NAME (Print): ______________________________

SIGNATURE: ______________________________

Chemistry 310N
Dr. Brent Iverson
3rd Midterm
April 23, 2009

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.

For synthesis problems GO FOR PARTIAL CREDIT EVEN IF YOU DO NOT KNOW THE ENTIRE ANSWER!!!WRITE DOWN WHAT YOU DO KNOW IS 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		(29)
2	deleted	(-)
3		(29)
4		(17)
5		(24)
6		(20)
7		(23)
8		(26)
9		(21)
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13		(16)
14		(22)
15		(28)
16		(23)
Total		(324)
%		
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Total Grade		

(HW score + Exam Grade) ⟹ Total 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	H-Cl	-7
Protonated alcohol	$RCH_2OH_2^{\oplus}$	-2
Hydronium ion	$H_3O^{\oplus}$	-1.7
Carboxylic acids	R–C(=O)O-H	3-5
Ammonium ion	$H_4N^{\oplus}$	9.2
β-Dicarbonyls	RC(=O)–CH_2–C(=O)R'	10
β-Ketoesters	RC(=O)–CH_2–C(=O)OR'	11
β-Diesters	ROC(=O)–CH_2–C(=O)OR'	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	RCH_2–C(=O)Cl	16
Aldehydes	RCH_2–C(=O)H	18-20
Ketones	RCH_2–C(=O)R'	18-20
Esters	RCH_2–C(=O)OR'	23-25
Terminal alkynes	RC≡C—H	25
LDA	H-N(i-C_3H_7)$_2$	40
Terminal alkenes	R_2C=C(H)—H	44
Alkanes	CH_3CH_2-H	51

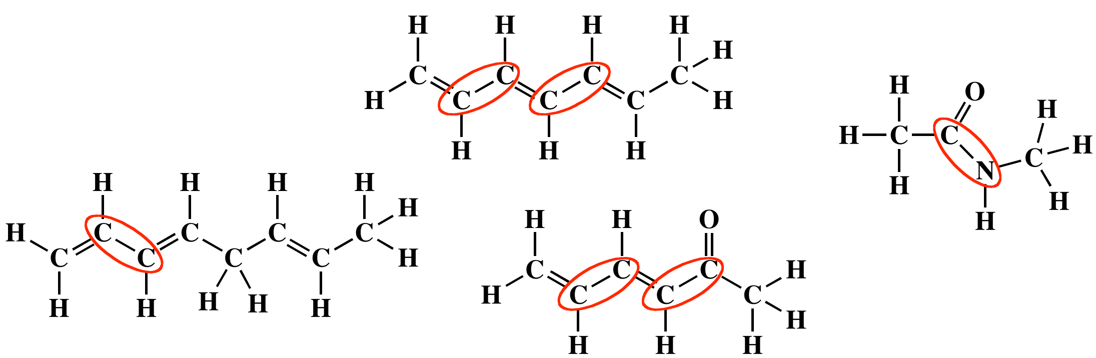
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minumum of 7 key points here.

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**.

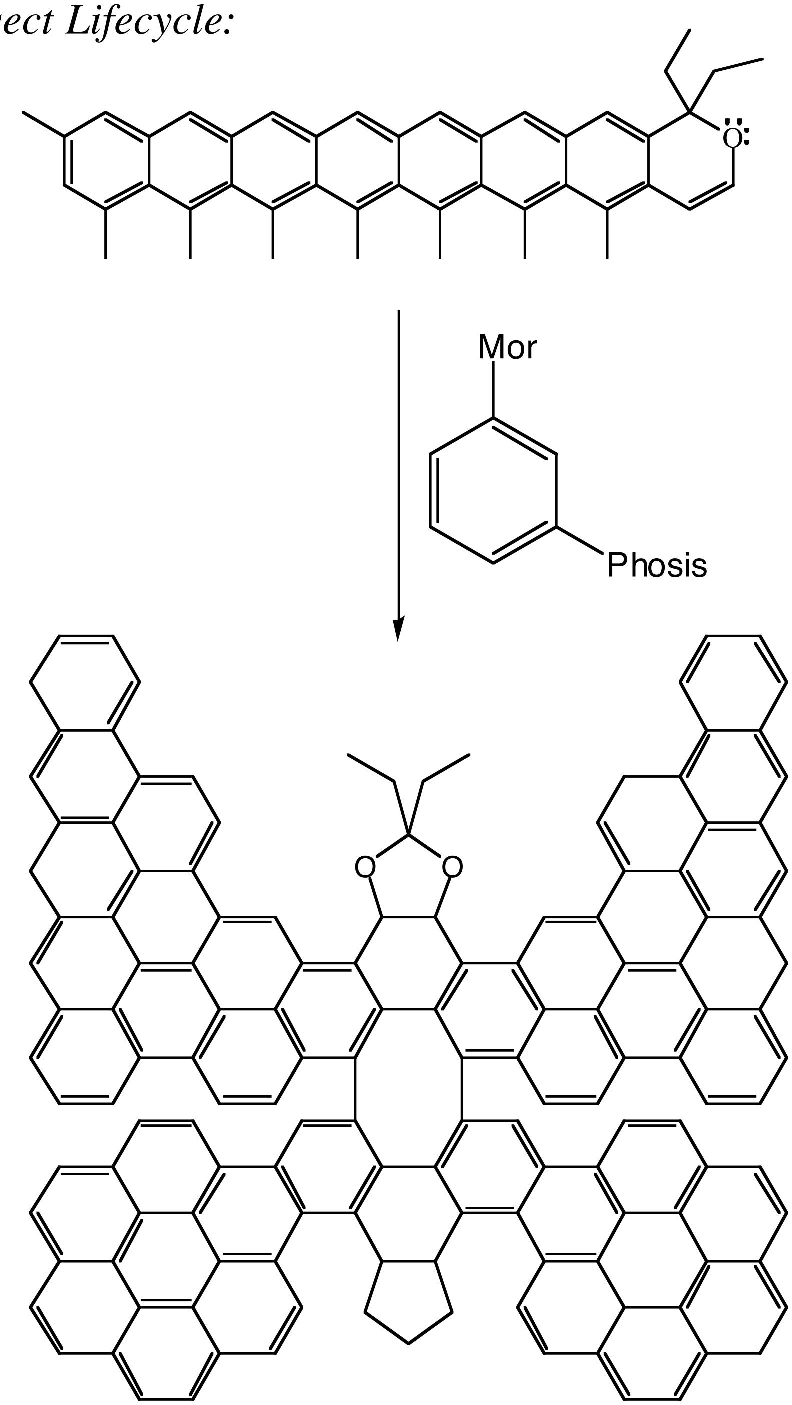
2. (8 points) Aromaticity is a term that refers to molecules with characteristic pi systems. A theorist named Hückel helped to derive several criteria that can be used to determine if a molecule is aromatic. List all four of these criteria:

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

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.

