

NAME (Print): _____

Chemistry 320N
Dr. Brent Iverson
Final
May 14, 2013

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.

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

Page Points

1		(25)
2		(24)
3		(16)
4		(14)
5		(14)
6		(19)
7		(32)
8		(29)
9		(19)
10		(18)
11		(38)
12		(18)
13		(17)
14		(18)
15		(17)
16		(13)
17		(19)
18		(16)
19		(4)
20		(16)
Total		(386)

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.

(Your signature)

Compound		pK _a
Hydrochloric acid	$\underline{\text{H}}\text{-Cl}$	-7
Protonated alcohol	$\text{RCH}_2\text{OH}_2^{\oplus}$	-2
Hydronium ion	$\underline{\text{H}}_3\text{O}^{\oplus}$	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\underline{\text{H}}$	3-5
Ammonium ion	$\underline{\text{H}}_4\text{N}^{\oplus}$	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\underline{\text{H}}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	10
Primary ammonium	$\underline{\text{H}}_3\text{N}^{\oplus}\text{CH}_2\text{CH}_3$	10.5
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\underline{\text{H}}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\underline{\text{H}}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	13
Water	$\text{HO}\underline{\text{H}}$	15.7
Alcohols	$\text{RCH}_2\text{O}\underline{\text{H}}$	15-19
Acid chlorides	$\text{RC}\underline{\text{H}}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RC}\underline{\text{H}}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RC}\underline{\text{H}}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	18-20
Esters	$\text{RC}\underline{\text{H}}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\underline{\text{H}}$	25
LDA	$\underline{\text{H}}-\text{N}(\textit{i}\text{-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\underline{\text{H}}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\underline{\text{H}}$	51

It has been an amazing year in many ways. I was worried after the second midterm, but you did great on the third one. It is the hope of the TA's and myself that you keep up the momentum and do well on this final.

This two-semester course has been an amazing journey. It started last fall with some simple but powerful ideas of structure and bonding, then took you through the increasingly complicated reactions of all the major functional groups, culminating in enolate chemistry. Along the way, we hope you learned how to predict the reactions and properties of organic molecules. If so, you will understand how the world operates in a whole new way, setting the stage for all of the biochemistry or other advanced chemistry courses you will be taking. Most important, we hope that for the rest of your life you will continue to notice and decipher the molecular phenomena that will surround you always.

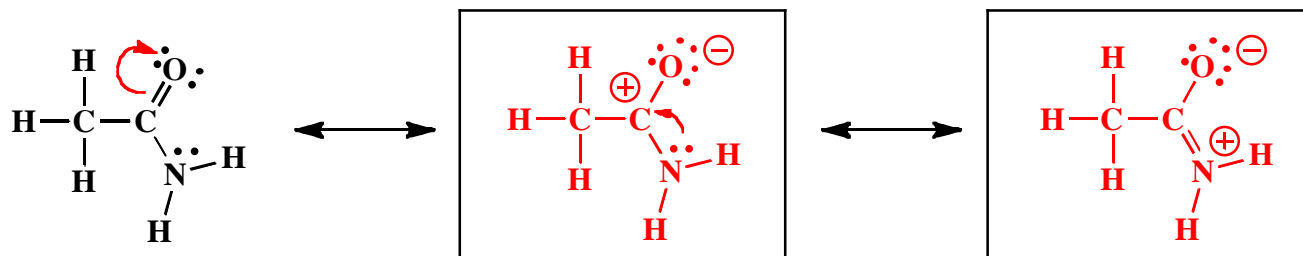
Have a safe summer and remember to run every chance you get. Staying fit for the rest of your life is the best way to enjoy the success you are working right now to achieve. I hope to see you on campus or on the trail running in coming years. If so, make sure to give me a “where are the electrons?” shout out so I know you are there!

Brent Iverson

1. (4 pts) What is the most important question in chemistry?

Where are the electrons?

2. (8 pts) On the left is drawn the Lewis structure of a simple amide. Draw the two next most important contributing structures in the spaces provided. Be sure to show all lone pairs and formal charges. You do not need to draw arrows on the structures, but you can if it helps you.



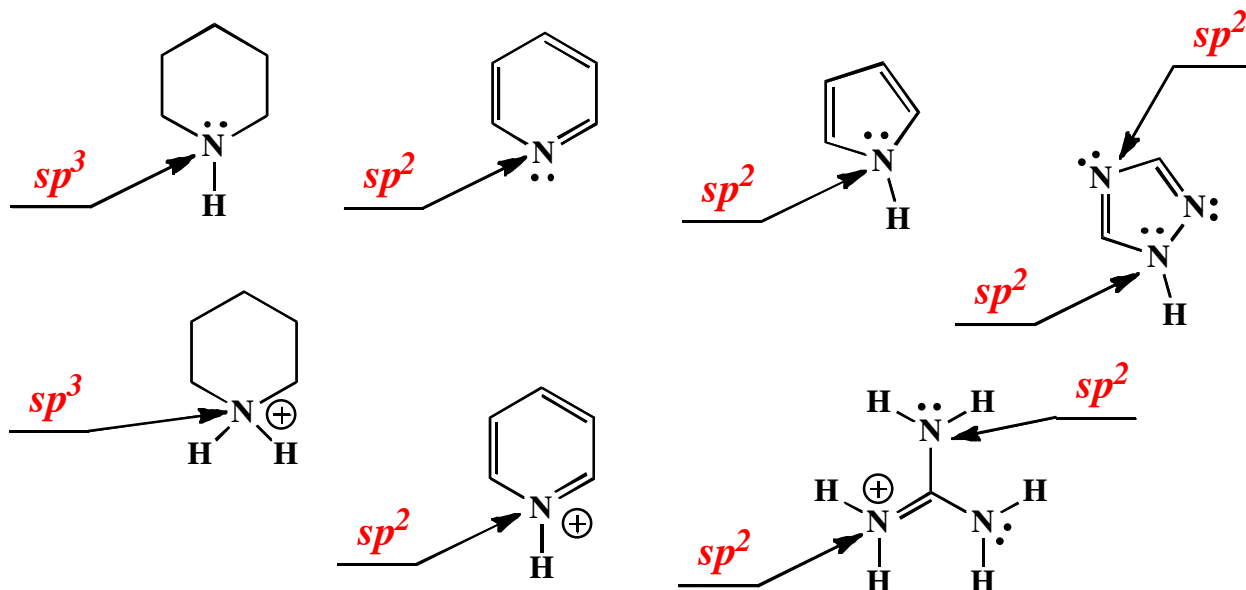
3. (2 pts) For the amide of problem 2., state what kind of orbital contains the lone pair on the nitrogen atom.

A 2p orbital

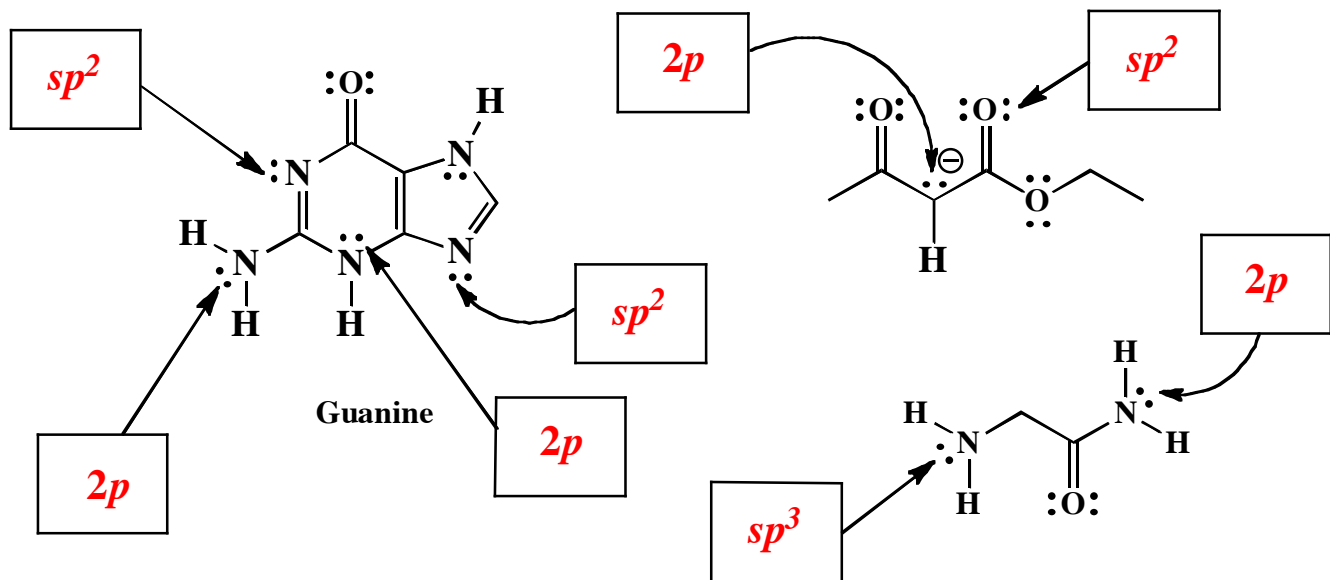
4. (2 pts) For the amide of problem 2., state the hybridization state of the N atom.

sp^2 hybridization

5. (9 pts) On the line provided, state the hybridization state of the N atom indicated by the arrow.

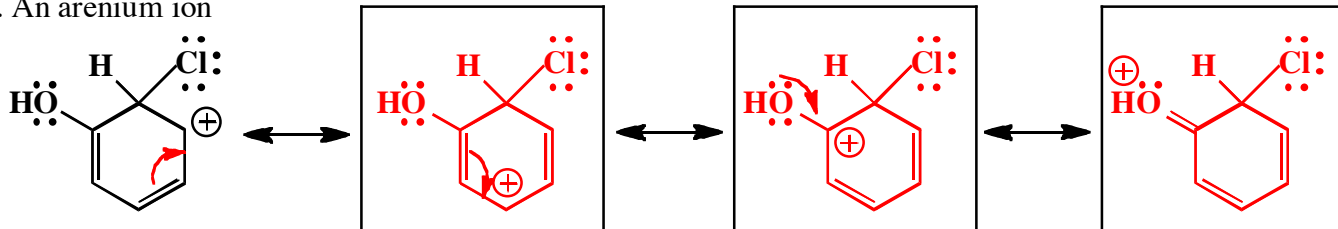


6. (8 pts) In the boxes provided write the type of atomic orbital that contains the indicated lone pair of electrons.

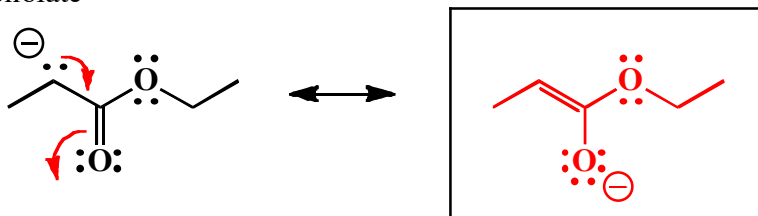


7. (16 pts) Resonance contributing structures are important for both enolates and aromatic molecules. On the following, **draw the indicated number of most important resonance contributing structures**. Show all lone pairs, pi bonds and formal charges. Use arrows to indicate the redistribution of electrons 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.

