

NAME (Print): _____

Chemistry 320N
Dr. Brent Iverson
3rd Midterm
April 21, 2016

SIGNATURE: _____

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

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Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

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

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

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

Page	Points
1	(53)
5	(24)
6	(18)
7	(23)
8	(10)
9	(20)
10	(18)
11	(10)
12	(19)
13	(23)
14	(16)
15	(15)
16	(8)
Total	(257)

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	$\text{RCH}_2\text{O}^+\text{H}_2$	-2
Hydronium ion	H_3O^+	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Ammonium ion	H_4N^+	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	10
Primary ammonium	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	10.5
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	18-20
Esters	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

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 (16 pts) True false questions.
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
 1.13 True False 1.14 True False
 1.15 True False 1.16 True False

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

- 2.1 alkoxide
 2.2 LDA
 2.3 Michael
 2.4 aldol / dehydration (OK not to say dehydration)

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

- 3.1 2p
 3.2 flat
 3.3 monocyclic
 3.4 pi
- } these can be in either order

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

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

Question 5, page 4 (17 pts) For each molecule, write "Aromatic" or "Not Aromatic"

- 5.1 Aromatic 5.2 Not aromatic
 5.3 Not aromatic 5.4 Not aromatic
 5.5 Aromatic 5.6 Not aromatic
 5.7 Aromatic 5.8 Aromatic
 5.9 Aromatic 5.10 Aromatic
 5.11 Aromatic 5.12 Aromatic
 5.13 Not aromatic 5.14 Not aromatic
 5.15 Aromatic 5.16 Not aromatic
 5.17 Not aromatic

Question 6, page 4 (6 pts) State the hybridization state of the atom indicated by the arrow.

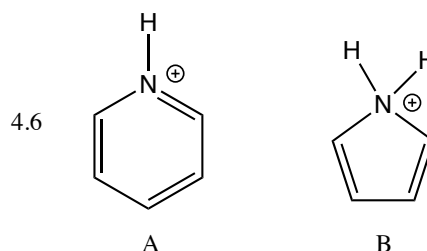
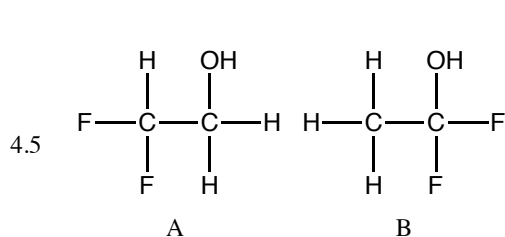
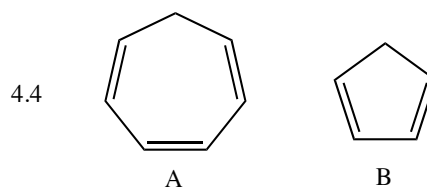
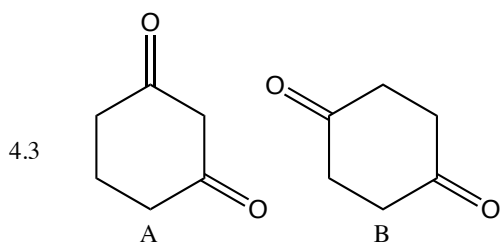
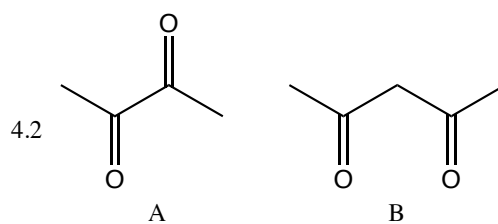
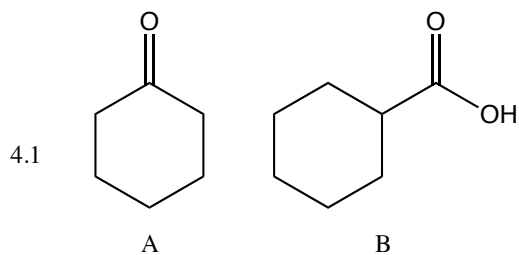
- 6.1 sp² 6.2 sp² 6.3 sp²
 6.4 sp³ 6.5 sp² 6.6 sp²

