

NAME (Print): _____

Chemistry 310N
Dr. Brent Iverson
3rd Midterm
April 26, 2007

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!!!!

Page	Points	
1		(27)
2	deleted	(-)
3		(24)
4		(19)
5		(31)
6		(18)
7		(22)
8		(26)
9		(19)
10		(22)
11		(16)
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13		(16)
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15		(19)
16		(19)
Total		(313)
HW		
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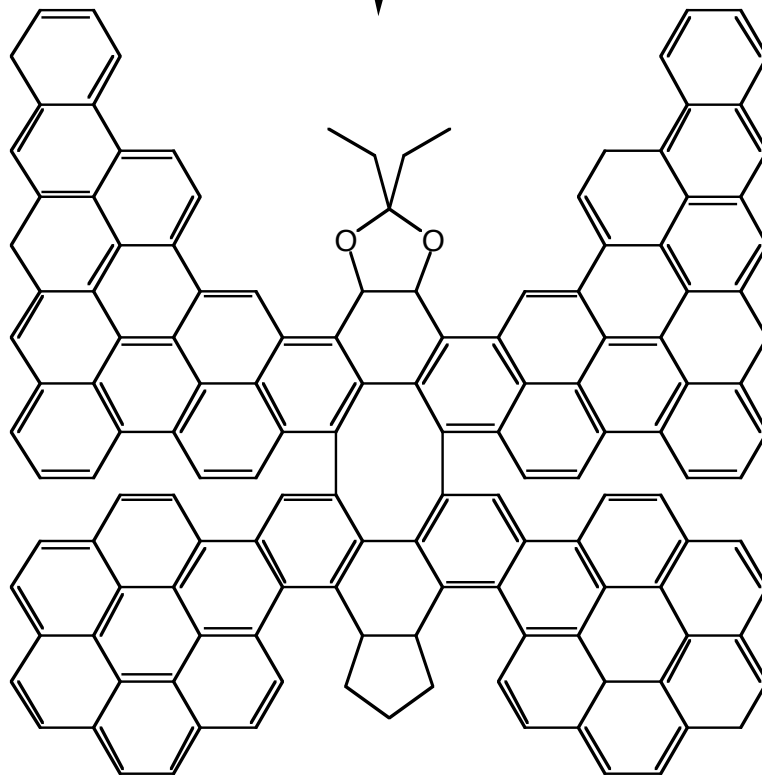
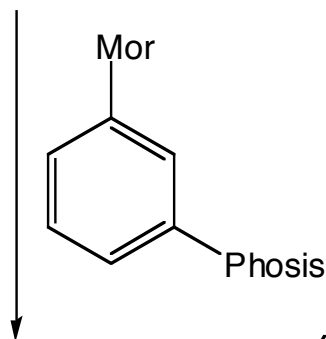
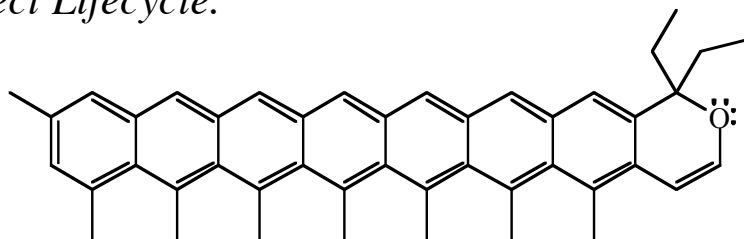
Honor Code

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	$\text{RCH}_2\text{O}\overset{\oplus}{\text{H}}_2$	-2
Hydronium ion	$\overset{\oplus}{\text{H}}_3\text{O}$	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\underline{\text{H}}$	3-5
Ammonium ion	$\overset{\oplus}{\text{H}}_4\text{N}$	9.2
β-Dicarbonyls	$\overset{\text{O}}{\parallel}{\text{RC}}-\underline{\text{CH}}_2-\overset{\text{O}}{\parallel}{\text{CR}'}$	10
β-Ketoesters	$\overset{\text{O}}{\parallel}{\text{RC}}-\underline{\text{CH}}_2-\overset{\text{O}}{\parallel}{\text{COR}'}$	11
β-Diesters	$\overset{\text{O}}{\parallel}{\text{ROC}}-\underline{\text{CH}}_2-\overset{\text{O}}{\parallel}{\text{COR}'}$	13
Water	$\text{HO}\underline{\text{H}}$	15.7
Alcohols	$\text{RCH}_2\text{O}\underline{\text{H}}$	15-19
Acid chlorides	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{CCl}}$	16
Aldehydes	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{CH}}$	18-20
Ketones	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{CR}'}$	18-20
Esters	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{COR}'}$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\underline{\text{H}}$	25
LDA	$\underline{\text{H}}\text{-N}(i\text{-C}_3\text{H}_7)_2$	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

Aromatic Insect Lifecycle:



I put this here to help you relax. You will do better on the exam in a relaxed frame of mind. (If the above equation made you laugh or even smile, you may be a chem nerd, but nobody has to find out.)

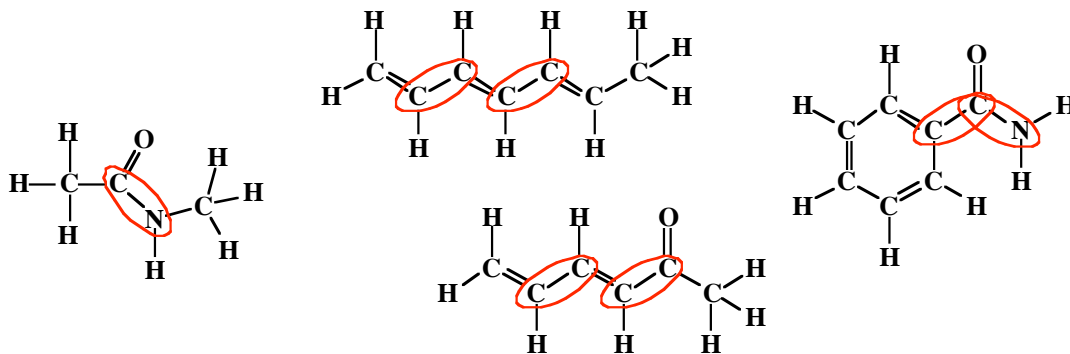
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons by radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field gradients** are used to gain imaging information, and **rotation of the gradient around the center of the object** gives imaging in an entire plane (**i.e. slice inside patient**). In an MRI image, you are looking at **individual slices that when stacked make up the three-dimensional image of relative amounts of protons, especially the protons from water and fat, in the different tissues.**

