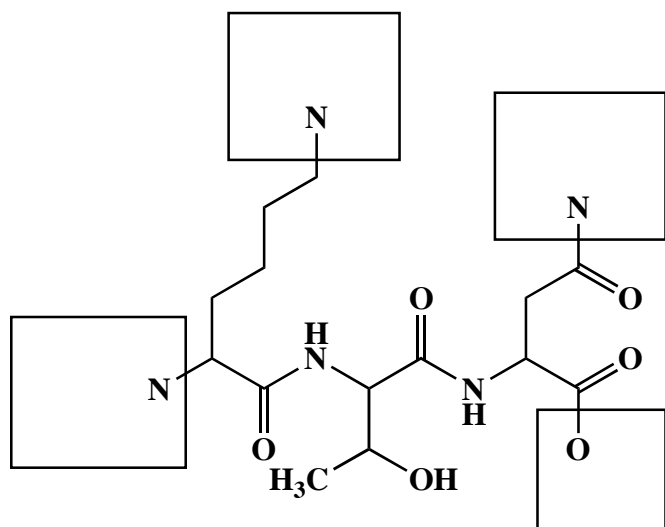
Absorbance of a photon by a molecule corresponds to promotion of a(n) \_\_\_\_\_ from a filled \_\_\_\_\_ to an unfilled \_\_\_\_\_.

\_\_\_\_\_ . In the visible region, this usually involves \_\_\_\_\_ bonding and antibonding molecular orbitals, and conjugation \_\_\_\_\_ the wavelength of absorption.

Molecules appear to our eye to be a combination of the wavelengths \_\_\_\_\_ (not \_\_\_\_\_).

According to the Huckel definition of aromaticity, molecules will be aromatic if they are 1) \_\_\_\_\_, 2) \_\_\_\_\_, 3) all the ring atoms are \_\_\_\_\_ hybridized (sp in rare cases) and 4) there are  $4n + 2$  \_\_\_\_\_ electrons, where  $n = 0, 1, 2, 3, 4, 5, 6, \dots$ . The 36 kcal/mol extra stability (unreactivity) of aromatic species derives from putting all the \_\_\_\_\_ electrons in low energy molecular orbitals that extend over the \_\_\_\_\_ hybridized ring atoms. These molecular orbitals involve overlap (in phase and out of phase) of the \_\_\_\_\_ atomic orbitals on each atom of the ring.

4. (16 points) A) This semester we have learned a great deal about both carboxylic acids and amines. Here is an apply what you know problem. The following three amino acid sequence (Lysine-Threonine-Asparagine) is found in a prion protein, an infectious species that does not contain nucleic acid. Its structure is shown below. **Complete the following peptide structure by adding all appropriate hydrogen atoms, lone pairs, and formal charges that will be present when this peptide is in buffered water at pH 7.0.** Assume the pKa value for a protonated amine ( $\text{RNH}_3^+$ ) is 9.2, pKa value for a carboxylic acid is 4.0, and the pKa for a protonated amide ( $\text{RC(O)NH}_3^+$ ) is -0.5 .



What is the total charge on this peptide at pH 7.0?

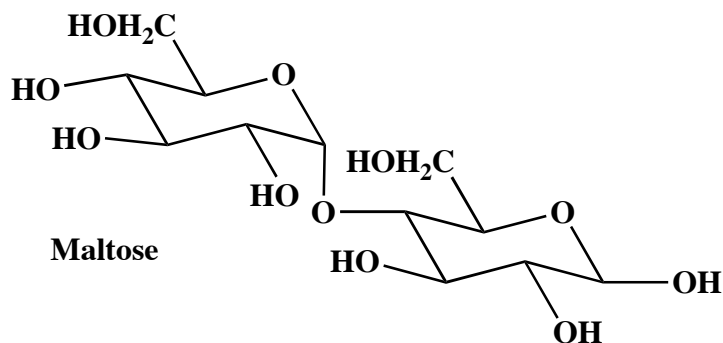
What is the total charge on this peptide at pH 2.0?

What is the total charge on this peptide at pH 11.0?

How many chiral centers are in this molecule?

5. (16 points) A) On the following disaccharide called maltose, **circle** the O atoms of all acetal functional groups, and **draw a box** around the O atoms of all hemiacetal functional groups.

B) Next **draw a triangle** around each anomeric carbon atom.



C) Are the two carbohydrates pentoses or hexoses? \_\_\_\_\_

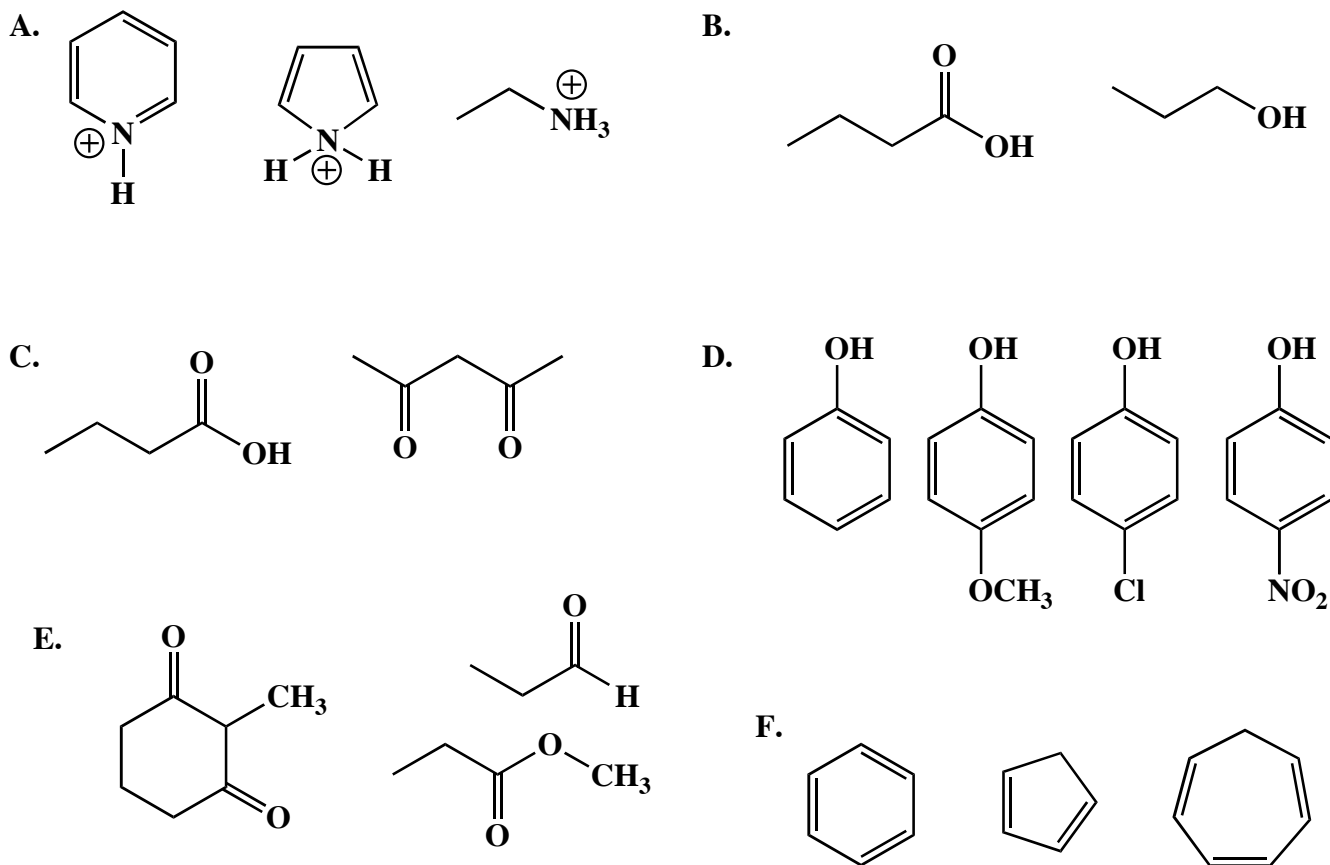
D) Is the carbohydrate on the left in the  $\alpha$  or  $\beta$  form? \_\_\_\_\_