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

1. (16 pts). On page 1, circle True or False to indicate whether each of the following statements is true or false.
 - 1.1 Photons in the visible region are absorbed by organic molecules when an electron in a filled molecular orbital is excited to an unfilled, antibonding molecular orbital.
 - 1.2 Photons in the visible region are absorbed by organic molecule when an electron in a lower atomic orbital on a single atom such as a $1s$ orbital is excited to a higher orbital such as a $2s$ or $2p$ orbital.
 - 1.3 A material appears to our eyes to be the combination of wavelengths absorbed minus the wavelengths reflected.
 - 1.4 A material appears to our eyes to be the combination of wavelengths reflected minus the wavelengths absorbed.
 - 1.5 In calculating the number of molecular orbitals, you get as many new molecular orbitals as the number of atomic orbitals used to construct them.
 - 1.6 Pi electron density delocalization occurs through overlapping $2p$ orbitals, so to take part in pi electron density delocalization atoms must be sp^2 or sp hybridized and reside in the same plane.
 - 1.7 Pi electron density cannot delocalize onto or through sp^3 hybridized atoms because an sp^3 atom has no $2p$ orbital.
 - 1.8 An enolate reacts at carbon because a product with a $C=C$ bond is lower in energy.
 - 1.9 An enolate reacts at oxygen because a product with a $C=O$ bond is lower in energy.
 - 1.10 An enolate reacts at carbon because the carbon has greater negative charge.
 - 1.11 An enolate reacts at oxygen because the oxygen has greater negative charge.
 - 1.12 H-X adds to conjugated dienes to give both 1,2 and 1,4 addition products, via a resonance stabilized allylic cation intermediate.
 - 1.13 Conjugated dienes equilibrate between the *s-cis* and *s-trans* geometry, referring to the conformation of the single bond between the double bonds. The *s-cis* geometry predominates.
 - 1.14 Conjugated dienes equilibrate between the *s-cis* and *s-trans* geometry, referring to the conformation of the single bond between the double bonds. The *s-trans* geometry predominates.
 - 1.15 For Diels-Alder reactions, the diene must be in the *s-cis* geometry to react with a dienophile.
 - 1.16 For Diels-Alder reactions, the diene must be in the *s-trans* geometry to react with a dienophile.

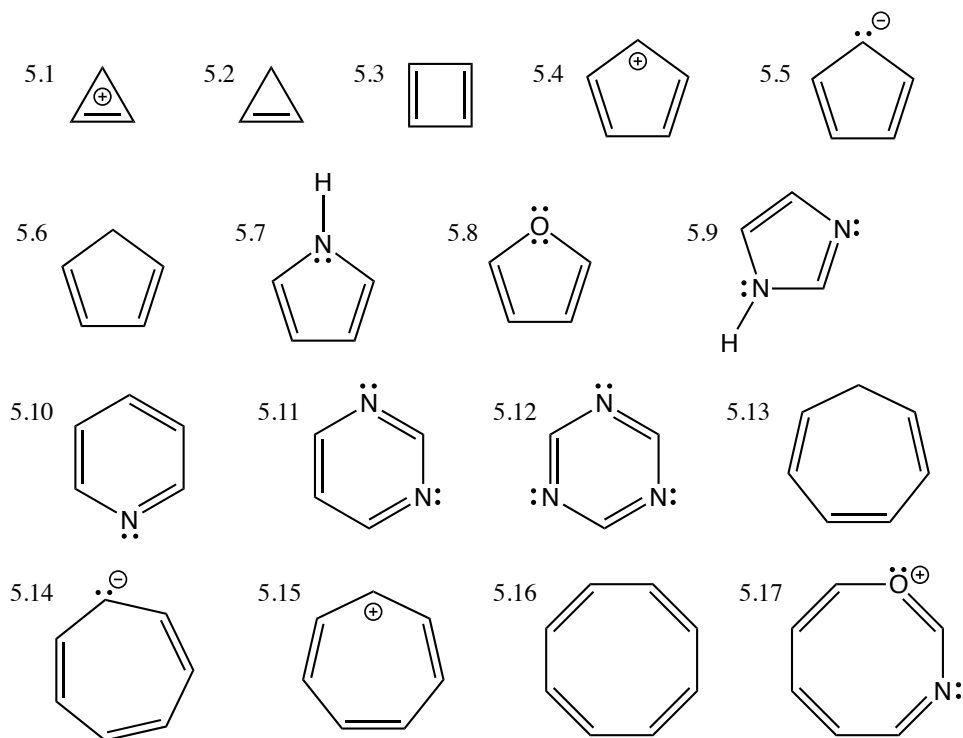
Write your answers to these questions on the answer sheet on page 1

2. (4 pts). On page 1, fill in each blank with the word that best completes the following sentences.
- Using _____ (alkoxide/LDA) (2.1) as the base creates only a small amount of enolate from a starting ester at equilibrium.
 - Using _____ (alkoxide/LDA) (2.2) as the base creates essentially a quantitative amount of enolate from a starting ester at equilibrium.
 - The Robinson annulation involves a _____ (2.3) reaction followed by an _____ (2.4) reaction to make a six-membered ring.
3. (4 pts). On page 1, fill in each blank with the word or symbol that best completes the following sentences.
- According to the four Hückel's rules, for a molecule to be aromatic:
- All of the ring atoms have a _____ (3.1) orbital.
 - The molecule must be _____ (3.2).
 - The molecule must be _____ (3.3).
 - There are $4n + 2$ _____ (3.4) electrons.
4. (6 pts). On page 1, for each pair of molecules, **write the letter (A or B)** corresponding to the MORE ACIDIC molecule.

