NAME (Print): ______________________________

SIGNATURE: ______________________________

Chemistry 320N
Dr. Brent Iverson
3rd Midterm
April 23, 2015

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		(44)
5		(24)
6		(18)
7		(23)
8		(26)
9		(11)
10		(22)
11		(10)
12		(13)
13		(19)
14		(13)
15		(18)
16		(8)
Total		(249)

Student Honor Code

"As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity."

____

(Your signature)

Compound		pK$_a$
Hydrochloric acid	H-Cl	**-7**
Protonated alcohol	$RCH_2OH_2^{+}$	**-2**
Hydronium ion	H_3O^{+}	**-1.7**
Carboxylic acids	$R-C(=O)O-H$	**3-5**
Ammonium ion	H_4N^{+}	**9.2**
β-Dicarbonyls	$RC(=O)-CH_2-C(=O)R'$	**10**
Primary ammonium	$H_3N^{+}CH_2CH_3$	**10.5**
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	$RC\equiv C-H$	**25**
LDA	$H-N(i\text{-}C_3H_7)_2$	**40**
Terminal alkenes	$R_2C=CH-H$	**44**
Alkanes	CH_3CH_2-H	**51**

Signature__________________________ Pg 1 _____________(44)

DO NOT TEAR OUT THIS PAGE!!

We are trying something new to improve grading accuracy. You must write the answers for the questions on the next three pages on this single sheet.

Question 1, page 2 (12 pts) True false qustions. As appropriate, circle True or False in each space corresponding to the statements on page 2.

1.1 True (False) 1.2 (True) False
1.3 (True) False 1.4 True (False)
1.5 (True) False 1.6 (True) False
1.7 (True) False 1.8 (True) False
1.9 True (False) 1.10 True (False)
1.11 True (False) 1.12 (True) False

Question 2, page 3 (4 pts) Write the word that best completes the sentences.

2.1 Reflected
2.2 Absorbed
2.3 Red (Red or Green)
2.4 Green (Red or Green)

Question 3, page 3 (3 pts) Write the word or symbol that best completes the sentences.

3.1 Flat
3.2 2p
3.3 Pi

Question 4, page 3 (6 pts) Write the letter (A or B) of the more acidic molecule.

4.1 A 4.2 B 4.3 A
4.4 B 4.5 A 4.6 A

Question 5, page 4 (12 pts) For each molecule, write "Aromatic" or "Not Aromatic"

5.1 Aromatic 5.2 Aromatic
5.3 Aromatic 5.4 Aromatic
5.5 Not aromatic 5.6 Not aromatic
5.7 Aromatic 5.8 Not aromatic
5.9 Aromatic 5.10 Aromatic
5.11 Aromatic 5.12 Not aromatic

Question 6, page 4 (7 pts) State the type of orbital containing the lone pair of electrons indicated by the arrow.

6.1 2p 6.2 sp^2 6.3 2p
6.4 sp^2 6.5 2p 6.6 sp^3
6.7 2p

Write your answers to these questions on the answer sheet on page 1

1. (12 pts). On page 1, circle True or False to indicate whether each of the following statements is true or false.

1.1 When **HBr** adds to conjugated dienes, the 1,4 addition product is the product that predominates when the reaction is considered to be under kinetic control.

1.2 When **HBr** adds to conjugated dienes, the 1,4 addition product is the product that predominates when the reaction is considered to be under thermodynamic control.

1.3 When **HBr** adds to conjugated dienes, thermodynamic control of the reaction will occur at higher temperatures and kinetic control will occur at lower temperatures.

1.4 When **HBr** adds to conjugated dienes, thermodynamic control of the reaction will occur at lower temperatures and kinetic control with occur at higher temperatures.

1.5 When trying to understand molecular orbitals in aromatic molecules it is best to think of electrons as waves.

1.6 In molecular orbital theory, the number of molecular orbitals generated equals the number of atomic orbitals used to construct them. For example, six 2p orbitals will combine to give six new pi molecular orbitals.

1.7 Fluorescence occurs when an electron is excited to an unfilled orbital upon absorption of a photon, then a new photon is emitted as the electron immediately returns to the orbital from where it originated (ground state).

1.8 Chemiluminescence occurs when the product of a reaction happens to be generated in an electronically excited state, and a photon is emitted as the electron returns to the ground state orbital.

1.9 Chemiluminescence occurs when an electron is excited to an unfilled orbital upon absorption of a photon, then the electron is trapped in this excited state for a while. After a time, a new photon is emitted as the electron returns to the orbital from where it originated (ground state).

1.10 Phosphorescence occurs when the product of a reaction happens to be generated in an electronically excited state, and a photon is emitted as the electron returns to the ground state orbital.

1.11 The greater the number of atoms taking part in conjugation (larger “pi-way”), the larger the energy gap between the highest energy filled pi molecular orbital and the lowest energy unfilled pi molecular orbital.

1.12 The greater the number of atoms taking part in conjugation (larger “pi-way”), the smaller the energy gap between the highest energy filled pi molecular orbital and the lowest energy unfilled pi molecular orbital.

Write your answers to these questions on the answer sheet on page 1

2. (4 pts). On page 1, fill in each blank with the word that best completes the following sentences.

The color we see for an object is the determined by the combination of wavelengths of light that are ___________________________________(2.1) minus the wavelengths of light that are ___________________________________(2.2) This is precisely why the _______________(2.3) (red or green) laser was able to shine through my finger while the _______________(2.4) (red or green) laser was completely absorbed by hemoglobin, the main colored pigment in our tissues.

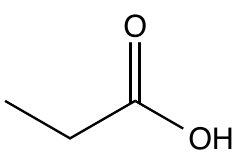
3. (3 pts). On page 1, fill in each blank with the word or symbol that best completes the following sentences.

According to Hückel's rules, for a monocyclic molecule to be aromatic:

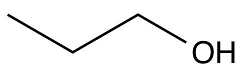
A. The ring must be _____________________(3.1).
B. All of the ring atoms have a ____________________(3.2) orbital.
C. There are 4n + 2 _________________(3.3) electrons.

4. (6 pts). On page 1, for each pair of molecules, **write the letter (A or B)** corresponding to the MORE ACIDIC molecule.