E) Is the glycosidic bond best described as  $\alpha 1,4$ ;  $\alpha 1,6$ ;  $\beta 1,4$ ; or  $\beta 1,6$ ? \_\_\_\_\_

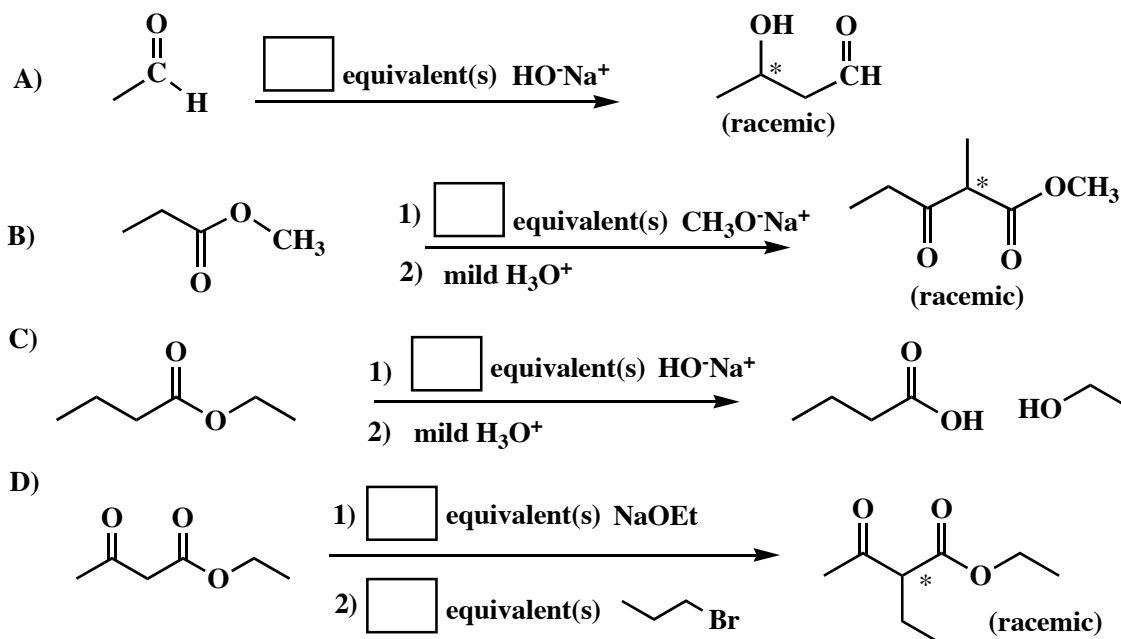
F) How many chiral centers does the molecule have? \_\_\_\_\_

G) Are the two carbohydrates aldoses or ketoses? \_\_\_\_\_

6. (2-4 points each) For each set, circle the MOST ACIDIC molecule.



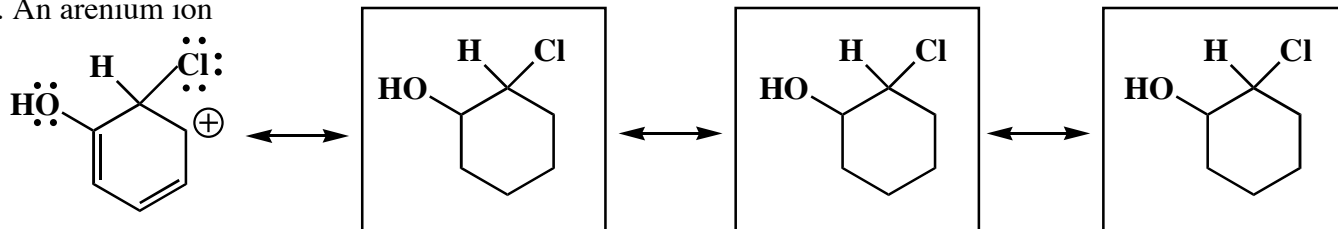
7. (2 pts each) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown to completion. If only a catalytic amount is needed, write "CAT". Note: You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.



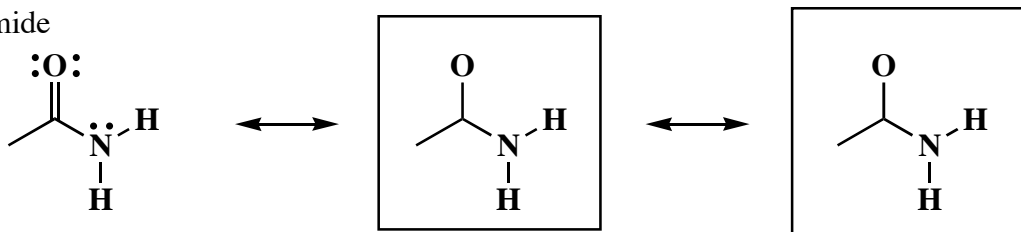


8. (20 pts) Resonance contributing structures are important for both units covered by this exam, namely enolates and aromatic molecules. On the following, **draw the indicated number of most important resonance contributing structures**. Show all lone pairs, pi bonds and formal charges. Use arrows to indicate the redistribution of electrons on each molecule to the left, that leads to the contributing structure you draw immediately to its right. (Only the structure on the farthest right on each line has no arrows on it). We drew template structures for you to save time.