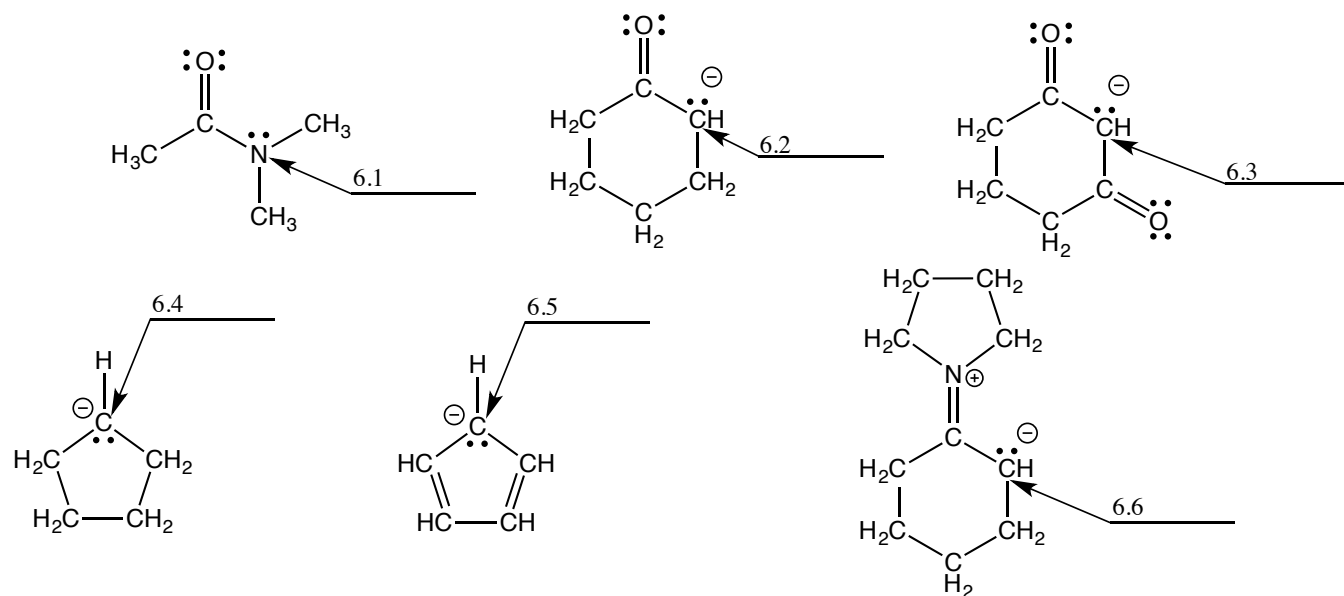


Write your answers to these questions on the answer sheet on page 1

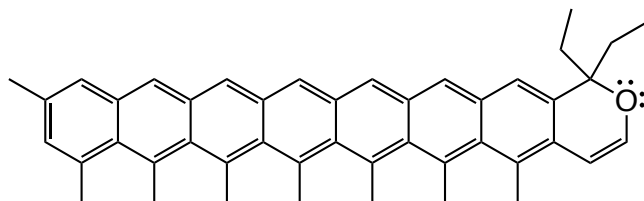
5. (17 pts). On page 1, for each molecule, in the spaces provided write "AROMATIC" if the molecule is aromatic according to the Hückel definition, write "NOT AROMATIC" if the molecule is not aromatic.



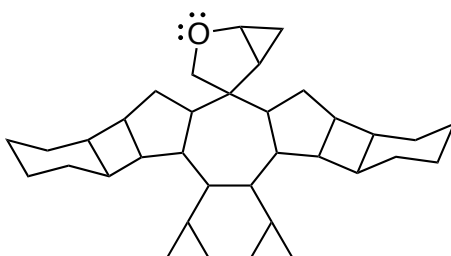
6. (6 pts). On page 1, in the spaces provided write the hybridization state of the atom indicated by the arrow.



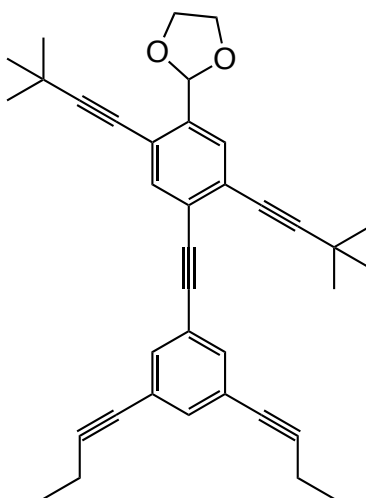
This would have been the nomenclature question page. Because your class ROCKED the Longhorn run with 161 runners, I have simply drawn a few of my favorite molecular creatures, complete with their official IUPAC name. No kidding, these are their real IUPAC names.