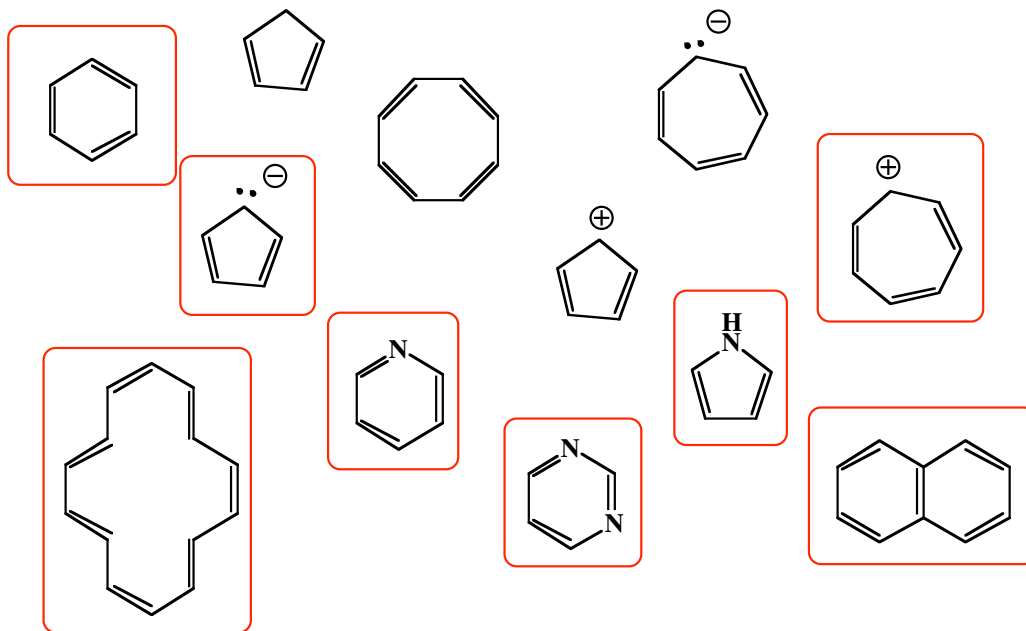
2. (6 points) Aromaticity is a term that refers to molecules with characteristic pi systems. A theorist named Hückel helped to derive several criteria that can be used to determine if a **monocyclic** compound is aromatic. List at least three of these criteria:

1. The molecule is flat
2. All atoms of the ring must be sp^2 (or sp in rare cases) hybridized
3. There must be " $4n + 2$ " pi electrons in the pi system, where $n = 0, 1, 2, 3, 4, 5, \dots$

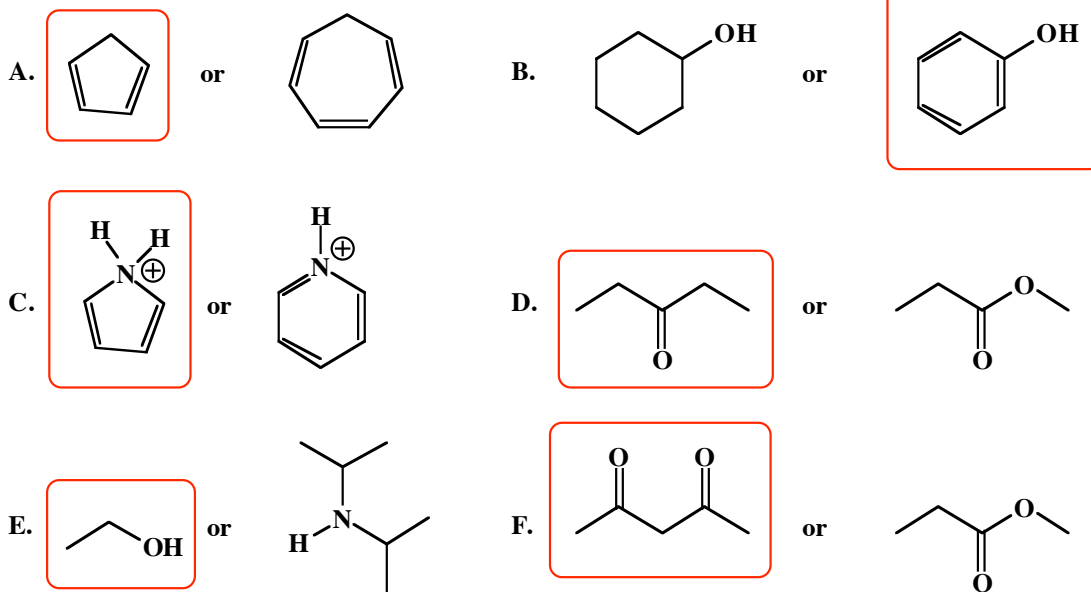
3. (7 points) We have now run into cases in which bonds that look like normal sigma single bonds in a Lewis structure, actually have partial double bond character in the molecule. **In the following set of molecules, circle the single bonds that have double bond character** (i.e. hindered bond rotation at room temperature). NOTE: You DO NOT have to circle any bonds WITHIN an aromatic ring.



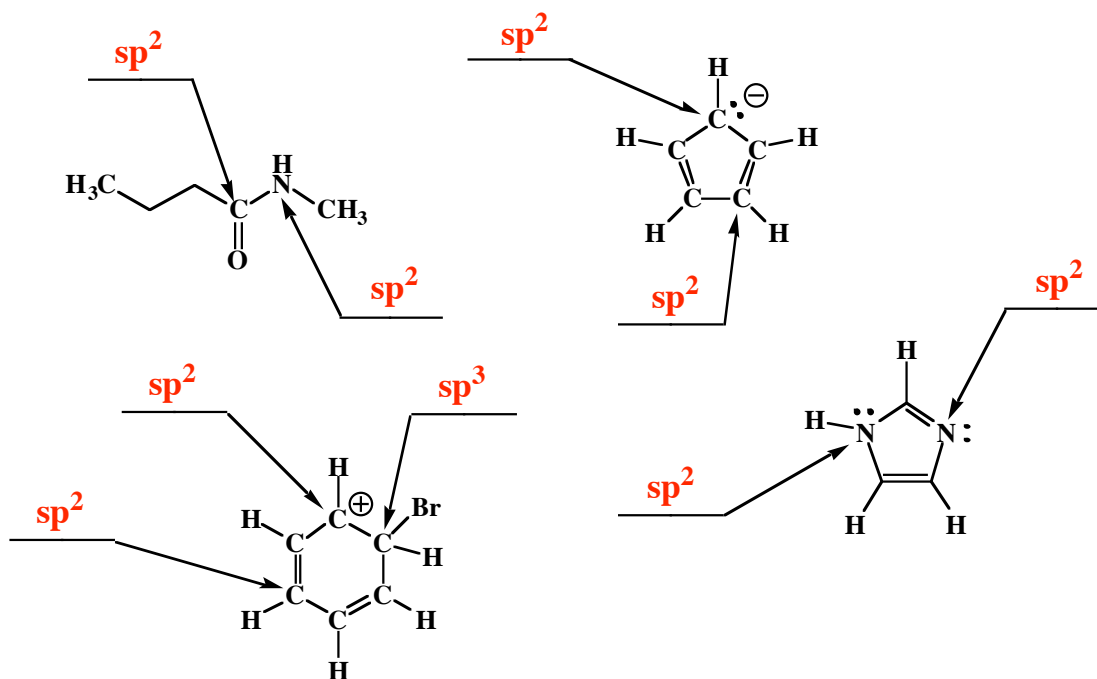
5. (12 points) Draw a circle around all of the molecules below that can be considered aromatic.