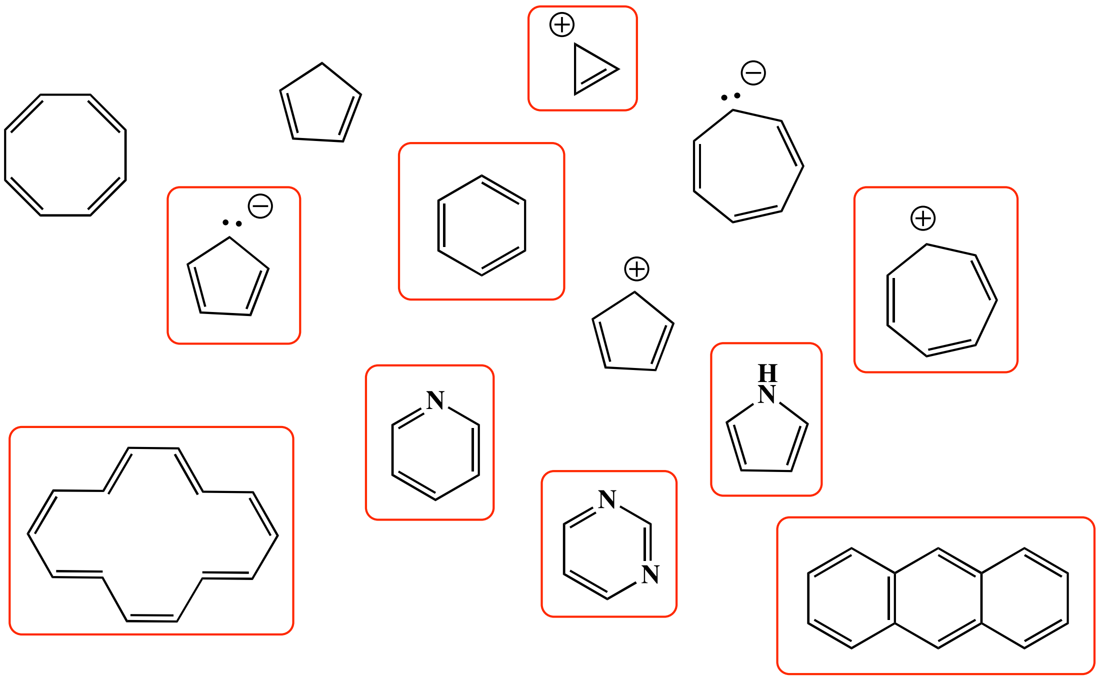


Aromatic Insect Lifecycle:

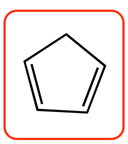
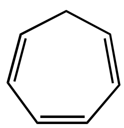


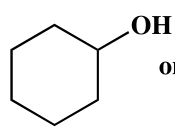
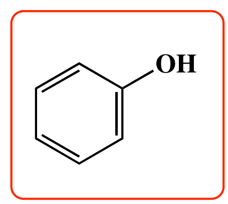
I put this here to help you relax. You will do better on the exam in a relaxed frame of mind. (If the above equation made you laugh or even smile, you may be a chem nerd, but nobody has to find out.)

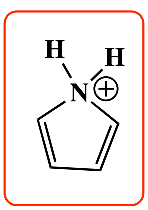
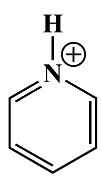
5. (13 points) **Draw a circle around** all of the molecules below that **can be considered aromatic.**

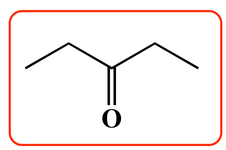
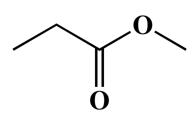


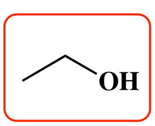
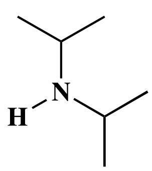
6. (16 points) **For each pair of molecules, circle the one that is more acidic.**

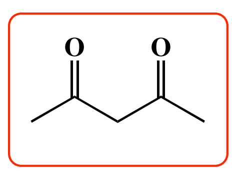
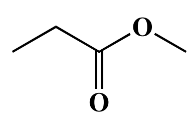
A.  or 

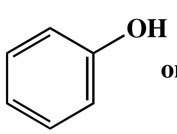
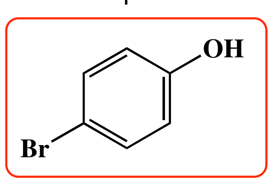
B.  or 

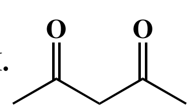
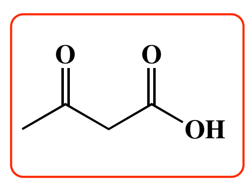
C.  or 