1,1-diethyl-5,6,7,8,9,10,11,13-octamethyl-1*H*-hexaceno[2,3-*g*]isochromene



(1*eR*,5*aS*,8*bR*,12*aS*)-triacontahydro-4'-oxaspiro[benzo[3,4']cyclobuta[1',2':3,4]cyclopenta[1,2- β]benzo[3,4]cyclobuta[1,2- α]dicyclopropa[3,4:5,6]benzo[1,2-*h*]azulene-7,2'-bicyclo[3.1.0]hexane]



2-(4-((3,5-di(but-1-yn-1-yl)phenyl)ethynyl)-2,5-bis(3,3-dimethylbut-1-yn-1-yl)phenyl)-1,3-dioxolane

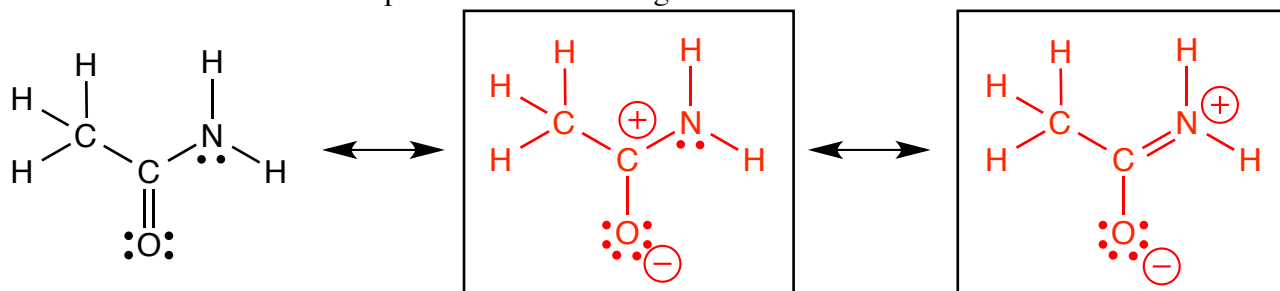
7. (2 pts) What is the most important question in chemistry?

Where are the electrons ?

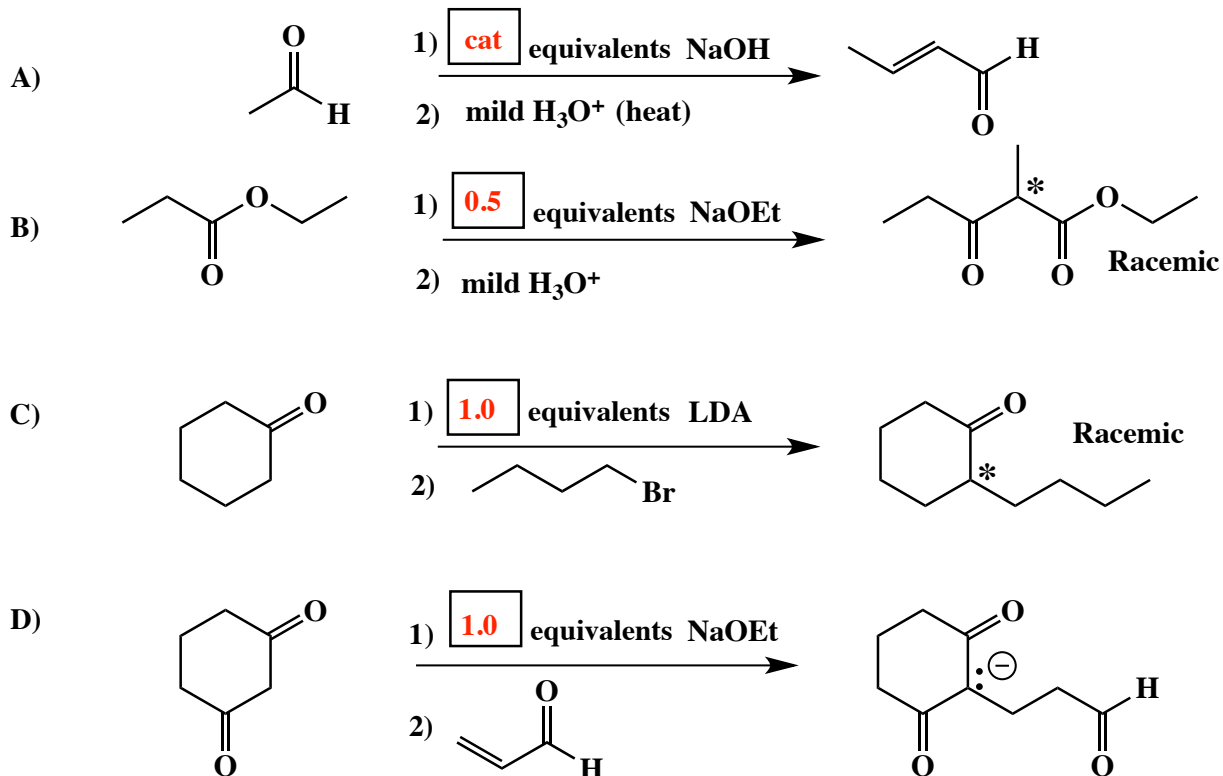
8. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