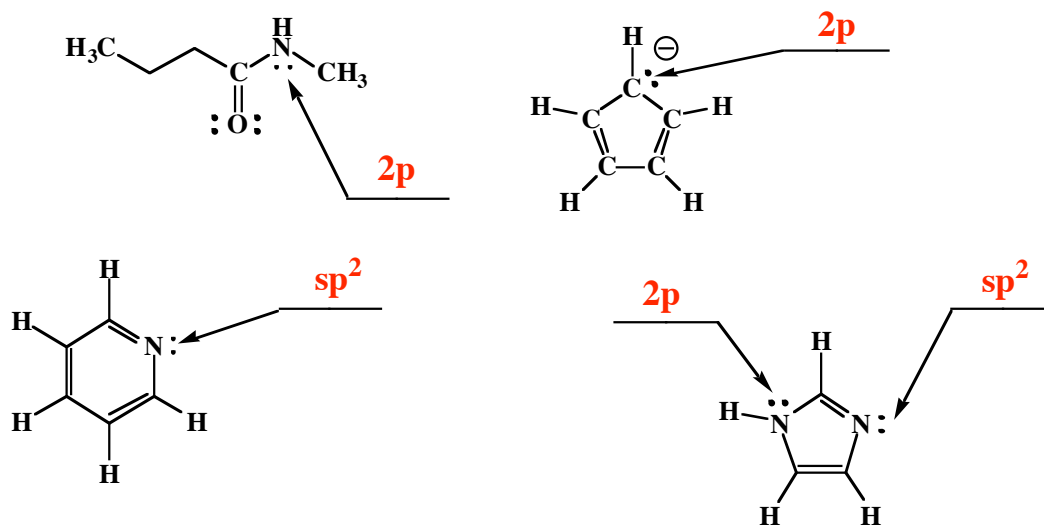
6. (12 points) For each pair of molecules, circle the one that is more acidic.



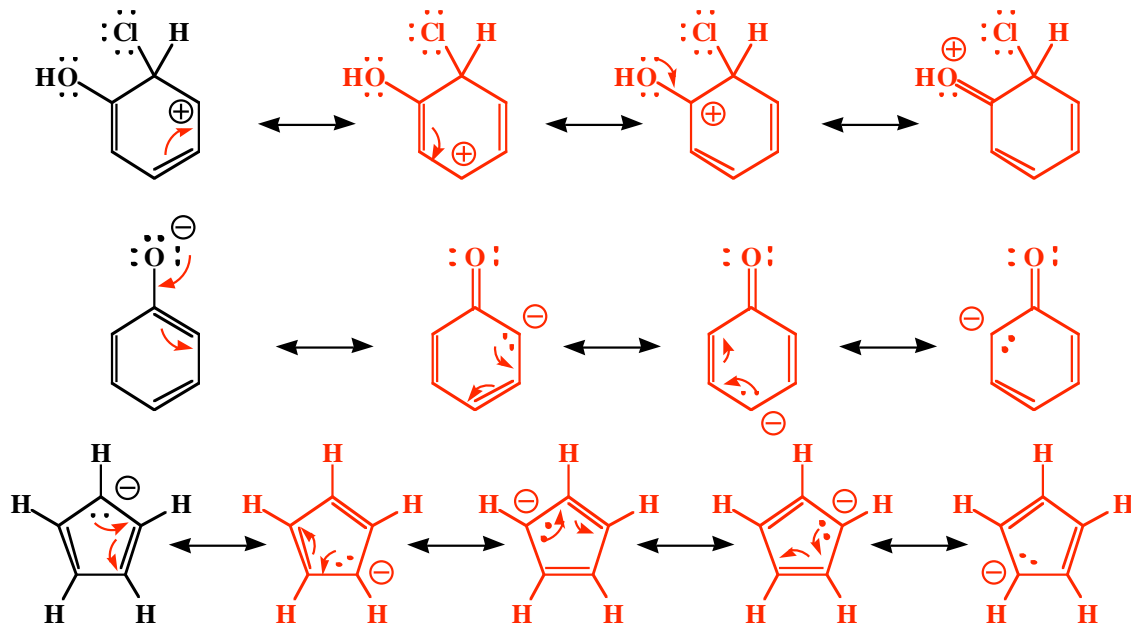
7. (9 points) On the lines provided, state the **hybridization state of the atom** indicated by the arrow.



8. (10 points) On the lines provided, state the **atomic orbital that contains the lone pair** of electrons indicated by the arrow.

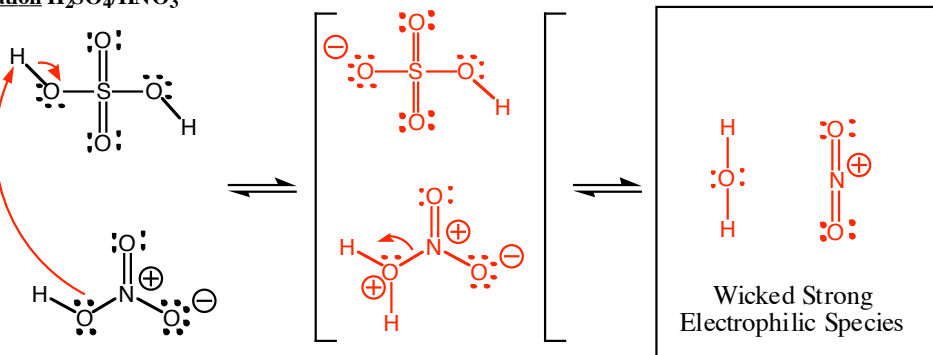


9. (20 points) **In the spaces provided, draw all the important resonance contributing structures of the indicated species.** We have provided template molecules to help you do this more quickly. You must draw all pi bonds, lone pairs of electrons and all formal charges on each of your structures. You DO NOT need to draw arrows to show electron movement.