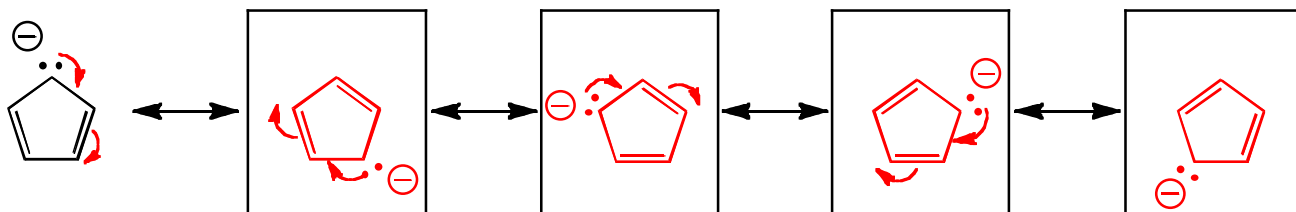
A. An arenium ion



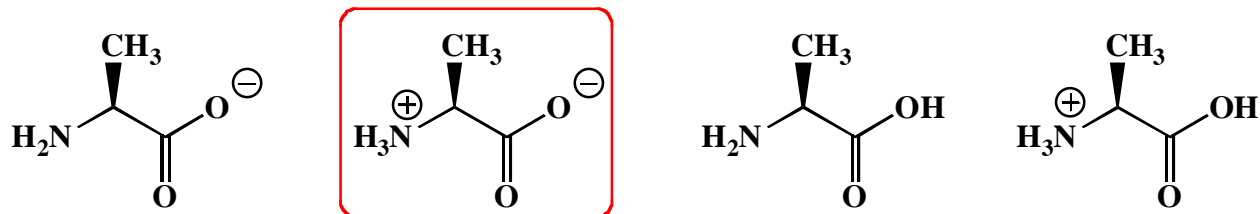
B. An enolate



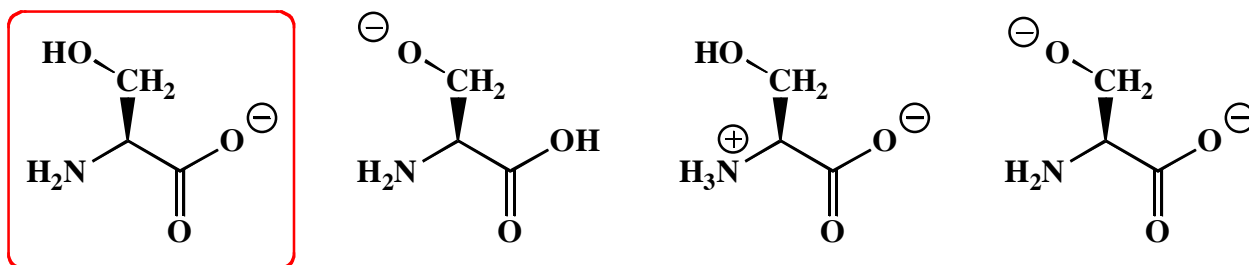
C. An aromatic anion



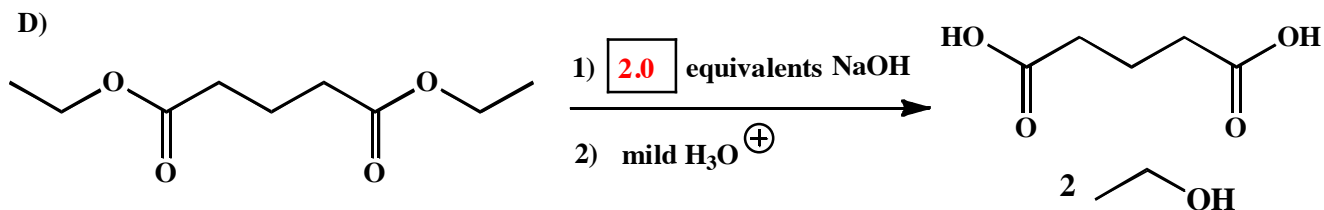
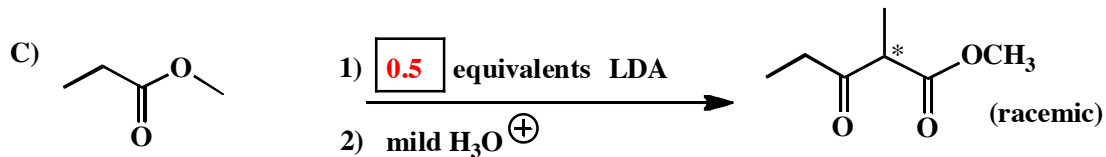
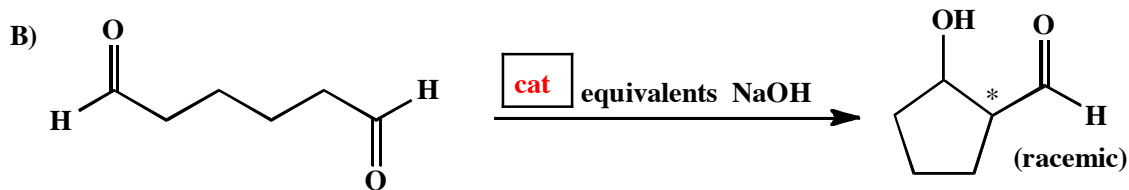
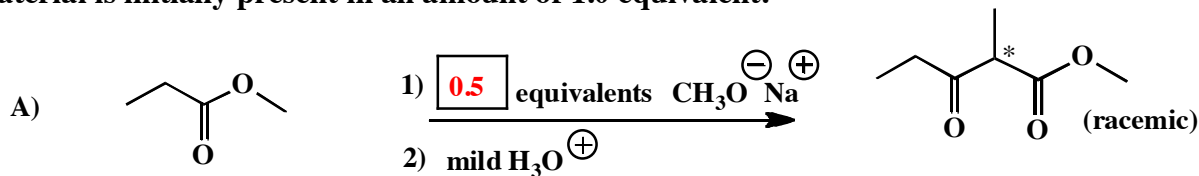
8. (8 pts) A) Circle the predominant species present at pH 7.0



B) Circle the predominant species present at pH 11.0



9. (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.**



10. (2 pts each) I know you were wondering how we were going to test the carbohydrate material. Here is what we came up with. Yes, it looks a lot like last year's test, but we changed the structures. For the following structures, draw a circle around the terms that provide the most accurate description.

Aldohehexose
 Ketohehexose
Aldopentose
 Ketopentose
 Pointy toes
 Fred

α-1,6-Glycosidic bond
 β-1,6-Glycosidic bond
 α-1,5-Glycosidic bond
 β-1,5-Glycosidic bond
 α-1,4-Glycosidic bond

β-1,4-Glycosidic bond
 α-1,3-Glycosidic bond
 β-1,3-Glycosidic bond
 α-1,2-Glycosidic bond
 β-1,2-Glycosidic bond
 Fred

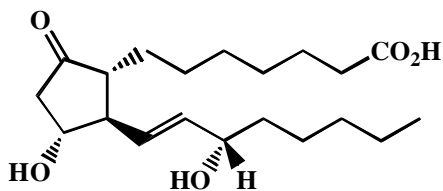
Monomeric carbon
Anomeric carbon
 Polymeric carbon
 Aldehyde carbon
 Fred

This structure is a:
 Furanose
Pyranose
 Comatose
 Bloody nose
 Fred

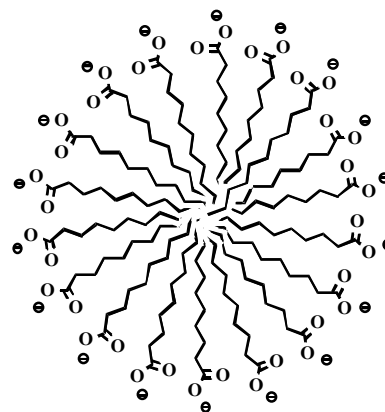
This structure is a:
Furanose
 Pyranose
 Comatose
 Bloody nose
 Fred

α-D-Glucose
β-D-Glucose
 ββ-D-Glucose
 Δ-D-Glucose
 Fred

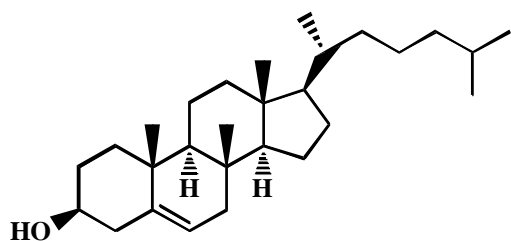
11. (2 pts each) Below are several structures. On the line under each of them, write the appropriate name taken from the list at the bottom of the page.



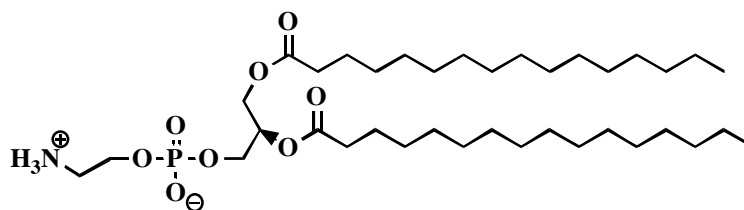
A prostaglandin



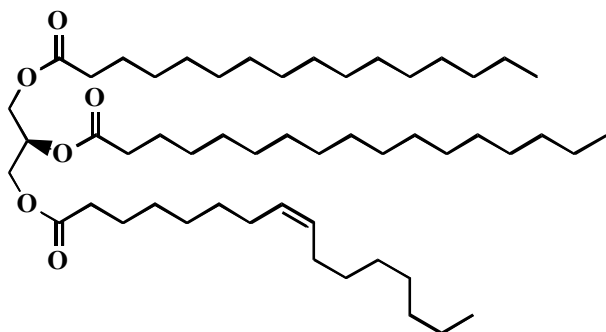
A micelle



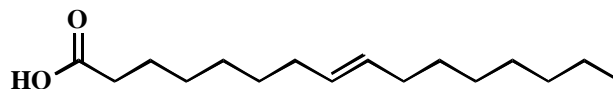
A steroid



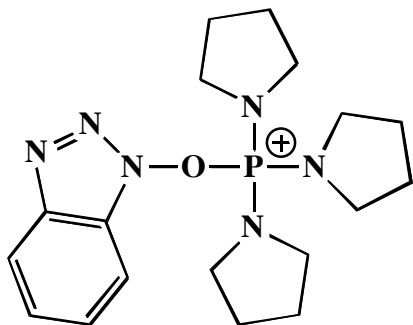
A phospholipid



A triglyceride



A trans fat

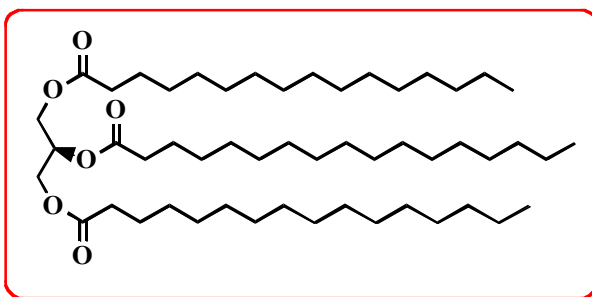
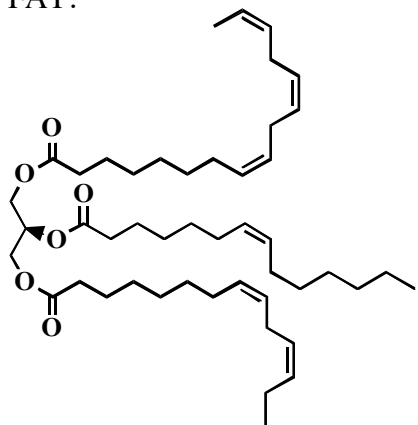


PyBOP

Possible names

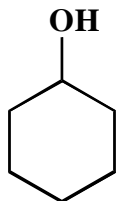
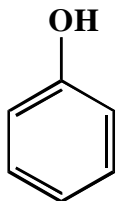
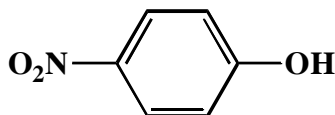
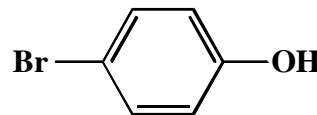
- | | |
|-----------------|----------------|
| A protein | A micelle |
| A triglyceride | A phospholipid |
| A prostaglandin | PyBOP |
| A trans fat | A steroid |
| An amino acid | A nucleic acid |

12. (4 pts) For the following molecules, one is a fat and one is an oil. DRAW A CIRCLE AROUND THE FAT.