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.**

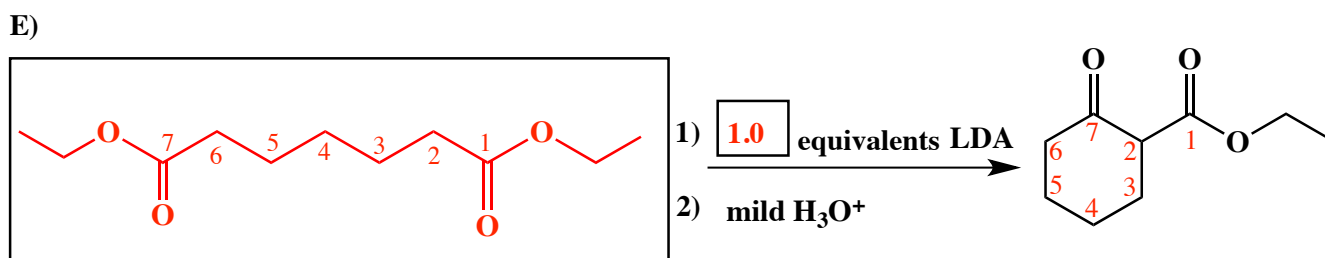
9. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



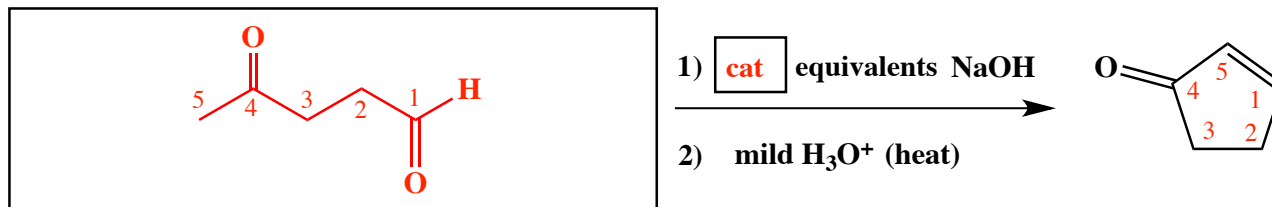
10. (18 pts) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write "CAT". Note: You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.



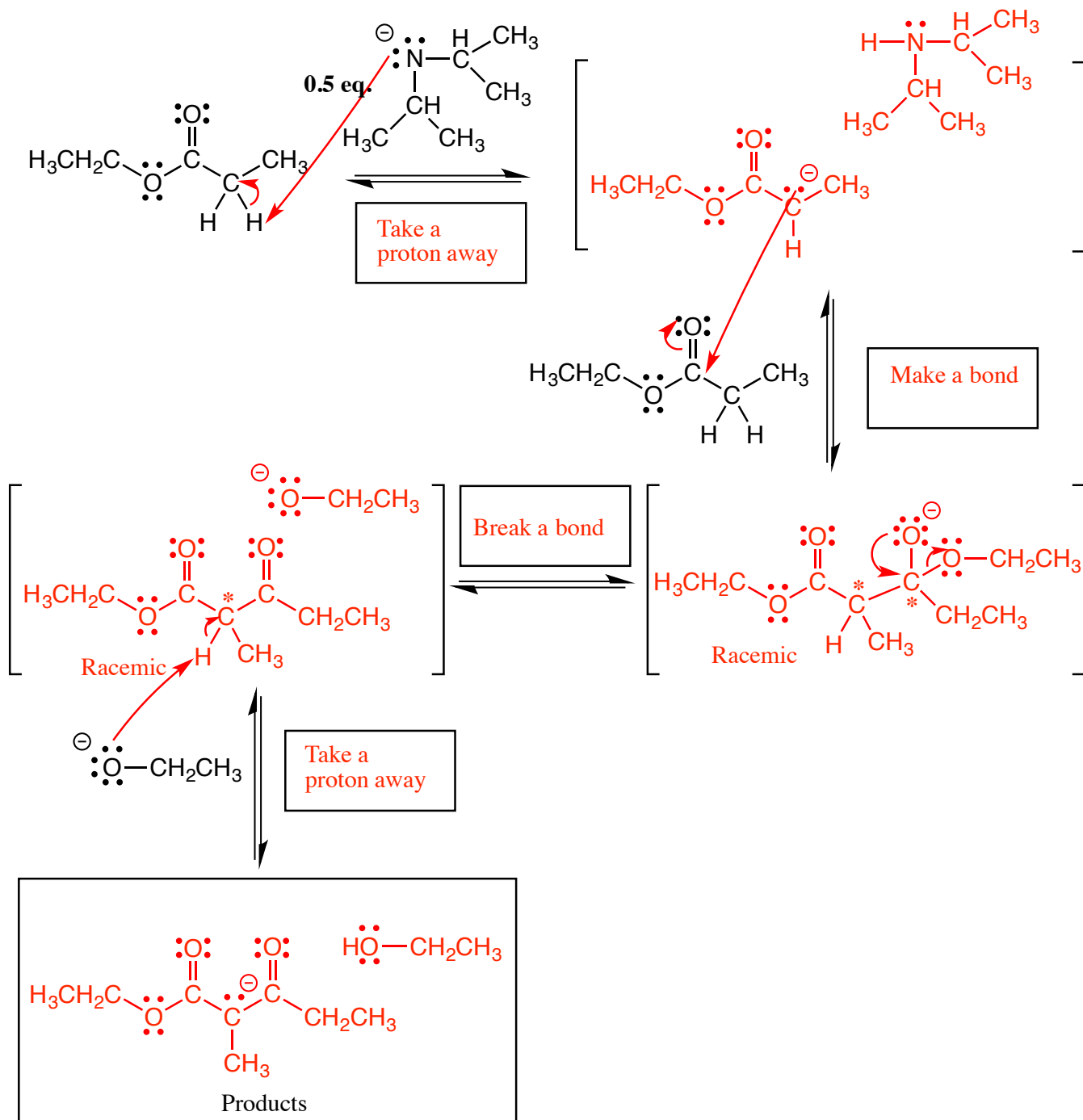
For these next two we have provided the product, you need to draw the starting material as well as fill in the number of equivalents.