D.  or 

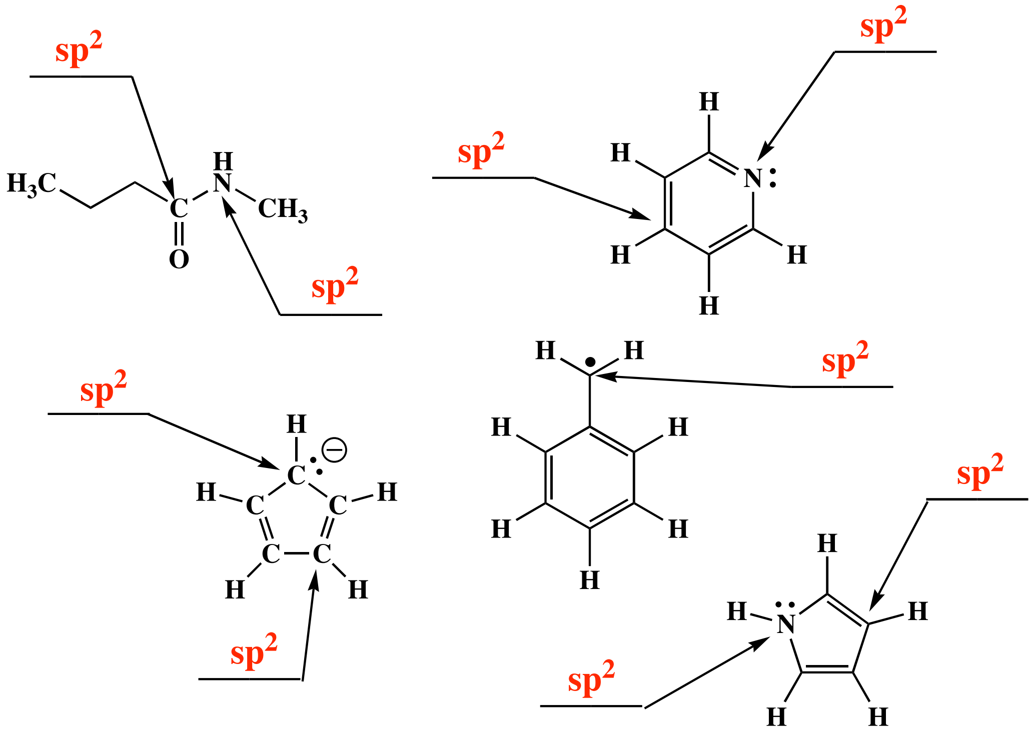
E.  or 

F.  or 

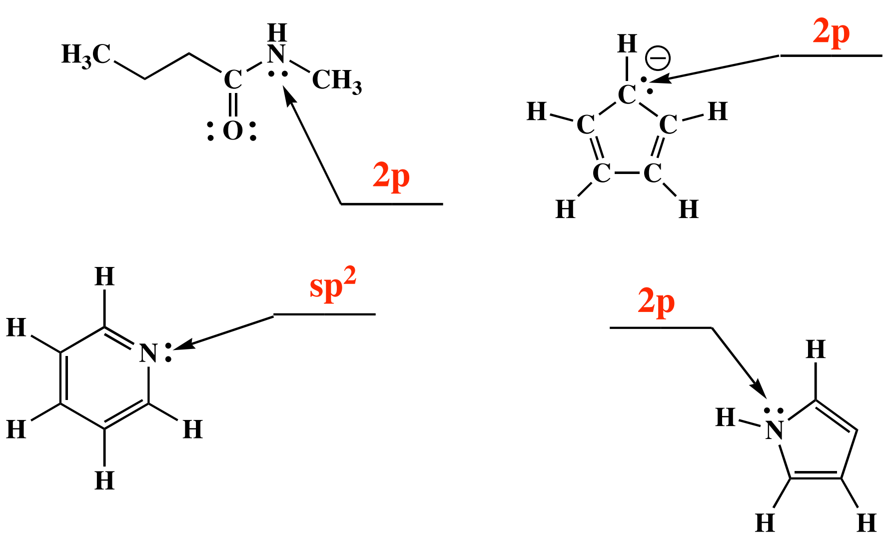
G.  or 

H.  or 

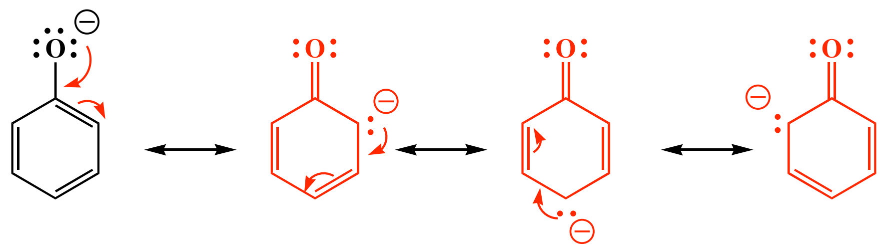
7. (9 points) On the lines provided, state the **hybridization state of the atom** indicated by the arrow.

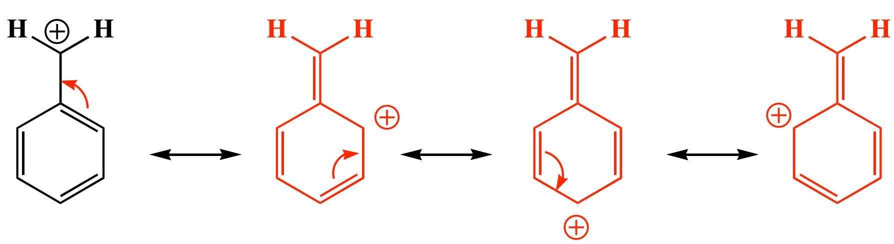


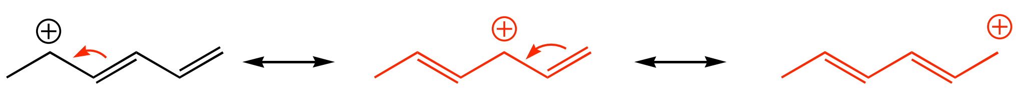
8. (8 points) On the lines provided, state the **atomic orbital that contains the lone pair** of electrons indicated by the arrow.

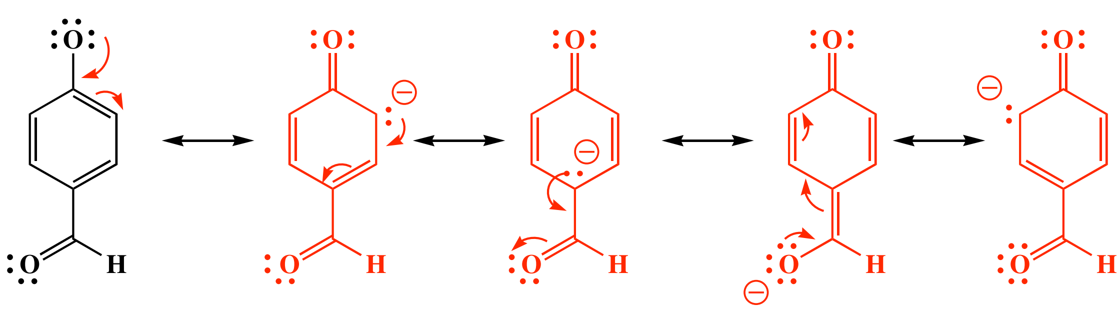


9. (24 points) An important theme that you have encountered throughout organic chemistry is that charge delocalization through resonance is stabilizing. For the following ions, draw the indicated number of most important resonance contributing structures. For each contributing structure, **you must show all formal charges and all lone pairs of electrons. In addition, you must use arrows to show movement of electrons leading to the structure immediately to the right.** This means the right most structures will be the only ones without arrows.



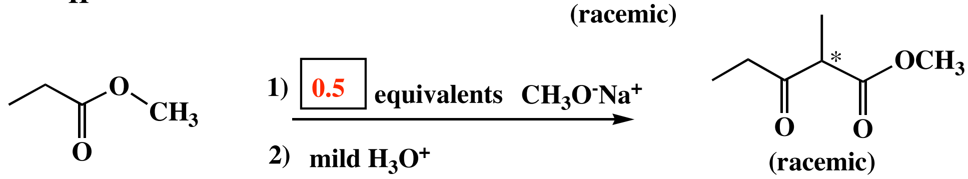






11. (2 pts each) In each of the boxes over an arrow, **write the minimum number of equivalents** of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write **"CAT"**. Note: **You must assume the carbonyl compound starting material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

A)


B)


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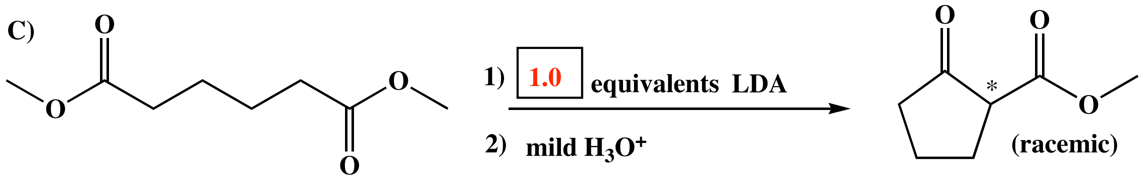

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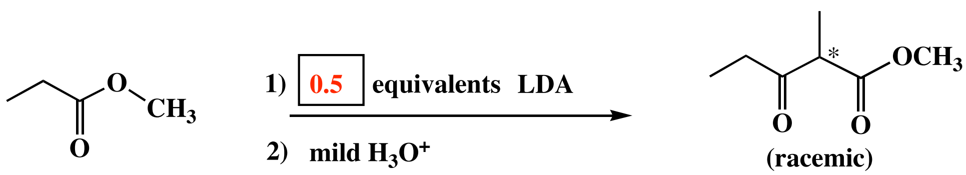

E)


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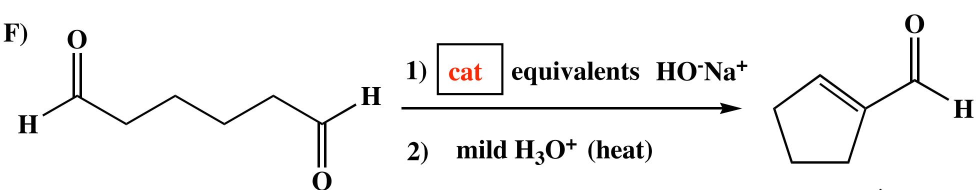