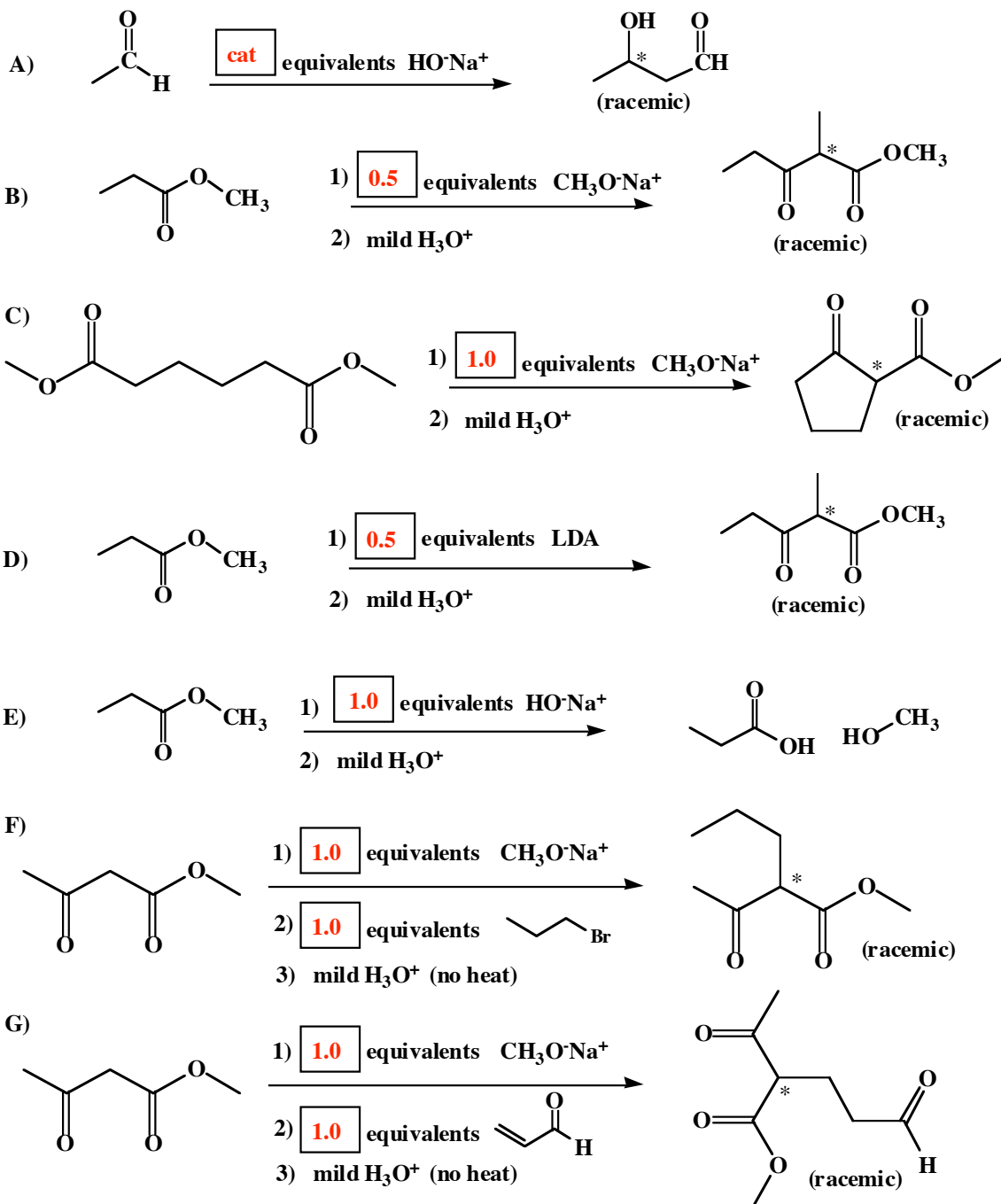


10. (11 points) Complete the mechanism below that shows how the wicked strong electrophilic species is produced that goes on to react with an aromatic ring. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. Your answer should end with formation of the wicked strong electrophilic species, you do not need to show reaction with an aromatic ring. Make sure to show all new species produced in each step.

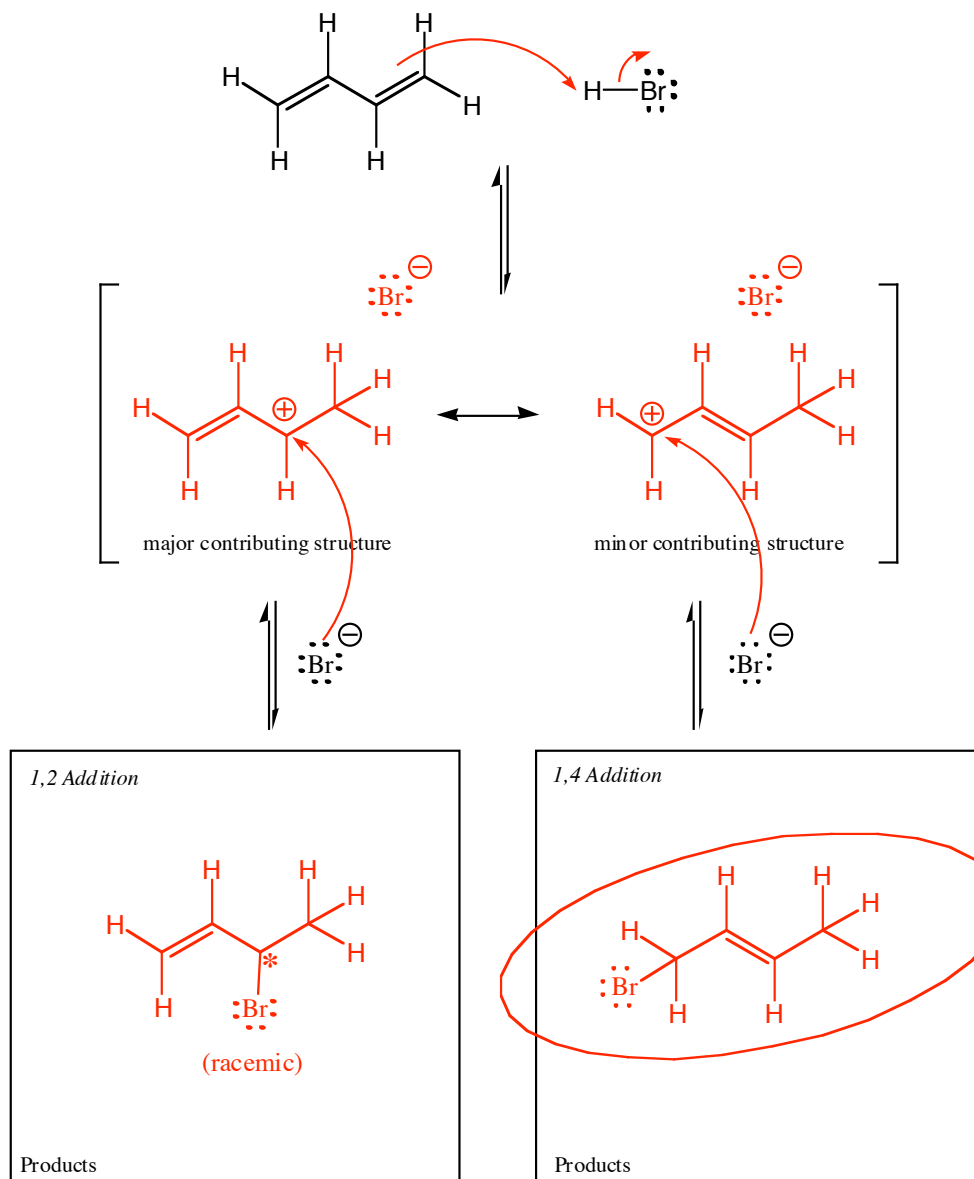
Nitration $\text{H}_2\text{SO}_4/\text{HNO}_3$



11. (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.