F) This one might take you a while so you might want to save it until the end.



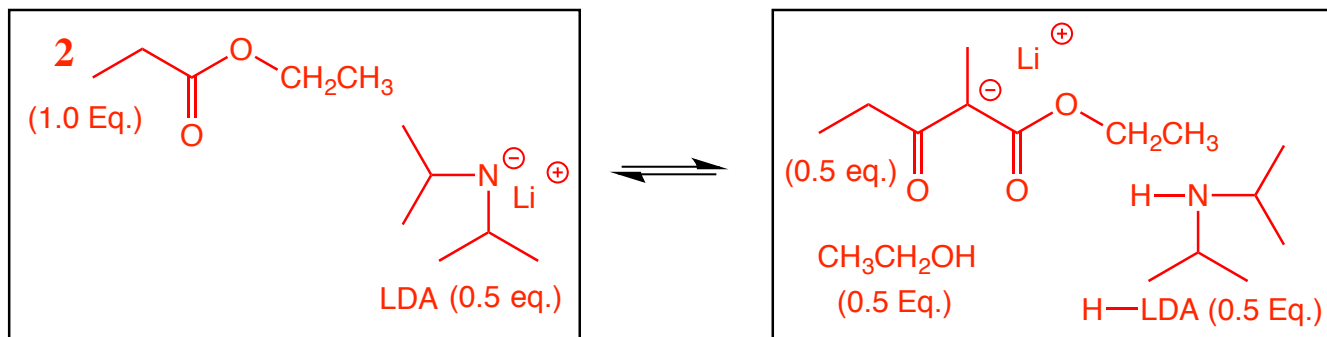
11. (23 pts) Complete the mechanism for the following Claisen reaction using LDA. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED 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.).



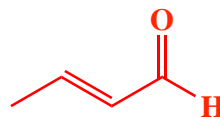
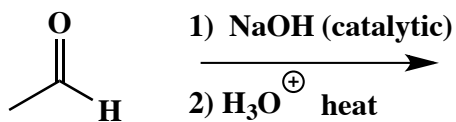
Note you will have to write a balanced equation for the above mechanism on PAGE 8

12. (10 pts) Write a BALANCED equation for the mechanism that you drew on page 7. Note that because we want balanced equations **you will need to specify the amount of each of the reagents you start with as well as the equivalents of each of the products made.**

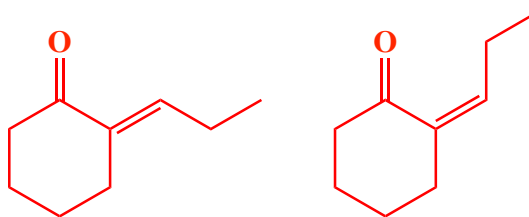
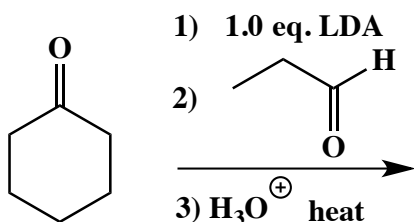
Write a balanced equation for the overall process described by the mechanism from page 7



13. (3, 4, 5 or 7 pts.) Write the predominant carbon containing product or products that will occur for each transformation. If there are multiple carbon containing products, WRITE ALL OF THEM. 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. If an E,Z mixture is formed you must draw both. Also, do not worry about balancing these equations, you just need to show us the major carbon-containing products of these transformations.