4.1

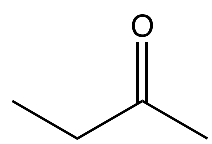


A

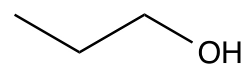


B

4.2

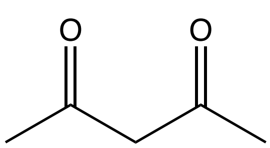


A

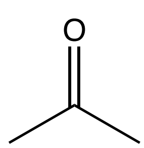


B

4.3

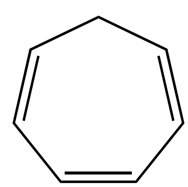


A

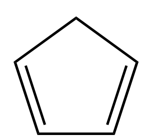


B

4.4

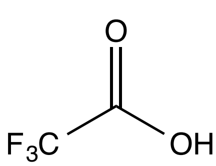


A

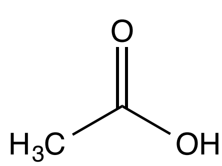


B

4.5

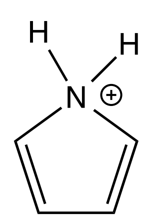


A

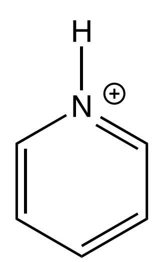


B

4.6



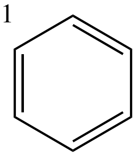
A

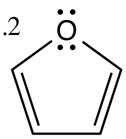


B

Write your answers to these questions on the answer sheet on page 1

5. (12 pts). On page 1, for each molecule, in the spaces provided write "AROMATIC" if the molecule is aromatic according to the <u>Hückel</u> definition, write "NOT AROMATIC" if the molecule is not aromatic.

5.1


5.2


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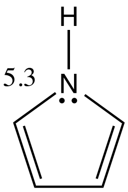

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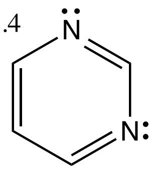
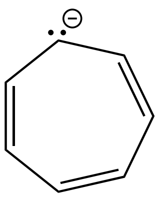


5.5


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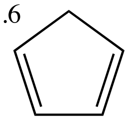

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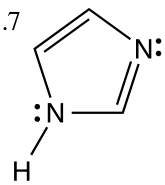

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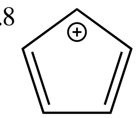
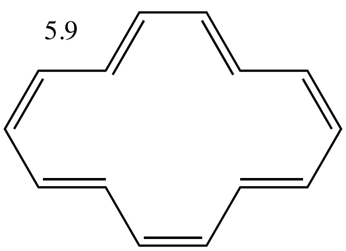
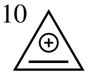
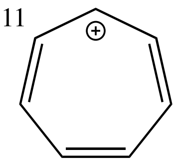
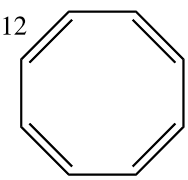


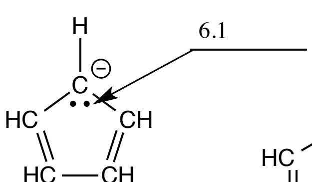
5.9


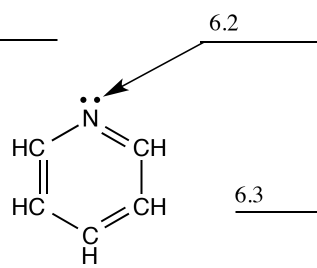
5.10


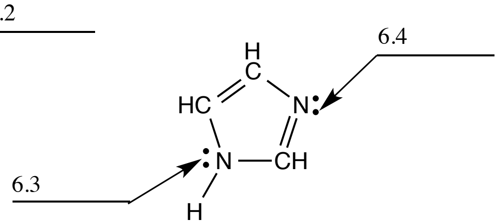
5.11


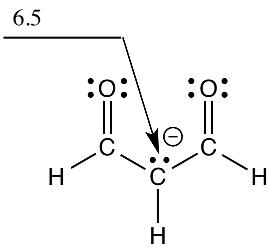
5.12


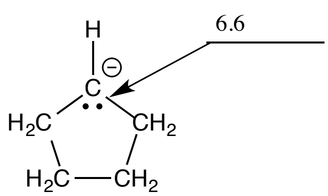
6. (7 pts). On page 1, in the spaces provided write the type of atomic orbital (sp^3, 2p, etc.) that contains the electron pair indicated by the arrow.

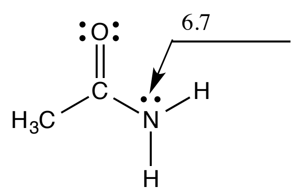












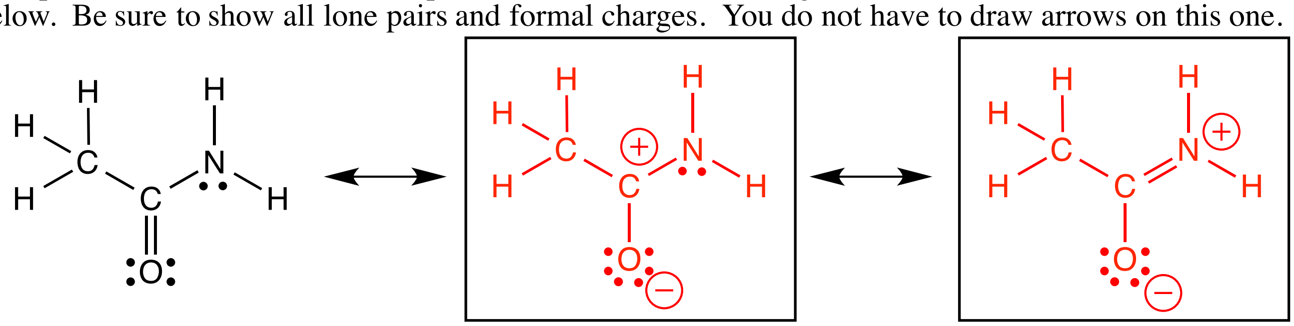
7. (2 pts) What is the most important question in chemistry?

Where are the electrons ?

8. (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.

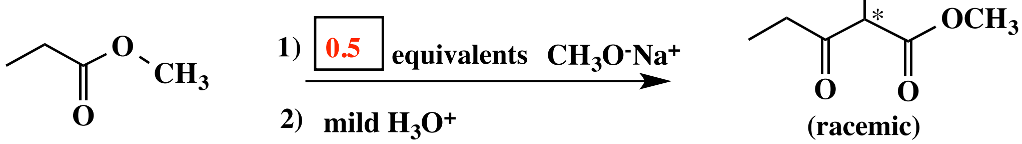
The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons** by **radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field 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**.