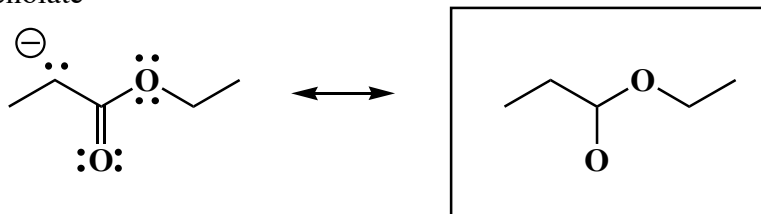
A. An arenium ion



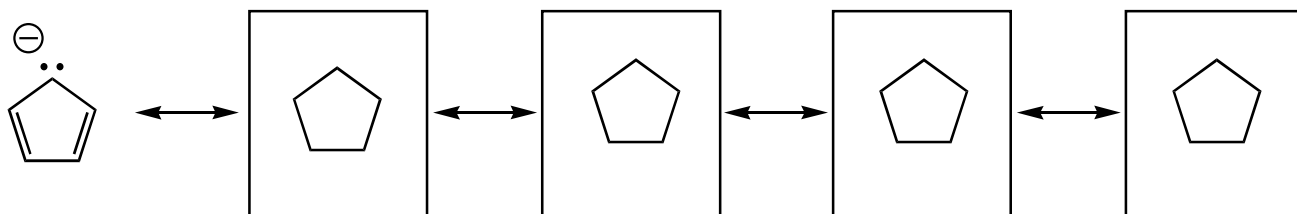
B. An amide



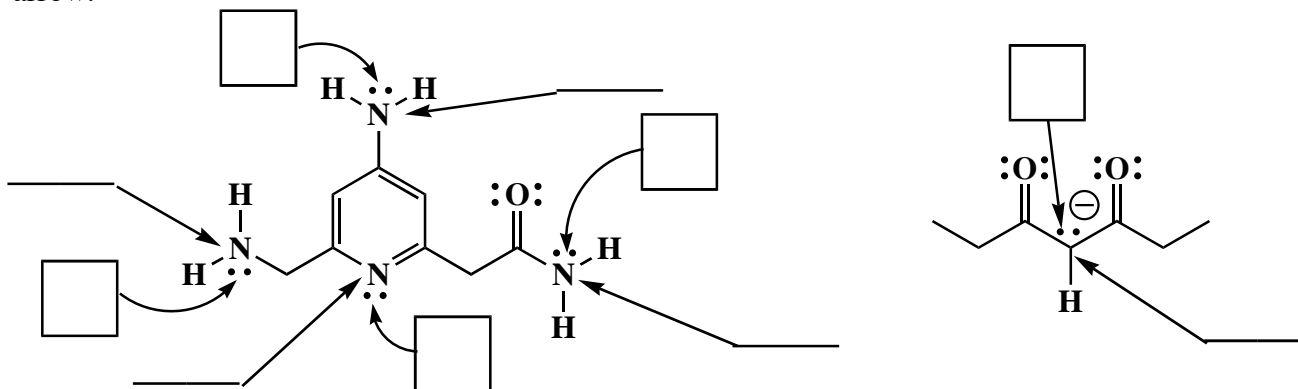
C. An enolate



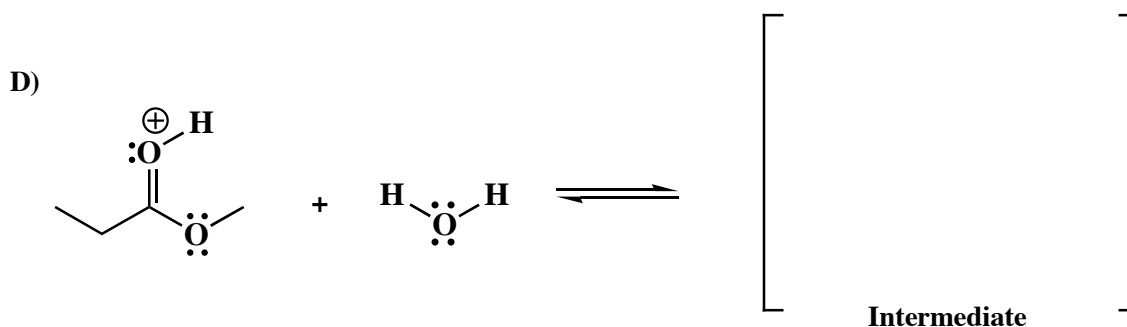
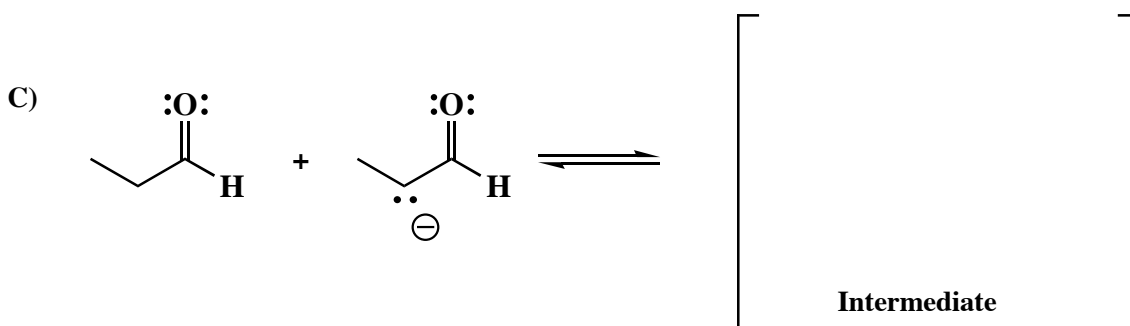
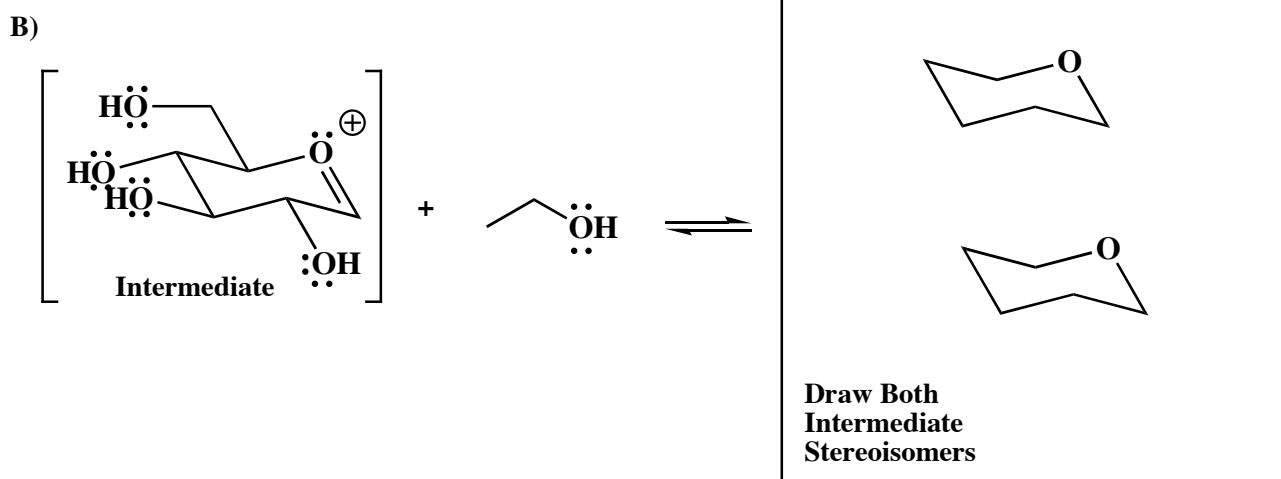
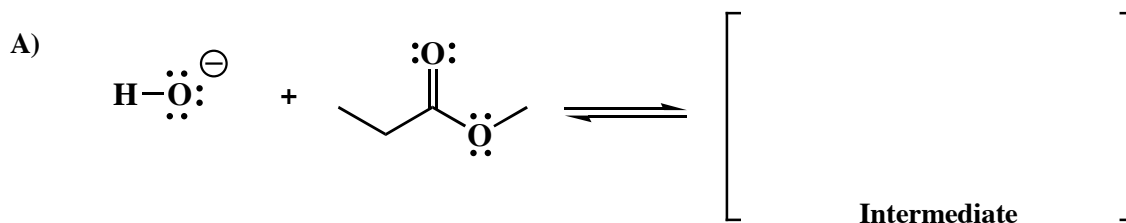
D. An aromatic anion



9. (2 pts each) **On the lines provided**, state the hybridization state of each atom indicated in the following molecule. **In the box provided**, state what type of atomic orbital contains the lone pair indicated by the arrow.