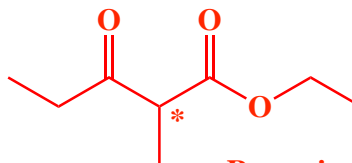
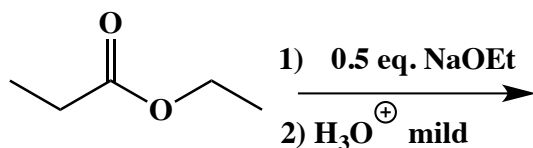


Aldol followed by dehydration



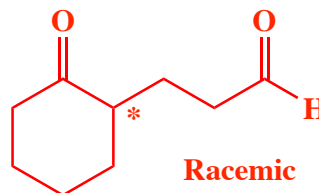
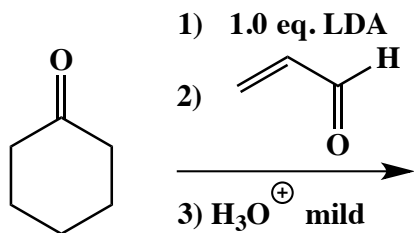
E,Z mixture

Aldol followed by dehydration



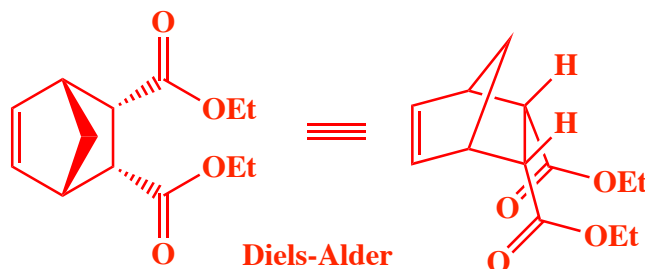
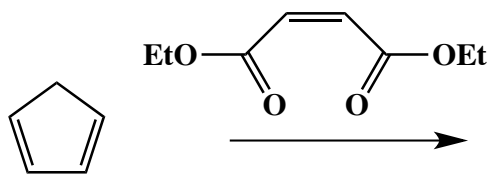
Claisen

Racemic



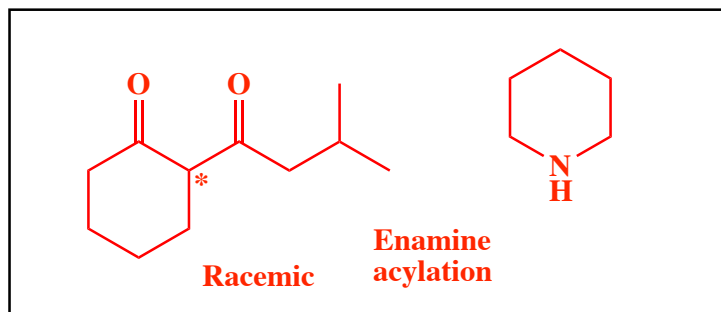
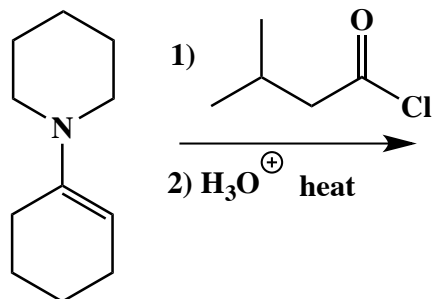
Michael

Racemic

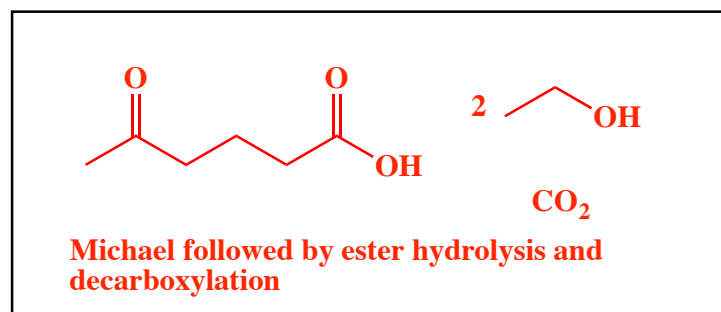
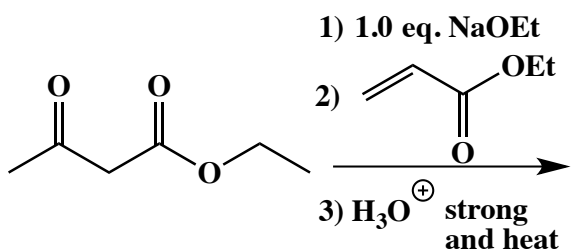
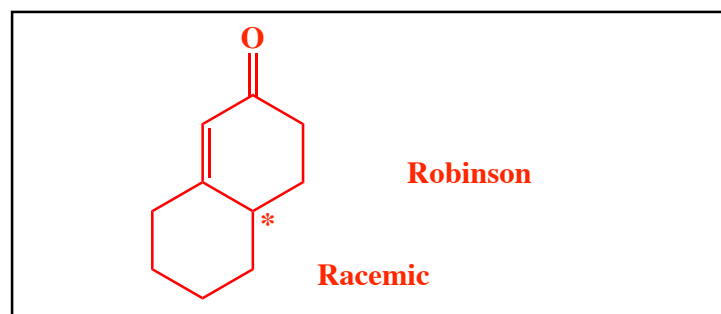
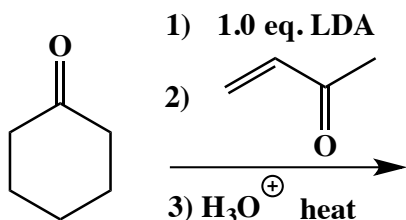
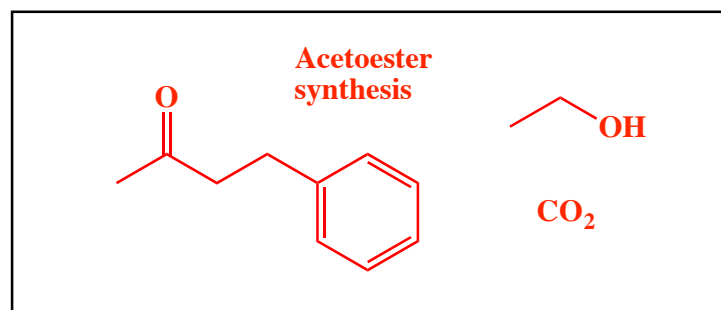
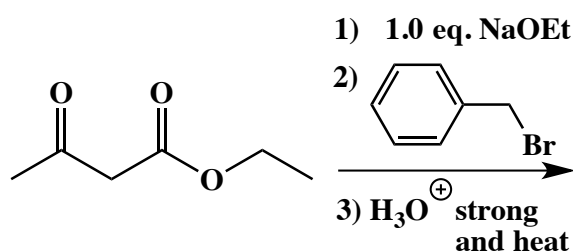