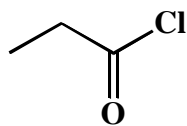
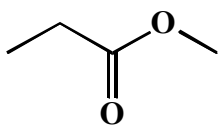
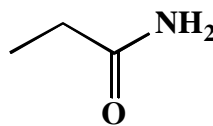
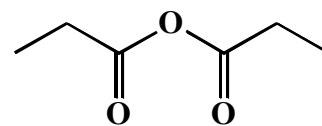
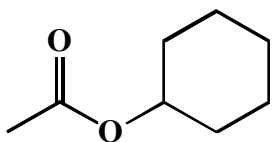
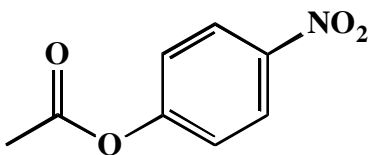
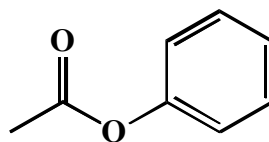
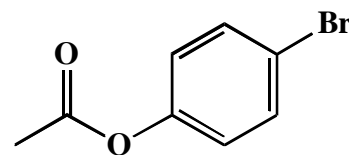


13. (4 or 3 pts each) For the following, rank the molecules according to the directions given.

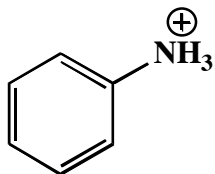
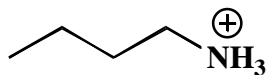
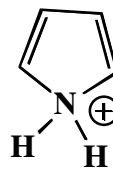
A. Rank from least to most acidic, with a 1 under the least acidic and a 4 under the most acidic molecule.

**1****2****4****3**

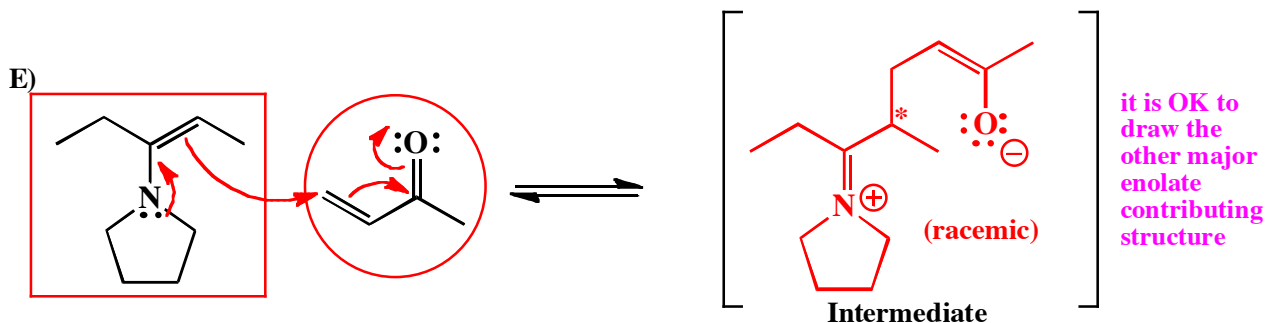
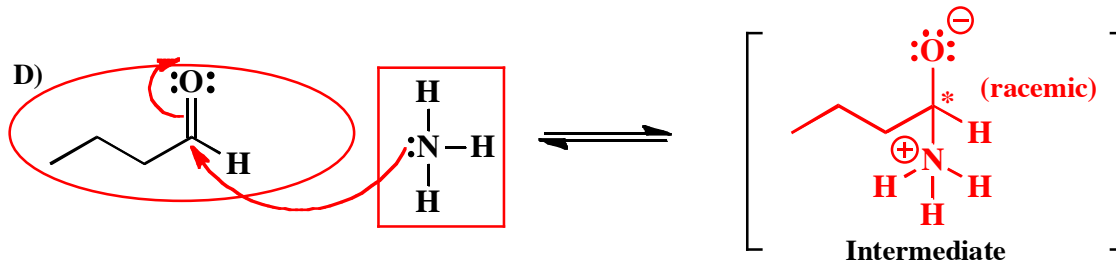
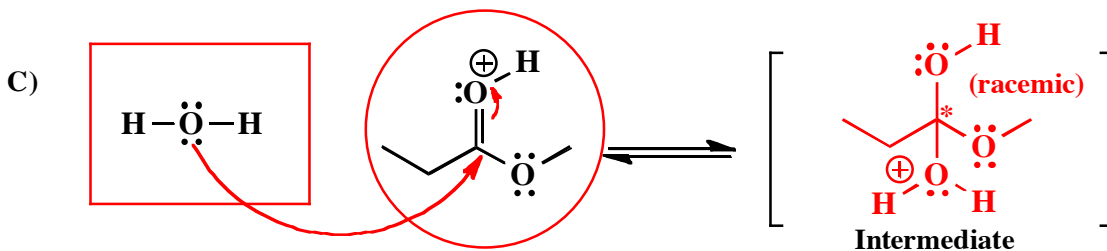
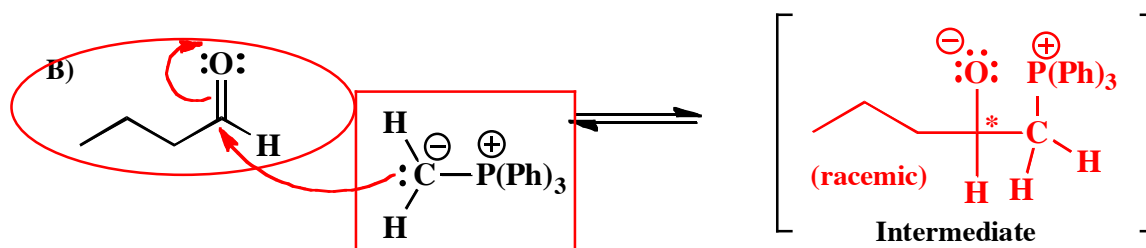
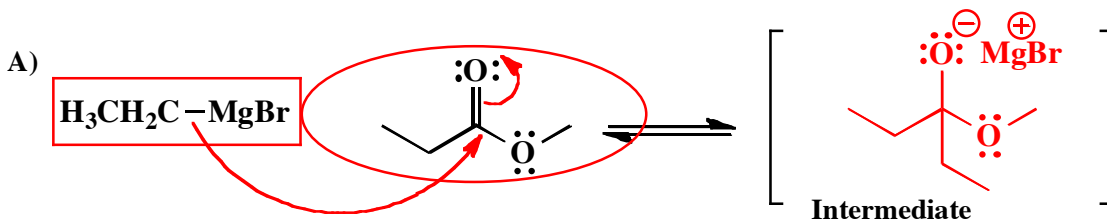
B. Rank from least to most reactive with nucleophiles, with a 1 under the least reactive and a 4 under the most reactive molecule.

**4****2****1****3****1****4****2****3**

C. Rank from least to most acidic, with a 1 under the least acidic and a 3 under the most acidic molecule.

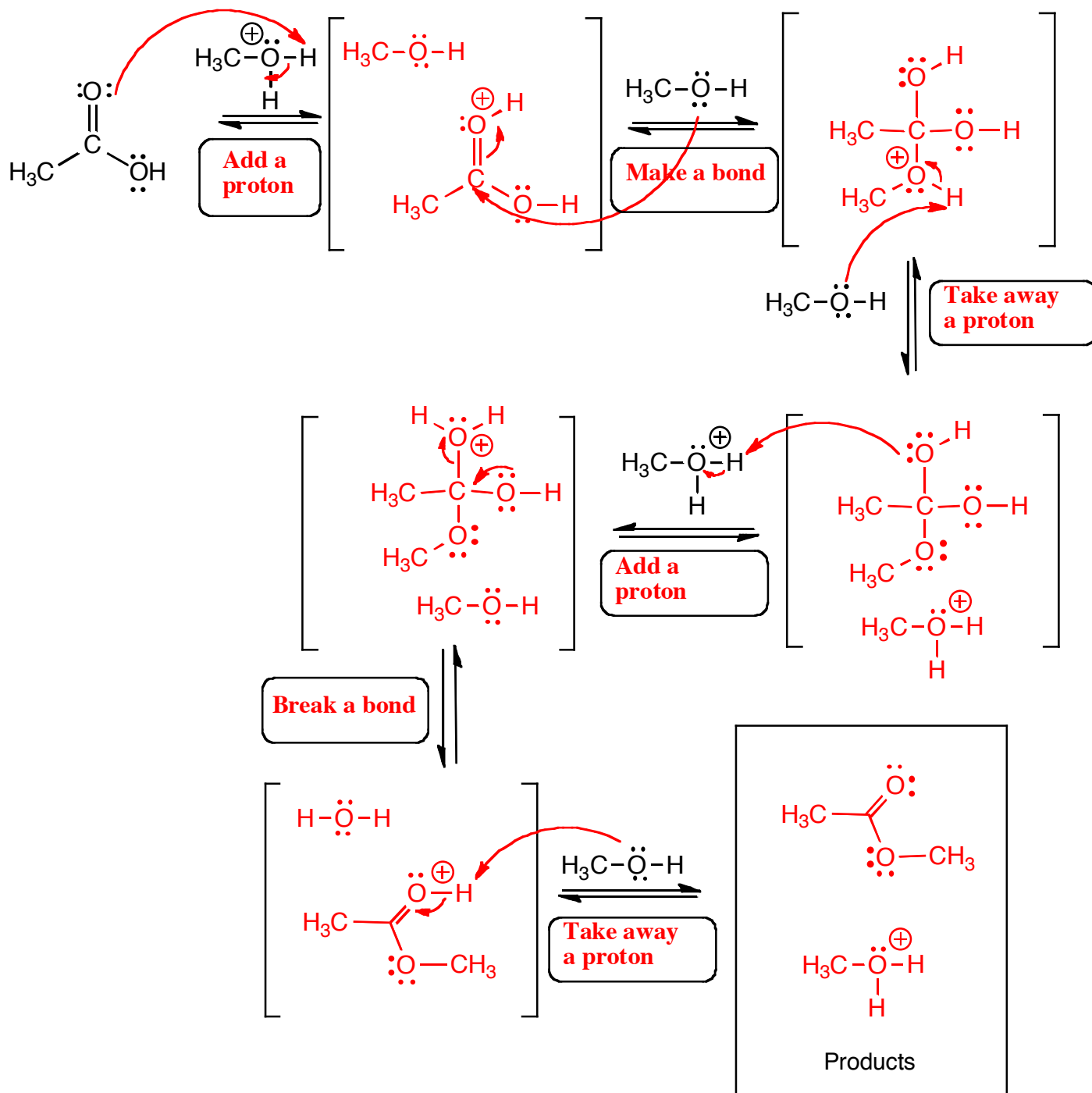
**2****1****3**

14. (32 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 final products or any further steps of the mechanisms. You do not have to worry about labeling chiral centers or writing "racemic" on this one. You might want to read these directions again so you know what we want.