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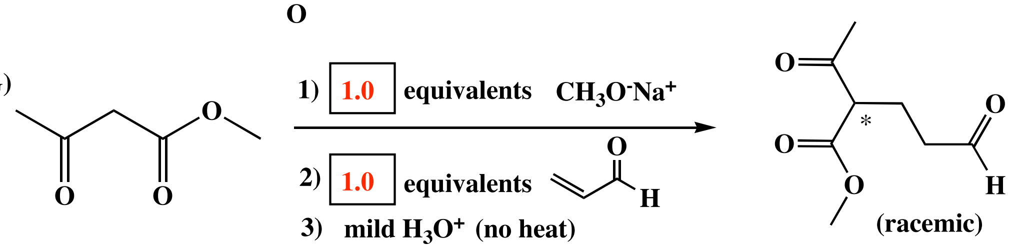

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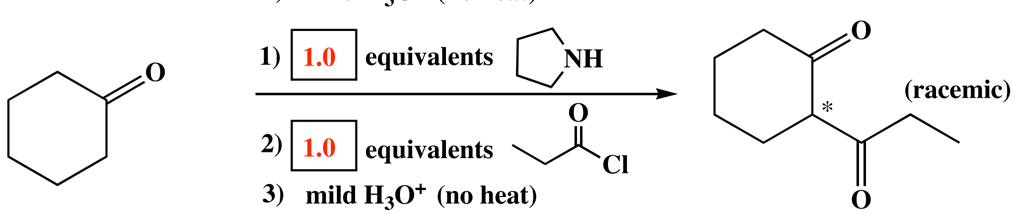
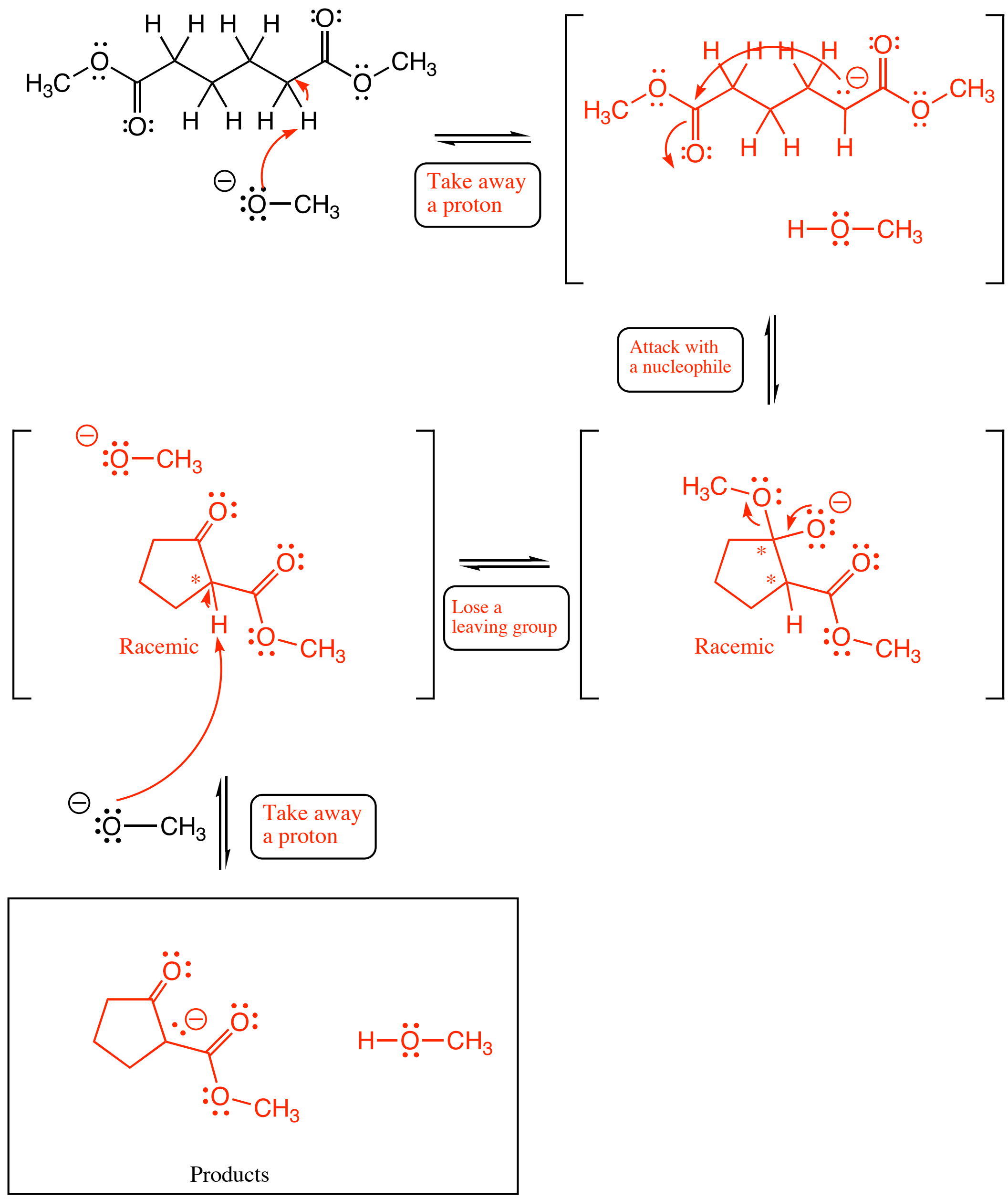
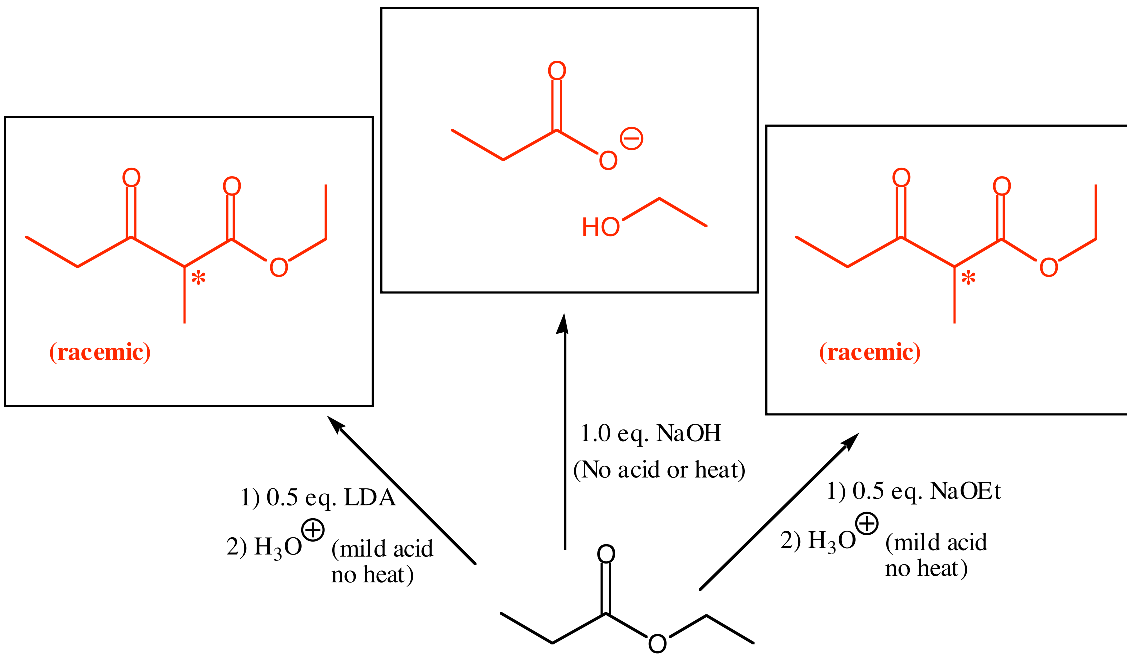
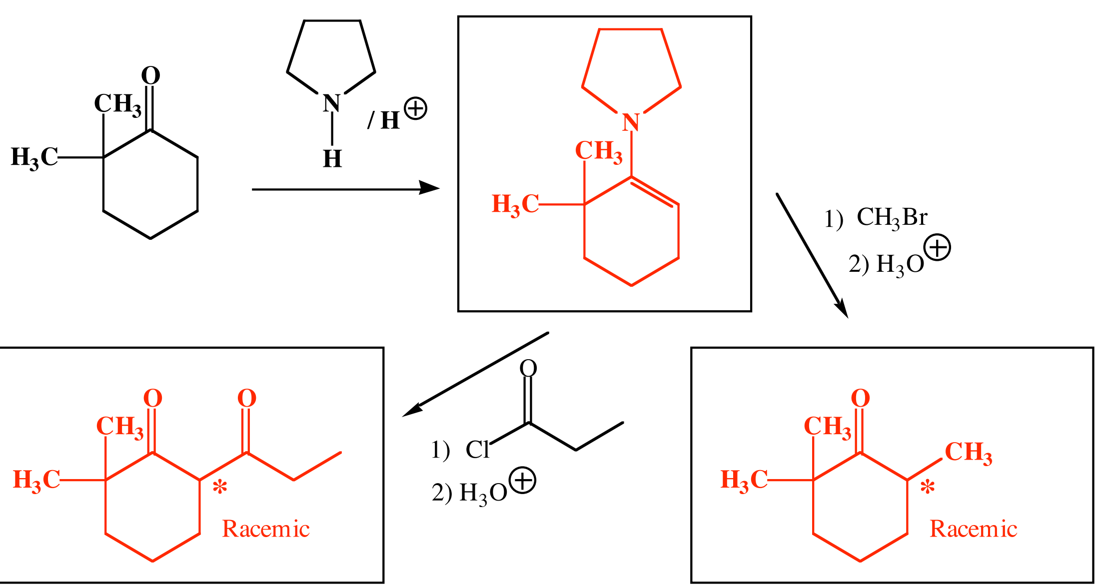


