

CH320N
Spring 2013

Anslyn

March 19th, 2013

Exam 2 Key

Please **PRINT** the first three letters of your last name in the three boxes.

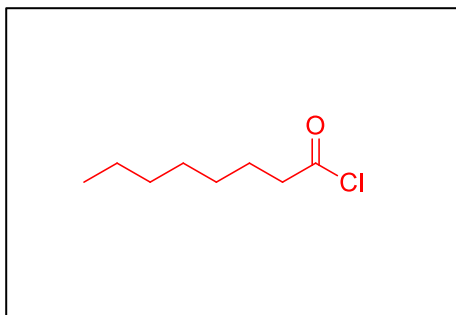
--	--	--

PRINT Name _____

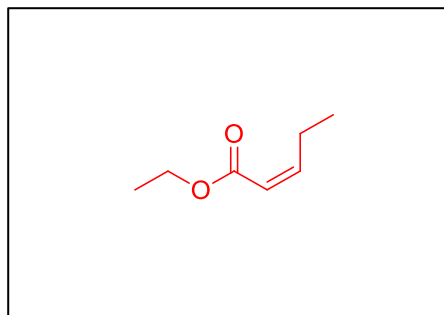
UT-EID _____

Problem 1. (2 points each, 10 pts total)

a) Draw the chemical structures for the following IUPAC names. (From homework 18.12)

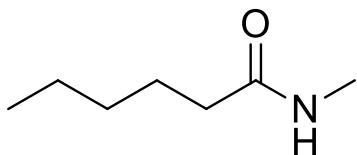


octanoyl chloride

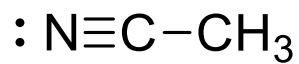


ethyl (Z)-2-pentenoate

b) Give the IUPAC names for the following molecules. (From homework 18.13 and notes)

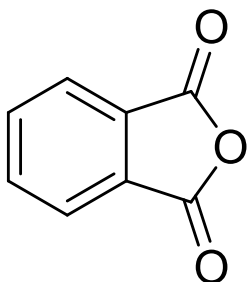


N-methylhexanamide



acetonitrile

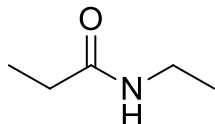
c) Give the common name for the following molecule. (From notes)



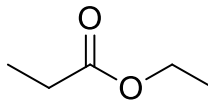
phthalic anhydride

Problem 2. (16 points total)

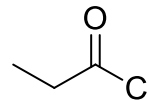
- a) (3 points) Rank the following carboxylic acid derivatives in order from most reactive (1) to least reactive (3).



3

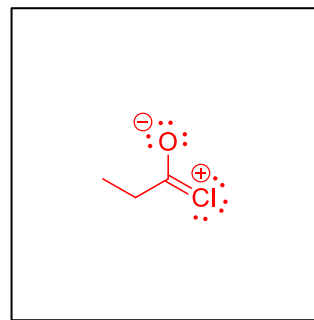
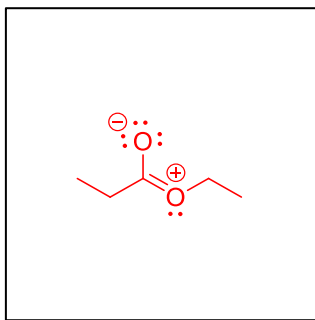
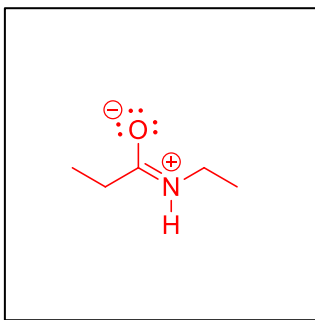


2

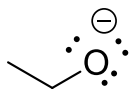


1

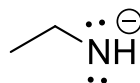
- b) (6 points) Draw one resonance structure, where carbon has full valence, for each carboxylic acid derivative shown in **part a**.



- c) (3 points) Rank the following leaving groups in order from best (1) to worst (3).



2



3



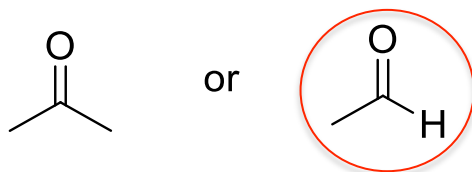
1

- d) (4 points) Give two one-sentence answers that explain your answer to **part a**.

- The order of electrophilicity of the carbonyl carbon is acid chloride>ester>amide due to
 - the strength of the inductive effect from each of these heteroatoms which is in the order $\text{Cl} > \text{O} > \text{N}$ (due to electronegativity order $\text{Cl} > \text{O} > \text{N}$)
 - the differing degree of orbital overlap between the orbitals on the carbonyl carbon and the heteroatom, which is in the order $\text{N} > \text{O} > \text{Cl}$.
 - favorability of placing a positive charge on the heteroatom in the resonance structures shown in part b above, which is in the order $\text{N} > \text{O} > \text{Cl}$ because of electronegativity order ($\text{Cl} > \text{O} > \text{N}$). Any **one** of the answers a-c was accepted as the second part of the statement.
- Chloride is a better leaving group than ethoxide, which is a better leaving group than amide anion (due to the electronegativity of the heteroatom carrying the negative charge).

Problem 3. (6 points)

- a) (2 points) Circle the better electrophile of the two molecules below.