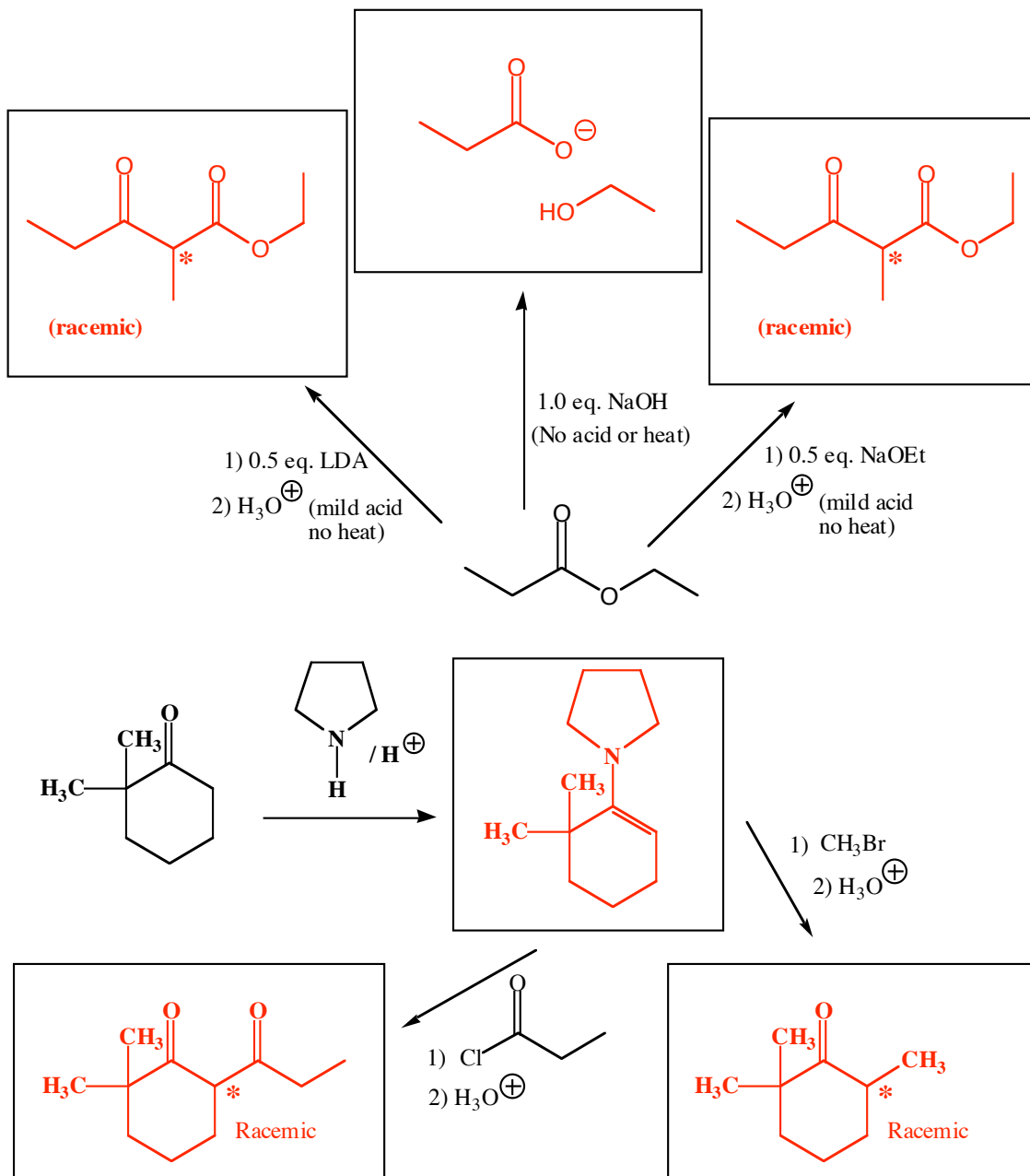
12. (18 pts) Complete the mechanisms below that shows how HBr adds to a conjugated diene to give both 1,2 addition and 1,4 addition. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. If a racemic product is formed, just put an asterisk (*) next to the chiral center and write "racemic" under it.



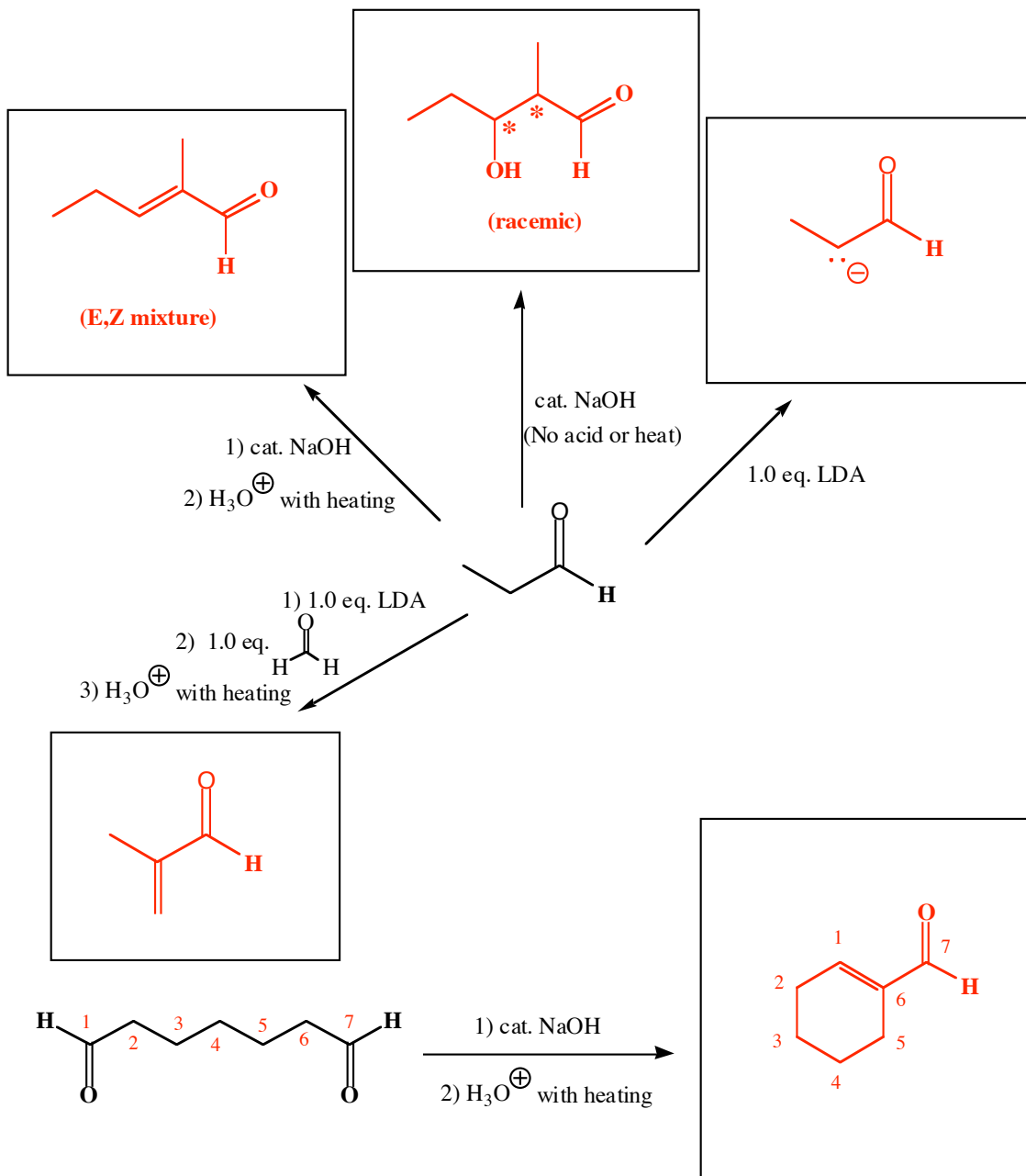
Notice this

(4 pts) Draw a circle around the product you drew that will predominate when the reaction is run under conditions of **thermodynamic control**.