11. (35 pts) Complete the mechanism for the following Dieckmann reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN 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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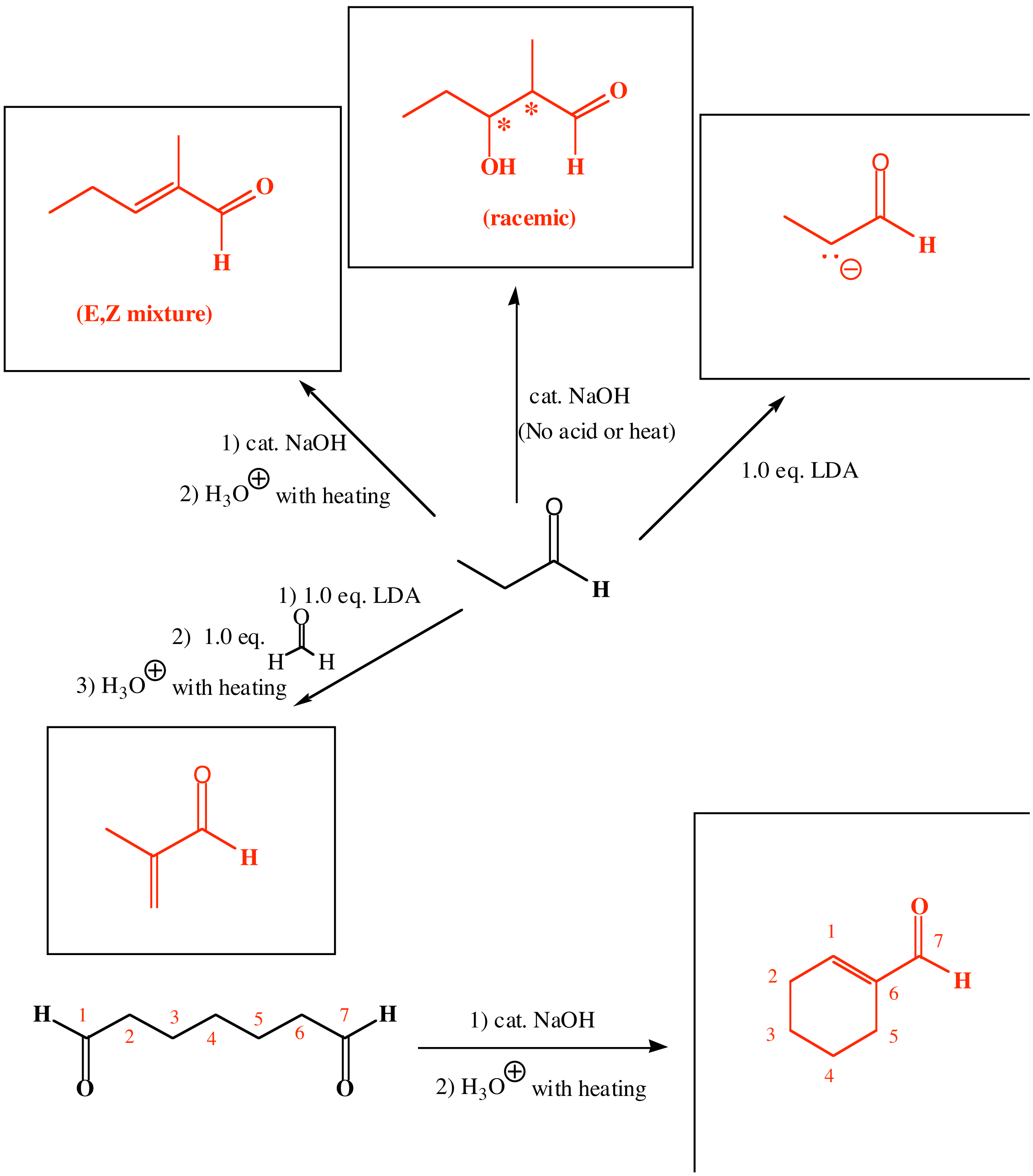