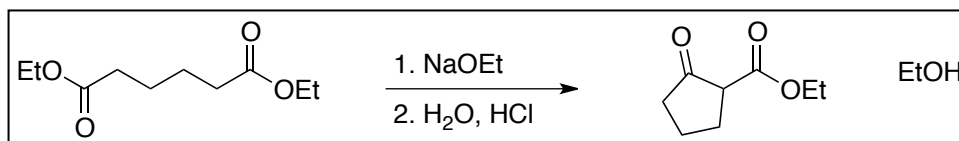


*An aldehyde hydrogen like the one shown above on the right is **not** an alpha hydrogen. Alpha hydrogens are the ones on the alkyl groups next to the carbonyl.

- b) (4 points) Give two one-sentence answers that explain your answer to **part a**).

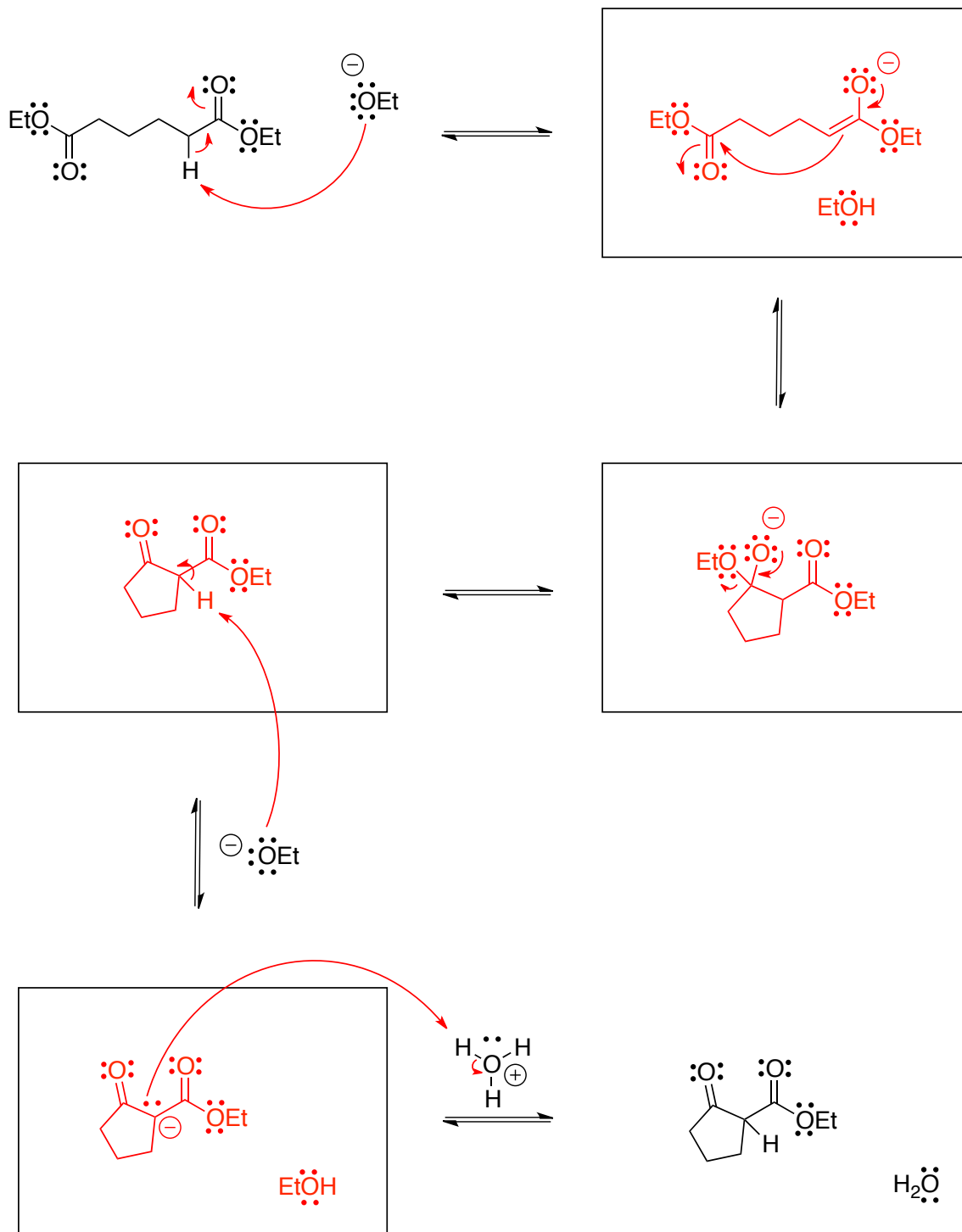
1. The aldehyde is less sterically hindered.
2. The partial positive charge of the carbonyl is better stabilized by methyl groups than hydrogens, so the aldehyde is more electrophilic.

Problem 4. (22 points) Using the boxes provided on the following page, write the mechanism for the Dieckmann condensation shown below. Draw all the arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all products for each step. This mechanism is from your notes.



