NAME (Print): _____

SIGNATURE: _____

Chemistry 310N
Dr. Brent Iverson
3rd Midterm
April 19, 2012

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

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 INCIDENCTS 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		(30)
2	XXXXX	(XX)
3		(20)
4		(21)
5		(18)
6		(25)
7		(29)
8		(17)
9		(20)
10		(14)
11		(10)
12	XXXXX	(XX)
13		(19)
14		(8)
15		(8)
Total		(239)
%		
T Score		
HW		
Total Grade		

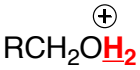
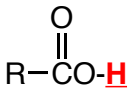
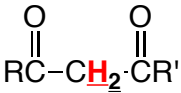
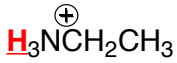
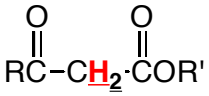
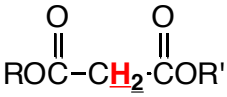
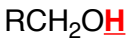
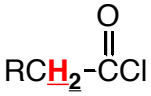
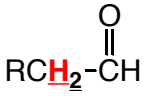
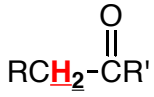
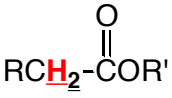
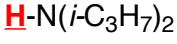
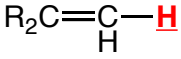
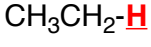
(HW score + Exam Grade) ⟹

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.

_____

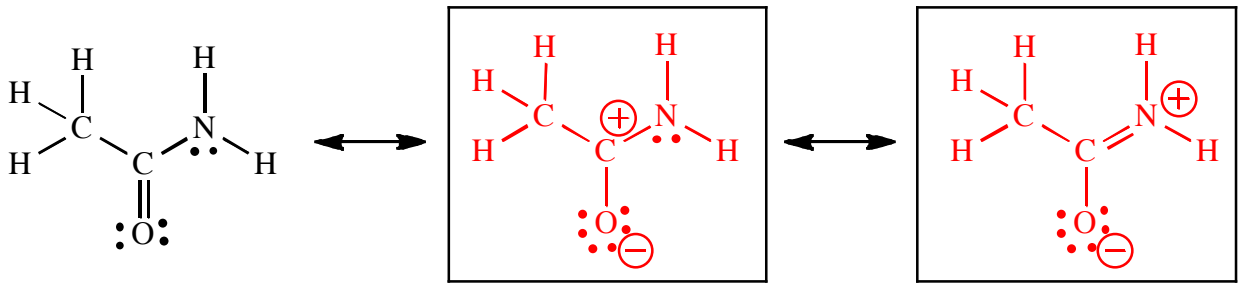
(Your signature)

Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal alkynes		25
LDA		40
Terminal alkenes		44
Alkanes		51

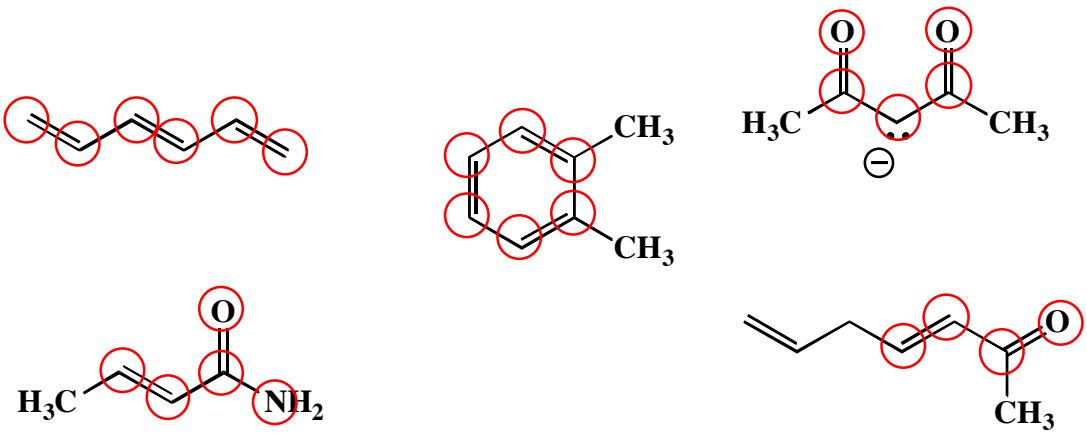
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We wil be looking for a minumum of 7 key points here.

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. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



3. (10 pts) On the following structures, circle all the **atoms** that have atomic orbitals that are involved in the delocalized pi electron orbitals (π-ways).



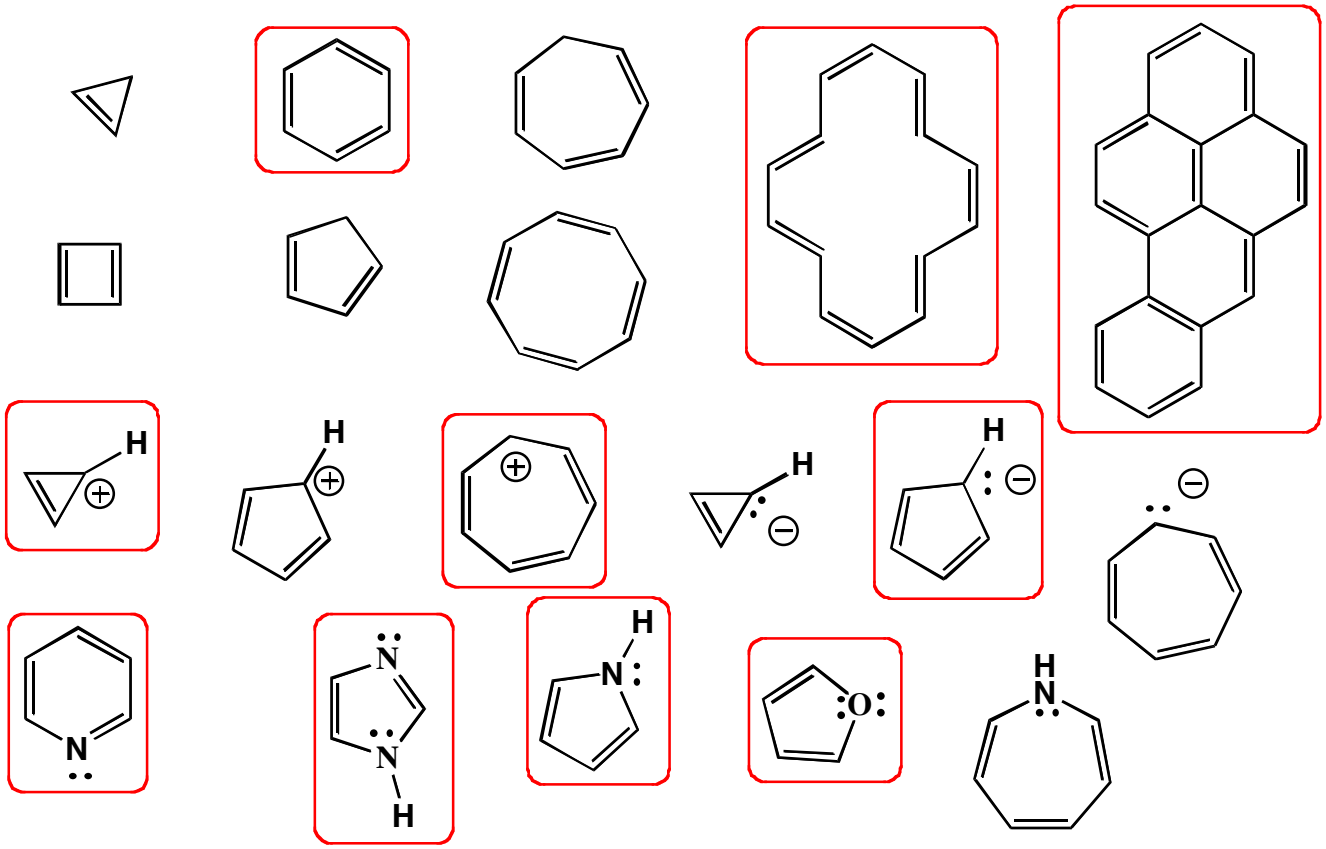
4. (2 pts) What is the most important question in chemistry?