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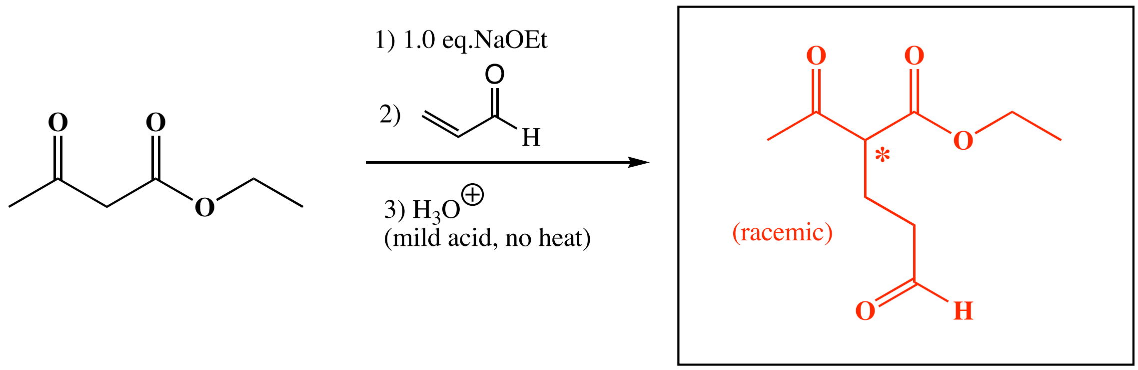
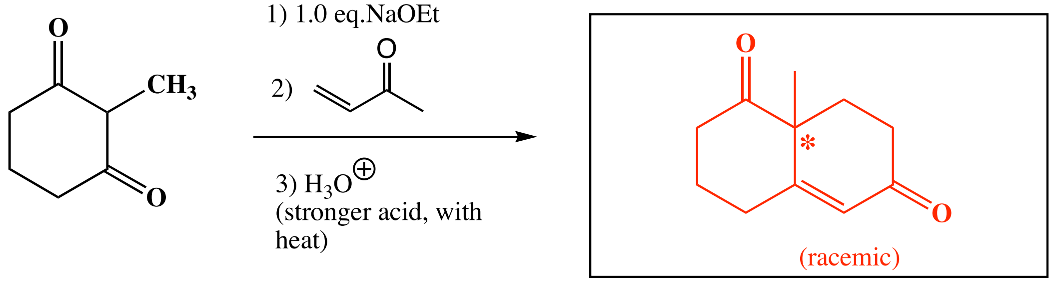
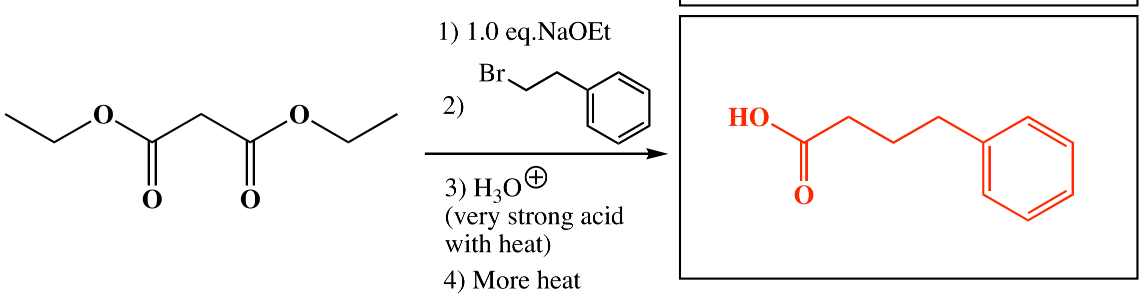
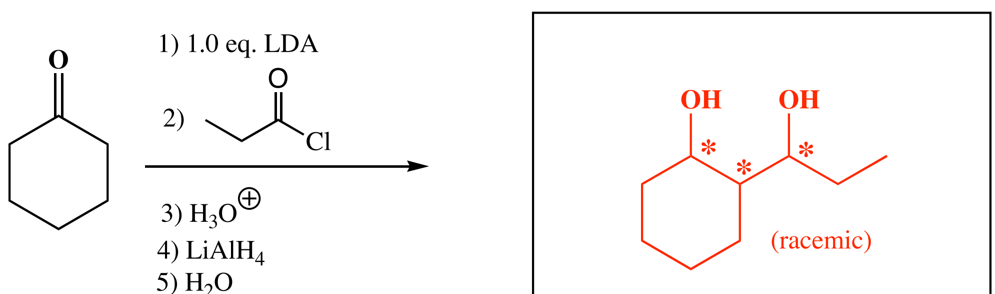


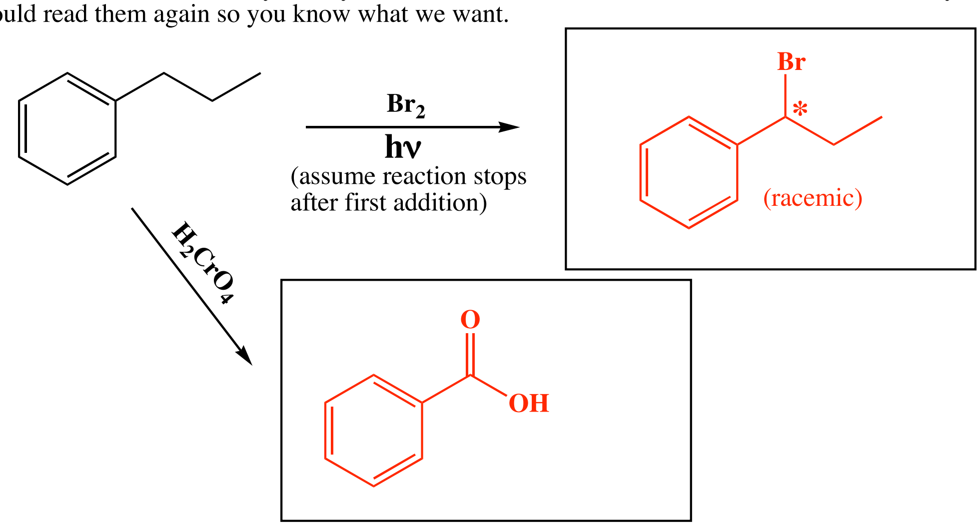




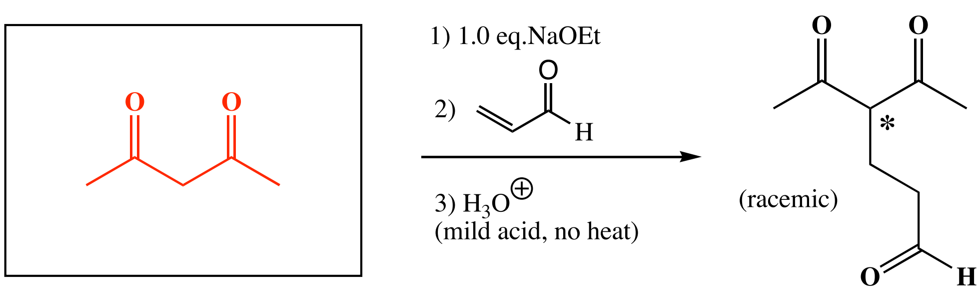


NOTICE THIS ⟹ **How many stereoisomers are possible for this product?** 8

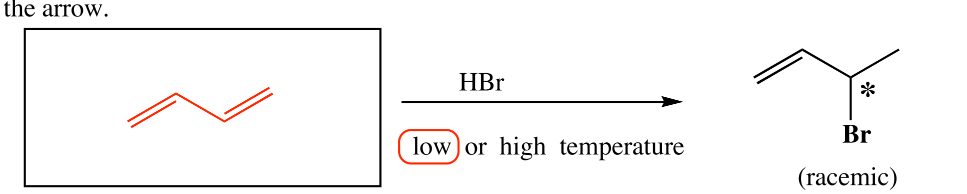
13. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration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

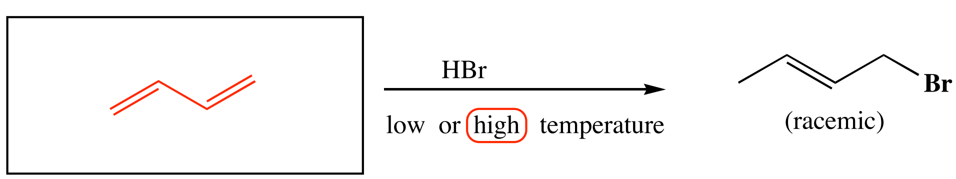


14. (3 pts each) For the following reactions, analyze the products and reagents and predict the appropriate starting material.