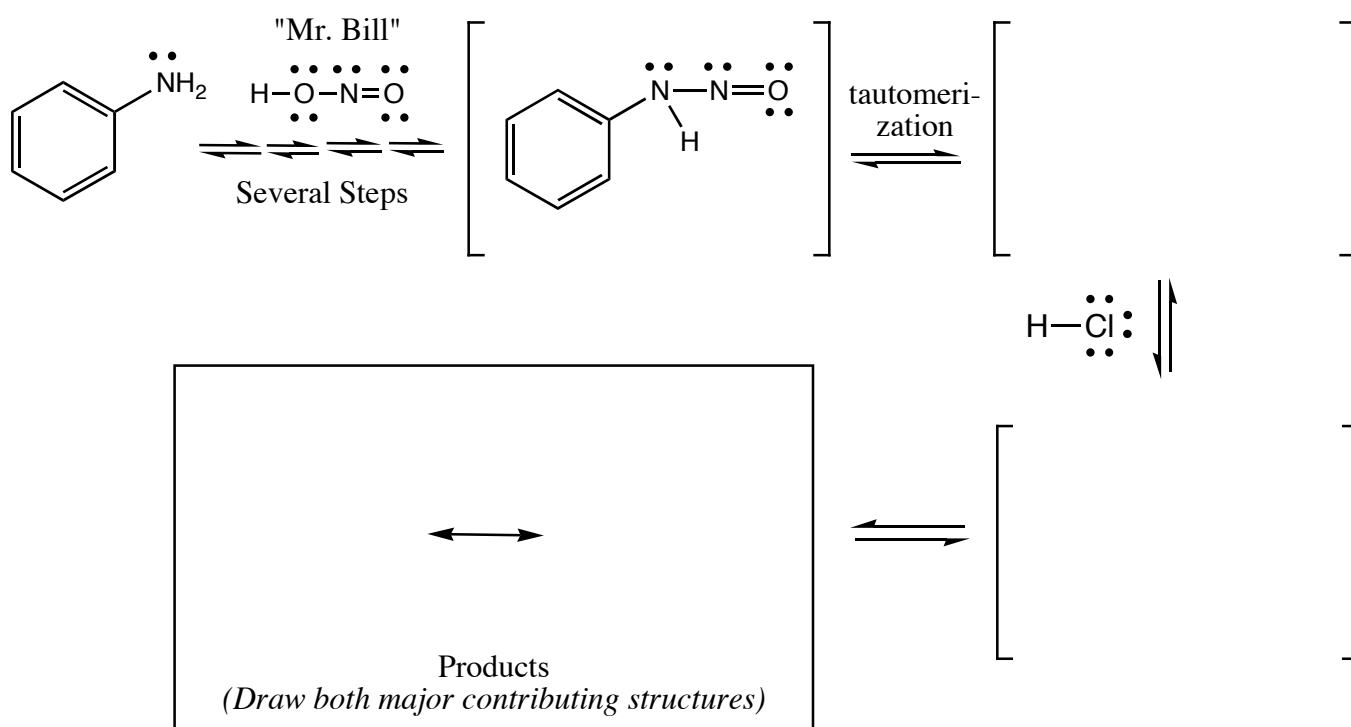
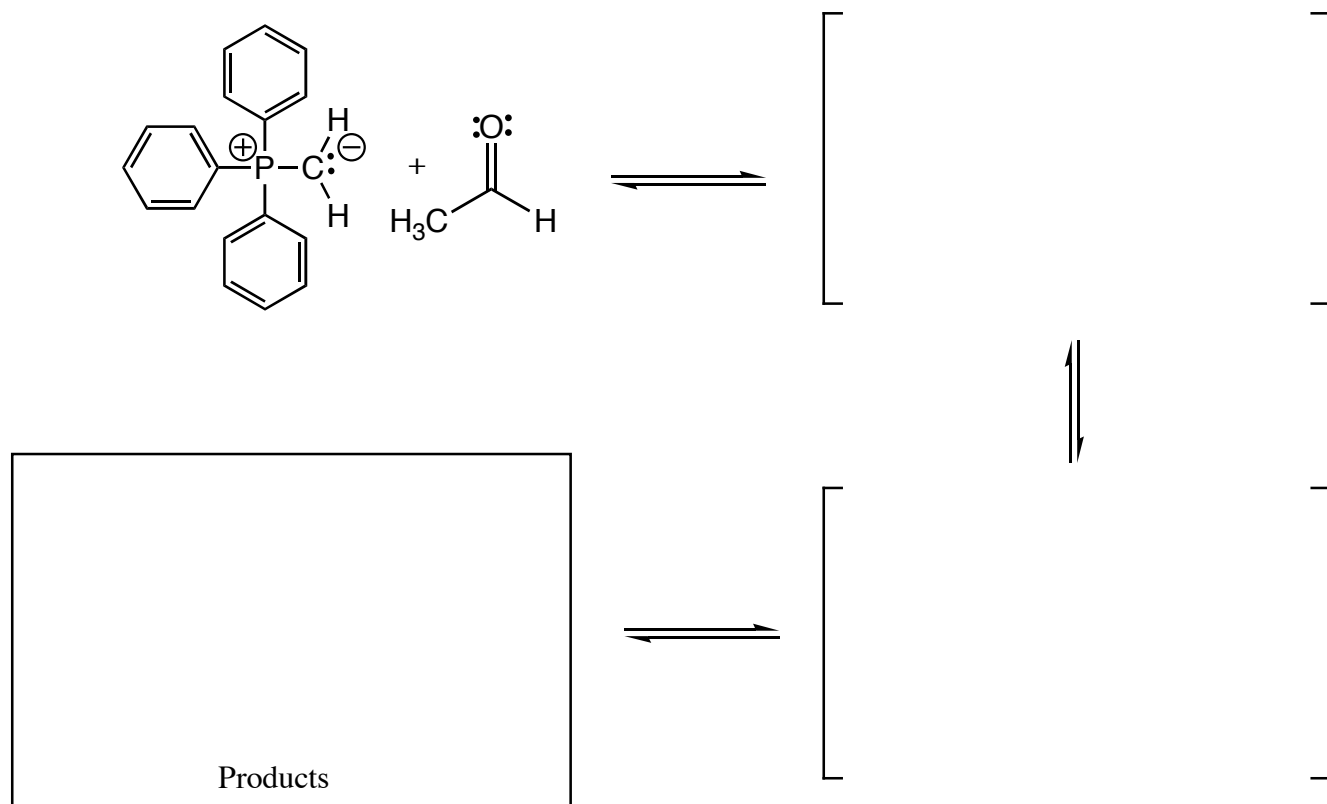


10. (26 points) Many of the reactions we have learned this semester involve steps with nucleophiles reacting with electrophiles. For the following examples of steps in mechanisms we have seen this semester, 1) **Draw the intermediate that will be formed when the two molecules react.** 2) **Draw all formal charges and lone pairs on the intermediates.** 3) **Draw arrows on the starting materials to indicate the flow of electrons that leads to the intermediate.** 4) **Finally, draw a box around the nucleophile and a circle around the electrophile in each case.** There is no need to draw products or any further steps of the mechanisms. You might want to read these directions again so you know what we want.

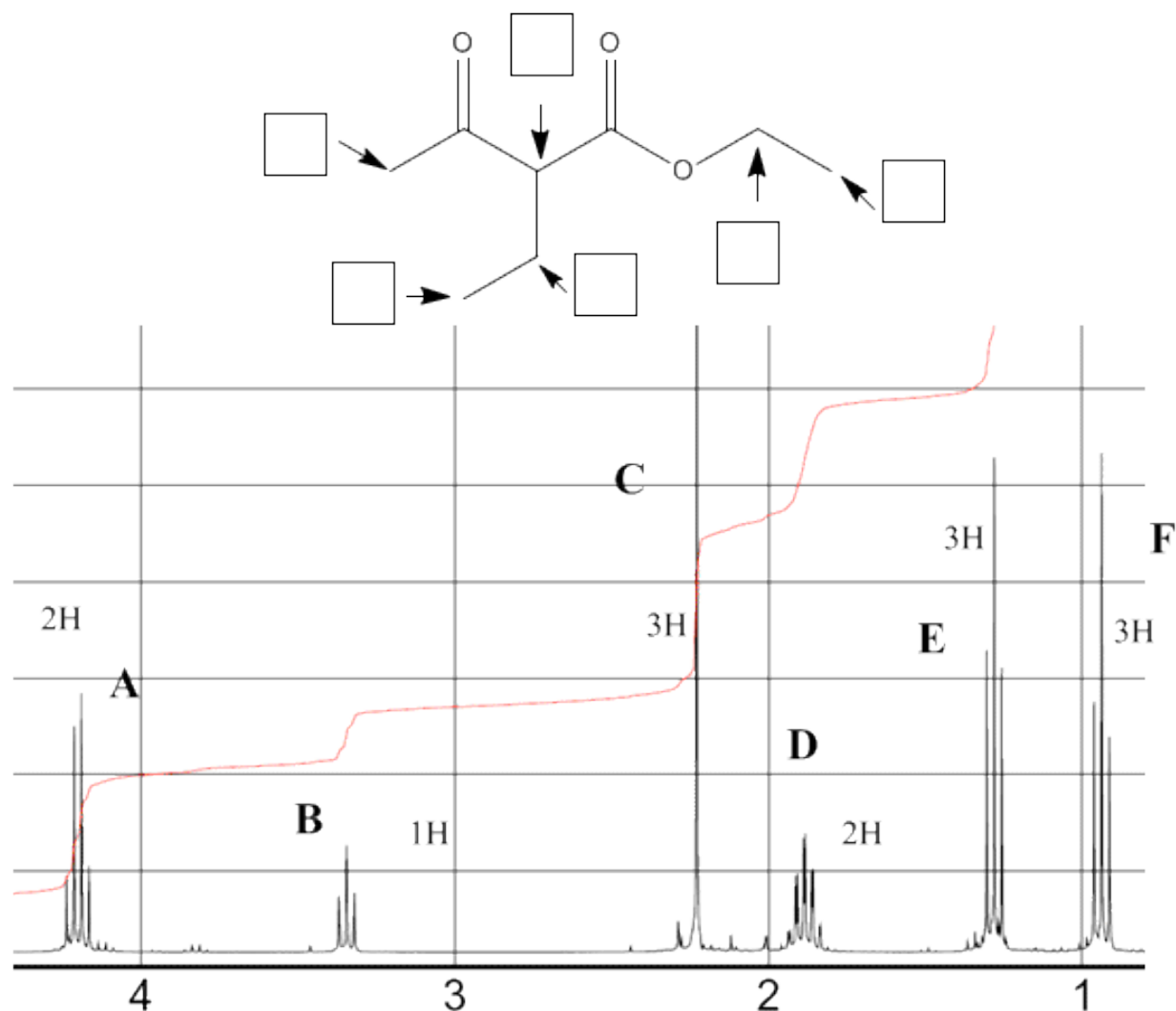


*Did you remember to draw boxes and circles?*

11. (28 pts) Complete the mechanisms below for a Wittig reaction and the Mr. Bill reaction. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. If a racemic product is formed, just put an asterisk (\*) next to the chiral center and write "racemic" under it.