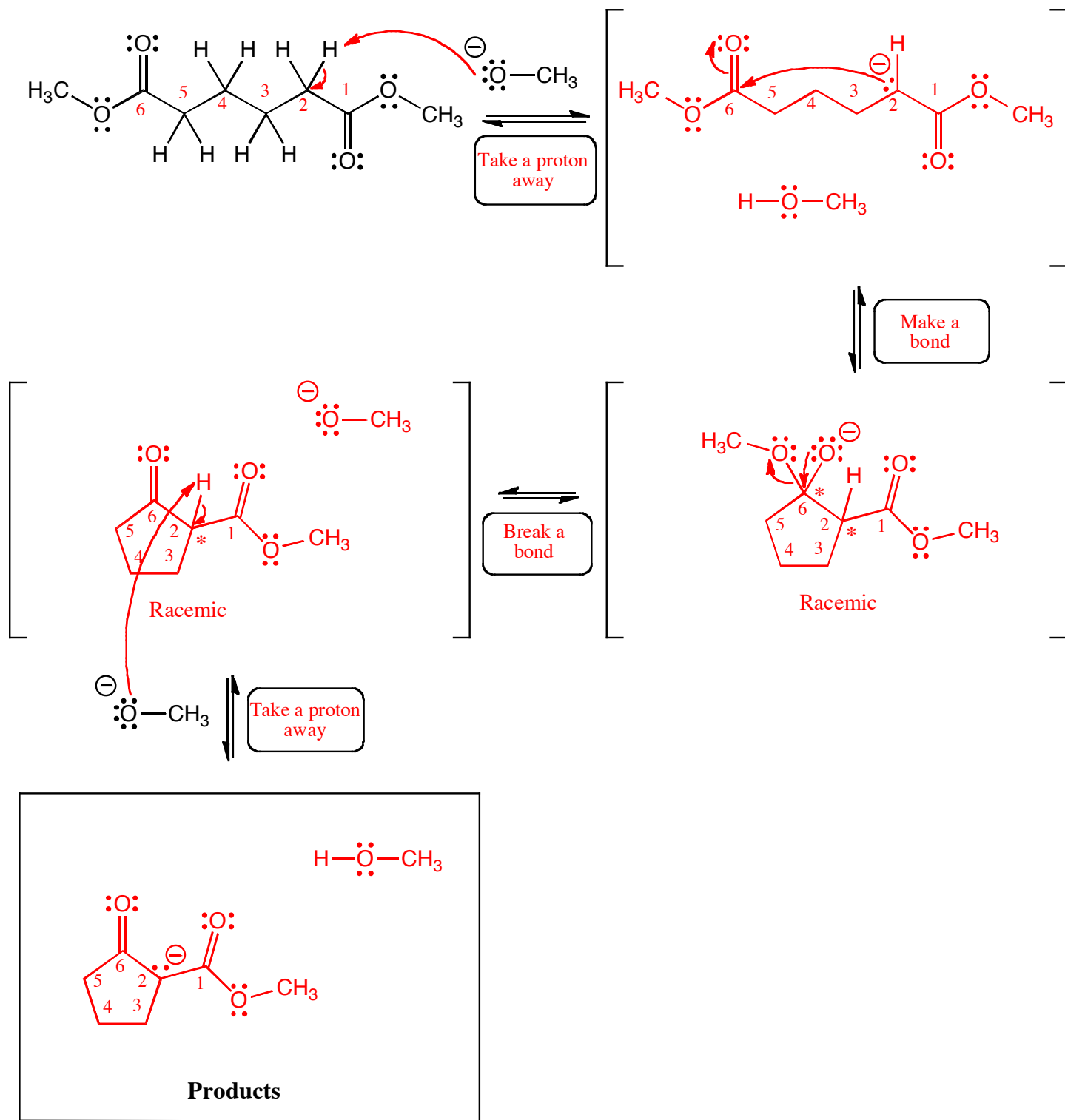


Did you remember to draw boxes and circles?

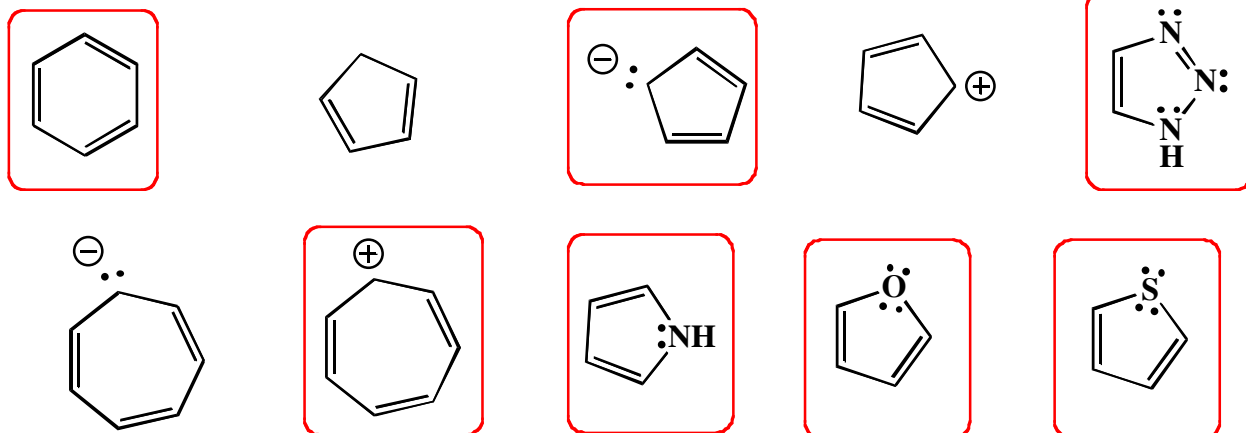
15. (29 points) Complete the mechanism below for Fisher esterification. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. You do not have to worry about labeling chiral centers or writing "racemic" on this one either. **Remember, you must show all products for each step.** Fill in the boxes below or beside each set of arrows to indicate which type of mechanistic element is involved, i.e. "add a proton", "break a bond", etc.



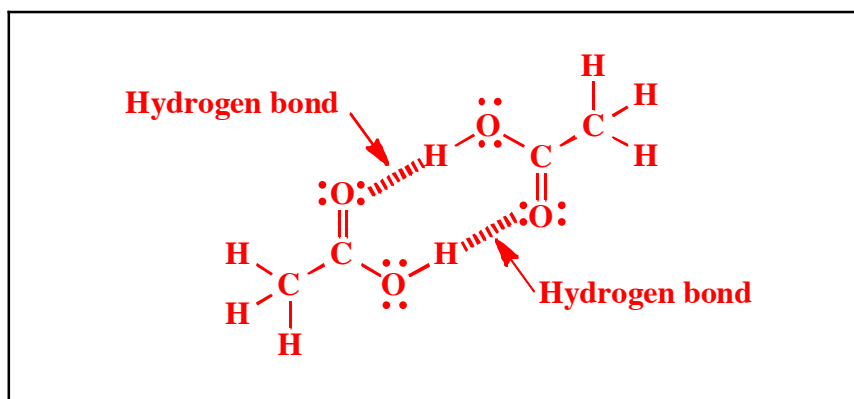
16. (19 pts total) Complete the mechanism below for a Dieckmann condensation. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. You do not have to worry about labeling chiral centers or writing "racemic" on this one either. **Remember, you must show all products for each step.** Fill in the boxes below or beside each set of arrows to indicate which type of mechanistic element is involved, i.e. "add a proton", "break a bond", etc.



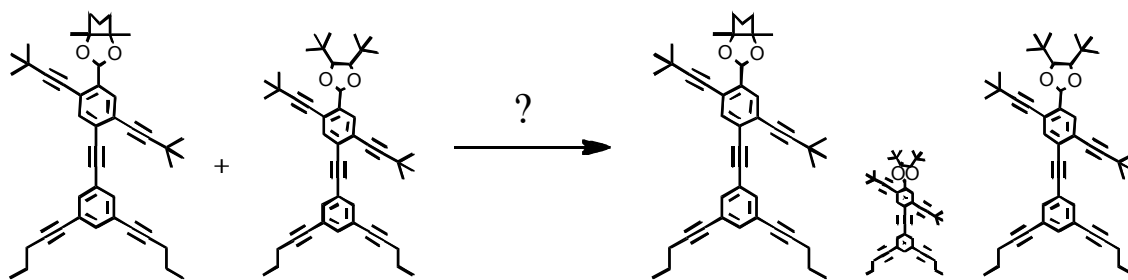
17. (10 pts total) Circle all of the following molecules that are aromatic.



18. (8 pts) Carboxylic acids such as acetic acid exist in solution in a characteristic orientation. In the space provided, draw two acetic acid molecules in the characteristic orientation. Be sure to include all lone pairs of electrons in your diagram.