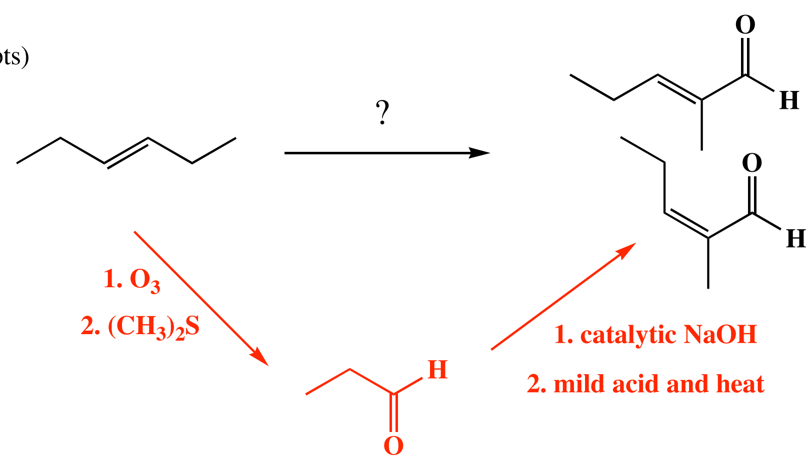
For the next two reactions circle the appropriate temperature regime, "high" or "low" temperature under the arrow.





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!

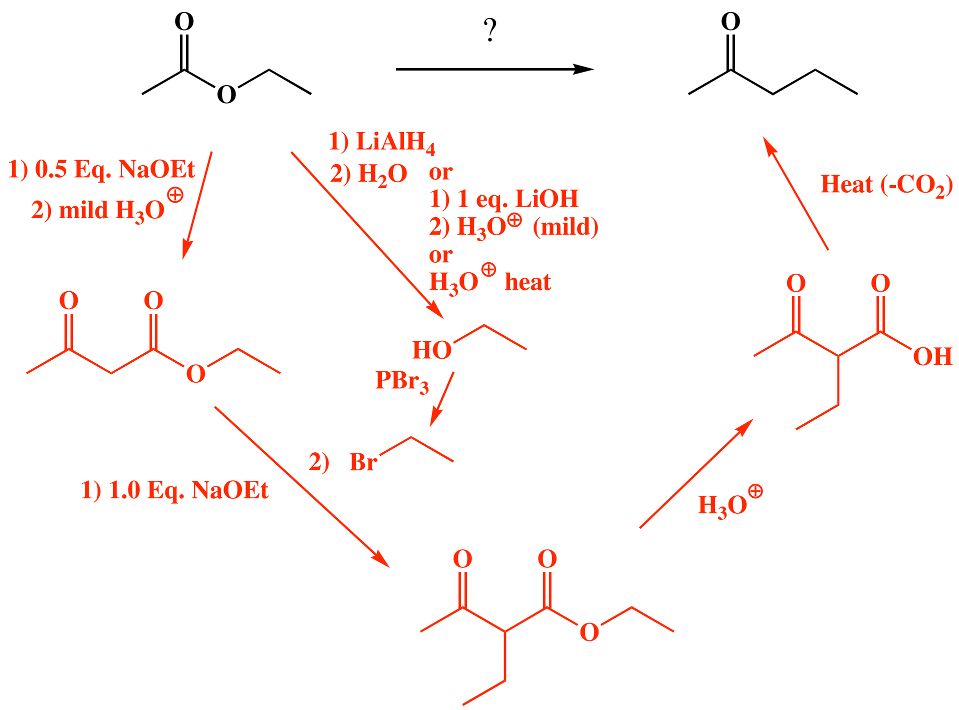
A) (4 pts)



Recognize the product as an α,β-unsaturated aldehyde, the KRE of an aldol reaction followed by dehydration. The required aldehyde is propanal, which can be conveniently prepared through ozonalysis of the starting *E*-3-hexene.

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!

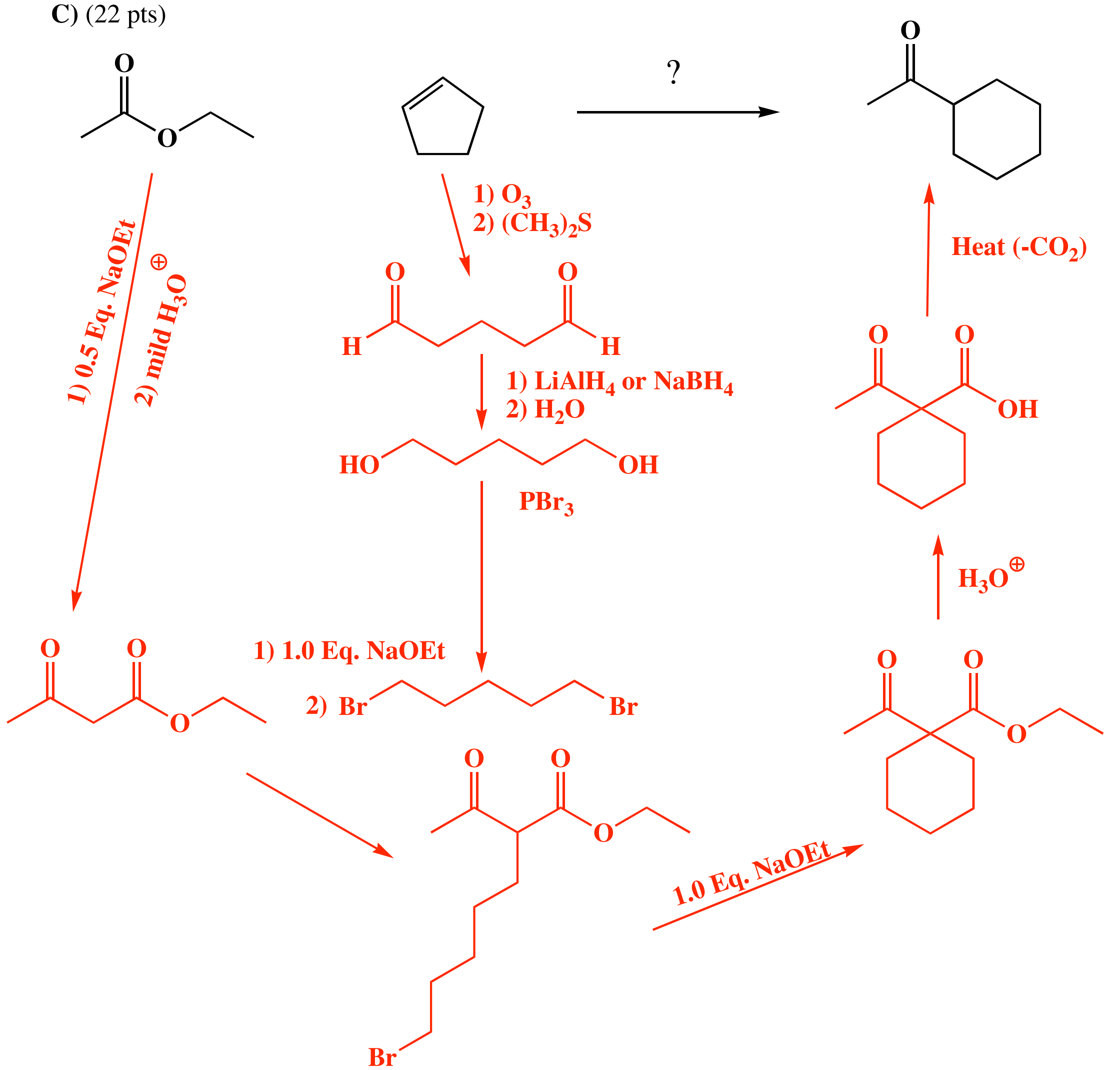
B) (16 pts)