Where are the electrons?

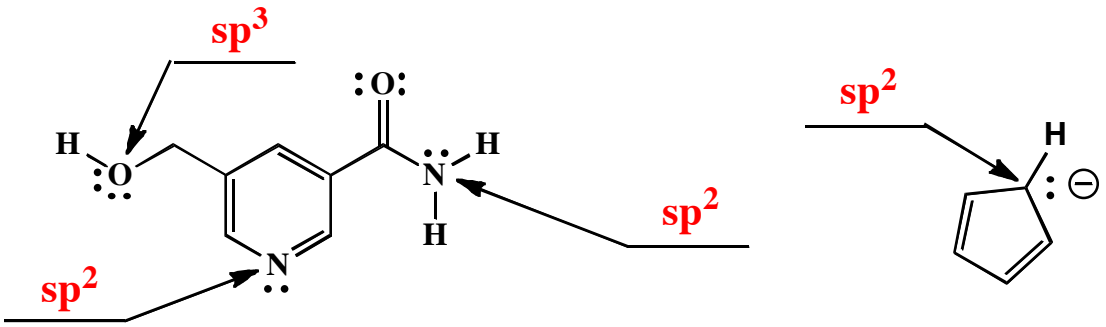
5. (1 pt. each) Here are a number of statements regarding aromaticity or other general aspects of organic chemistry. Do not second guess yourself, this is not meant to be tricky! **Check the appropriate box to indicate whether the statement is true or false.**

	True	False
A. When using molecular orbital theory, it is best to think of electron density as being like waves, since it is described mathematically using wave equations.	X	
B. According to Huckel's rule, aromatic molecules are flat, monocyclic, all ring atoms have a 2p orbital (no sp3 ring atoms) and there are 4n + 2 pi electrons (i.e. 2, 6, 10, 14.....).	X	
C. A reaction is said to be under kinetic control if the ratio of products is dependent on the relative energy barriers leading to the products.	X	
D. A reaction is said to be under kinetic control if the ratio of products is dependent on the relative energies of the products.		X
E. A reaction is said to be under thermodynamic control if the ratio of products is dependent on the relative energies of the products.	X	
F. When drawing mechanisms, arrows are used to indicate the flow of electrons from nucleophiles to electrophiles.	X	
G. A strong resonance effect due to aromaticity can stabilize a postive charge, negative charge, or unpaired electron density on an atom attached to an aromatic ring.	X	
H. Aromaticity makes pi electron density less reactive compared to simple alkenes	X	
I. When molecules absorb light, electrons are excited from an antibonding to a bonding molecular orbital.		X
J. If a substance absorbs red light, it will appear red to our eyes.		X
K. The positively charged intermediate produced when an aromatic ring reacts with a wicked strong electrophile has the positive charge located mostly meta to the location of where the electrophile bonded to the ring.		X
L. The positively charged intermediate produced when an aromatic ring reacts with a wicked strong electrophile has the positive charge located mostly ortho and para to the location of where the electrophile bonded to the ring.	X	
M. The last step of the general mechanism of aromatic rings reacting with wicked strong electrophiles is loss of a proton in a step that restores aromaticity to the ring.	X	

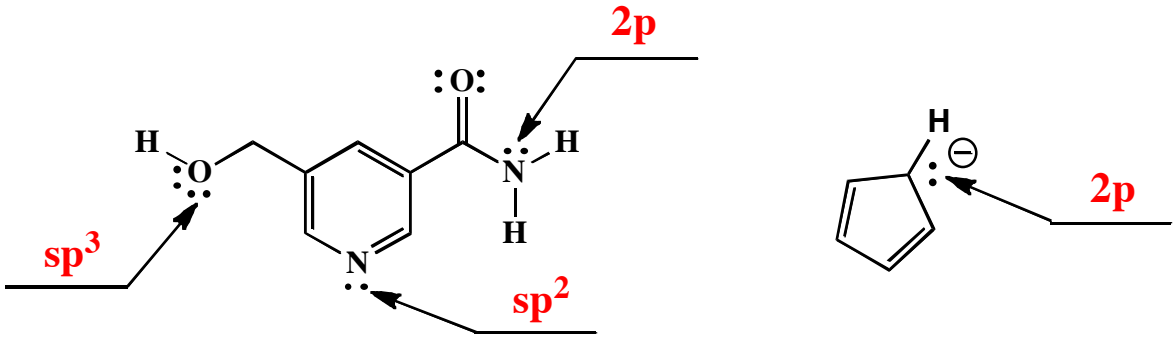
6. (19 points) **Draw a circle around** all of the molecules below that **can be considered aromatic.**



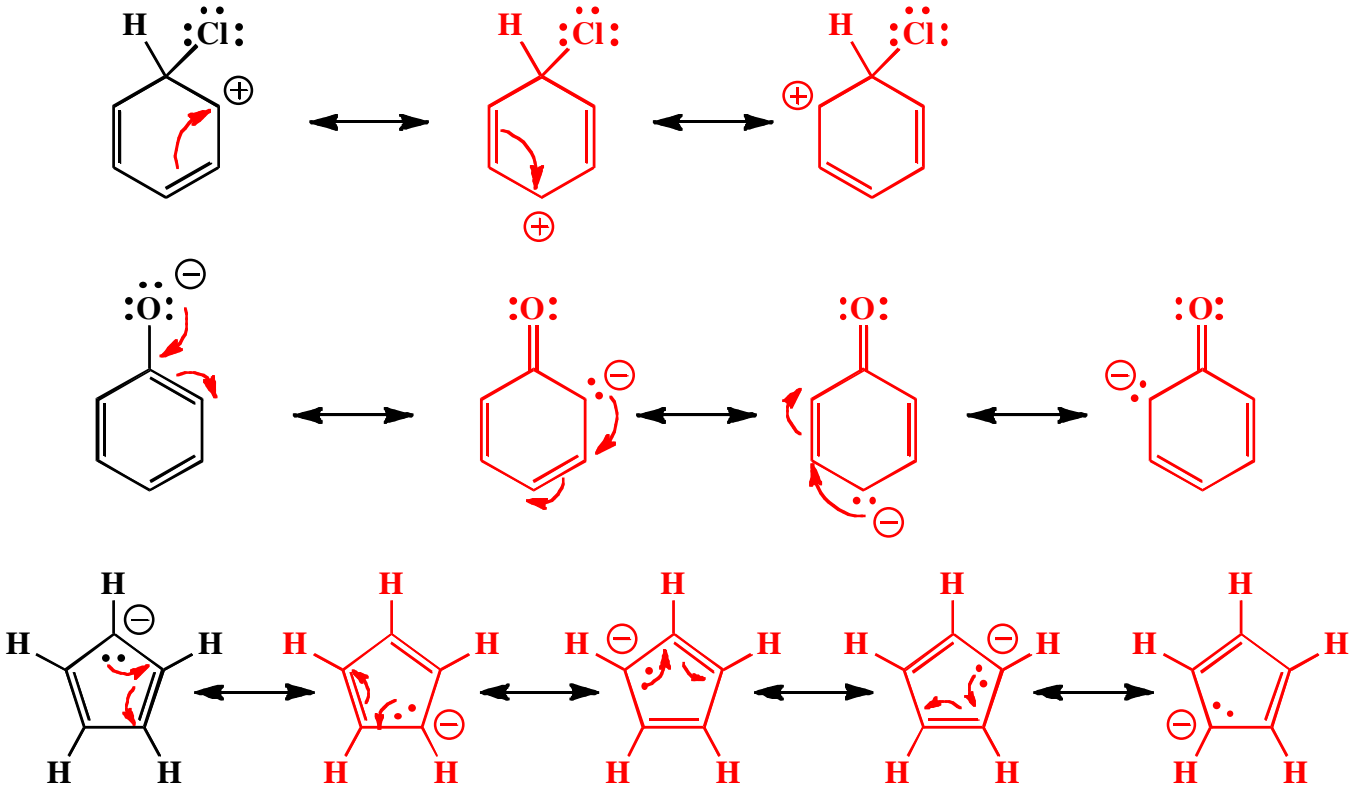
7. (4 pts) On the lines provided, state the **hybridization state of the atom** indicated by the arrow.