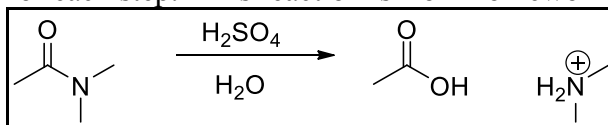
WRITE YOUR ANSWER ON THE NEXT PAGE

THIS IS PROBLEM 4

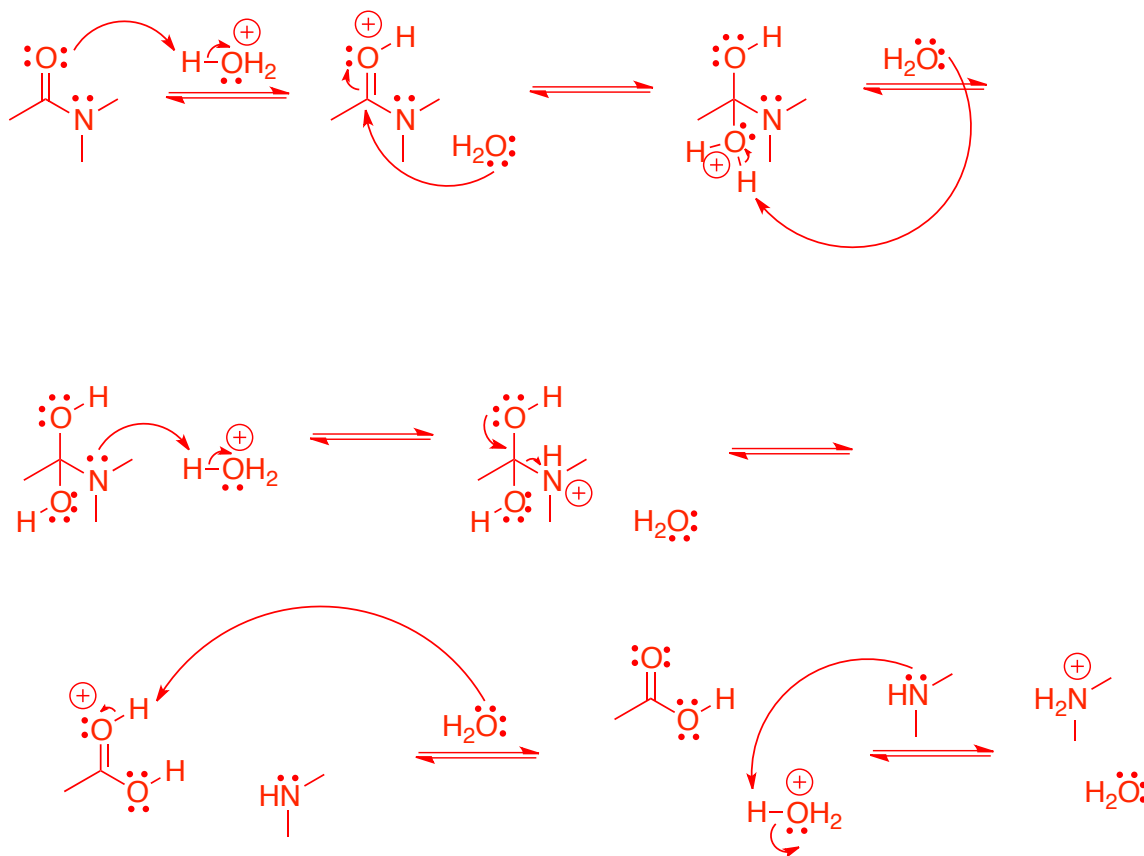


* Alternate **correct** resonance structures were accepted where applicable. FYI: tautomers are not resonance structures of one another.

Problem 5. (34 points) On this page, write the mechanism for the hydrolysis of the amide shown below. Draw all the arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all products for each step. This reaction is from homework problem 18.56(a).



WRITE YOUR ANSWER BELOW



* Deprotonation of the carbonyl by the amine was accepted. Showing proton transfers in one step that should have been multiple separate steps or doing proton transfers in the wrong order was accepted for full credit. You had to show lone pairs attacking properly in your arrow pushing in order to get points for those arrows (i.e., from a lone pair you drew out on a correct atom). Sulfuric acid was accepted for use in proton transfers, but you had to do it correctly for credit.

What is the *minimum* amount of H_2SO_4 needed to drive the above reaction to completion? (Circle **one** of the options below for 2 points)

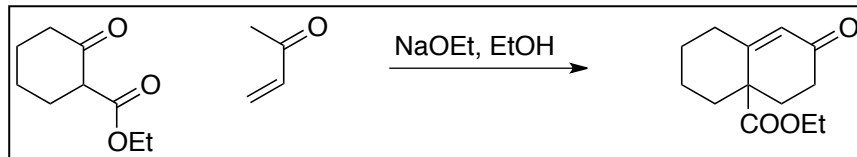
catalytic

1 equiv.

2 equiv.