12. A) (12 points) Each signal in the NMR spectrum below is assigned a letter. In the boxes below, write the letter of the signal that corresponds to the **protons attached to** the carbon indicated.



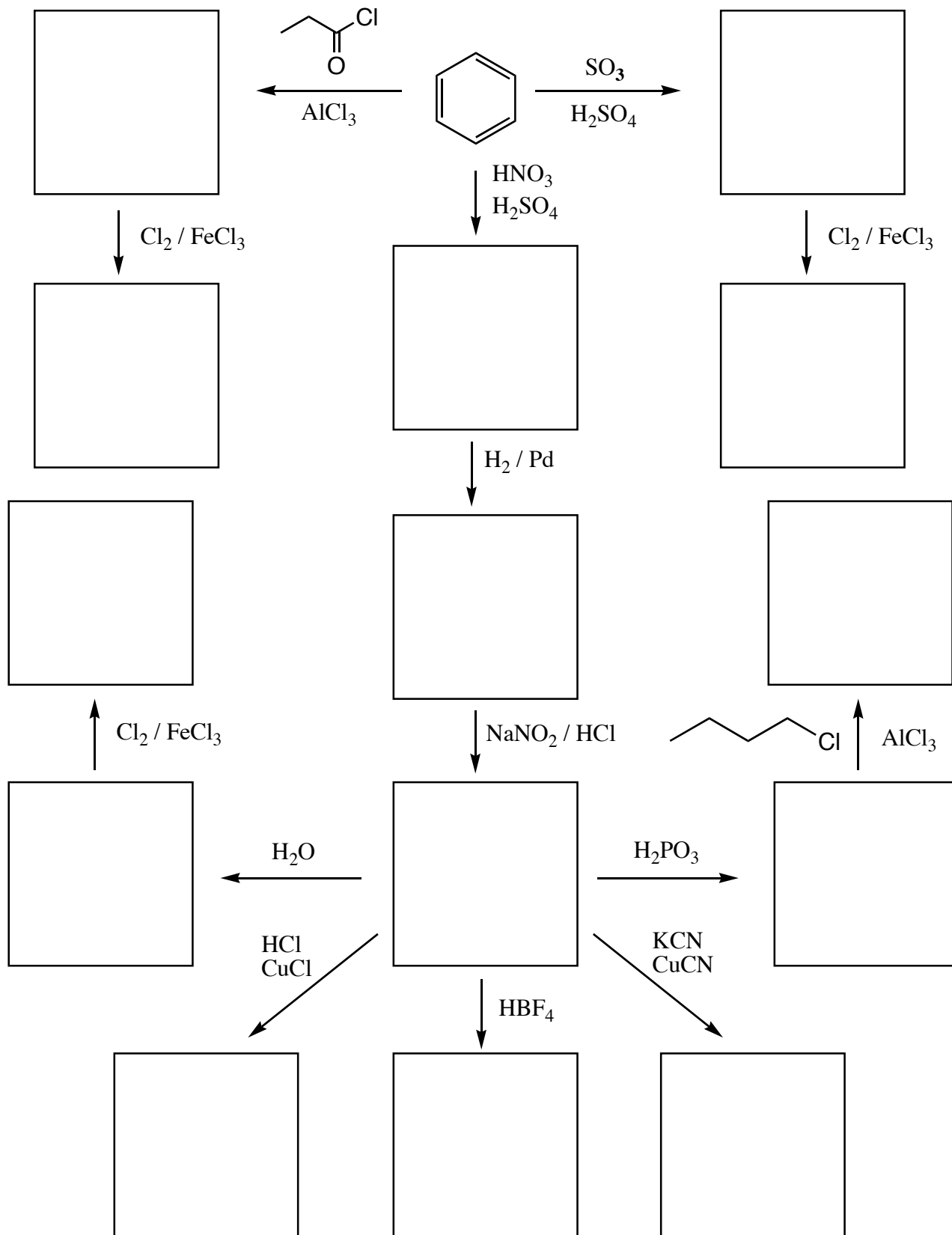
In 1 to 3 words, give an example of a reaction you have learned that will produce a product with the following characteristic feature (3 points each):

B) a new C=C bond to a former carbonyl carbon \_\_\_\_\_

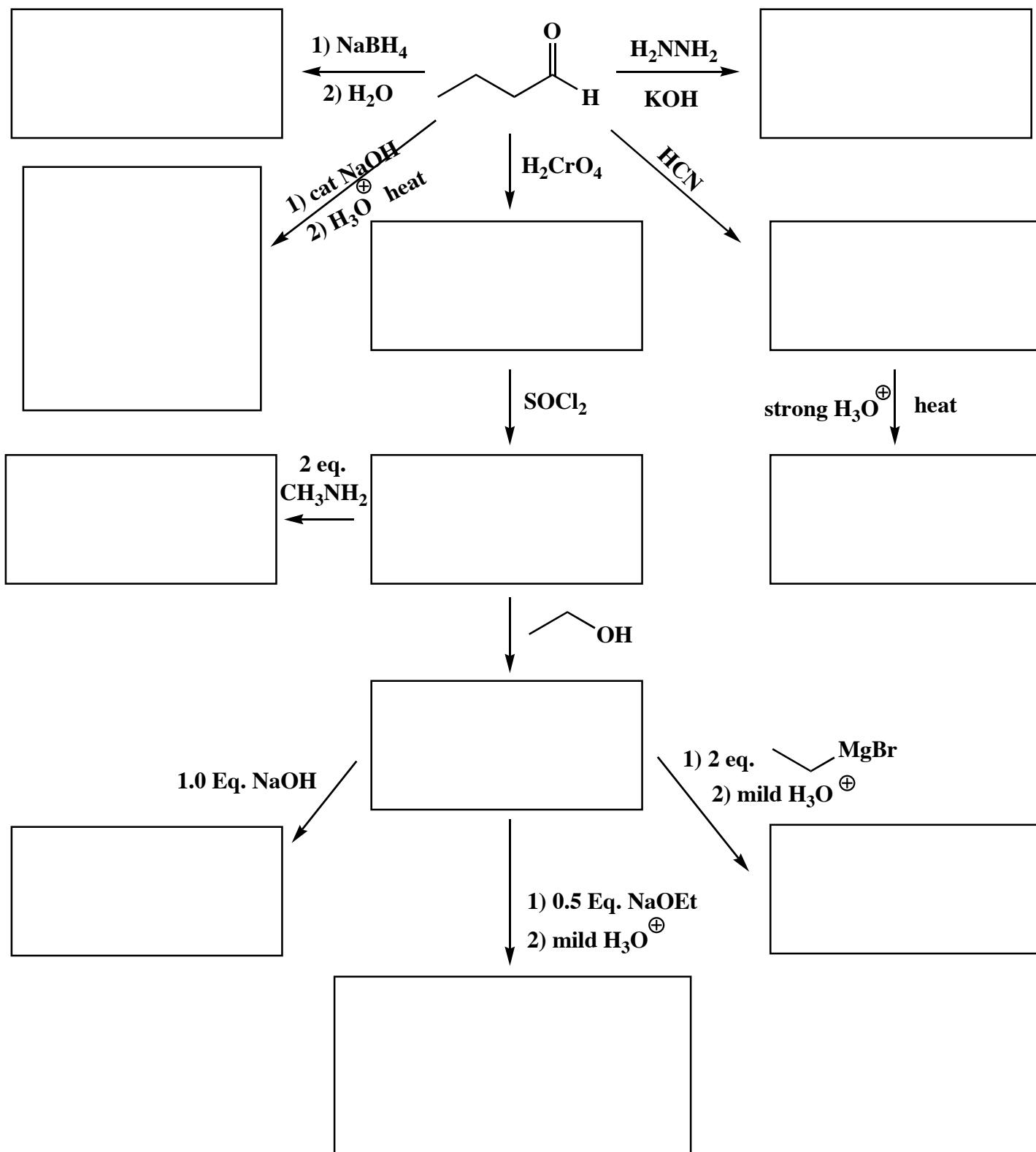
C) a new C-C bond to a carbon alpha to a carbonyl carbon \_\_\_\_\_