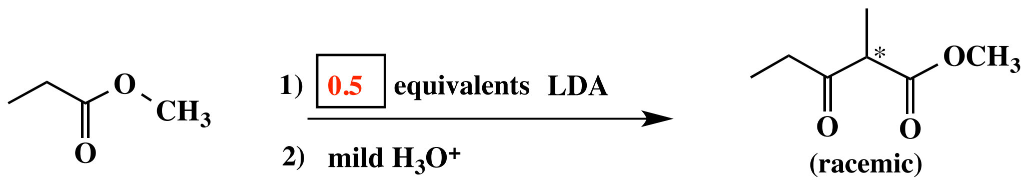
9. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



10. (10 pts) 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 **<u>to completion</u>**. 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.**

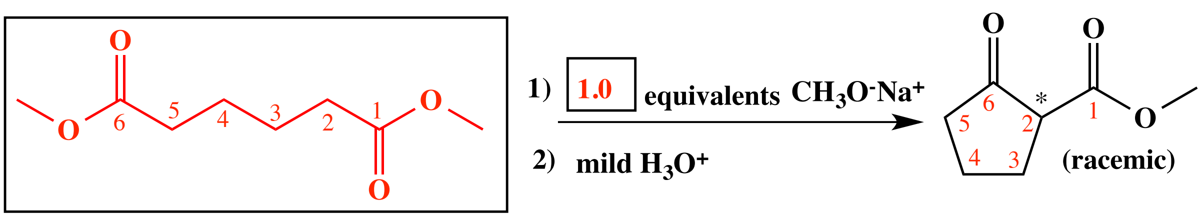
A)

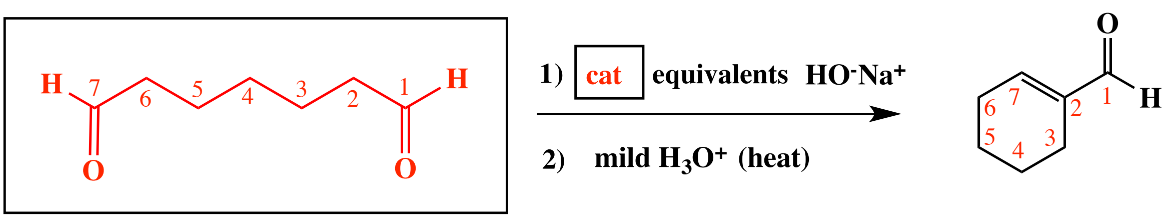

B)


C)


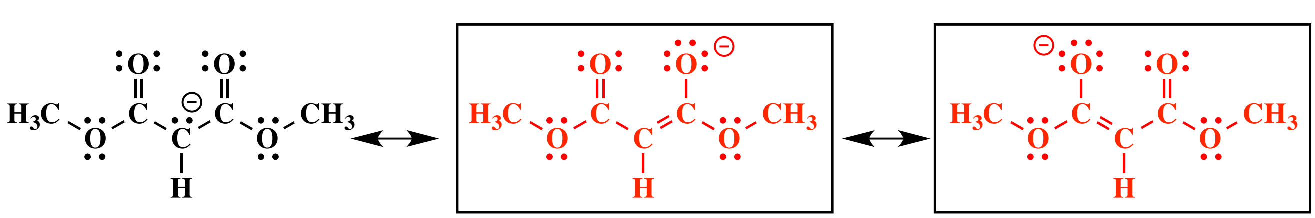
D)


For these next two we have provided the product, you need to draw the starting material as well as fill in the number of equivalents.

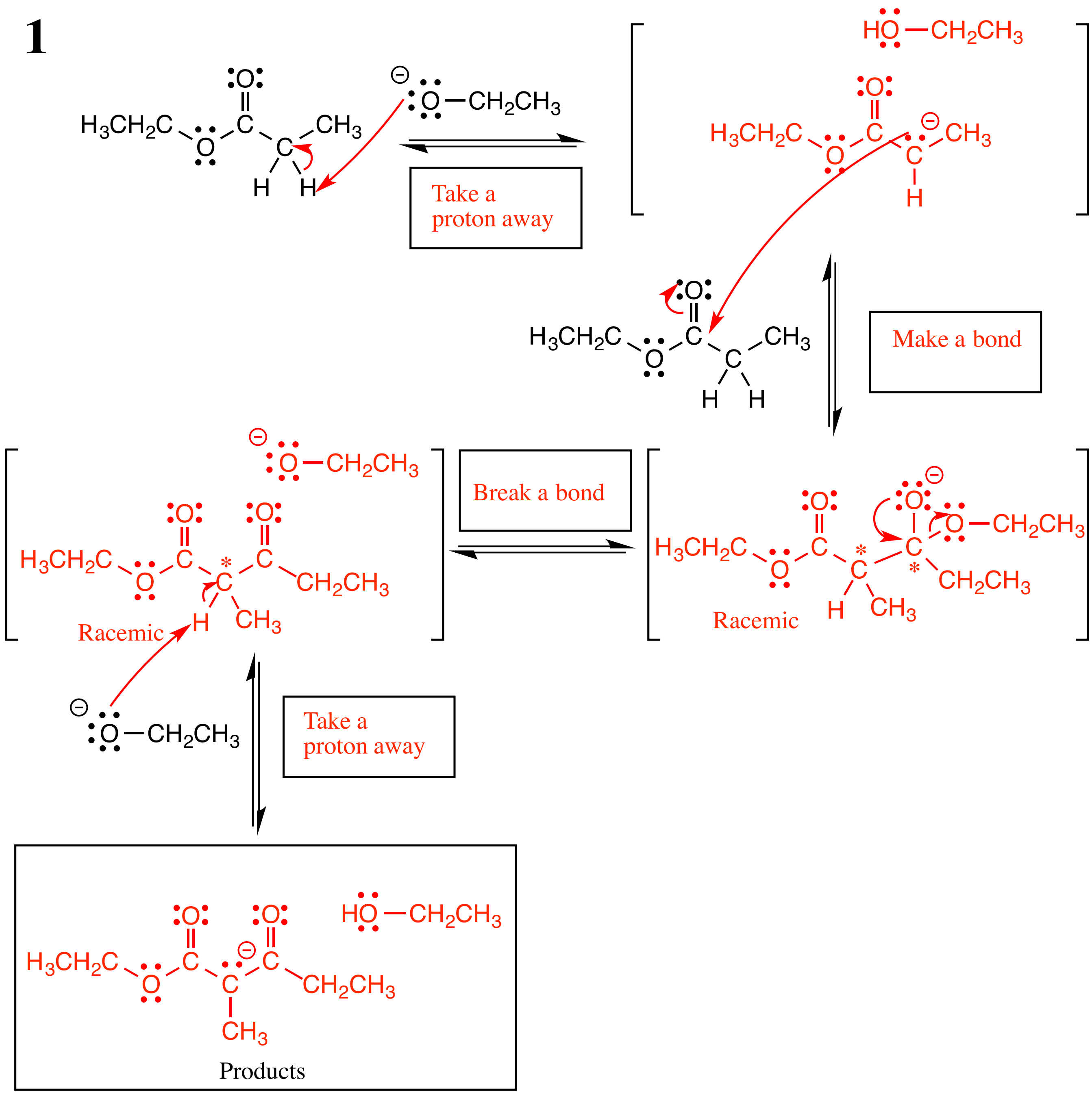
E)


F)


11. (8 pts) For the following enolate, draw the two other most important contributing structures. You do not need to draw arrows here, but be sure to show all lone pairs and formal charges.