8. (4 pts) On the lines provided, state the **atomic orbital that contains the lone pair** of electrons indicated by the arrow.

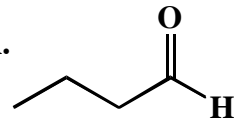


9. (18 points) **In the spaces provided, draw all the important resonance contributing structures of the indicated species.** We have provided template molecules to help you do this more quickly. You must draw all pi bonds, lone pairs of electrons and all formal charges on each of your structures. You DO NOT need to draw arrows to show electron movement.

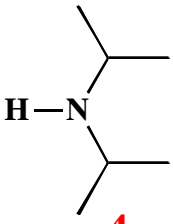


10. (8 pts) For each set of four, rank the following molecules with respect to acidity, with a **1** under the most acidic and a **4** under the least acidic. Please make sure that you do not rank them backwards!!!

A.



3



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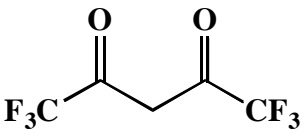
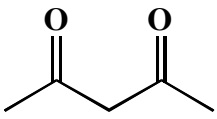
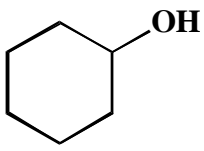


1

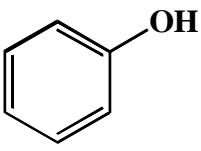


2

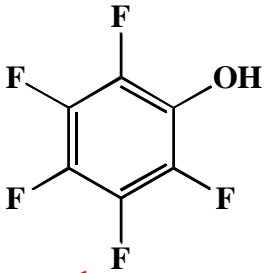
B.



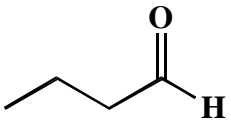
3



2

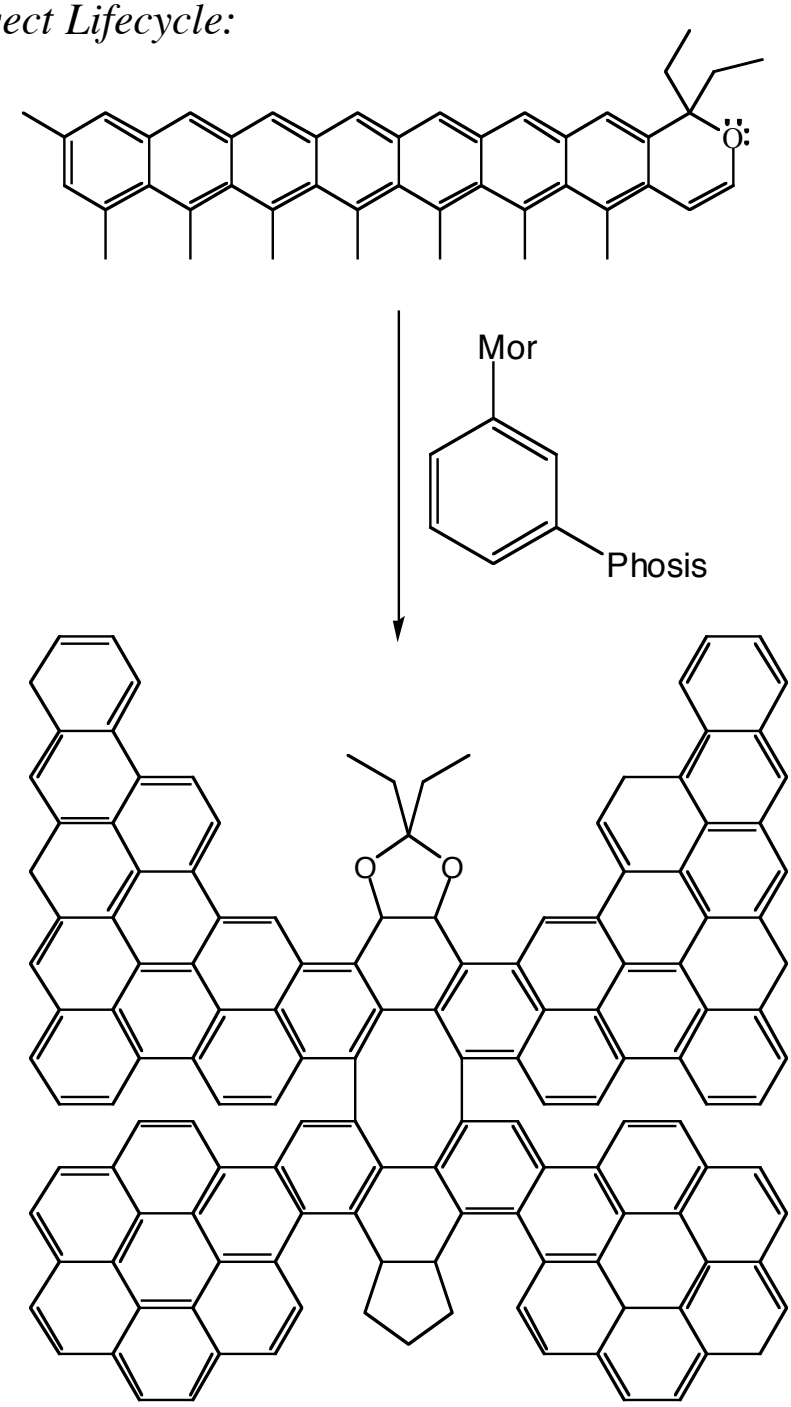


1



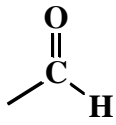
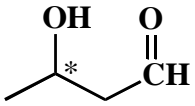
4

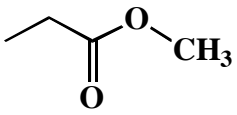
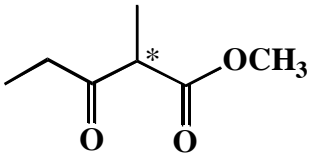
Aromatic Insect Lifecycle:

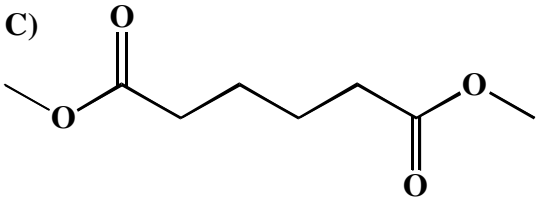
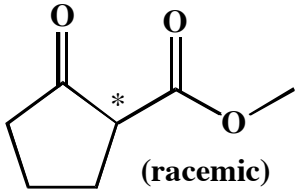


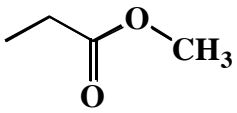
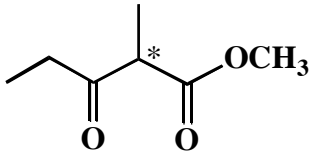
I put this here to help you relax. You will do better on the exam in a relaxed frame of mind. (If the above equation made you laugh or even smile, you may be a chem nerd, but nobody has to find out.)