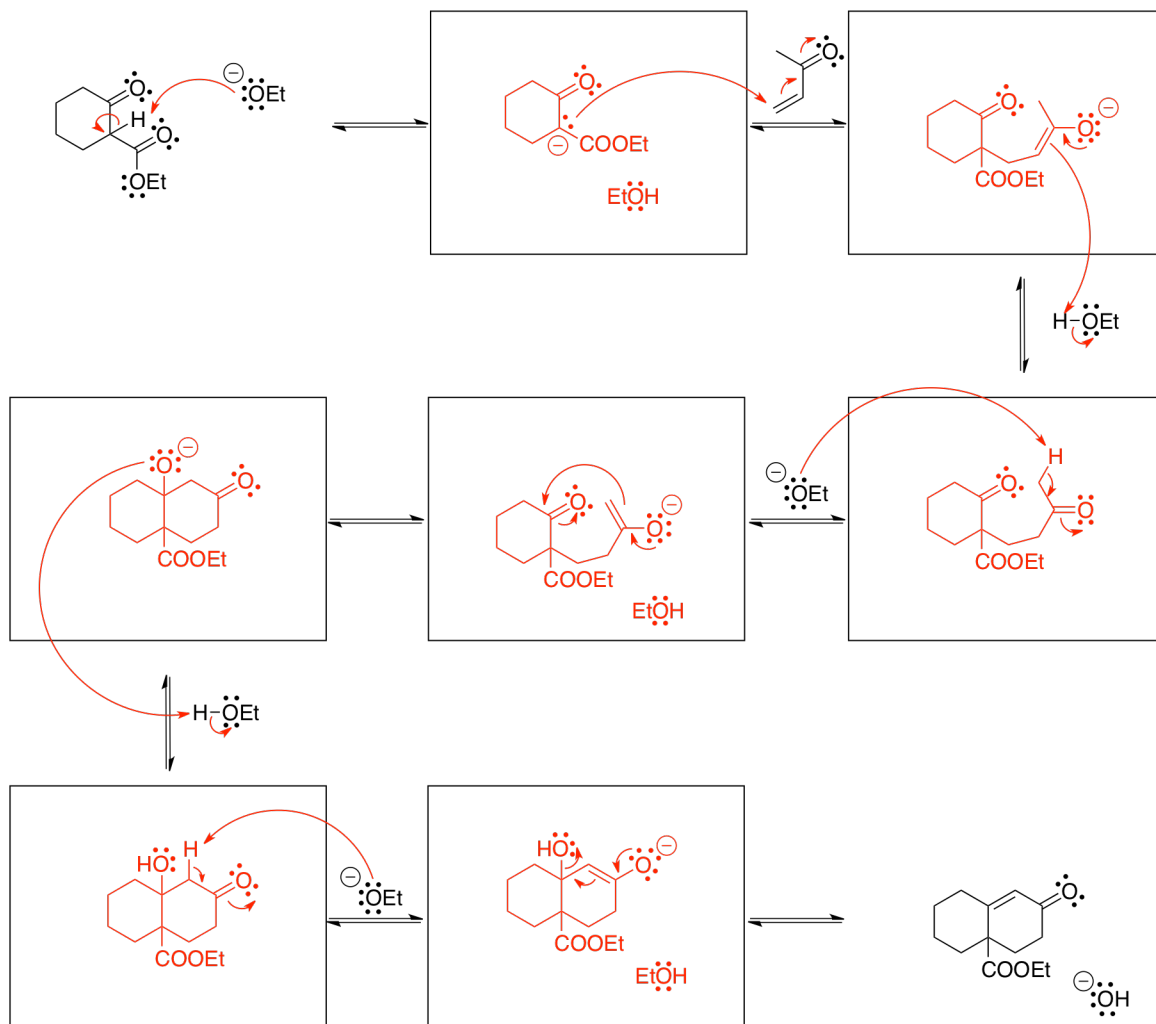
excess

Problem 6. (39 points) In the boxes on the following page, write the mechanism for the Robinson annulation shown below. Draw all the arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all products for each step. (It is acceptable to abbreviate the ethyl ester as COOEt without showing lone pairs as shown below). This mechanism is from your notes.



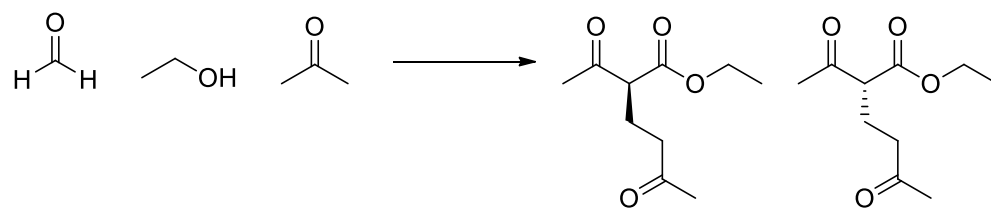
WRITE YOUR ANSWER ON THE NEXT PAGE

THIS IS PROBLEM 6

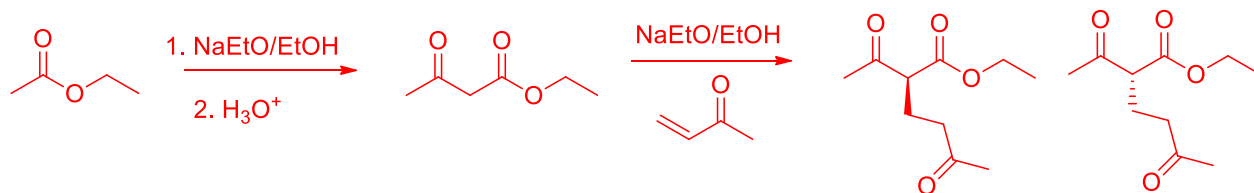
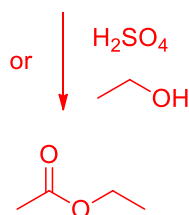
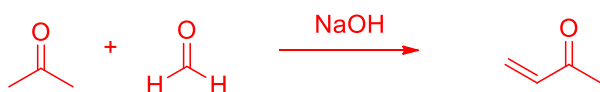


* Alternate **correct** resonance structures were accepted where applicable. FYI: tautomers are not resonance structures of one another.