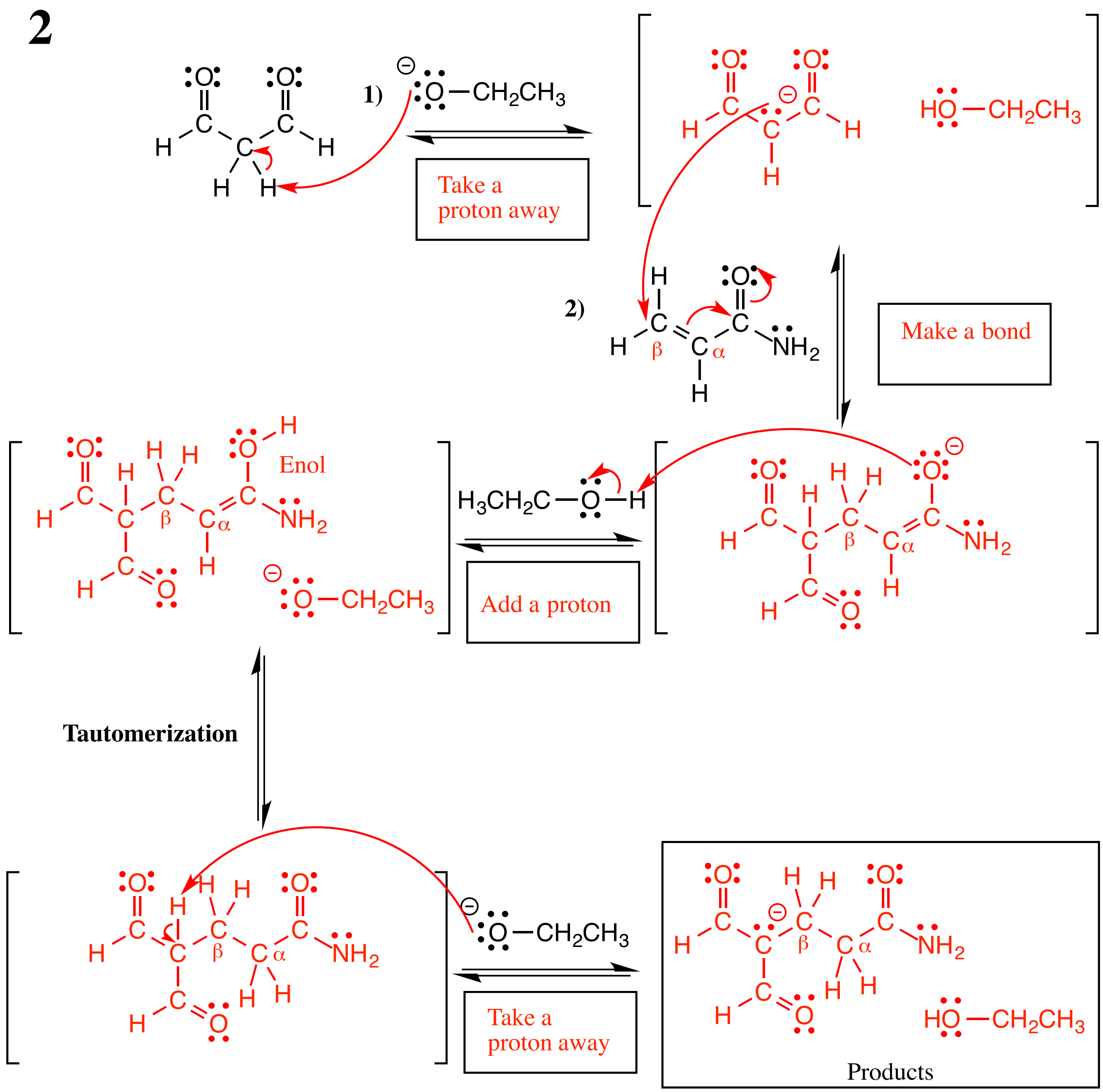
12. (23 pts) Complete the mechanism for the following Claisen reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE. In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).**



Note you will have to write a balanced equation for the above mechanism on PAGE 9

13. (26 pts) Complete the mechanism for the following Michael reaction. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE. In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).**

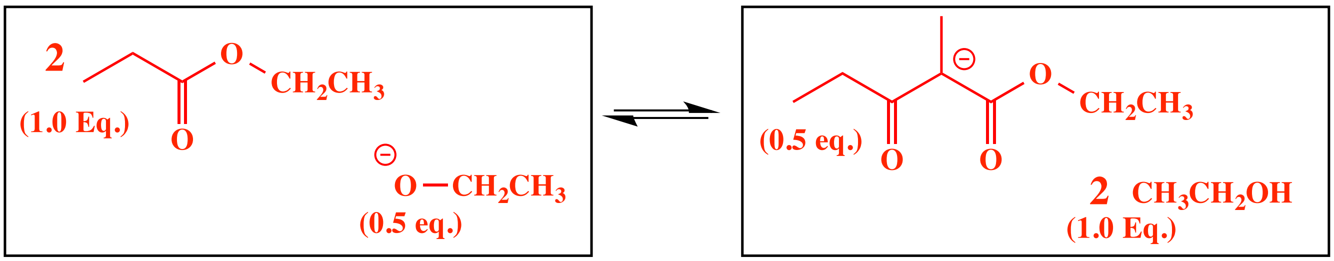
2



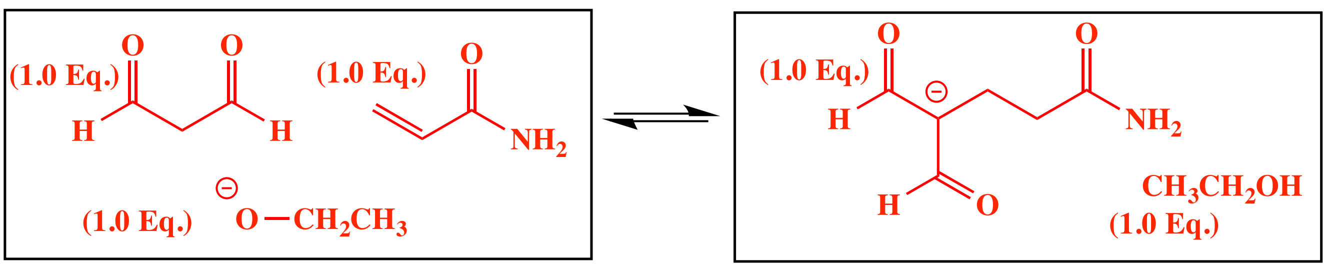
Note you will have to write a balanced equation for the above mechanism on PAGE 9

14. (11 pts) Write BALANCED equations for both mechanisms that you drew on the last two pages. Note that because we want balanced equations **you will need to specify the equivalents of <u>each</u> of the reagents you start with as well as the equivalents of <u>each</u> of the products made**. PLEASE READ THIS CAREFULLY, WE ARE NOT TRYING TO TRICK YOU SO MAKE SURE YOU READ THE WORD <u>EACH</u> IN THE LAST SENTENCE!!