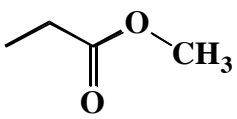
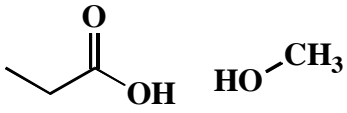
11. (2 pts each) In each of the boxes over an arrow, **write the minimum number of equivalents** of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write **"CAT"**. Note: **You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.**

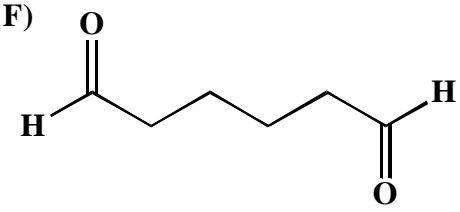
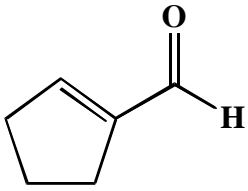
A)  cat equivalents HO^-Na^+  (racemic)

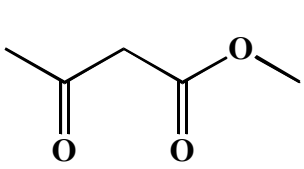
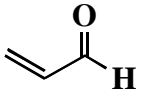
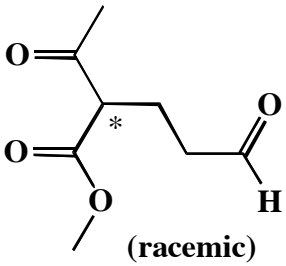
B)  1) 0.5 equivalents $CH_3O^-Na^+$ 2) mild H_3O^+  (racemic)

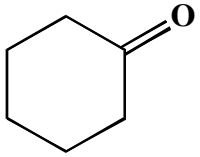
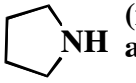
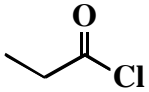
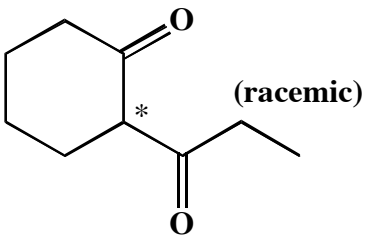
C)  1) 1.0 equivalents LDA 2) mild H_3O^+  (racemic)

D)  1) 0.5 equivalents LDA 2) mild H_3O^+  (racemic)

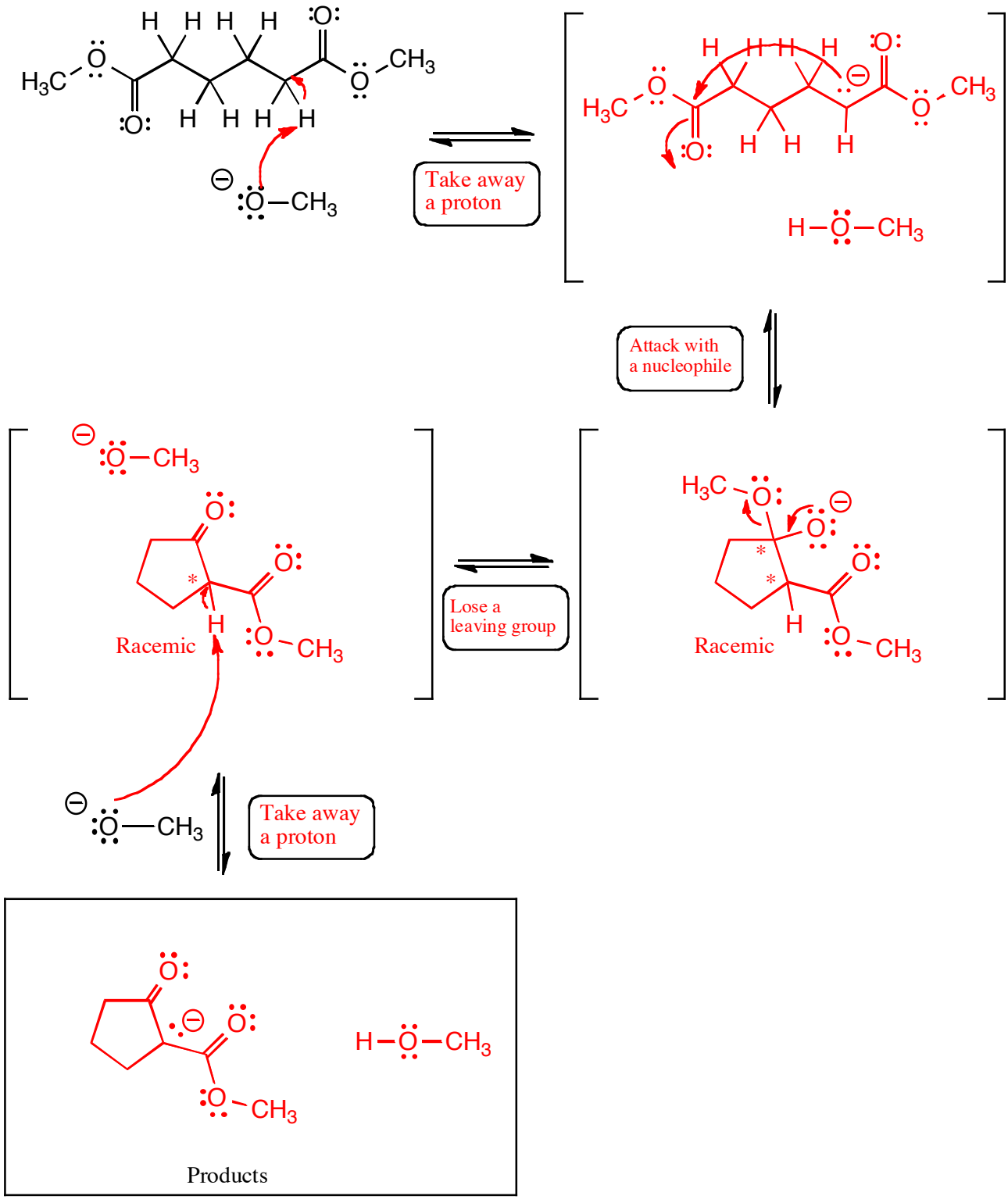
E)  1) 1.0 equivalents HO^-Na^+ 2) mild H_3O^+ 

F)  1) cat equivalents HO^-Na^+ 2) mild H_3O^+ (heat) 