Problem 7. (16 points) Using the following starting materials as your only source of all carbon atoms in the product, show how to synthesize ethyl 2-acetyl-5-oxohexanoate in the space below. Show all reagents and steps, and show all molecules synthesized along the way. If you make a racemic mixture, draw **both** enantiomers and write **racemic**. (From homework 19.76)

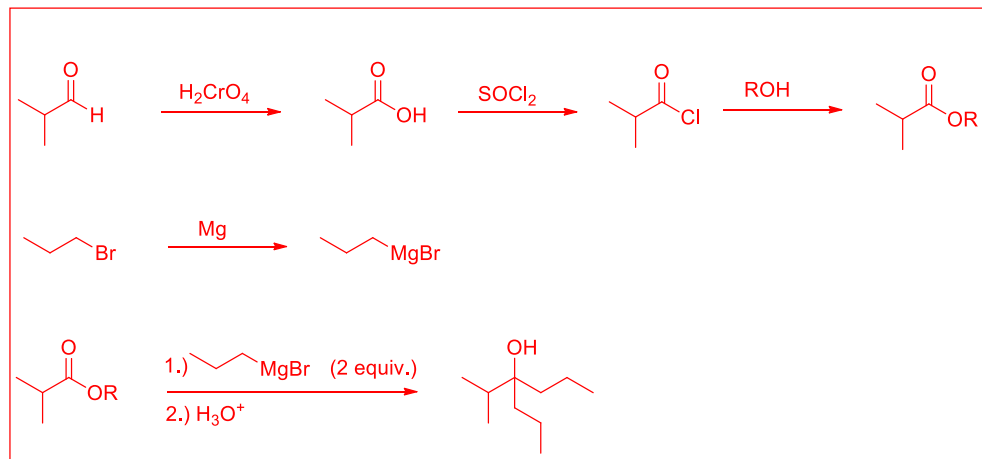
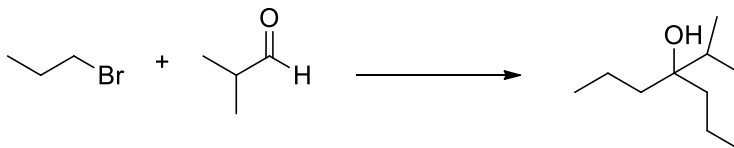


racemic

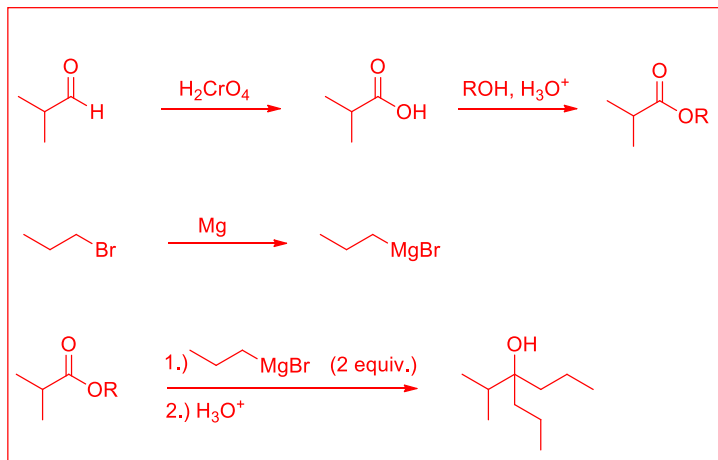


racemic

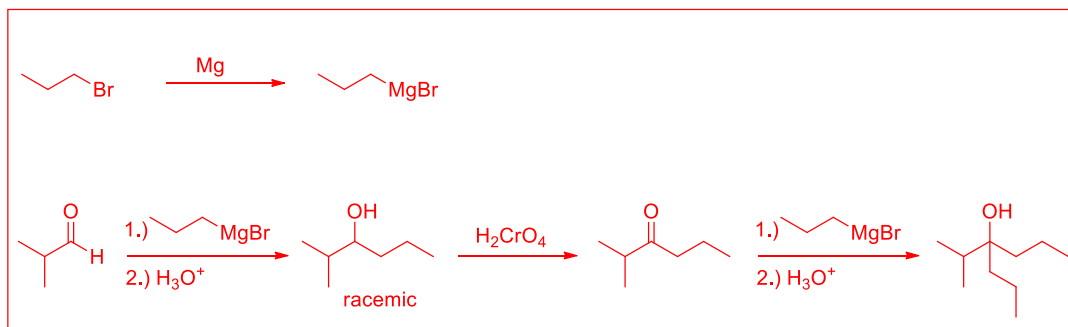
Problem 8. (13 points) Using the provided starting materials as your only source of all carbon atoms in the product, show how to synthesize the following alcohol. Show all reagents and steps, and show all molecules synthesized along the way. If you make a racemic mixture, draw **both** enantiomers and write **racemic**.