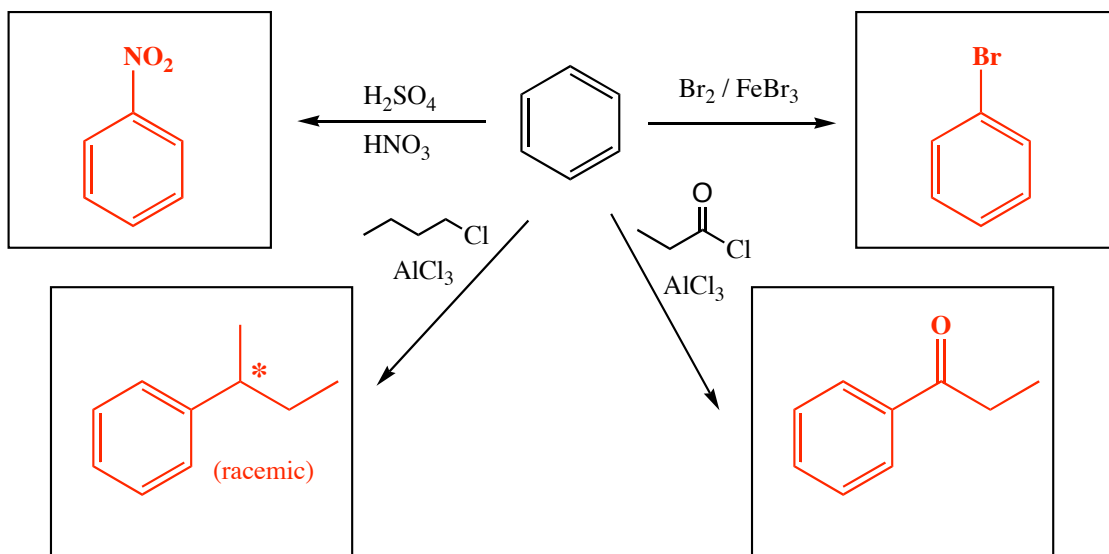
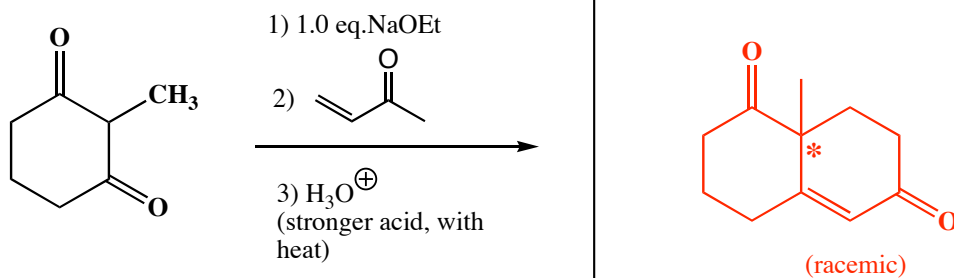
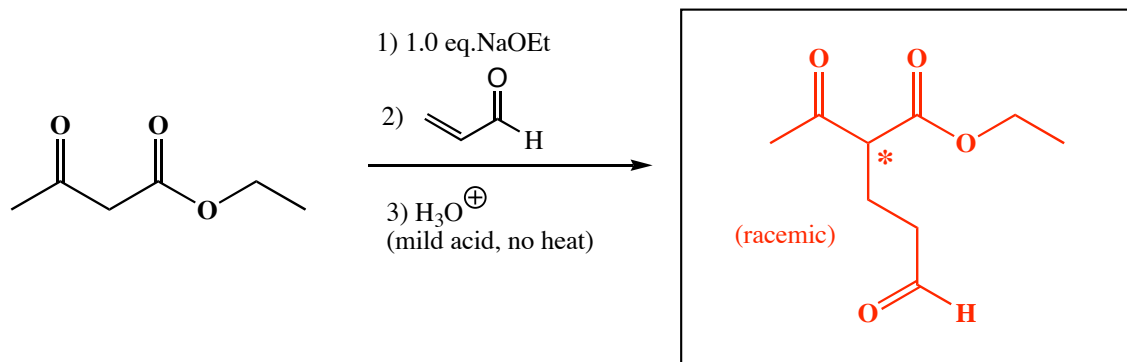
13. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration step, write "E,Z mixture", but you only have to draw one isomer, not both.** These directions are different than you may have seen before, and are intended to make it easier for you. You should read them again so you know what we want.



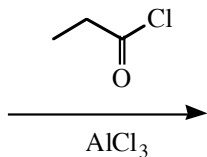
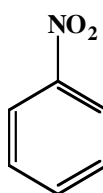
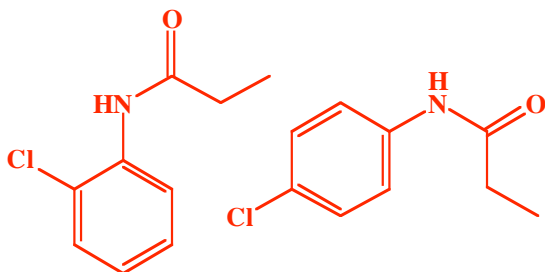
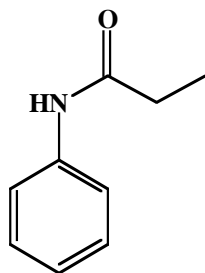
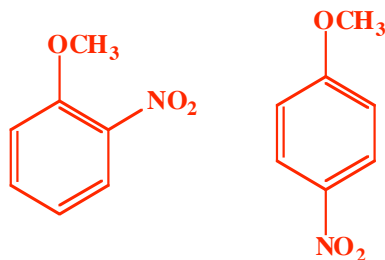
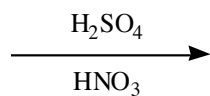
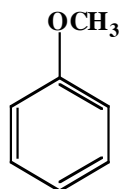
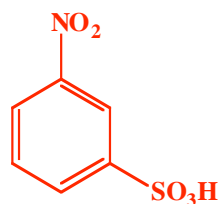
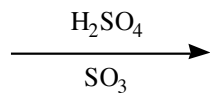
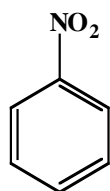
13. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration step, write "E,Z mixture", but you only have to draw one isomer, not both.** These directions are different than you may have seen before, and are intended to make it easier for you. You should read them again so you know what we want.



13. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration step, write "E,Z mixture", but you only have to draw one isomer, not both.** These directions are different than you may have seen before, and are intended to make it easier for you. You should read them again so you know what we want.

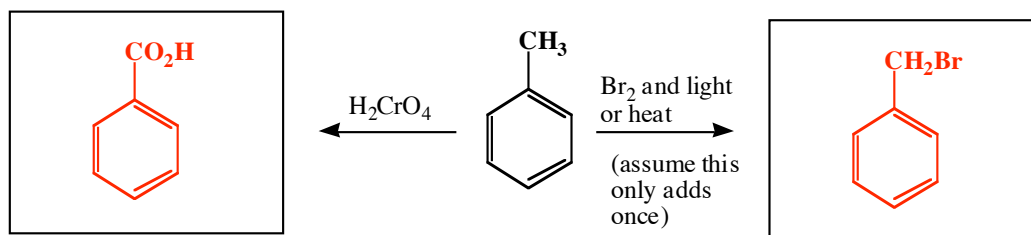


14. (3 or 5 pts each) For the following electrophilic aromatic substitution reactions, draw the predominant product or products in the boxes provided. **If an ortho/para mixture is expected to predominate, you must draw both.** If you predict that no reaction will occur, write "No Reaction" in the box.

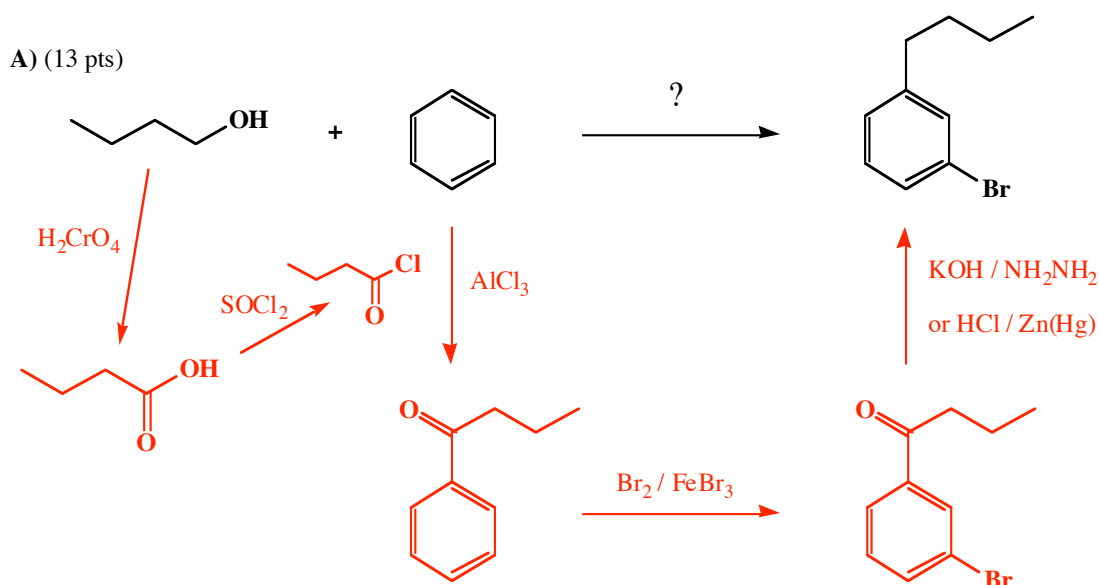


No reaction because the ketone group (bad) deactivates the aromatic ring.