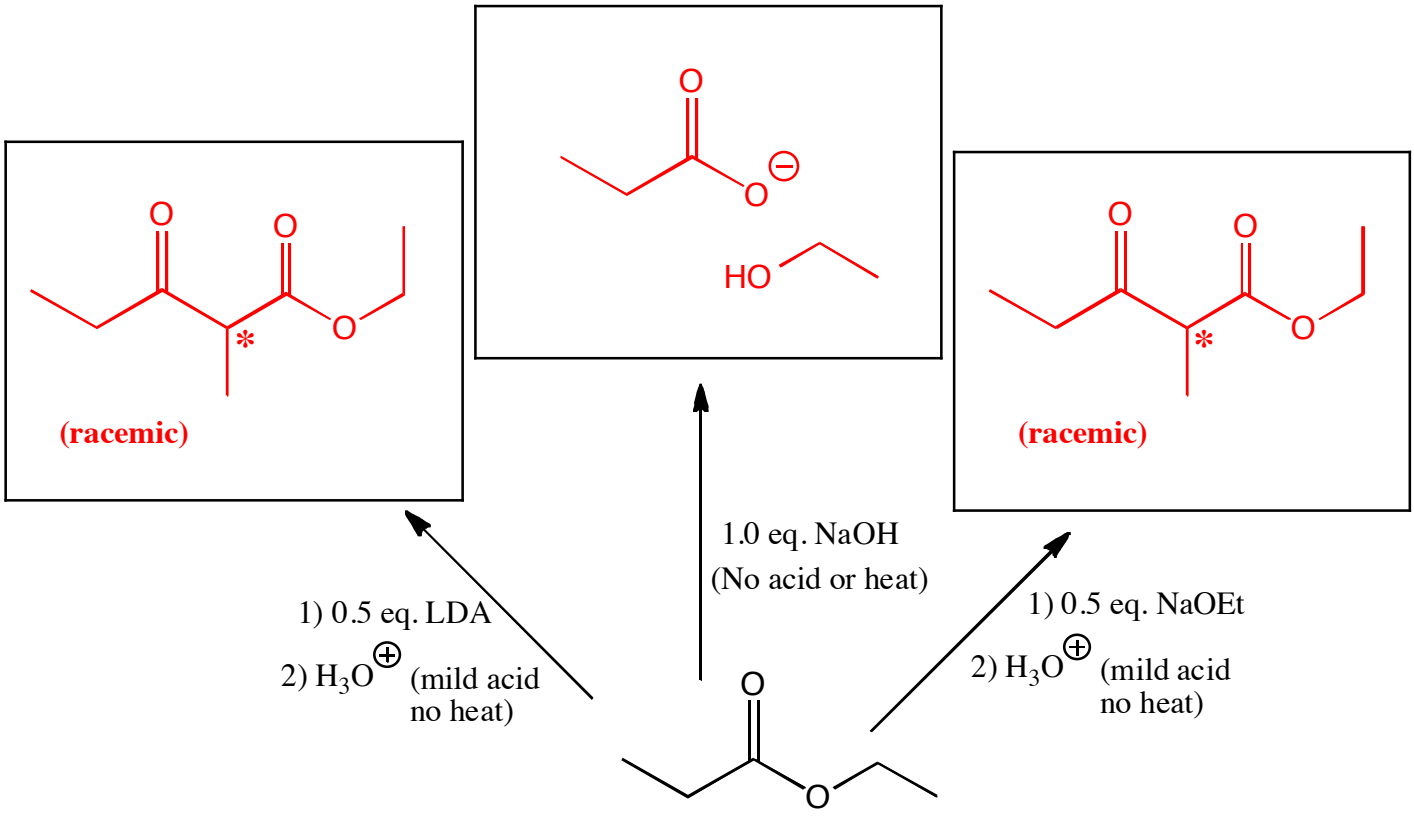
G)  1) 1.0 equivalents $CH_3O^-Na^+$ 2) 1.0 equivalents  3) mild H_3O^+ (no heat)  (racemic)

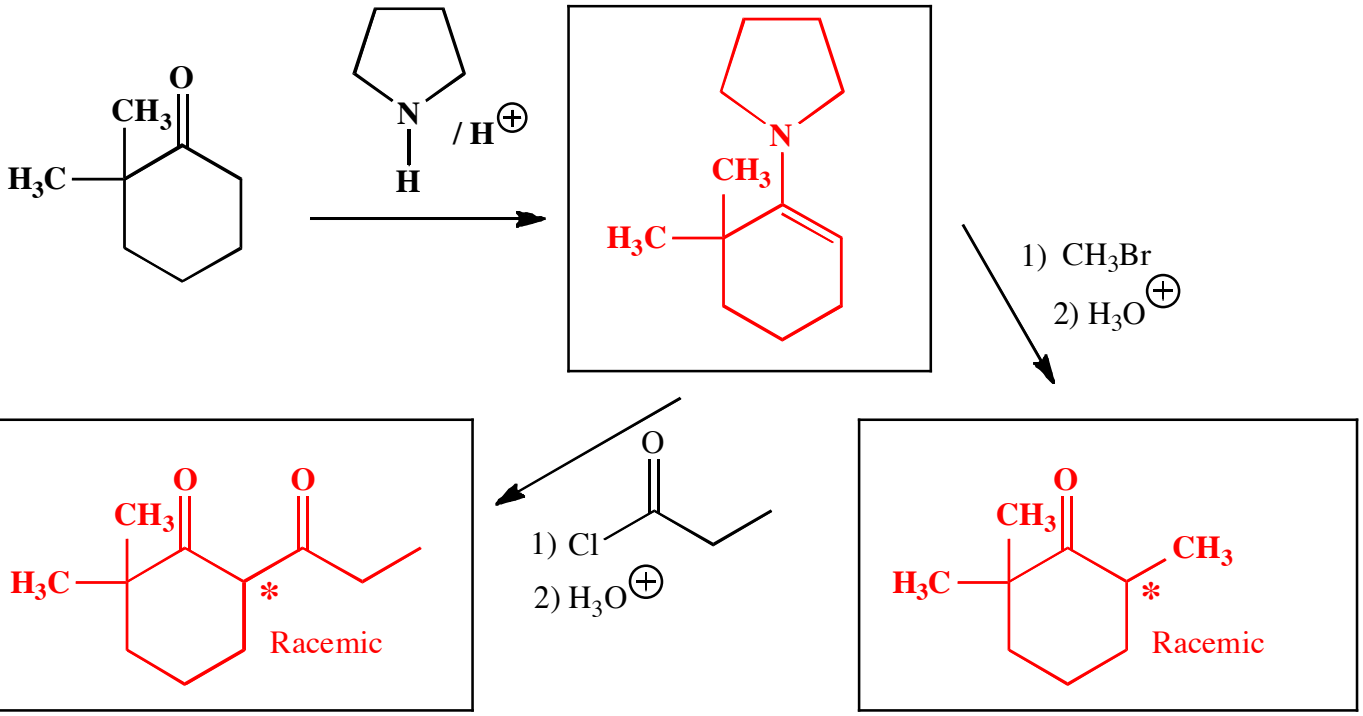
H)  1) 1.0 equivalents  (mild acid) 2) 1.0 equivalents  3) mild H_3O^+ (no heat)  (racemic)

11. (23 pts) Complete the mechanism for the following Dieckmann reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR THE PRODUCTS, MARK IT WITH AN ASTERISK AND LABEL AS "RACEMIC" IF RELEVANT. IN THE BOX BY EACH SET OF ARROWS, WRITE WHICH OF THE 4 MECHANISTIC ELEMENTS IS INDICATED IN EACH STEP OF YOUR MECHANISM (For example, "Add a proton").