D) a new C-C bond to a carbon beta to a carbonyl carbon \_\_\_\_\_

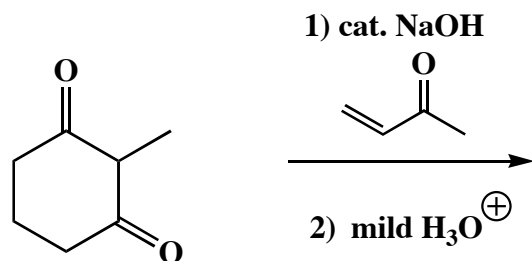
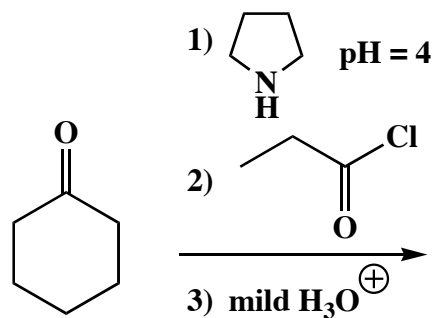
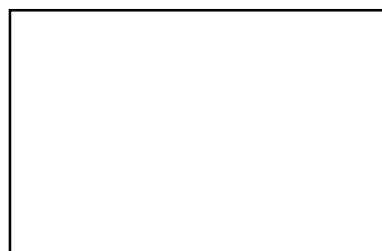
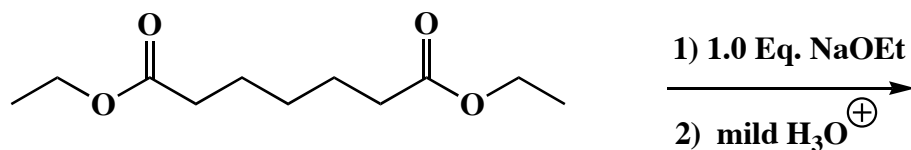
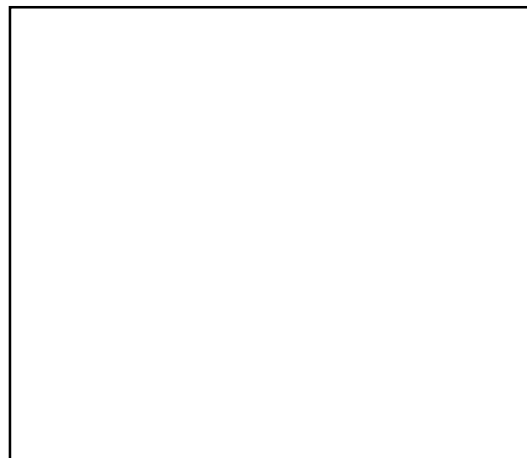
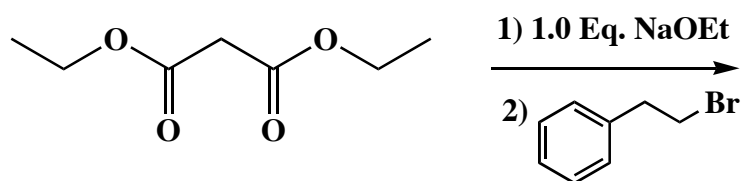
13. (46 pts.) Write the predominant product or products that will occur for each transformation. Assume each reagent only adds once to the ring. **If predominantly ortho/para products are predicted, you must draw both.** If a chiral center is created, use an asterisk and write "racemic" as appropriate.



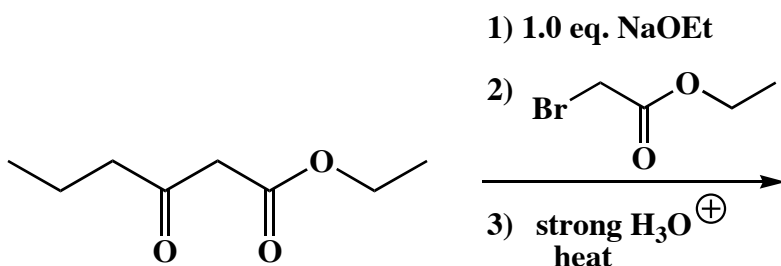
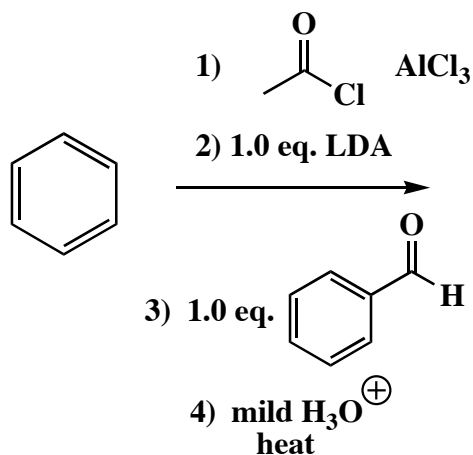
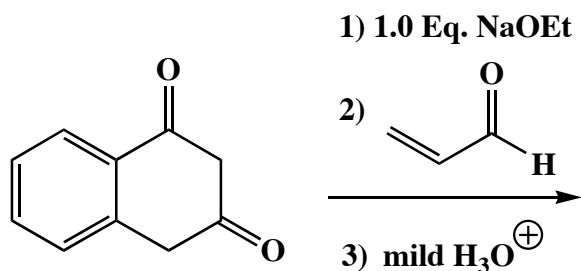
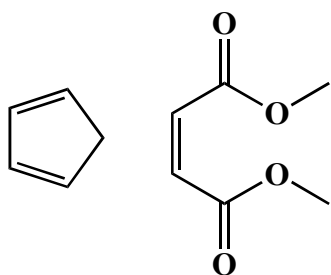
14. (44 pts.) Write the predominant product or products that will occur for each transformation. For aldol reactions, assume dehydration takes place and you must draw both E and Z products unless one predominates by a substantial margin. Label any new chiral centers with an asterisk and write "racemic" if appropriate.



15 (5 pts. each) These are a little harder, so take your time. Write the predominant product or products that will occur for each sequence of transformations. For aldol reactions, assume dehydration takes place and you must draw both E and Z products unless one predominates by a substantial margin. Label any new chiral centers with an asterisk and write "racemic" if appropriate.