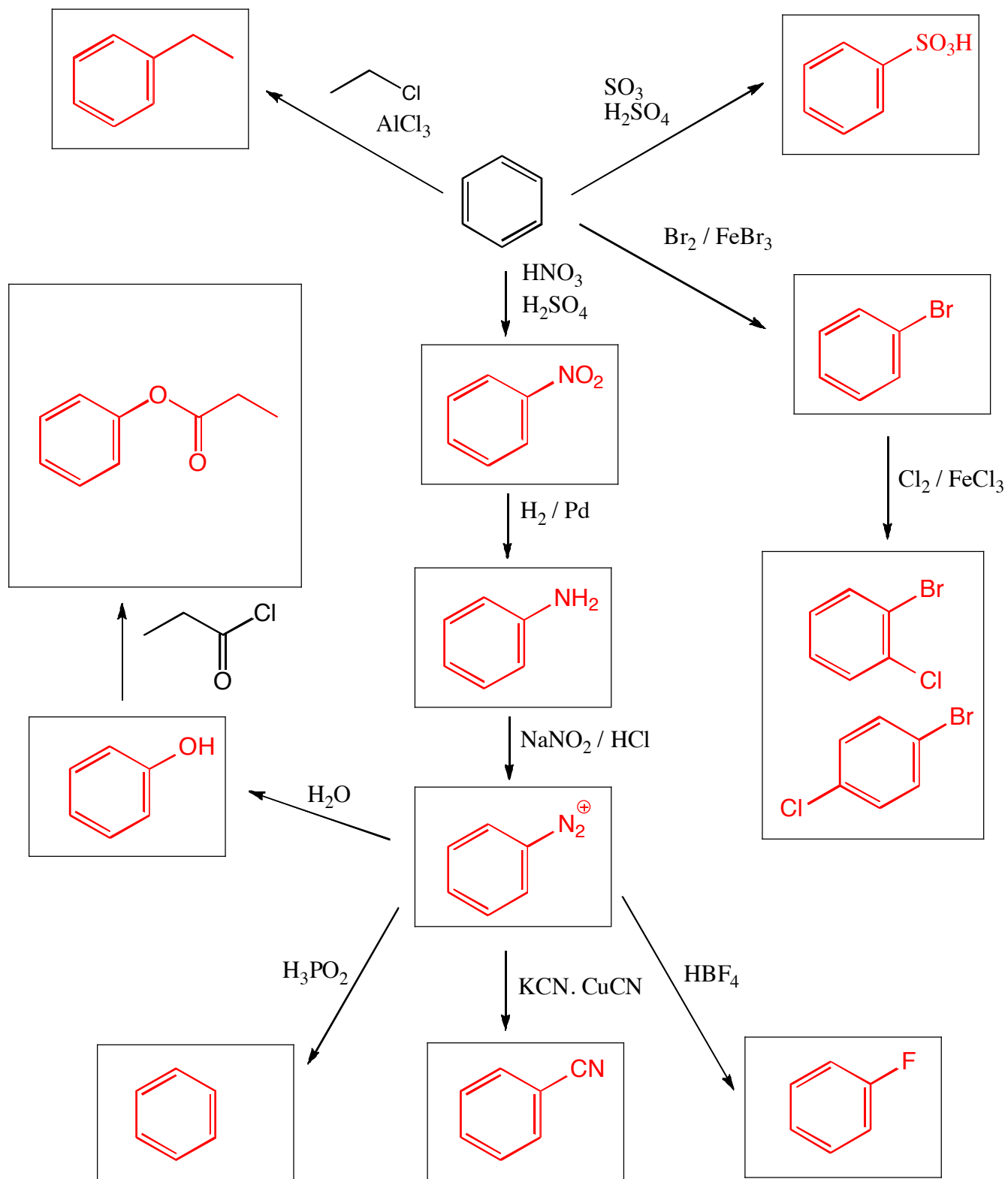


Synthesis Question for Chemistry Nerds

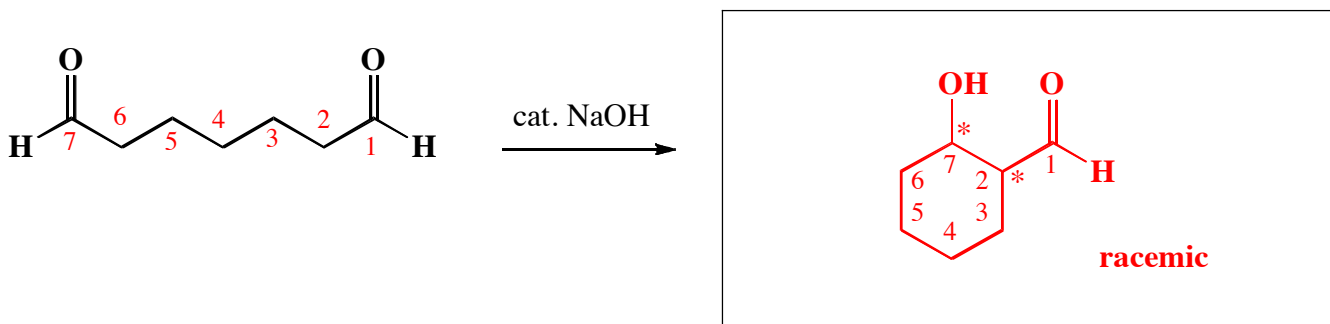
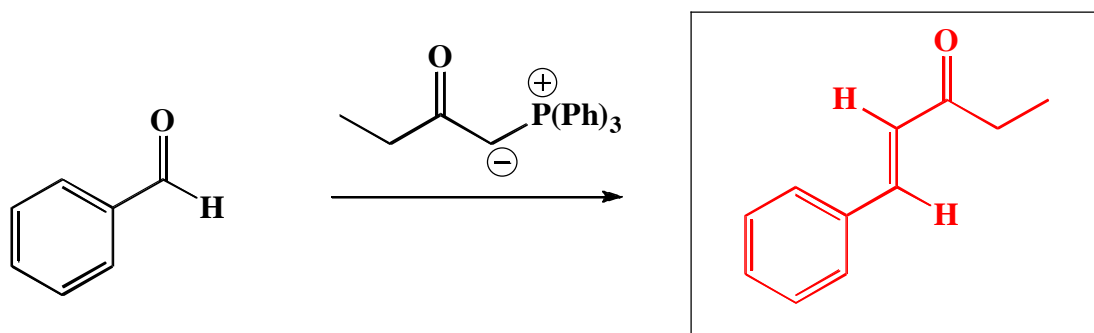
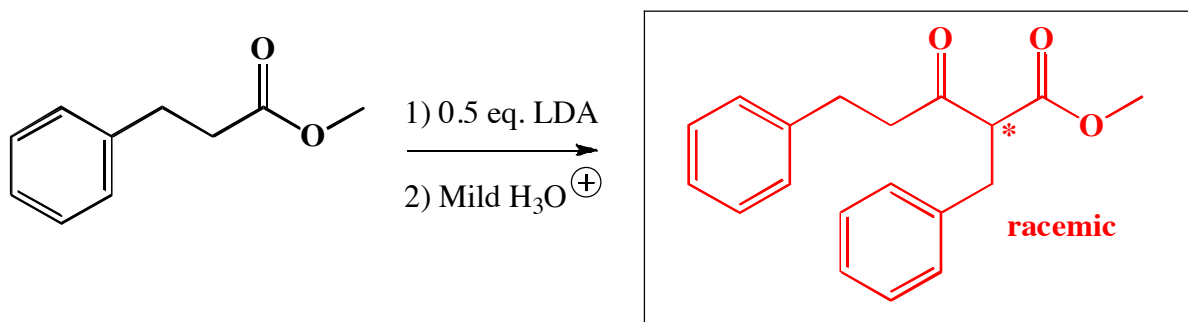
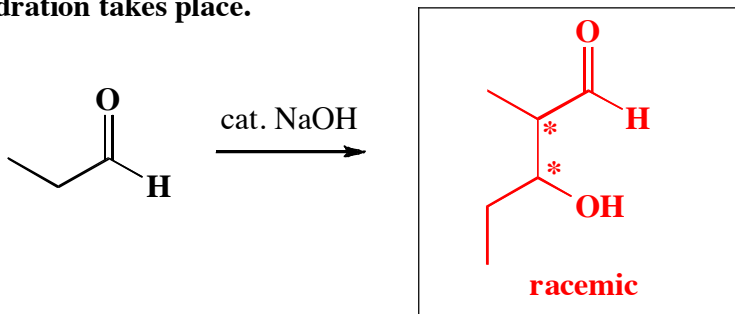


I realize it is a pretty nerdy form of humor, but what the heck, we are chemists.

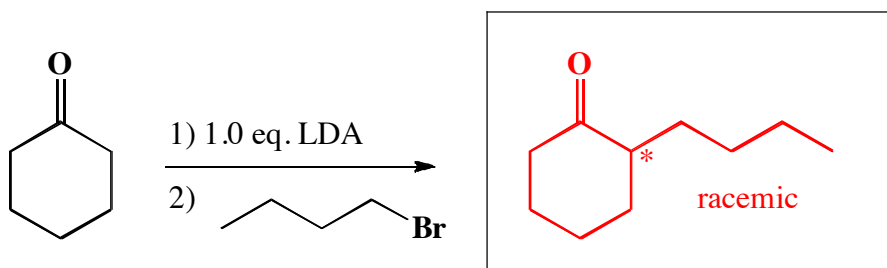
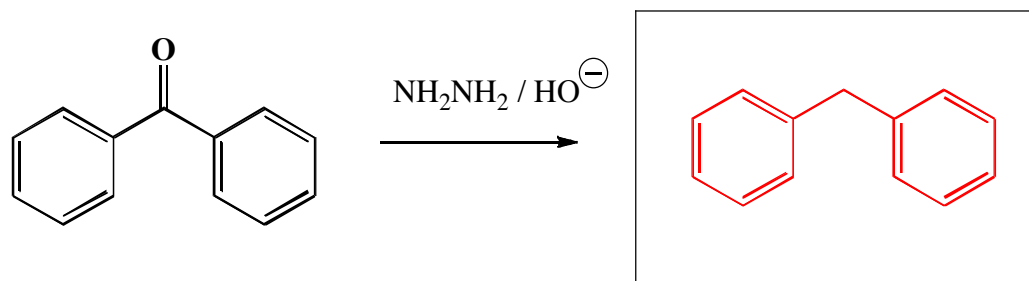
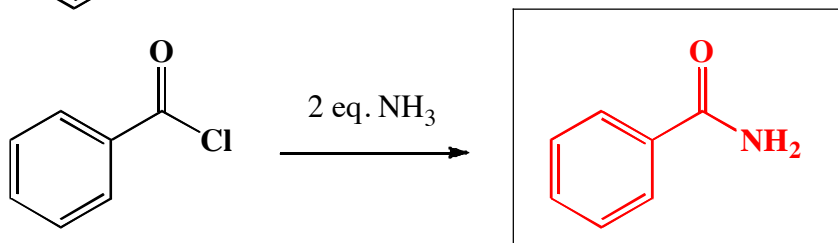
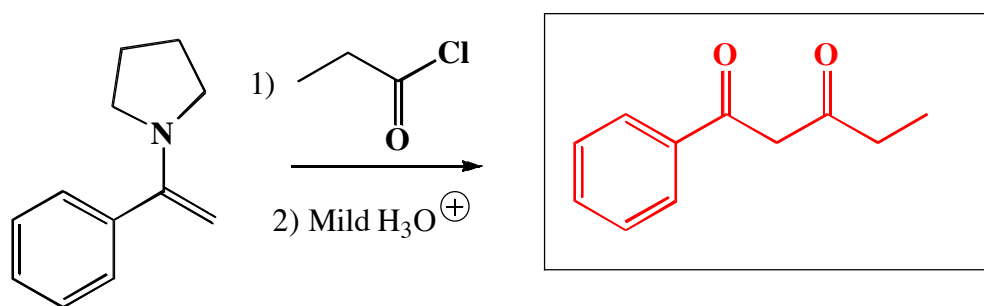
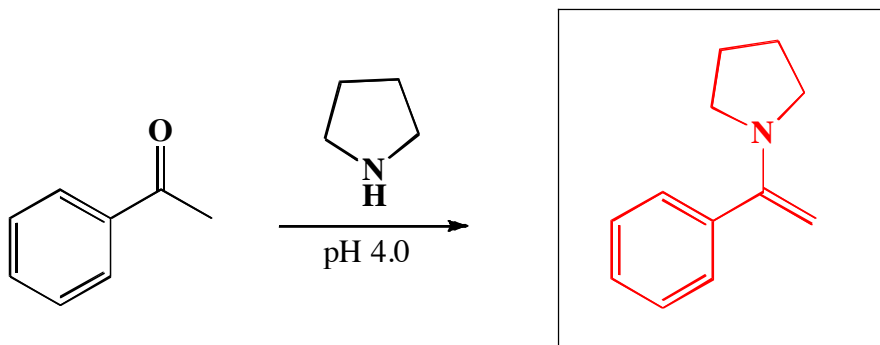
19. (38 pts.) Write the predominant product or products that will occur for each transformation. Assume each reagent only adds once to the ring. If predominantly ortho/para products are predicted, you must draw both.