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.





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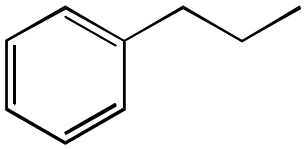
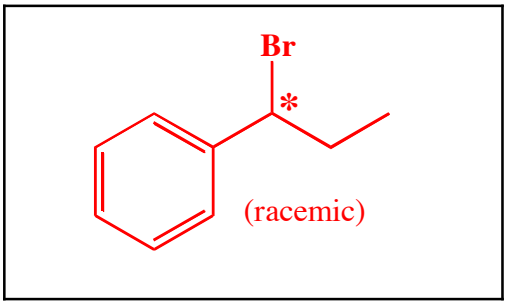
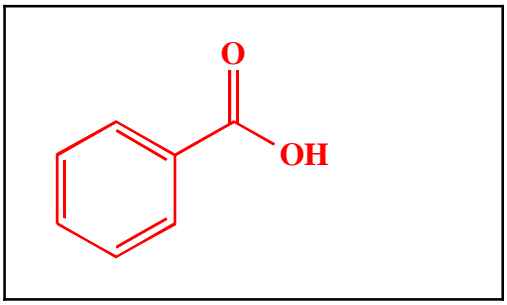
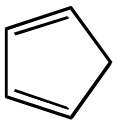


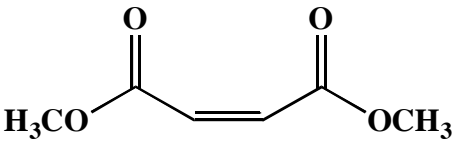
Br_2 / hν (assume reaction stops after first addition)

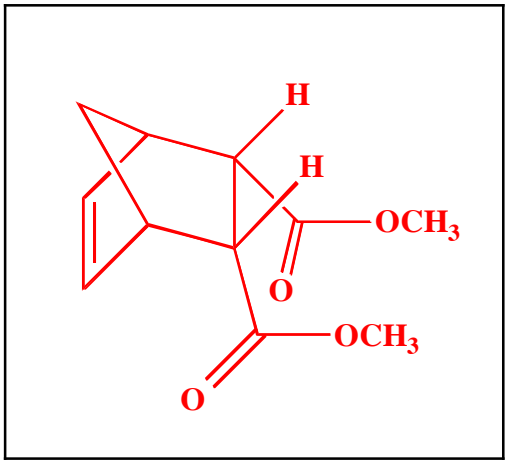


H_2CrO_4

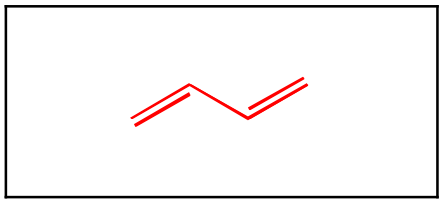






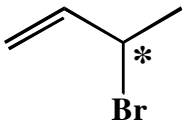


For the next two reactions draw the appropriate starting material then circle the appropriate temperature regime, "high" or "low" temperature under the arrow.

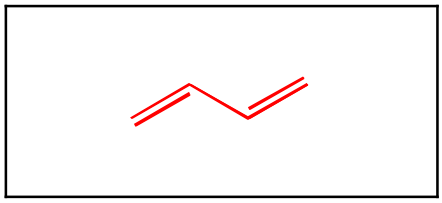


HBr

(low) or high temperature

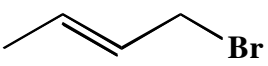


(racemic)



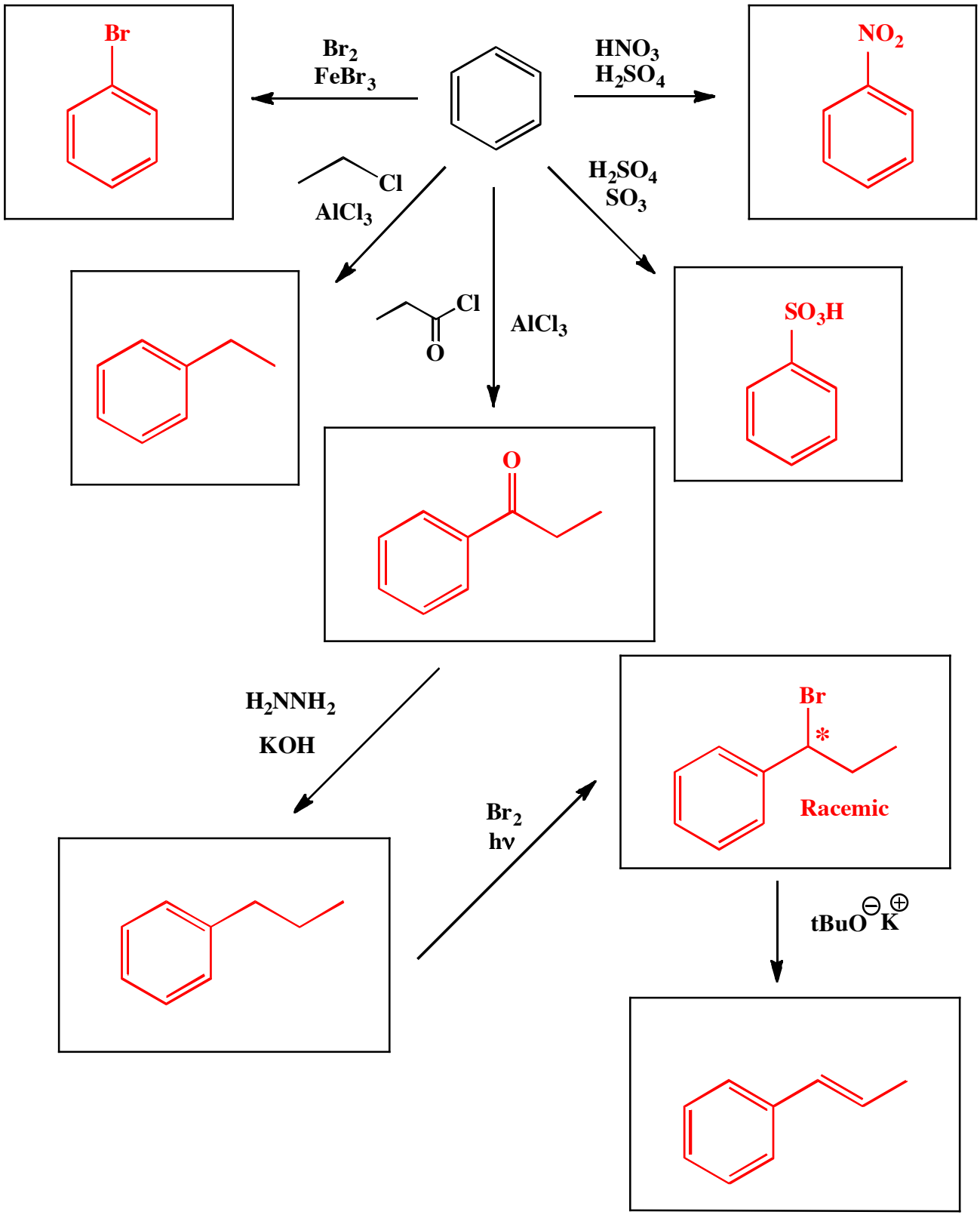
HBr

low or (high) temperature

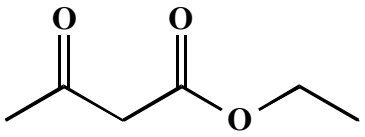


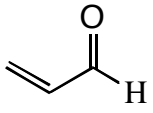
(racemic)

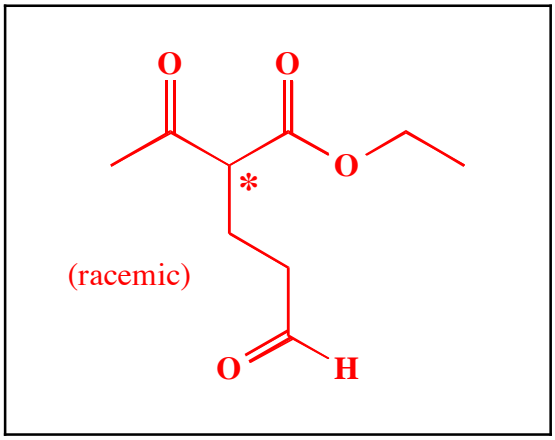
13. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration 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.