OR

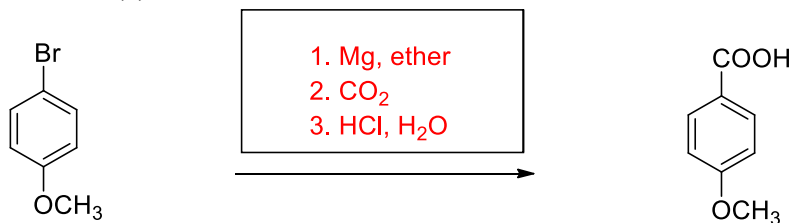


OR

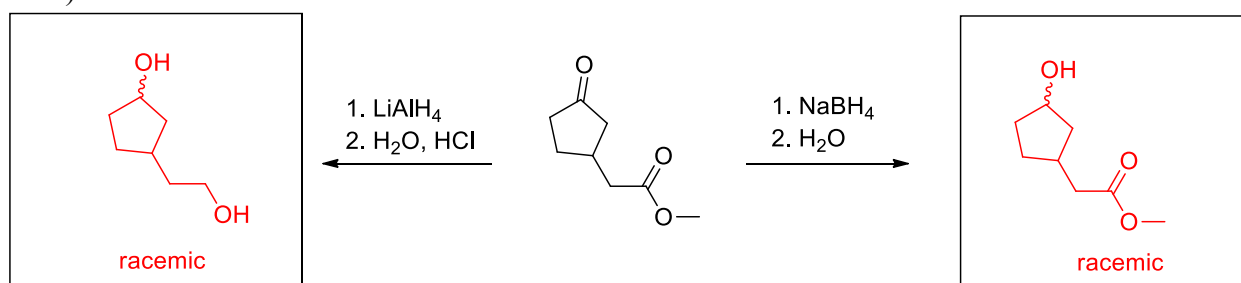


Problem 9. (30 points, 3 per box) Fill in the boxes with the appropriate reactant, reagents, or product to achieve the following transformation. Some boxes require more than one step. If you generate a racemic mixture, write **racemic** under the structure. To get full credit you only need to write the major organic product for these. You do not have to worry about the other products.

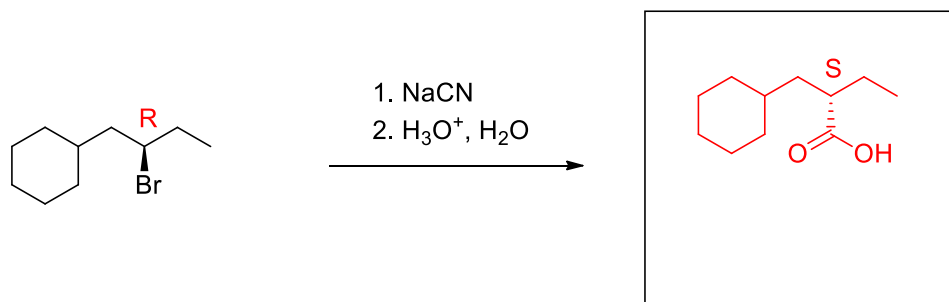
a) From homework 17.18(a).



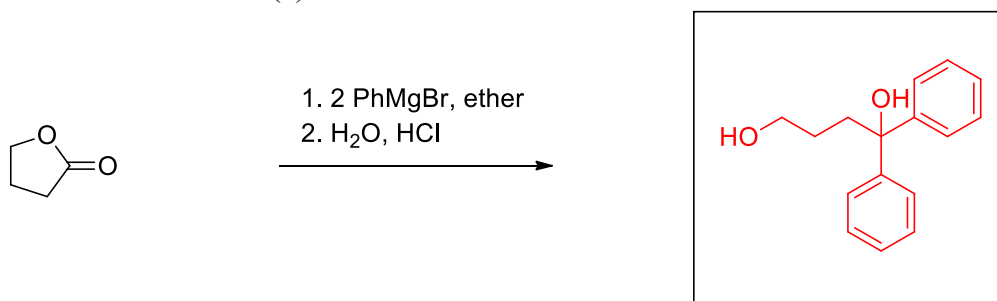
b)



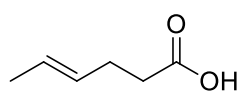
c)



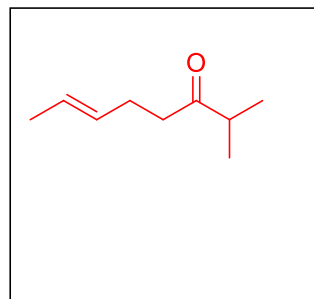
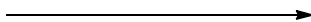
d) From homework 18.32(c).



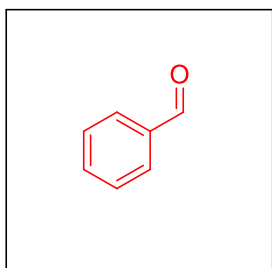
e)



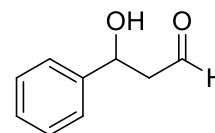
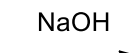
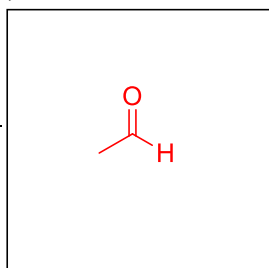
1. SOCl_2
 2. $(i\text{-(CH}_3)_2\text{CH})_2\text{CuLi}$
 3. H_2O



f) From homework 19.22(a).