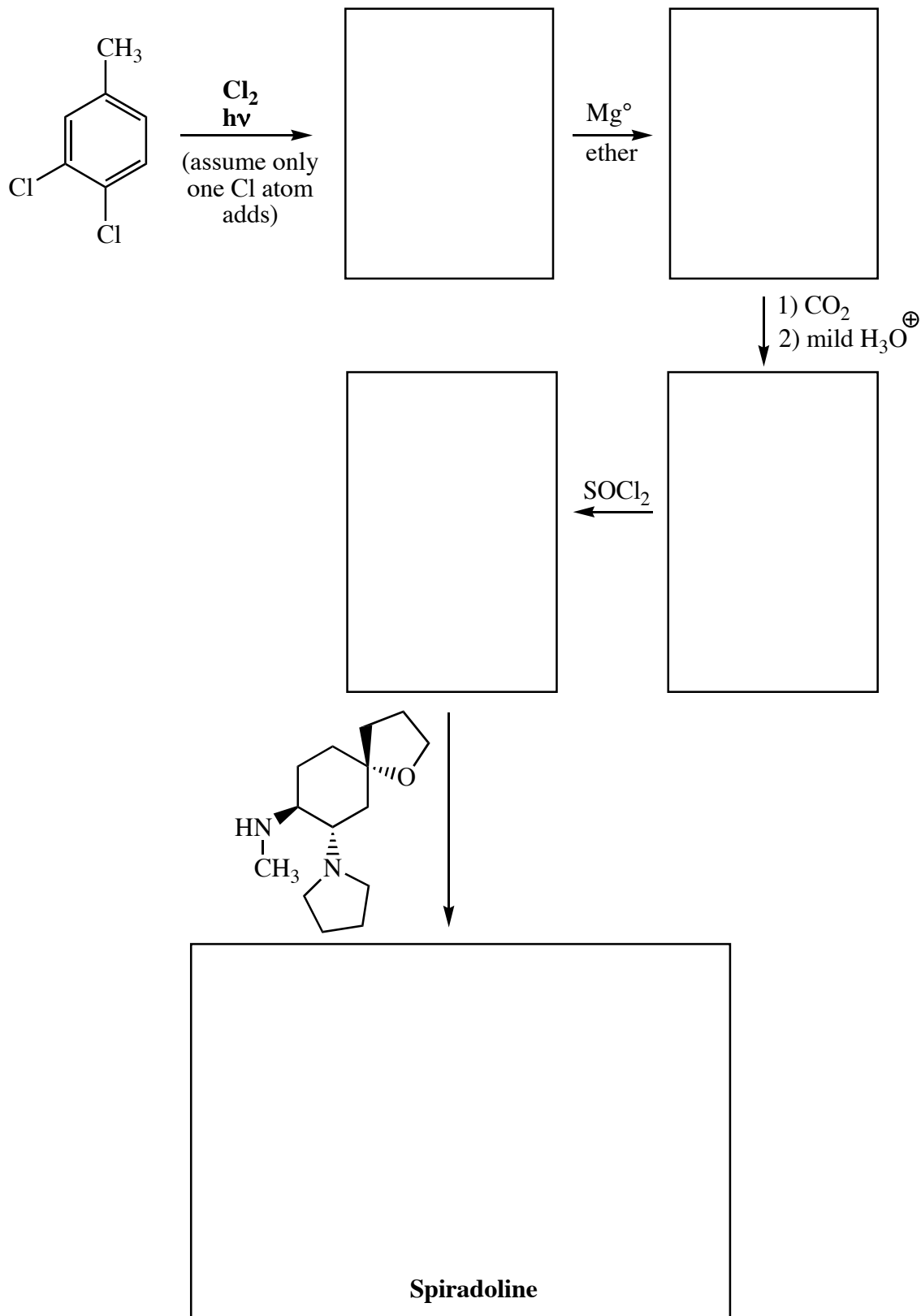


**15 cont.** (5 pts. each) These are a little harder, so take your time. Write the predominant product or products that will occur for each sequence of transformations. For aldol reactions, assume dehydration takes place and you must draw both *E* and *Z* products unless one predominates by a substantial margin. Label any new chiral centers with an asterisk and write "racemic" if appropriate.

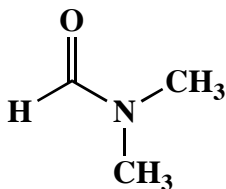




16. (17 pts) Here is the end of an actual synthesis of a powerful opioid analgesic called spiradoline. Fill in the boxes with the appropriate molecules. Use wedges and dashes to indicate the appropriate stereochemistry.



17. (10 points) *N,N*-Dimethylformamide (DMF) is a very popular solvent.



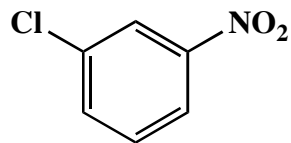
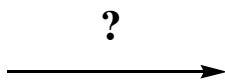
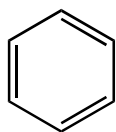
*N,N*-Dimethylformamide (DMF)

A) How many different signals would you expect in the  $^1\text{H-NMR}$  spectrum of DMF taken at room temperature? In no more than two sentences, explain your answer.

B) Would you expect DMF to be good at dissolving polar molecules? In no more than two sentences explain your answer.

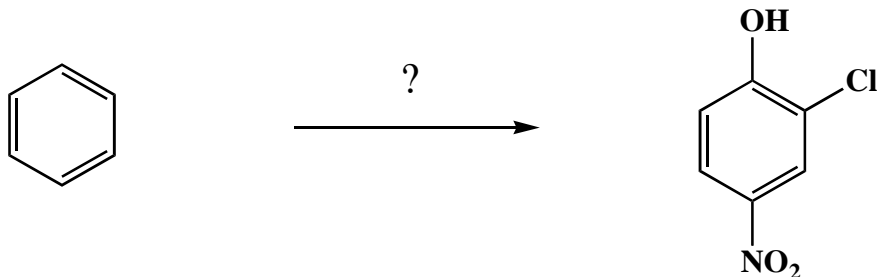
18. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! If an ortho/para mixture will be the major products of a reaction, you can choose whether you would like to isolate the ortho or para product for your synthesis.

A) (4 pts)



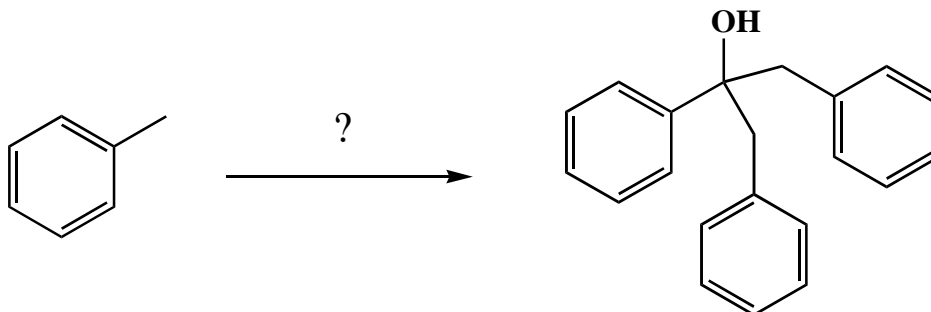
18. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! If an ortho/para mixture will be the major products of a reaction, you can choose whether you would like to isolate the ortho or para product for your synthesis.

B) (16 pts)



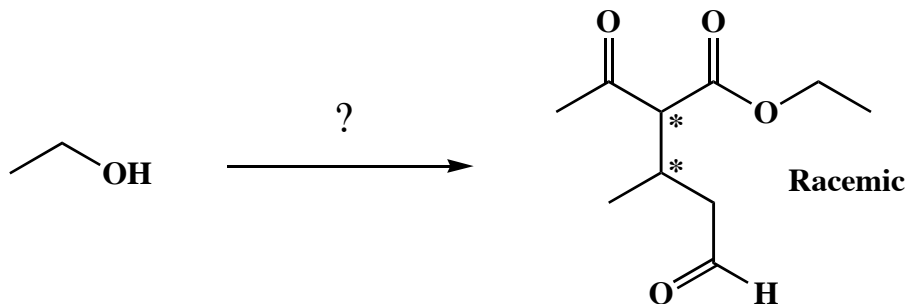
18. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! If an ortho/para mixture will be the major products of a reaction, you can choose whether you would like to isolate the ortho or para product for your synthesis.