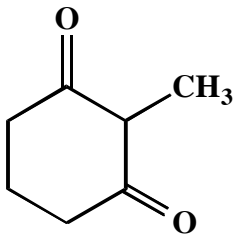


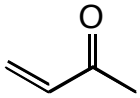
13. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration 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.

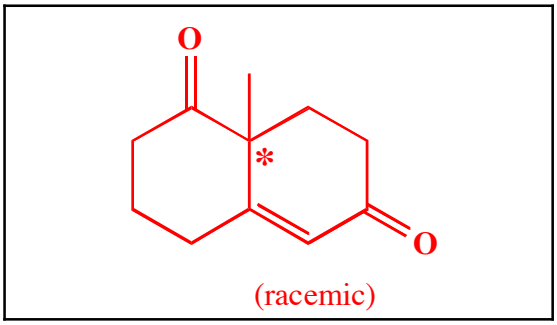


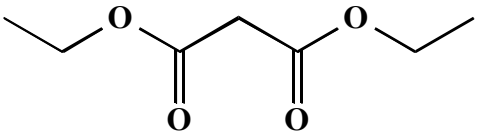
1) 1.0 eq.NaOEt
2) 
3) $H_3O^{\oplus}$
(mild acid, no heat)

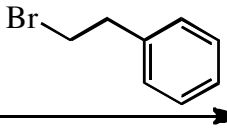


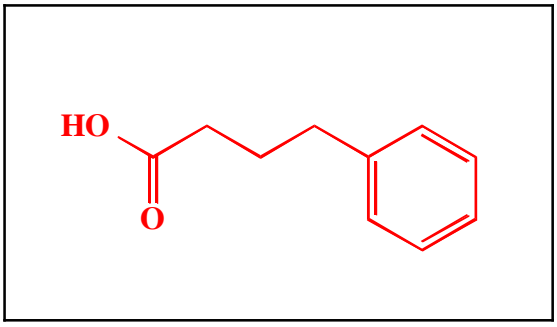


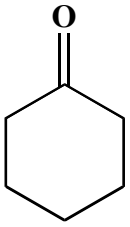
1) 1.0 eq.NaOEt
2) 
3) $H_3O^{\oplus}$
(stronger acid, with heat)

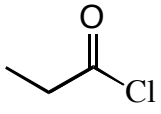


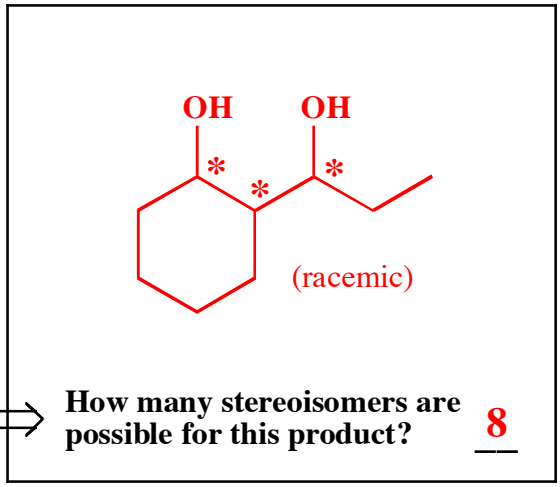


1) 1.0 eq.NaOEt
2) 
3) $H_3O^{\oplus}$
(very strong acid with heat)
4) More heat





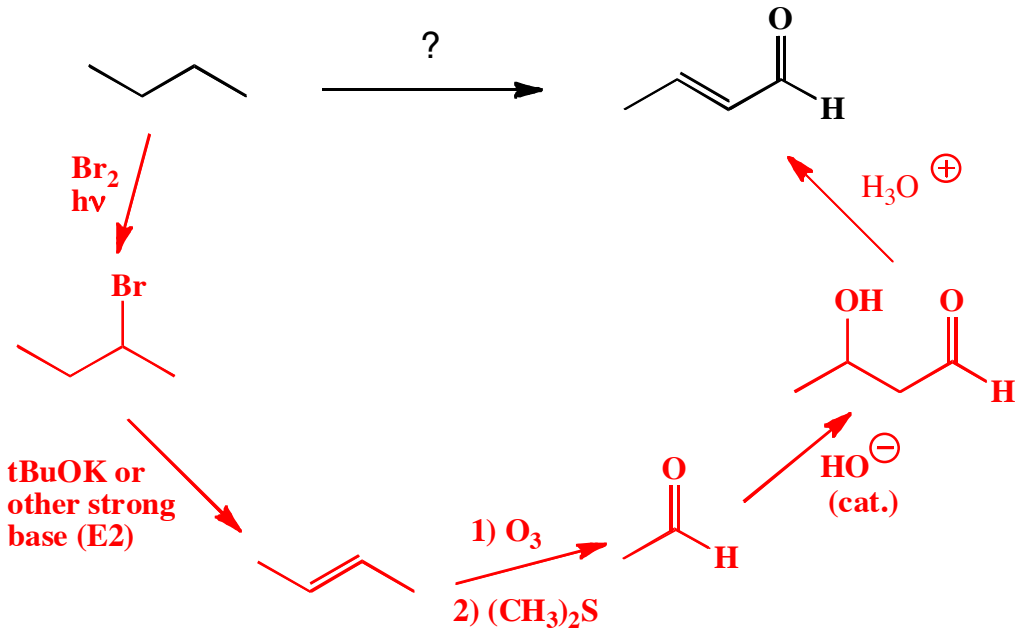
1) 1.0 eq. LDA
2) 
3) $H_3O^{\oplus}$
4) $LiAlH_4$
5) H_2O



NOTICE THIS ⟹ **How many stereoisomers are possible for this product?** **8**

14. (10 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate.