14. (3 or 5 pts each) For the following electrophilic aromatic substitution reactions, draw the predominant product or products in the boxes provided. **If an ortho/para mixture is expected to predominate, you must draw both.** If you predict that no reaction will occur, write "No Reaction" in the box.



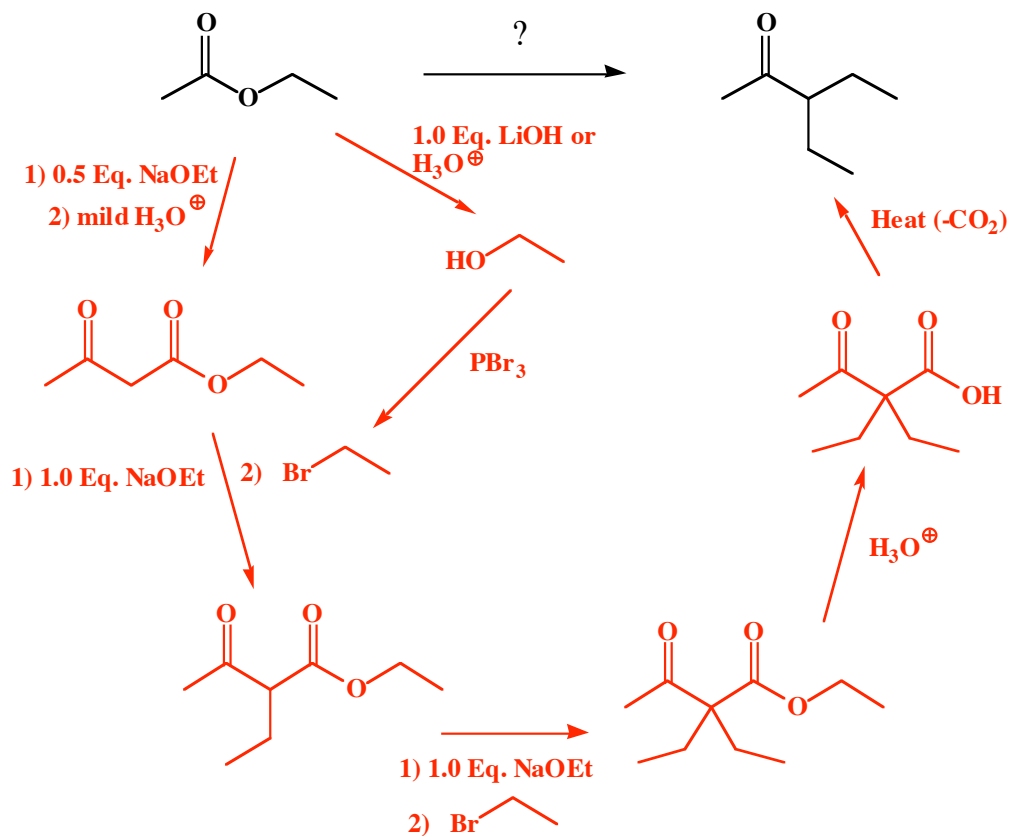
15. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!



Recognize that this synthesis requires a meta directing group, even though none are present in the product. Deduce that this means there was a meta director created at some point, the most likely candidate being a ketone derivative formed upon Friedel-Crafts *acylation* of benzene. Note that the absence of rearrangement (i.e. branching) in the product verifies that a Friedel-Crafts *alkylation* could not have created the product alkyl group in high yield. **Recognize** that the required acid chloride for the Friedel-Crafts acylation could be derived from oxidation of the starting 1-butanol, followed by SOCl_2 treatment. The Br atom is added to the ring with the ketone group present to provide meta direction, then Clemmensen or Wolff-Kischner reduction removes the carbonyl and gives the desired alkyl substituent.

15. 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 it doubt, draw the molecule!

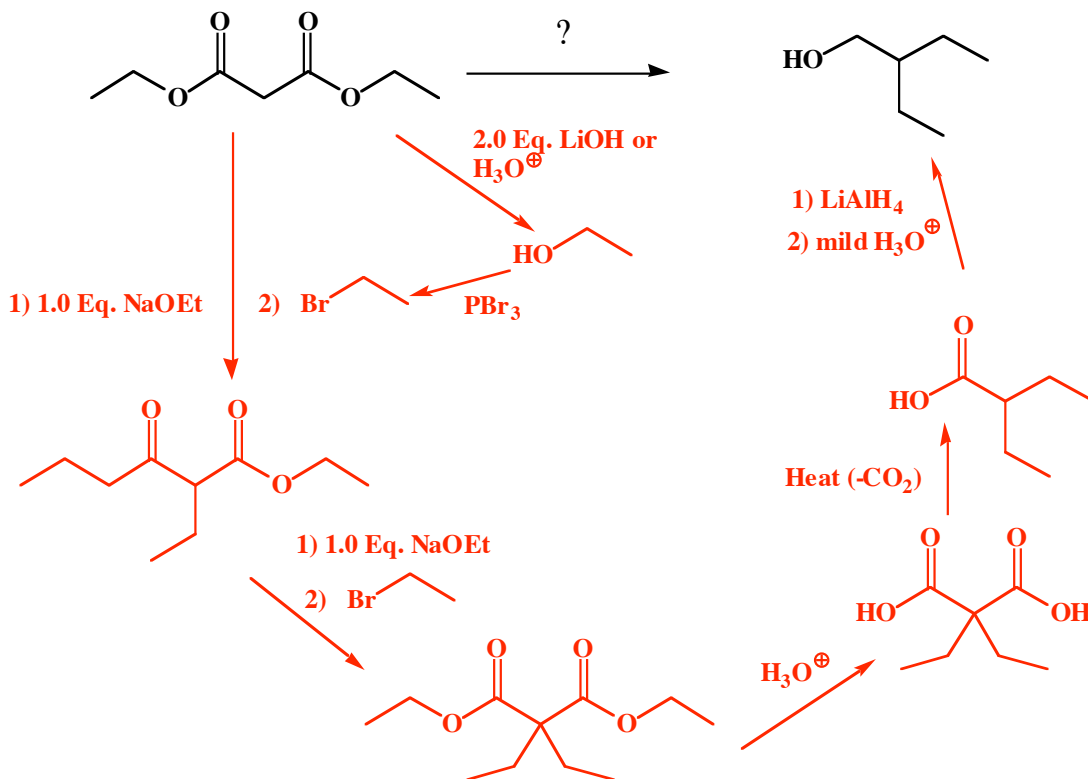
B) (16 pts)



Recognize this as the methyl ketone (KRE) product of an acetoester synthesis. Recognize also that acetoester is the product of a Claisen reaction derived from the starting ethyl acetate. Recognize also that the required two carbon unit needed for alkylation can be derived from hydrolysis of the starting ethyl ester, followed by reaction with PBr_3 .