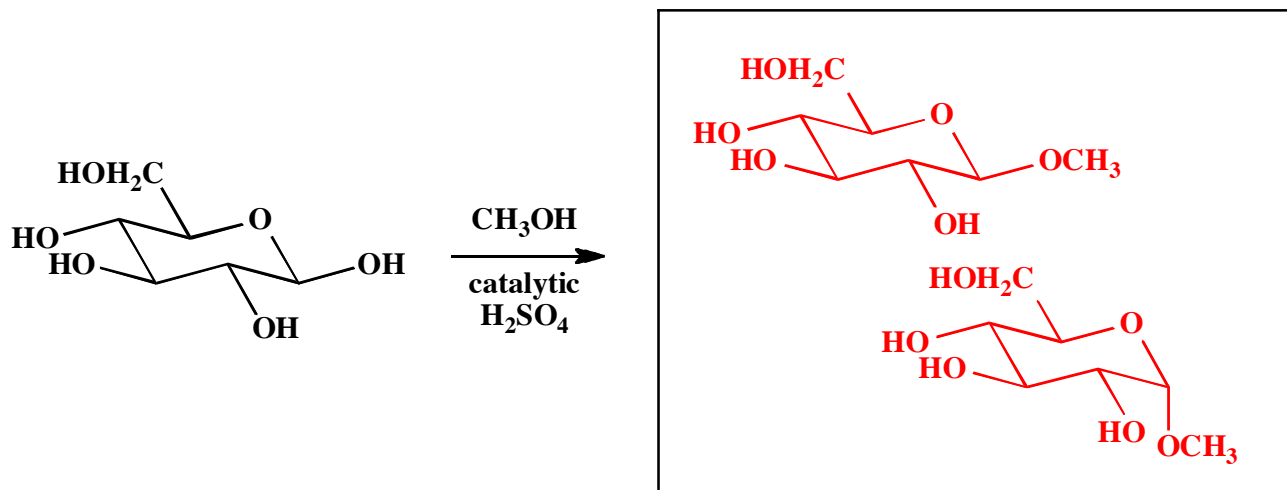
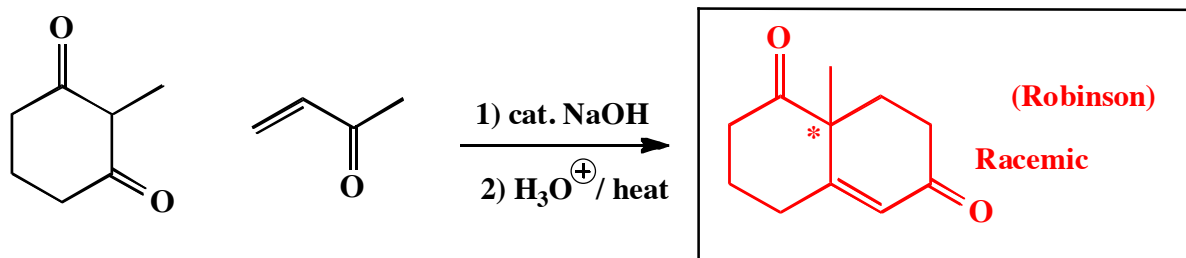
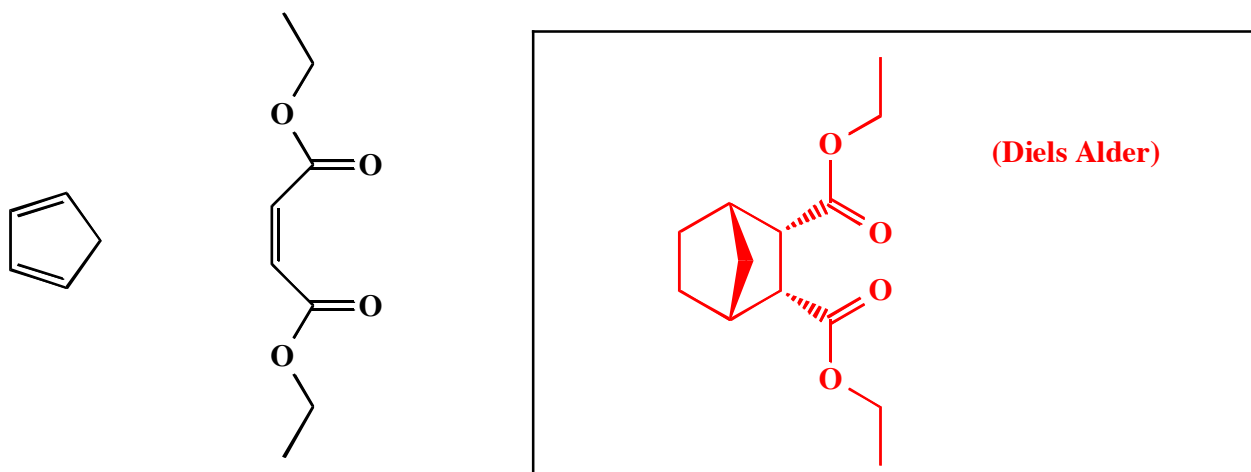
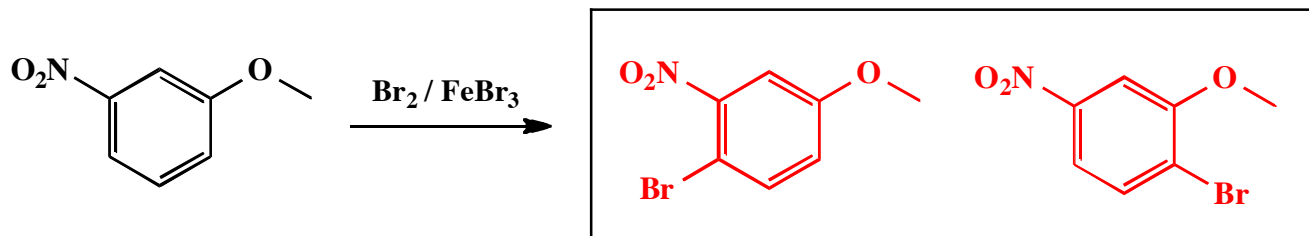
20. (18 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If there is an aldol reaction, draw the product before any dehydration takes place.**



21. (17 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure.** If there is an aldol reaction, draw the product before any dehydration takes place.

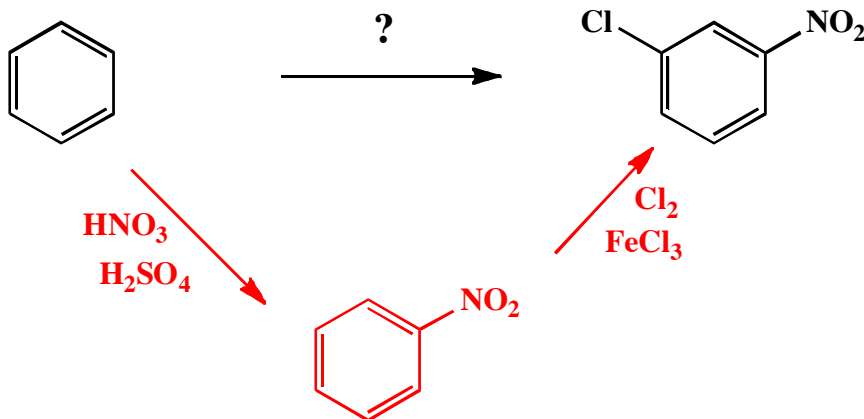


22. (18 pts.) You might find these are harder so take your time. Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If ortho/para products are made, you must draw both. Note, for this problem, aldols can dehydrate if heated in dilute acid.



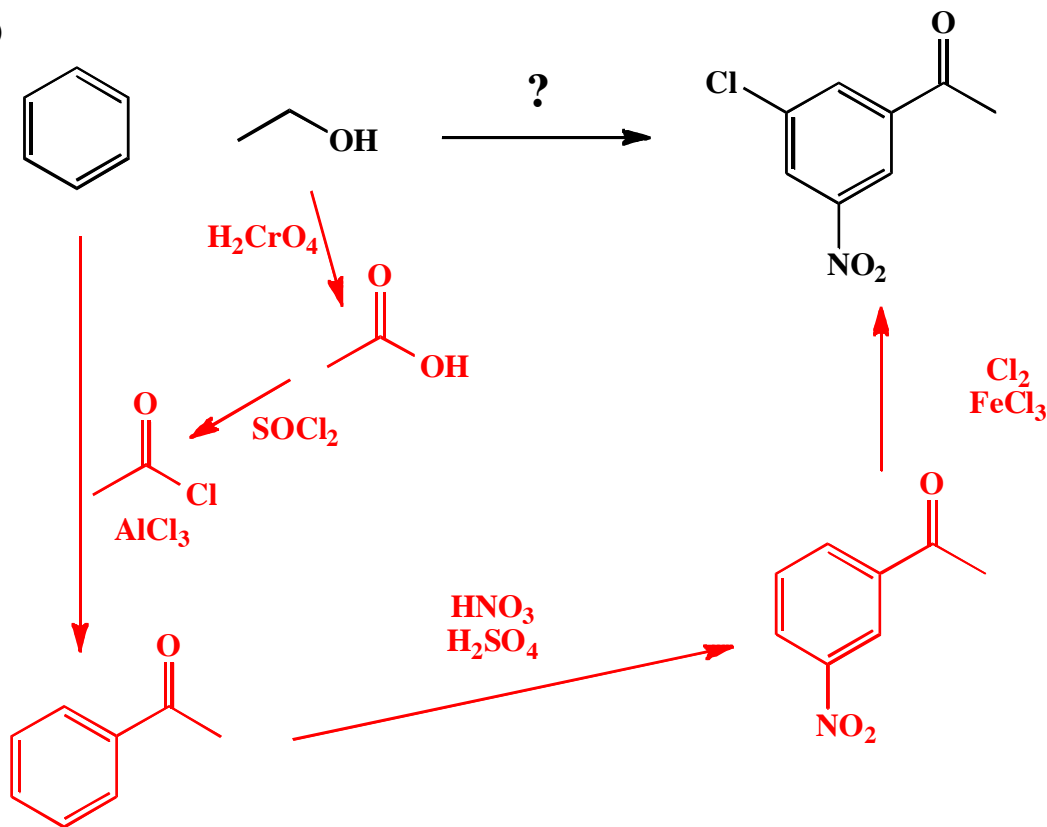
23. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

(4 pts)