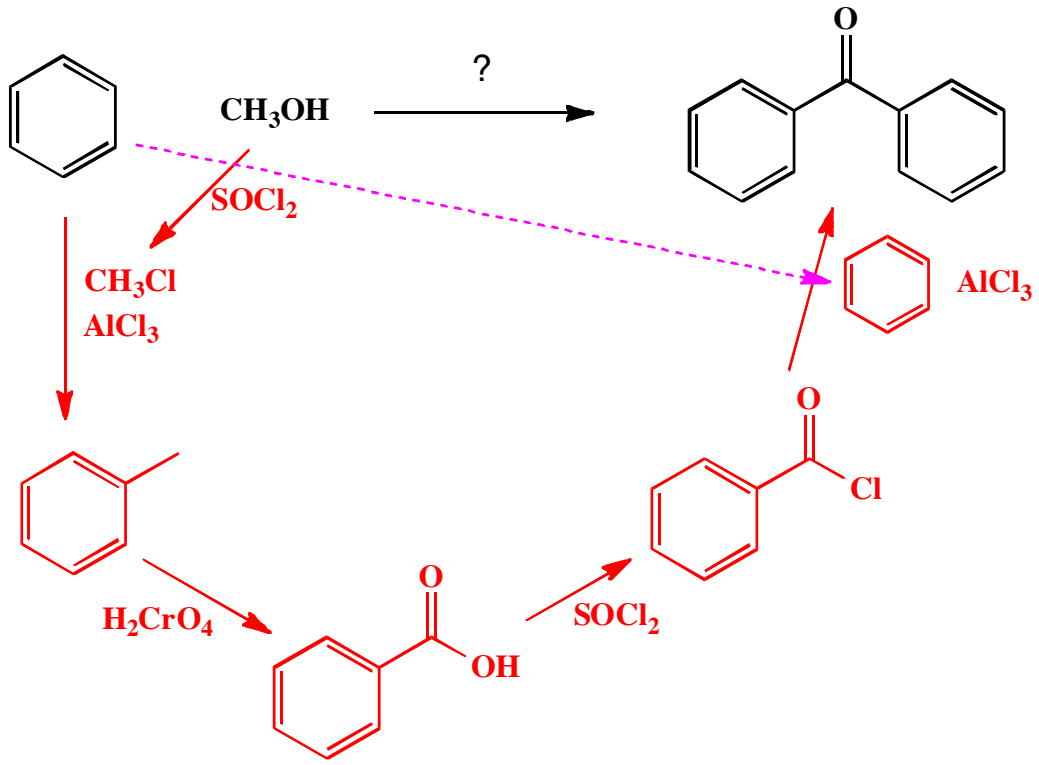
Remember, all of the carbons of the product must come from the given starting material.



Recognize the final product as resulting from dehydration of the aldol product (β-hydroxy aldehyde). The required aldehyde for the aldol reaction is acetaldehyde, which can be derived from the ozonolysis of 2-butene. **Recognize** that 2-butene can be derived from the starting material through the sequence of free radical halogenation followed by E2 elimination in base.

14. (cont. 13 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate.

Remember, all of the carbons of the product must come from the given starting material.

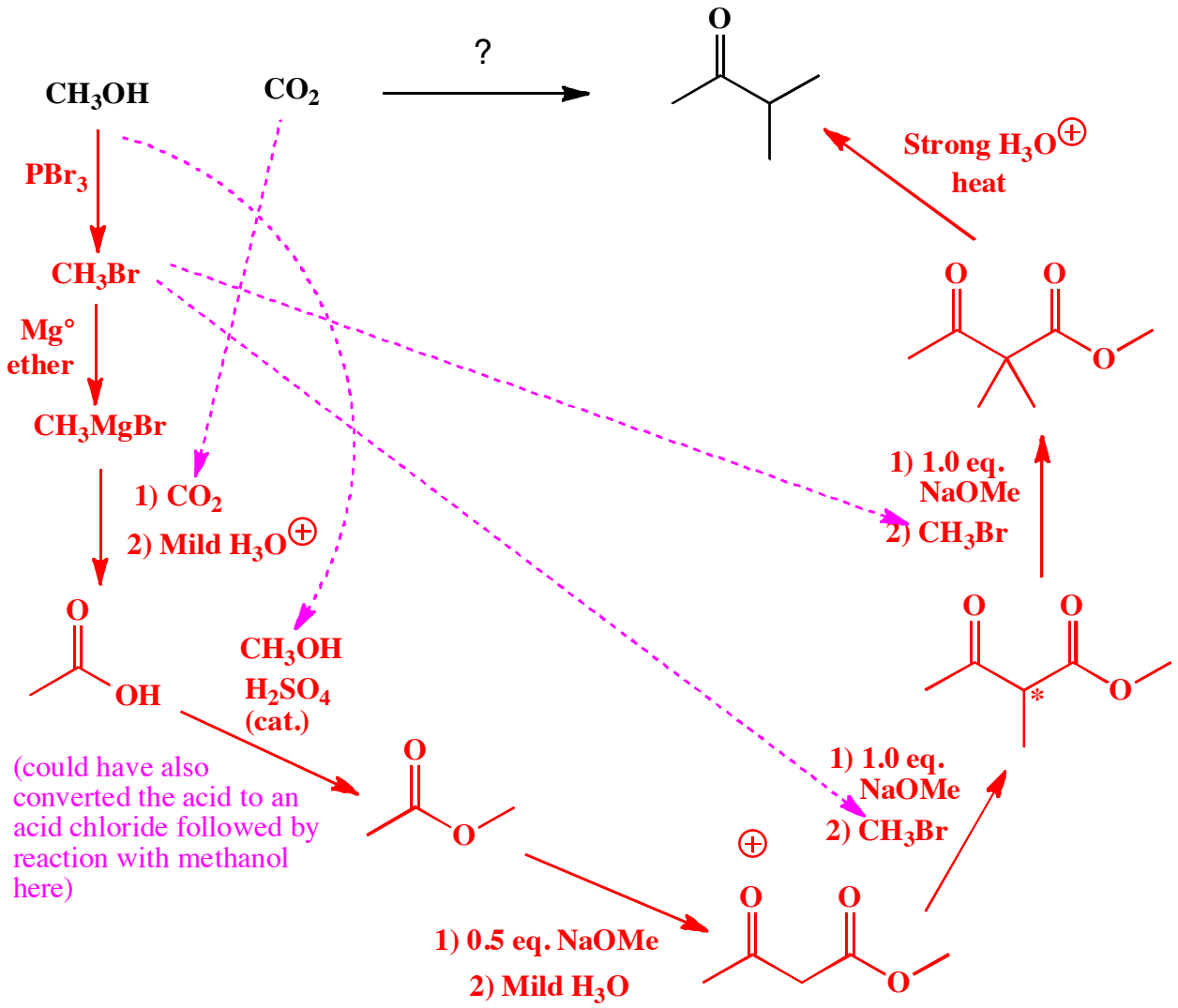


Recognize the product as a phenyl ketone, the KRE of a Friedel-Crafts acylation reaction between benzene and the acid chloride derived from benzoic acid. **Recognize** that benzoic acid can be made from the chromic acid oxidation of toluene, which can be made from the Friedel-Crafts alkylation of benzene with methyl chloride. Methyl chloride can be made from methanol using $SOCl_2$. Note that methyl bromide would also work on this step.

An alternative synthesis would be the same as shown above, except the last step would use the phenyl Gilman reagent reacting with the acid chloride. The phenyl Gilman reagent could be made by first reacting benzene with Cl_2 and $FeCl_3$ followed by reaction with Li° then CuI.

14. (cont. 22 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate.

Remember, all of the carbons of the product must come from the given starting material.



I consider this to be a difficult problem because of how many pieces from one carbon units (starting materials) need to be assembled to get to the product. Recognize the product as a methyl ketone derivative, the KRE for the acetoester synthesis. The required β-ketoacid derivative is acetoester that has been alkylated twice using methyl bromide, which is available from the starting methanol following reaction with PBr_3. **Recognize** that acetoester comes from the Claisen reaction of methyl acetate. **Recognize** further that methyl acetate comes from esterification of acetic acid. The required acetic acid can be made from the Grignard reagent derived from methyl bromide added to CO_2.