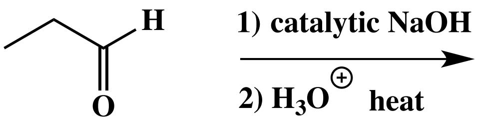
Write a balanced equation for the overall process described by mechanism 1 from page 7

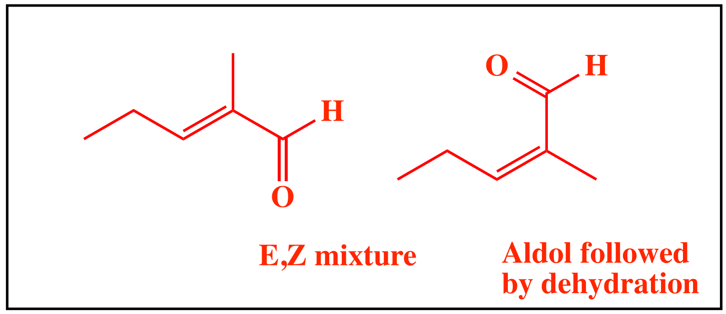


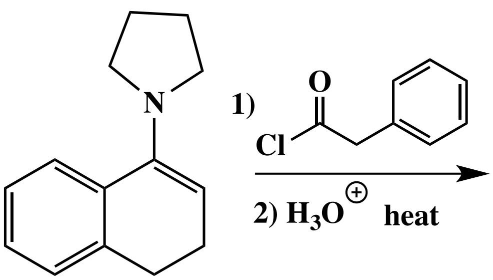
Write a balanced equation for the overall process (including adding both reagents) described by mechanism 2 from page 8

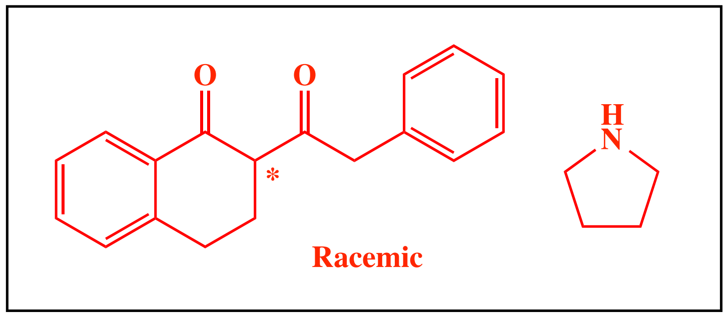


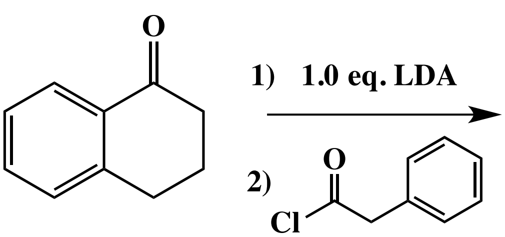
15. (3, 4 or 5 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes. Also, do not worry about balancing these equations, you just need to show us the major carbon-containing products of these transformations.**