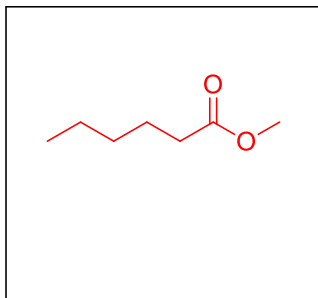


+

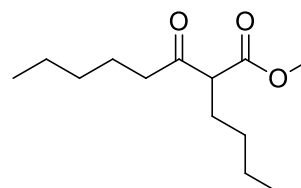


racemic

g) From homework 19.29(b).

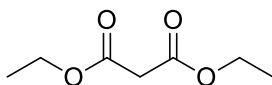


1. NaOMe/MeOH
 2. $\text{HCl, H}_2\text{O}$

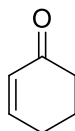


racemic

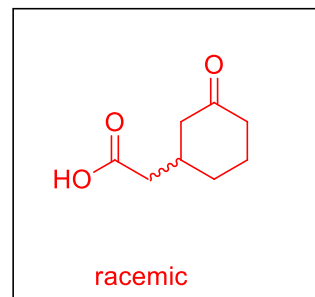
h)



1. NaOEt/EtOH
 2.

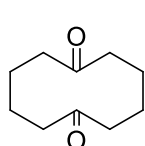
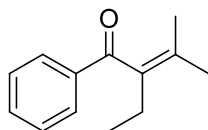
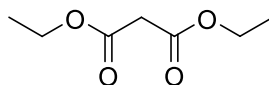
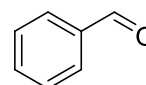
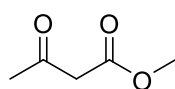
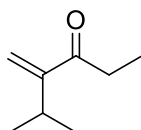
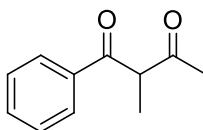
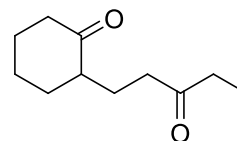
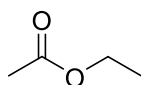
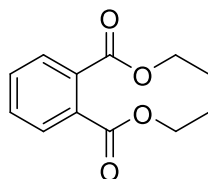
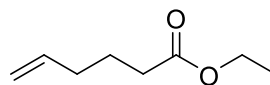
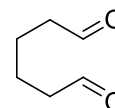
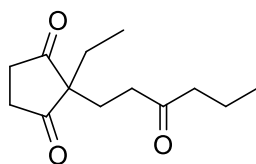
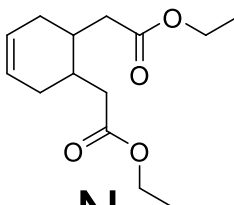
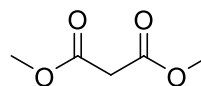
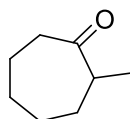
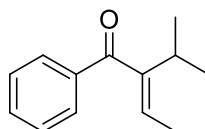


3. $\text{NaOH/H}_2\text{O}$
 4. $\text{HCl/H}_2\text{O}$
 5. heat



Problem 10. (27 points, 3 per box) This problem involves **retrosynthetic analysis**. In the boxes provided on page 16, write the **letter** of the corresponding starting material that will give you the indicated product. Possible starting materials are listed below.

Note: A molecule may only be chosen once, and not all of the provided molecules will be used.

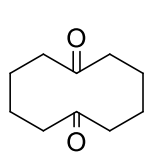
**A****B****C****D****E****F****G****H****I****J****K****L****M****N****O****P****Q**

THIS PAGE IS THE SAME AS THE PREVIOUS PAGE

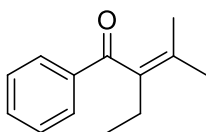
TEAR THIS PAGE OUT FOR EASY MATCHING

Write the ***letter*** that corresponds to the correct molecule in the boxes on page 16.

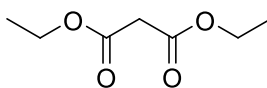
Note: A molecule may only be chosen once, and not all of the provided molecules will be used.