C) (16 pts)



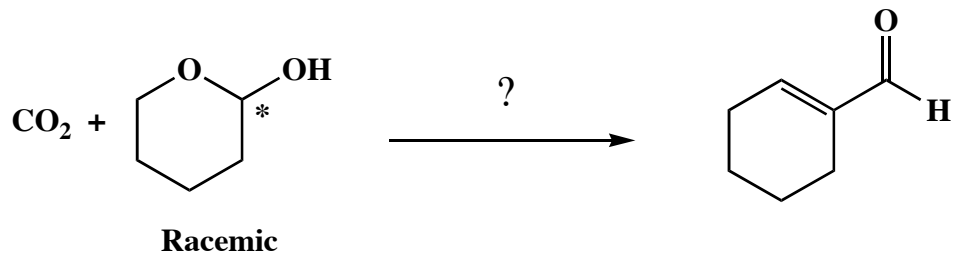
18. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! If an ortho/para mixture will be the major products of a reaction, you can choose whether you would like to isolate the ortho or para product for your synthesis.

D) (19 pts)



18. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! If an ortho/para mixture will be the major products of a reaction, you can choose whether you would like to isolate the ortho or para product for your synthesis.

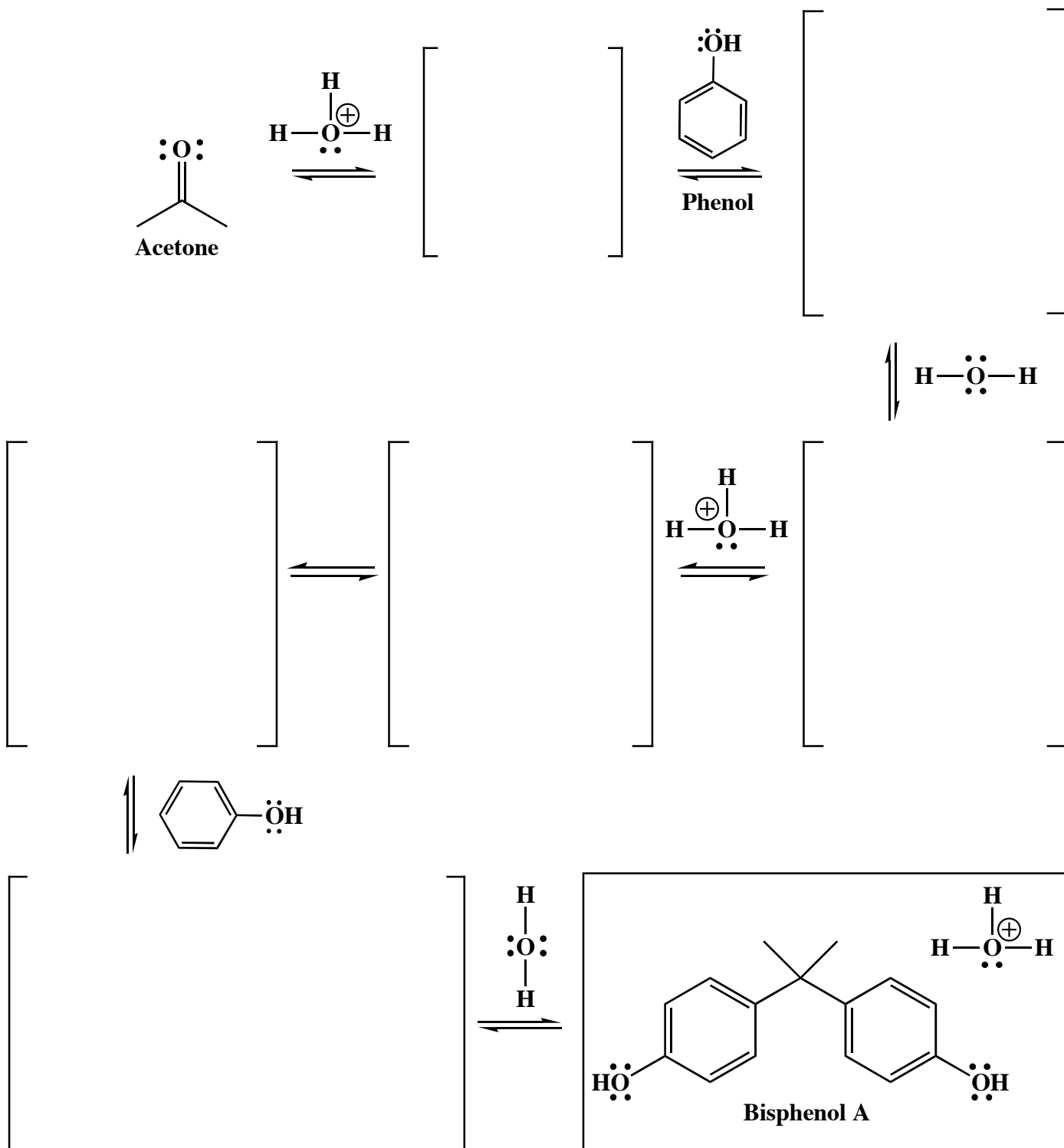
E) (22 pts)



19. (28 pts) Here is an all-time first for my class. This is an "apply what you know" mechanism question.

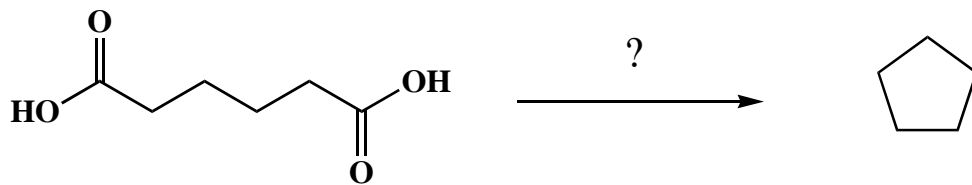
Even though you have not seen this before, **all of the steps are related to ones you have seen.**

**Bisphenol A** has been in the news lately for concerns about health as it leaches out of plastic Nalgene water bottles. Complete the mechanisms below that shows how bisphenol A is synthesized from phenol and acetone in strong acid. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. If a racemic product is formed, just put an asterisk (\*) next to the chiral center and write "racemic" under it. *Hint: there is no "hemi" in this one, and no acetal either because those structures are not stable for steric reasons.*



20. This is not worth a lot of points so I wanted you to save it until last. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule!

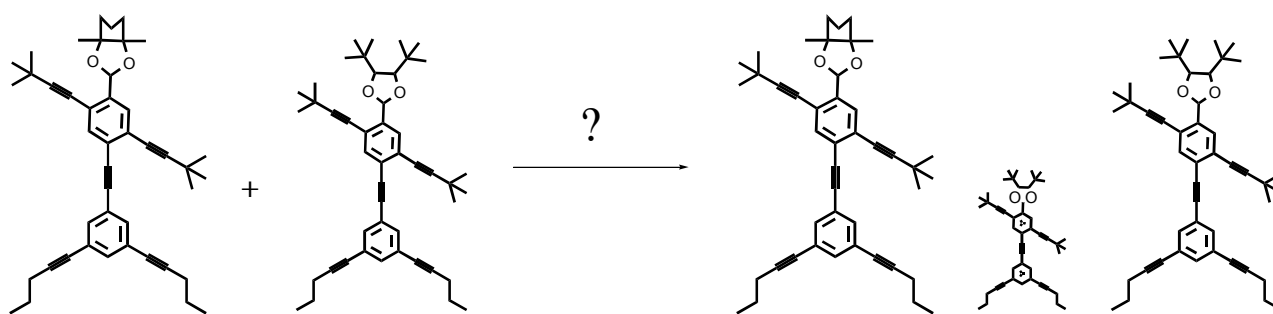
(10 pts)



Thank you for taking your Organic Chemistry journey with us. We enjoyed getting to know you and wish you all the success in the world. Remember to always ask “where are the electrons” when you see molecules, and run every chance you get to stay healthy!!!! Have a safe and productive summer.



Synthesis Question for Chemistry Nerds



Page	Points
1	(30)
2	(21)
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8	(21)
9	(46)
10	(44)
11	(20)
12	(20)
13	(17)
14	(14)
15	(16)
16	(16)
17	(19)
18	(22)
19	(28)
20	(10)
Total	(497)
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Total Grade	

(HW score + Exam Grade)  $\implies$