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. Finally, **recognize** that the required two carbon unit needed for akylation can be derived from reduction or 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!

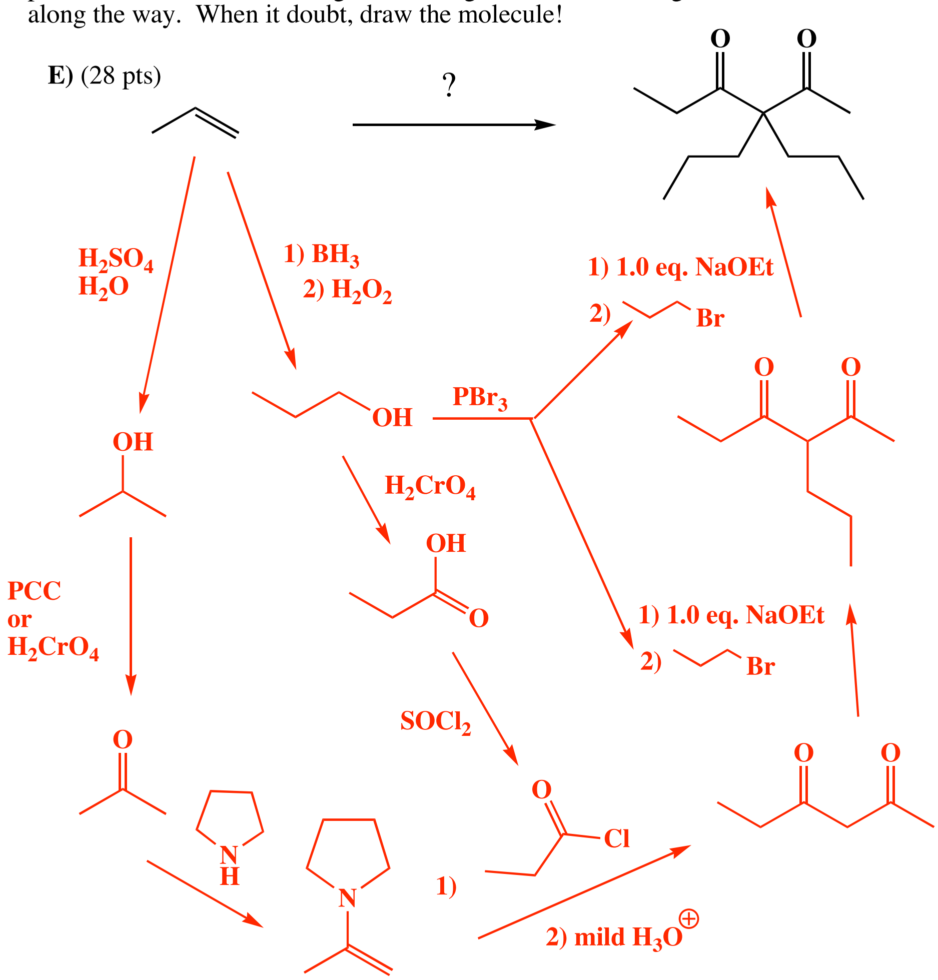
C) (22 pts)



Recognize the product as a methyl ketone, the KRE of the acetoester synthesis. The challenge in this one is to create the six membered ring. Analogous to the homework problem from last week, **recognize** that you need to use 1,5-dibromopentane in two sequential cycles of deprotonation/alkylation of ethyl acetoacetate. **Recognize** the ethyl acetoacetate as the product of a Claisen with the starting ethyl acetate. Finally, **recognize** that the five carbons of the 1,5-dibromopentane can be conveniently prepared from cyclopentene using the sequence of ozonolysis, reduction then 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!

E) (28 pts)



Recognize the product as being a β-diketone that was doubly akylated. This is not the KRE for any specific reaction, but rather, just a pattern of reactivity you have seen many times before (reaction at an α carbon between two carbonyls). Breaking down the alkylation reaction into the components needed, **recognize** that you need 1-bromopropane as the alkyl halide. Further **recognize** that 1-bromopropane can be prepared from 1-propanol via treatment with PBr_3. In turn, **recognize** 1-propanol as the non-Markovnikov product derived from hydroboration of the starting propene. **Recognize** the required β-diketone as the KRE of an enamine made from acetone with an acid chloride made from propanoic acid. **Recognize** acetone as coming from propene via a two reaction sequence of Markovnikov hydration (you could have used oxymercuration here as well) followed by oxidation of 2-propanol. **Recognize** the propanoyl chloride as coming from 1-propanol via oxidation with chromic acid followed by treatment with $SOCl_2$. Note there are other acceptable approaches to synthesizing the β-diketone, but space limitations prevent us from describing those here.

16. (18 pts) Here is an apply what you know problem. The following is a scan from a technical bulletin that accompanied a product we had purchased in my research laboratory. It is from a company called Clontech Laboratories, Inc. Whomever wrote this did not take my class!!! **It is not important** that you understand the product itself or the description of how it is used. However, there are problems with the figure **A. In no more than three sentences,say what is wrong with the figure**. **B. Draw your own version of the diagram that is entirely correct.**

TALON® Metal Affinity Resins User Manual

I. Introduction *continued*

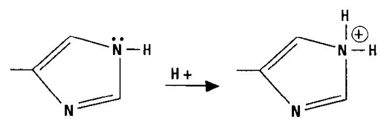


Figure 2. Elution mechanism of recombinant polyhistidine-tagged proteins from TALON® Resin. Elution occurs when the imidazole nitrogen (pKa = 5.97) is protonated, generating a positively charged ammonium ion which is repelled by the positively charged metal ion. Alternatively, the bound polyhistidine-tagged protein can be competitively eluted by adding imidazole to the elution buffer.

A. (8 pts) Explain what is wrong with the figure in no more than three sentences

Error 1: The lower nitrogen does not have a lone pair drawn on it and Error 2: The incorrect nitrogen was protonated. As drawn in the figure the lone pair on the upper nitrogen is in a 2p orbital, so aromaticity would be lost upon protonation and this costs too much energy to be realistic. The correct diagram will have the lower nitrogen protonated (see below), because the lone pair is in an sp^2 orbiral so it is the basic nitrogen atom and aromaticity is not lost upon protonation at that site.

B. (10 pts) Redraw the figure correctly.