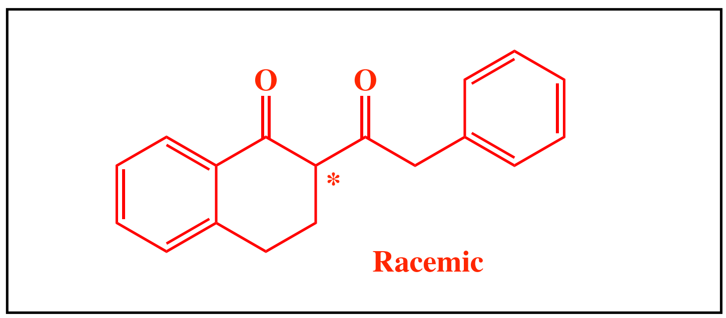


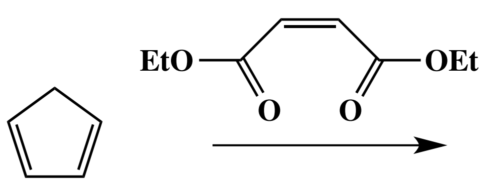


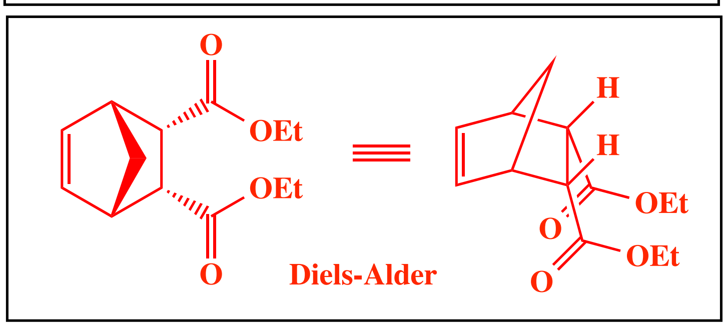


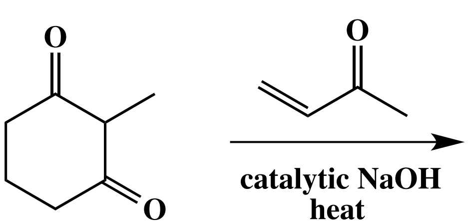


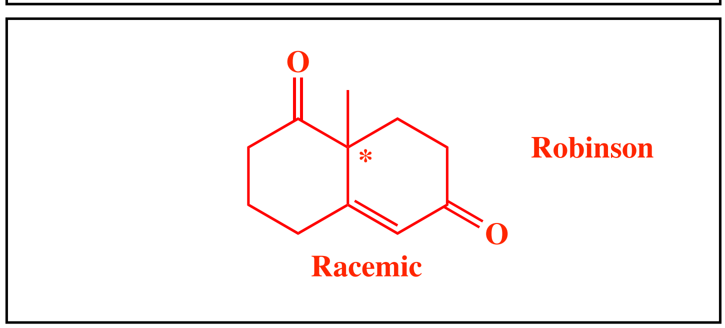








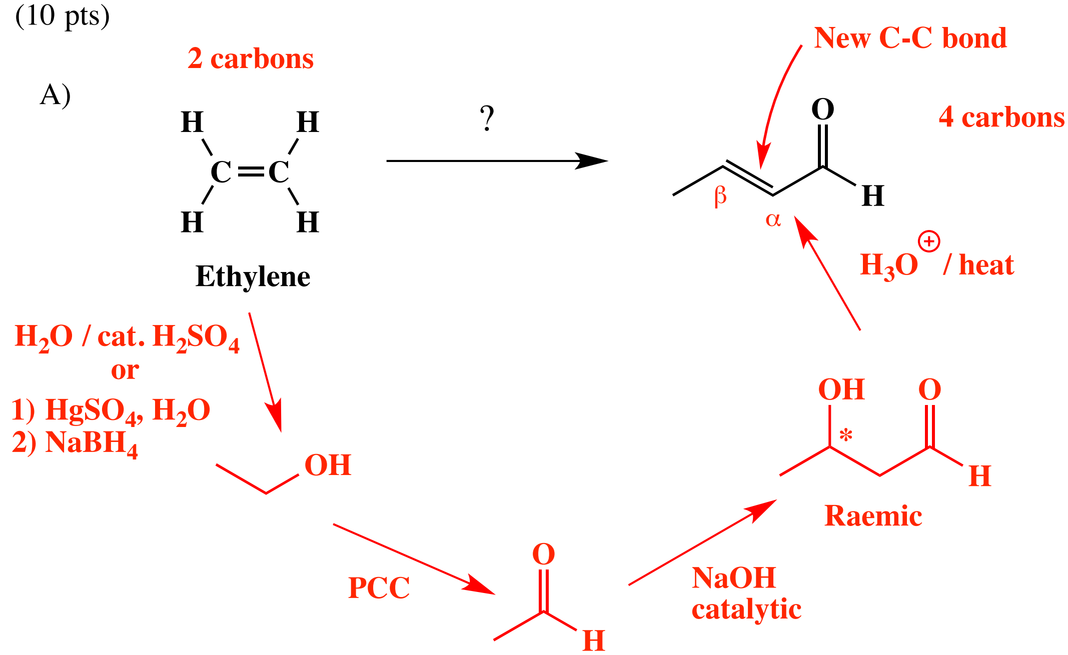




16. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate. You will notice a theme in these problems in that you will be starting with very simple structures and making more complex products.

Remember, all of the carbons of the product must come from the given starting material.
(10 pts)

A)

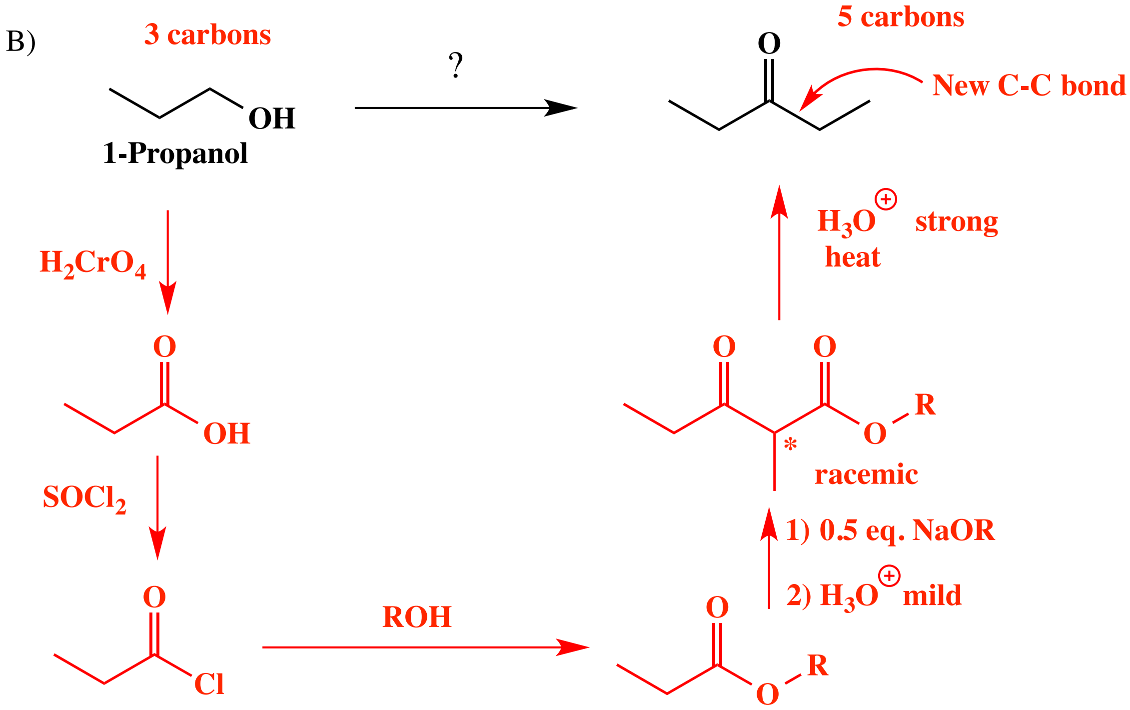


Recognize there are 4 carbons in the product, but 2 carbons in the starting material so 2 molecules of starting material must be assembled into the product. **Recognize** further the final product as an α,β-unsaturated aldehyde, the KRE of an aldol reaction follwed by dehydration. **Recognize** the required aldehyde as being derived from the starting ethylene via hydration using either aqueous acid or mercury followed by PCC.

16. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product 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. You will notice a theme in these problems in that you will be starting with very simple structures and making more complex products.