15. 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 it doubt, draw the molecule!

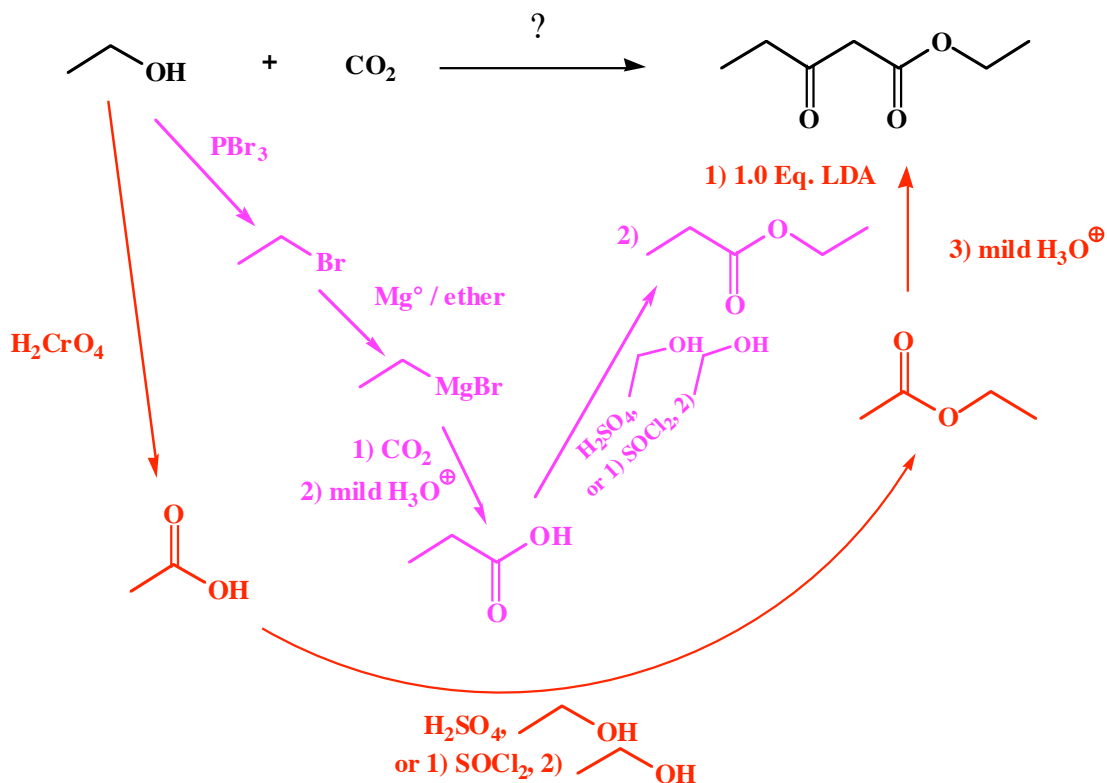
C) (16 pts)



Recognize this as a malonic ester synthesis because malonic acid is the starting material given. The required two carbon piece can be derived from ethanol liberated by hydrolysis of the diethyl malonate followed by conversion to a primary alkyl halide using PBr₃. The hard part of this one is seeing that the product does not have a KRE directly, but needs to be **recognized** as a reduced carboxylic acid, a transformation that requires LiAlH₄ and mild acid workup.

15. 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 it doubt, draw the molecule!

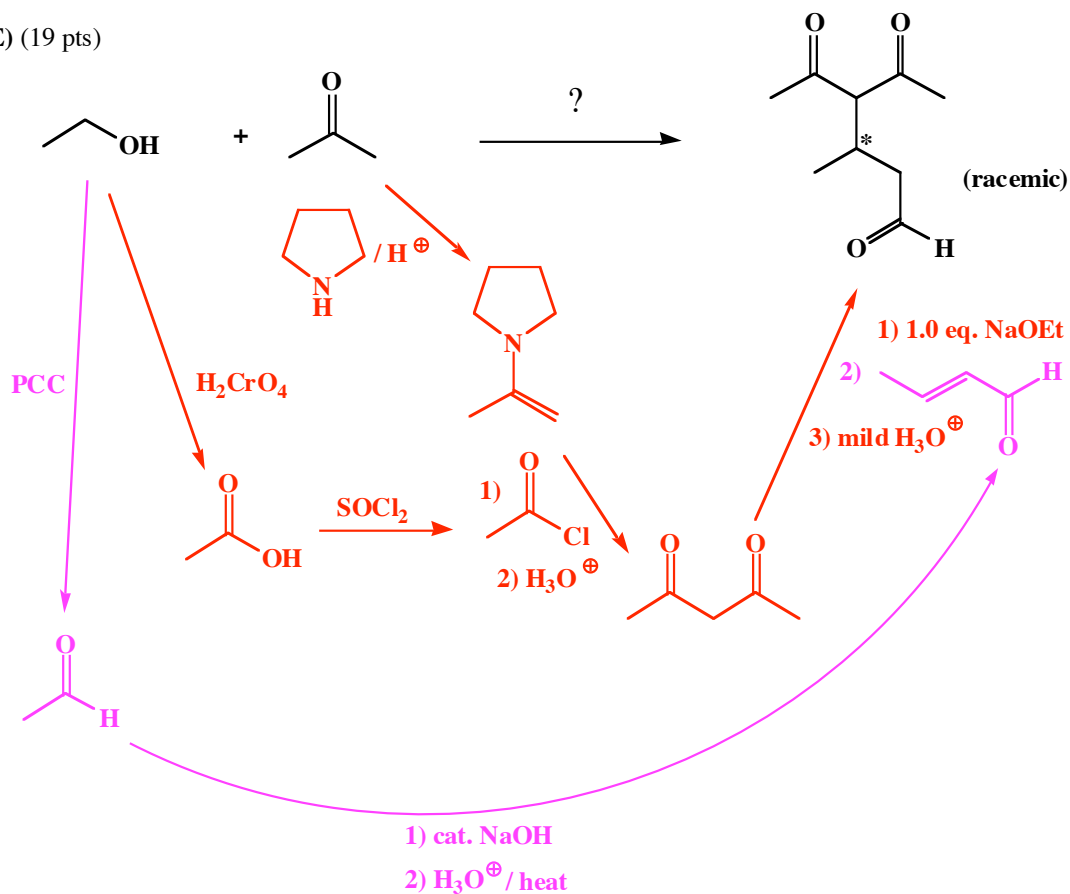
D) (19 pts)



Recognize this as a β -keto ester Claisen product, but a non-symmetrical one. We must carry out a crossed Claisen here between esters with two and three carbons in their acid portions, respectively. The two carbon acid containing ester must be the enolate portion as shown. The three carbon acid building block can be made using the CO₂ and a Grignard reaction.

15. 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 it doubt, draw the molecule!

E) (19 pts)



Recognize the product as being the result of a Michael reaction between a β -diketone and an α,β -unsaturated aldehyde as shown. **Recognize** the α,β -unsaturated aldehyde as being derived from an aldol reaction involving acetaldehyde, which in turn comes from PCC oxidation of the starting ethanol. **Recognize** the β -diketone as coming from the acylation of acetone with acetyl chloride, a transformation that is most easily accomplished using the symmetrical enamine derived from acetone. The acetyl chloride can be made from the oxidation of ethanol to give acetic acid, which is then reacted with thionyl chloride.