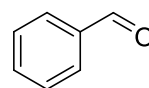
A



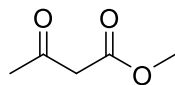
B



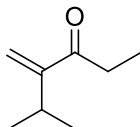
C



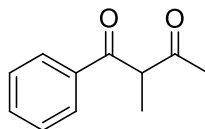
D



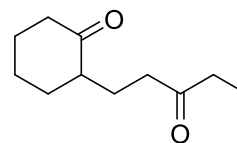
E



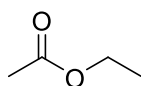
F



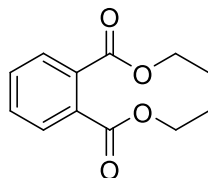
G



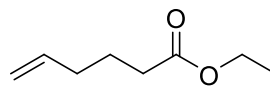
H



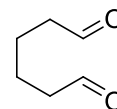
I



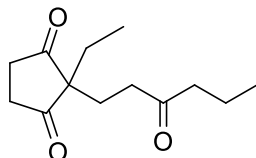
J



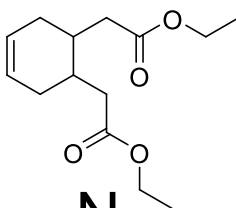
K



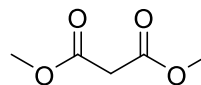
L



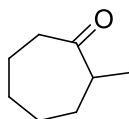
M



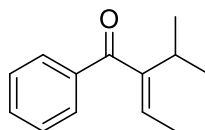
N



O

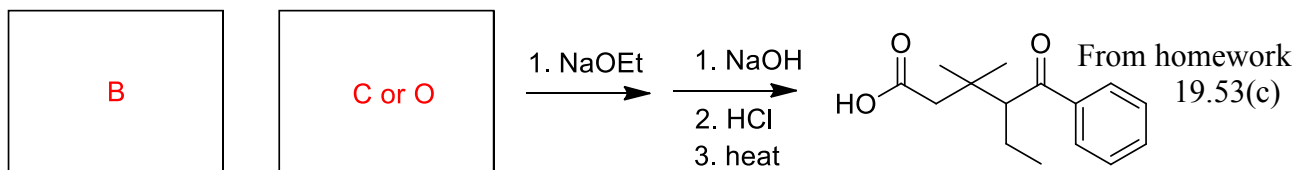
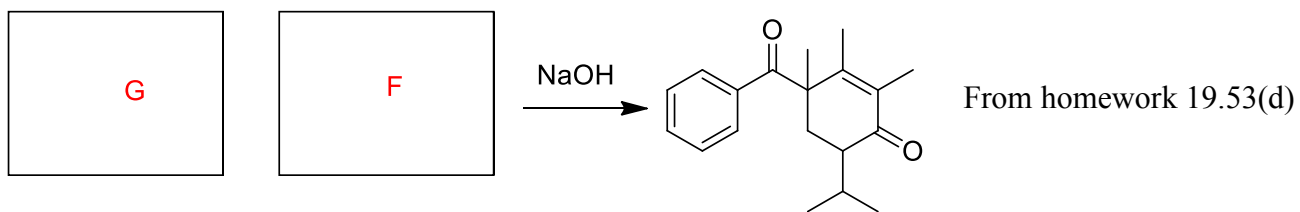
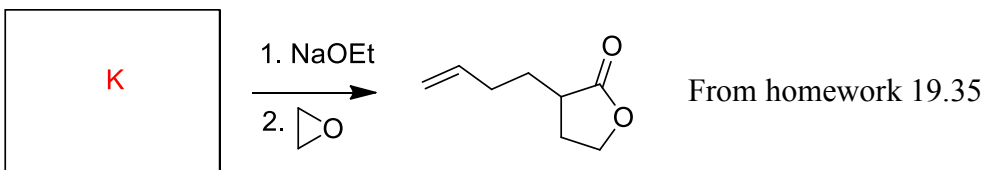
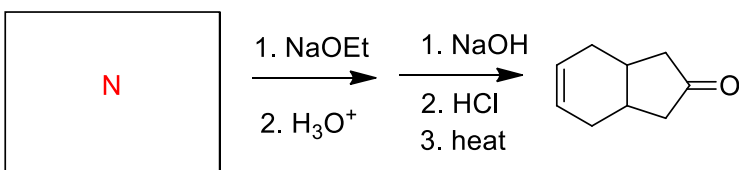
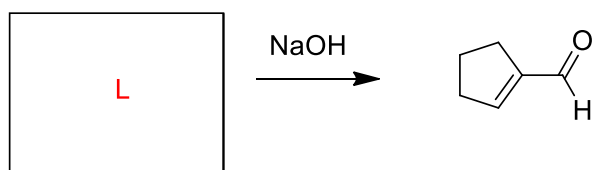
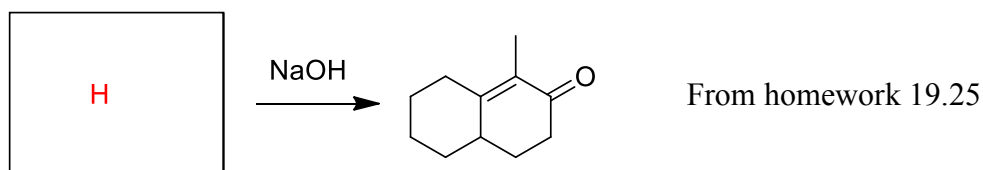
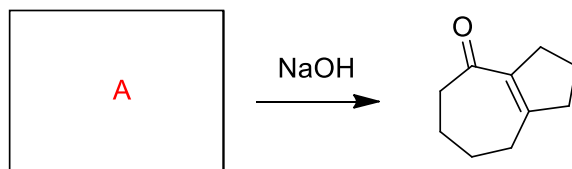


P



Q

IN THE BOX, WRITE THE **LETTER** OF THE CORRECT STRUCTURE



**THIS PAGE INTENTIONALLY LEFT BLANK.
PLEASE FEEL FREE TO USE IT AS SCRATCH**

Bonus Question. (3 points) In Dr. Anslyn's opinion, what is the best rock band from the late 1970s and early 1980s? **Yes**

**Anslyn CH320N
Spring 2013**

Second Midterm

March 19th, 2013

EXAM SCORE

2) _____ (10 pts)
3) _____ (16 pts)
4) _____ (6 pts)
6) _____ (22 pts)
7) _____ (34 pts)
9) _____ (39 pts)
10) _____ (16 pts)
11) _____ (13 pts)
12) _____ (15 pts)
13) _____ (15 pts)
16) _____ (27 pts)
Bonus) _____ (3 pts)

Total _____ (213 pts)