Remember, all of the carbons of the product must come from the given starting material.
(13 pts)

B)

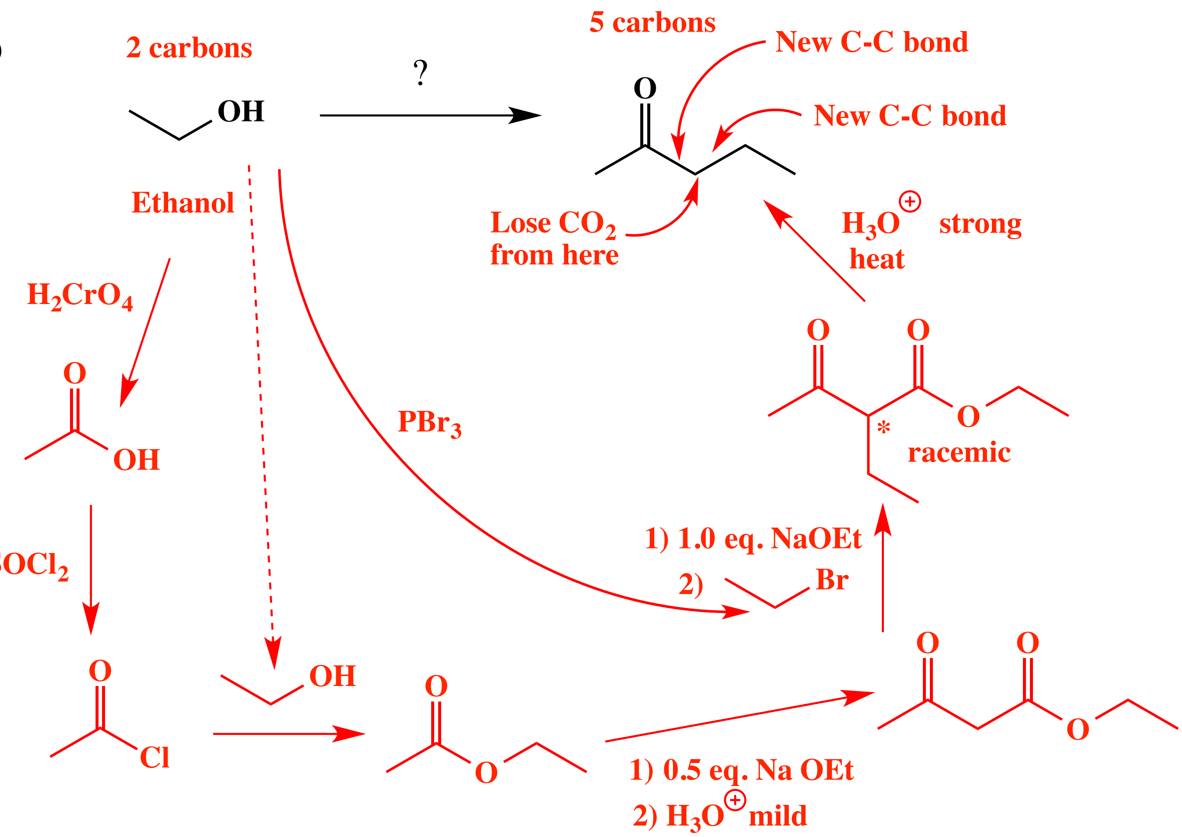


Recognize there are 5 carbons in the product, but 3 carbons in the starting material so, 2 molecules of starting material must be assembled into the product (minus 1 carbon) with the location of the new C-C bond as shown. Losing 1 carbon indicates a decarboxylation. **Recognize** further the final product as a symmetrcial ketone, the KRE of a Claisen reaction followed by ester hydrolysis/decarboxylation. **Recognize** that the Claisen product can be derived from a three carbon ester, that can be made from the three carbon alcohol starting material using chromic acid followed by $SOCl_2$ and reaction with an alcohol. Because the alcohol does not show up in the product, any alcohol can be used and I indicated that by designating the alcohol as ROH.

16. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product 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. You will notice a theme in these problems in that you will be starting with very simple structures and making more complex products.

Remember, all of the carbons of the product must come from the given starting material.
(19 pts)

C)



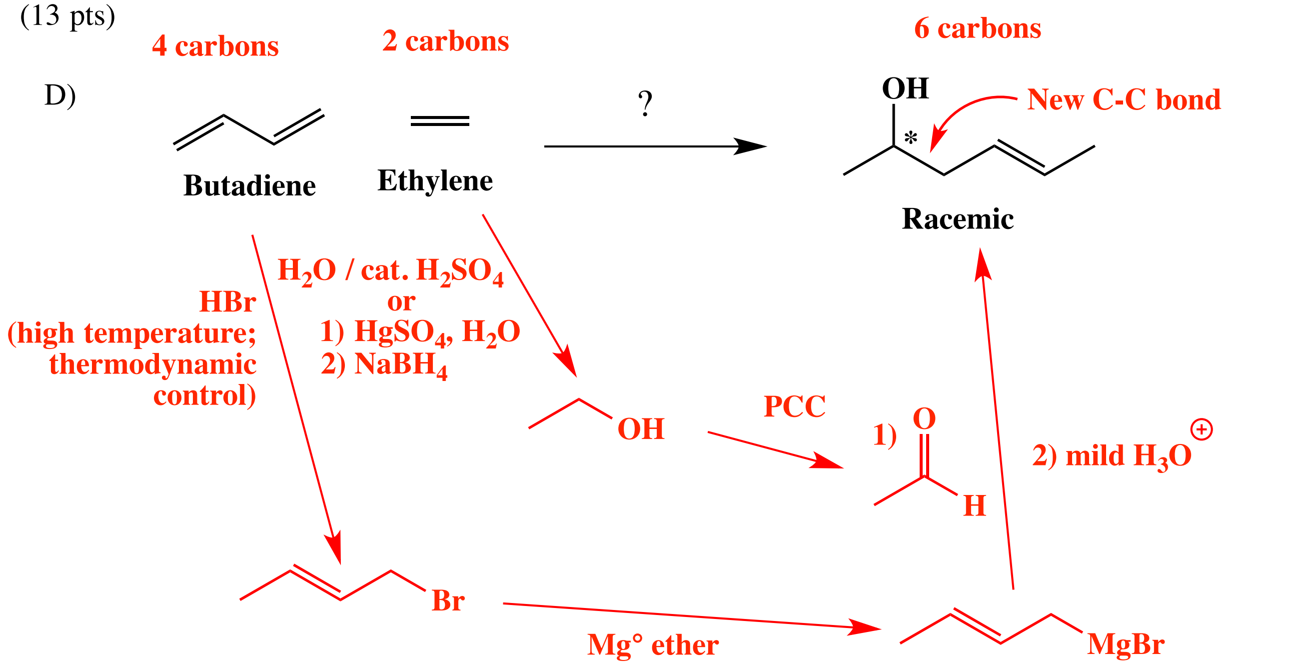
Recognize there are 5 carbons in the product, but 2 carbons in the starting material so 3 molecules of starting material must be assembled into the product. Since 1 carbon is missing assume that, like the last problem, a decarboxylation occured. **Recognize** further the final product as a methyl ketone, the KRE of an acetoester synthesis. **Recognize** that the last step of the acetoester synthesis is an ester hydrolysis, decarboxylation step from an ethyl-substituted β-keto ester. **Recognize** the ethyl substituted β-keto ester as being derived from reaction of acetoester with 1.0 eq. of base followed by ethyl bromide. The ethyl bromide can be derived from the starting ethanol using PBr$_3$. **Recognize** that acetoester can be derived from ethanol by oxidation to give acetic acid, reaction with SOCl$_2$ to give the acid chloride, reaction of the acid chloride with ethanol to give ethyl acetate and then a Claisen reaction to give acetoester.

16. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product 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. You will notice a theme in these problems in that you will be starting with very simple structures and making more complex products.

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

(13 pts)

D)



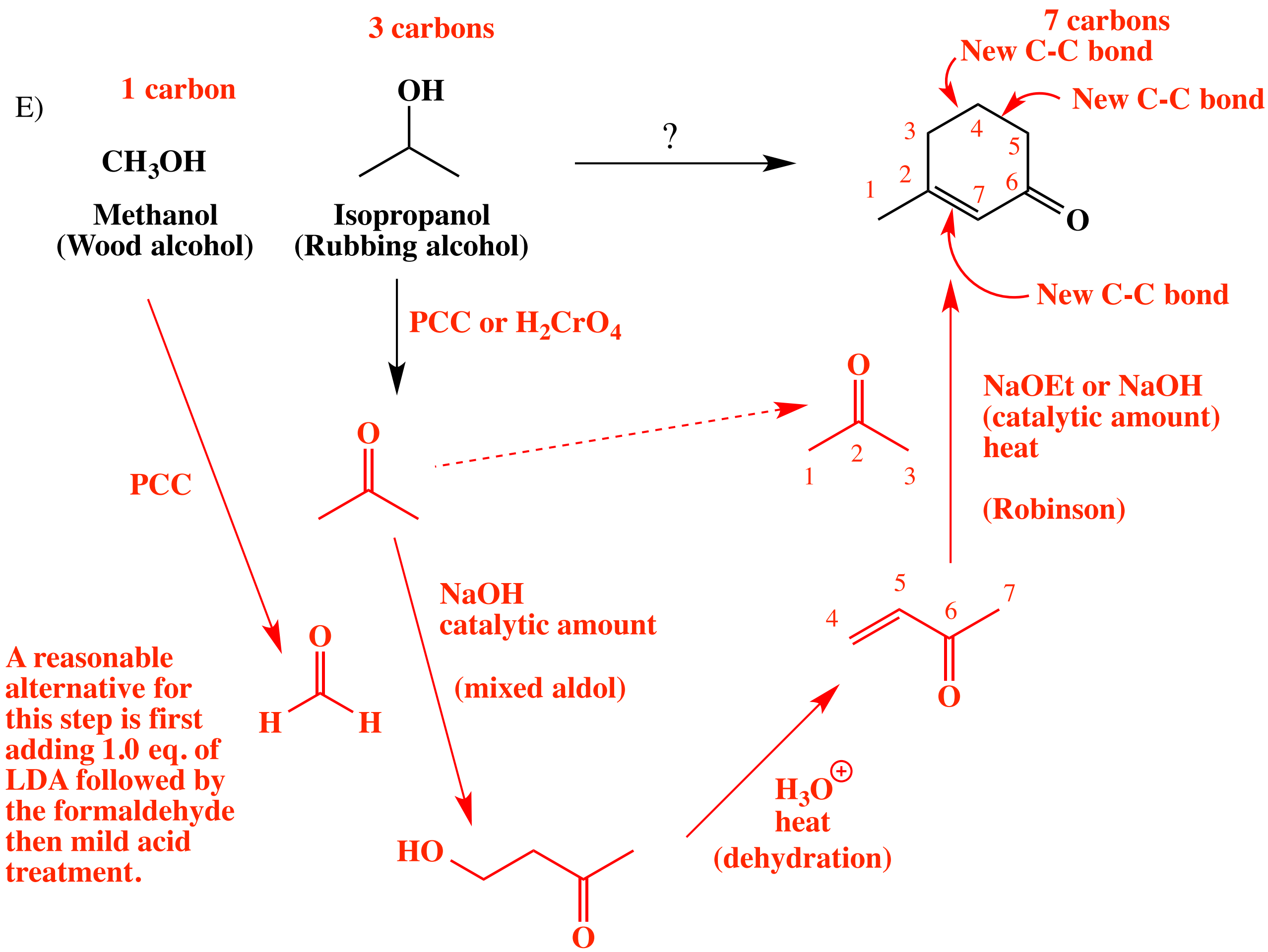
Recognize there are 6 carbons in the product, but 4 carbons and 2 carbons in the starting material, so the two starting materials must be assembled into the product. Assume the location of the new C-C bond based on your knowledge of KRE's. **Recognize** further the final product as an alcohol with a new C-C bond to the same carbon as the -OH, the KRE of a Grignard reaction with an aldehyde. **Recognize** that for the new C-C bond to be as shown, the aldehyde would have to be acetaldehyde and the Grignard reagent would have to contain an *E* double bond in the center. **Recognize** that acetaldehyde is made in two steps from ethylene via hydration then PCC. **Recognize** the Grignard as coming from the corresponding haloalkene, that in turn is made in one step from butadiene using high temperature to insure the thermodynamic product is formed in high yield.

16. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product 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. You will notice a theme in these problems in that you will be starting with very simple structures and making more complex products.

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

(13 pts) **You will get 5 bonus points for getting this one entirely correct!**

E)



Recognize there are 7 carbons in the product, but 1 carbon and 3 carbons in the starting materials, so assume you must add two of the 3 carbon pieces to one 1 carbon piece. **Recognize** the product as being the result of a Robinson annulation reaction. This Robinson recognition is clearly make or break for this synthesis. The ketone must be acetone and the Michael acceptor must be the α,β-unstaturated ketone shown to produce the Robinson product shown. **Recognize** the α,β-unstaturated ketone, (the KRE of aldol followed by dehydration) as having 4 carbons, so it must be derived from dehydration of the product from a mixed aldol reaction between formaldehyde and acetone. Note this is a useful example of a high yielding mixed aldol because formaldehyde has no α−hyddrogens and acetone connot form a stable aldol product with itself. As an alternative you could have used LDA with acetone followed by adding the formaldehye then mild acid. **Recognize** that the required acetone and formadehyde are available in one step from the starting alcohols by using PCC, or H_2CrO_4 in the case of 2-propanol going to acetone. Did you ever think you would know how to turn methanol and 2-propanol into such complicated structures?

Signature__________________________ Pg 16 ____________(8)

16. (8 pts) The reactions we have learned now are powerful enough to make some very sophisticated molecules. Using the reactions you know, draw the missing reagent or product in the box. In both cases, one of the four molecules listed (A-D) is the correct answer.