This was just a warmup

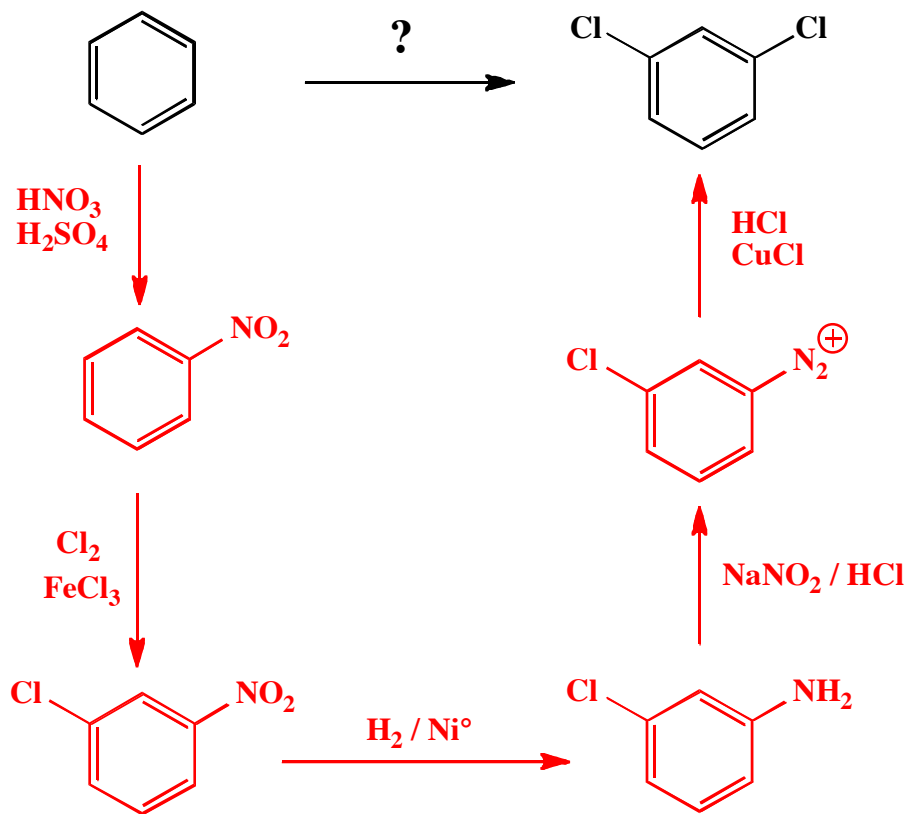
(13 pts)



Recognize that this is the only sequence of reactions that will work. The Friedel-Crafts acylation must be done first, because it does not work with a nitro group on the ring. The Cl must be added last so that the meta orientation is present. **Recognize** that the acetyl chloride needed for the acylation can be made by H_2CrO_4 oxidation of ethanol followed by treatment with SOCl_2 .

23. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule! **The product isomer shown must be the only predominant isomer you make during your synthesis.**

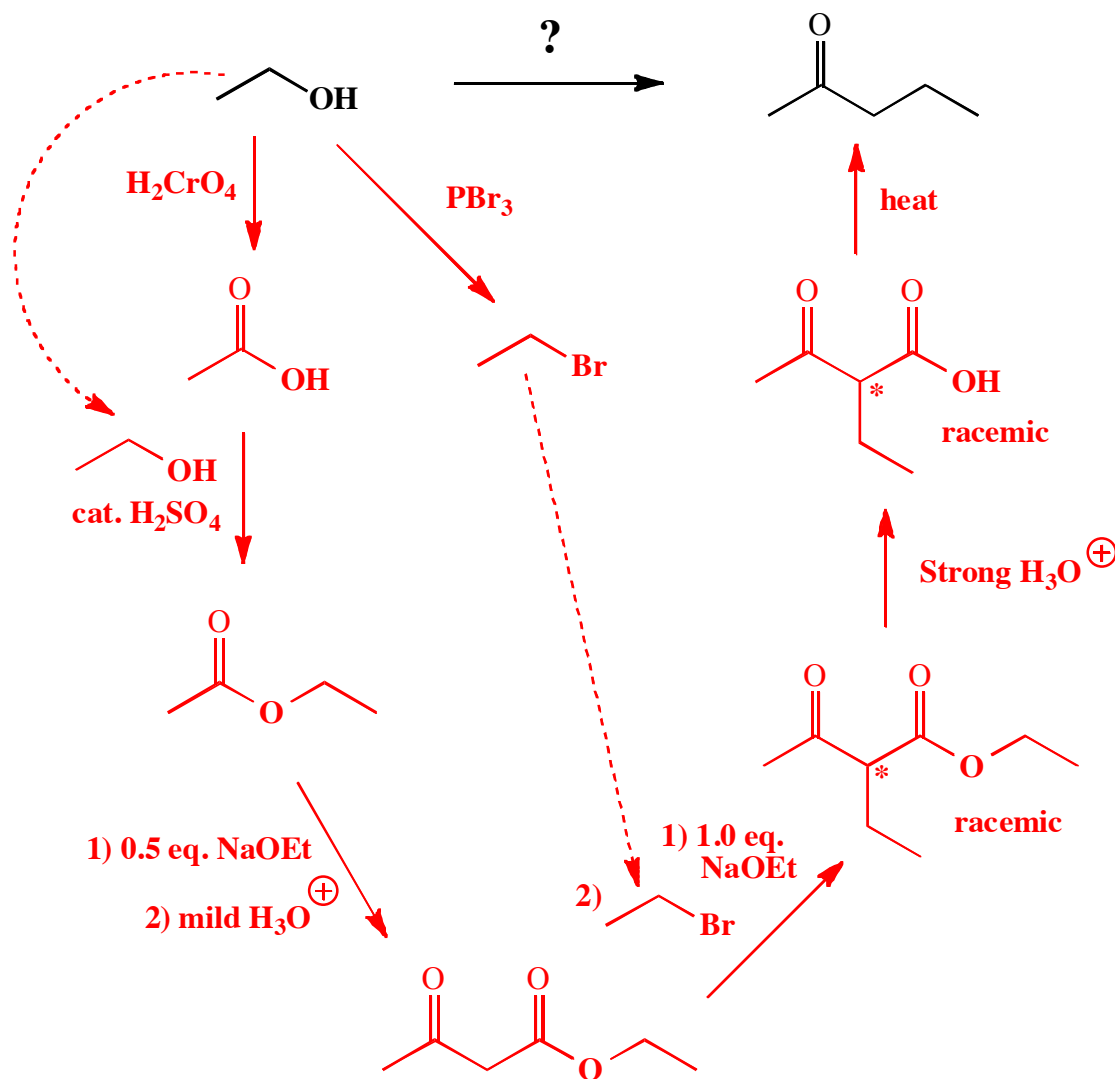
(13 pts)



Recognize that the product has two Cl atoms in a meta orientation, meaning this could not be the major product from a simple double chlorination reaction of benzene. **Recognize** that the Cl can be added by a Sandmeyer reaction starting from the corresponding diazonium species. As illustrated in the first synthesis problem on the previous page, to get the required meta orientation, start by nitration followed by the chlorination reaction. Then carry out the familiar sequence of reduction followed by the Mr. Bill reaction (HONO!!!) before ending with the Sandmeyer reaction to give the final dichloro product.

23. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the ethanol starting material, but you may use any carbon containing reagent along the way as long as its carbons do not end up in the product. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

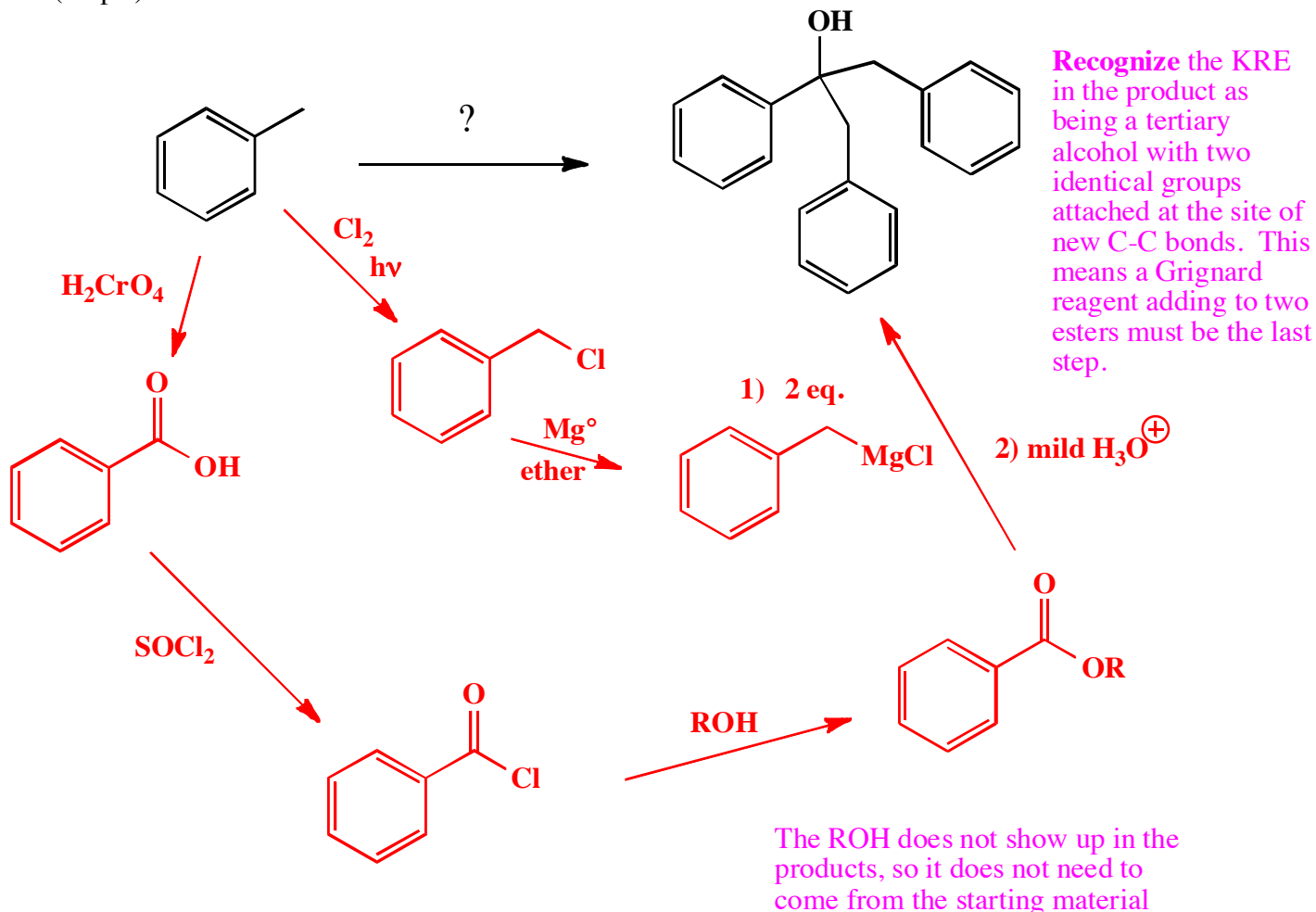
(19 pts)



Recognize the product as a methyl ketone, the KRE of the acetoester synthesis. **Recognize** further that there are two carbons added to the ketone α -carbon. That means we need to add a two carbon chain to acetoester just prior to the ester hydrolysis/decarboxylation sequence. The two carbon haloalkane can be made by treatment of the starting ethanol with PBr_3 to make bromoethane. You could have also used chloroethane, derived from treatment of ethanol with SOCl_2 . **Recognize** that acetoester can be derived from ethanol through a three-step sequence of H_2CrO_4 oxidation to give acetic acid, esterification to give ethyl acetate and a Claisen reaction to give acetoester. One of the most interesting aspects of second semester OChem is that we teach you how to turn simple starting materials like ethanol into more complex molecules such as 2-pentanone.

23. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

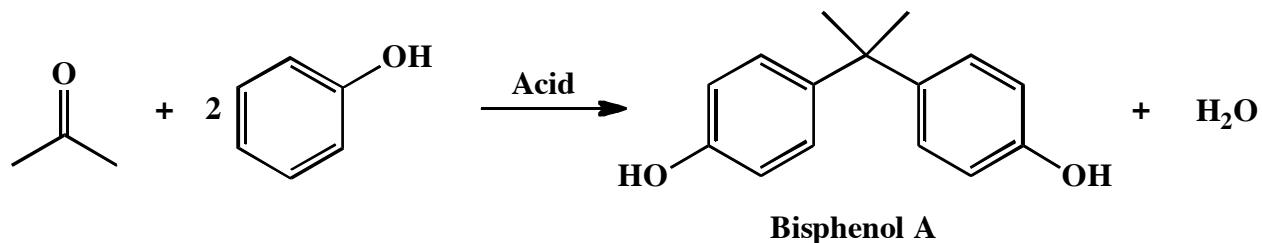
(16 pts)



Recognize the two pieces needed for the final reaction, the benzyl Grignard reagent and the benzoic acid ester, can both be derived from reactions unique to benzyl positions (H_2CrO_4 oxidation of the starting toluene to give benzoic acid, and free radical halogenation to give the benzyl halide). This is another example of starting with a relatively simple molecule and using it to construct a molecule that is much more complex. Note that in practice the final product would be tricky to isolate because it would tend to dehydrate to give a highly conjugated alkene.

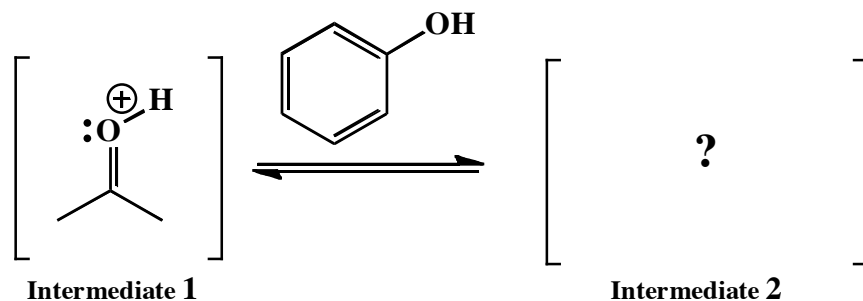
Here is an MCAT style passage question.

Bisphenol A is a compound that has received a lot of attention in recent years. It is used as a plasticizer, an additive to soften polymers. There are concerns that bisphenol A is an estrogen analog and can therefore cause health problems upon repeated exposure. Concerns about bisphenol A leeching from Nalgene water bottles a few years ago led to changes in how all water bottles are made. Bisphenol A is made from simple and readily available starting materials using chemistry that is very similar to the reactions you have learned. In particular, bisphenol A is synthesized from acetone and phenol in the presence of strong acid.

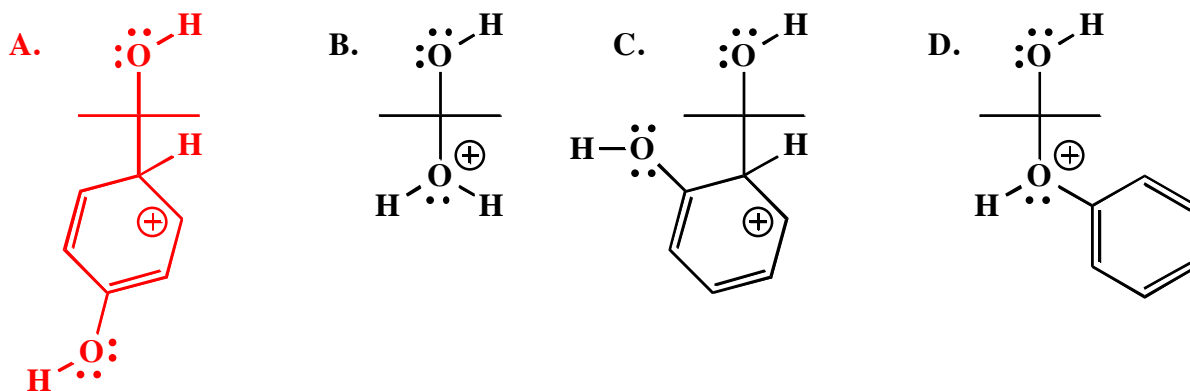


Refer to the last page for a mechanism sheet that is intended to help you answer the next five questions. We will NOT be grading the mechanism sheet, it is just added to help you think through the mechanism.

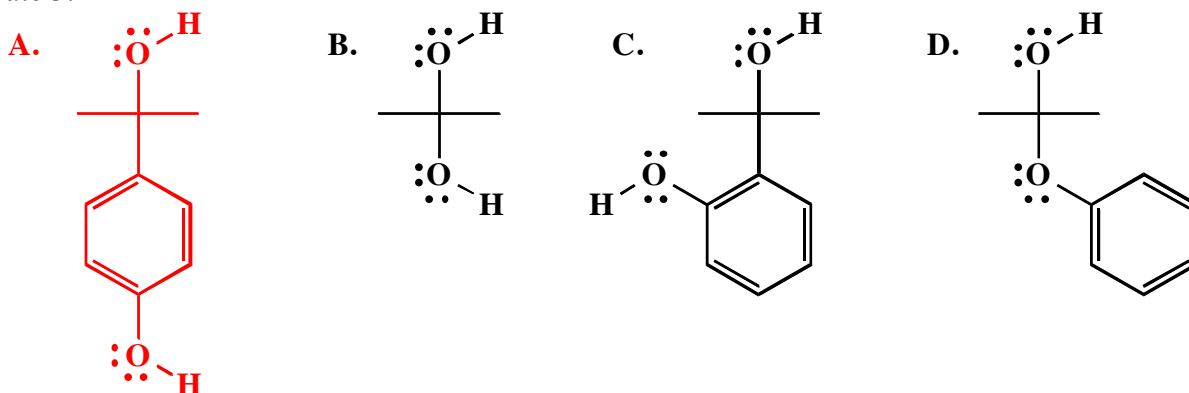
In the first step of the bisphenol A synthesis, acetone is protonated and then reacts with phenol



Circle the structure of the intermediate 2 that is formed in this first step. (Hint: you need to look at the product to determine which possible reaction is the one that actually occurs)



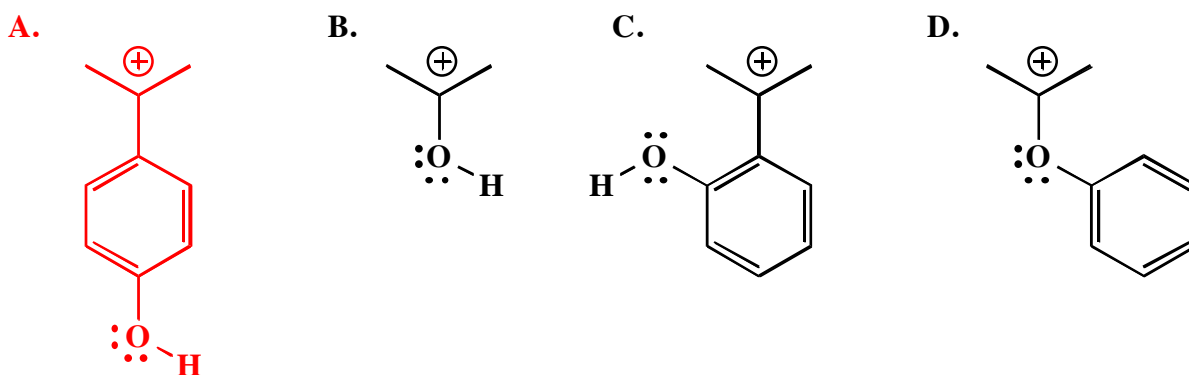
2) In the next step of this mechanism, a proton is lost to give a neutral intermediate 3. Circle the neutral intermediate 3.



3) The two-step sequence described in parts 1) and 2) of this question is referred to as

- A. Acetal formation
- B. Hemiacetal formation
- C. Electrophilic aromatic substitution
- D. Nucleophilic aromatic substitution

4) In the next two steps of the reaction, a proton is added to an -OH group followed by departure of water. This creates a carbocation intermediate 5. Circle the carbocation intermediate 5 that is formed.

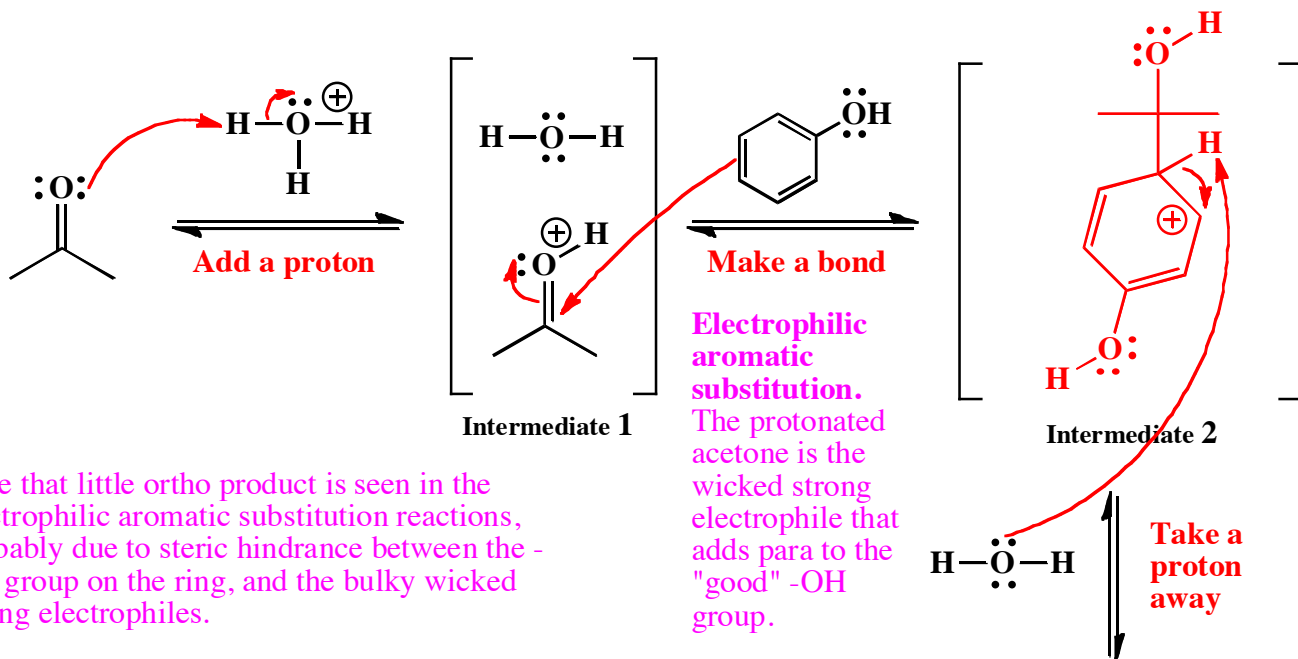


5) In the next two steps in the mechanism another molecule of phenol reacts to give bisphenol A. How many equivalents of acid is used in this process?

- A. A catalytic amount
- B. 0.5 equivalents
- C. 1.0 equivalents
- D. 2.0 equivalents.

Related to your answer in part 5), this overall reaction is considered to be a “green reaction” process because there are no organic byproducts to be disposed of, only water. The acid can be recycled from batch to batch.

This mechanism sheet is just for your reference, WE WILL NOT GRADE THIS PAGE



Note that little ortho product is seen in the electrophilic aromatic substitution reactions, probably due to steric hindrance between the -OH group on the ring, and the bulky wicked strong electrophiles.