Diels-Alder

13. (3, 4, 5 or 7 pts.) Write the predominant carbon containing product or products that will occur for each transformation. If there are multiple carbon containing products, WRITE ALL OF THEM. 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. If an E,Z mixture is formed you must draw both. Also, do not worry about balancing these equations, you just need to show us the major carbon-containing products of these transformations.



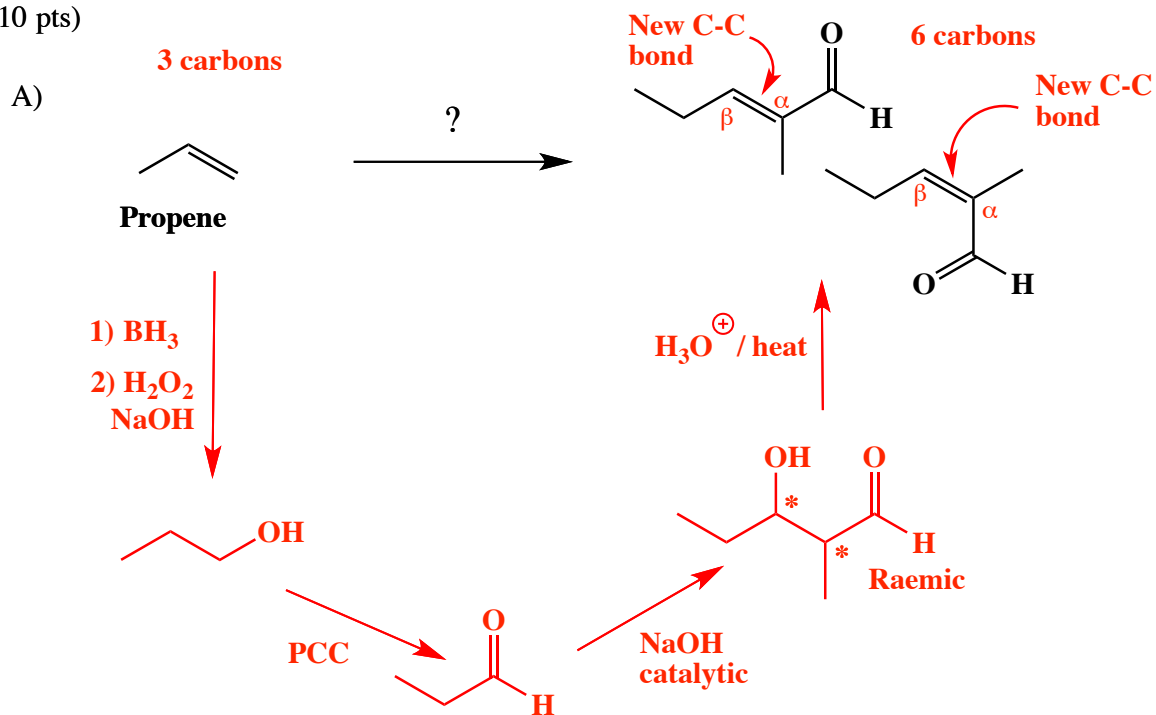
These next two are a little more complicated, they might take a bit more time. Be sure to write down all the carbon containing products.



14. Using any reagents turn the starting material into the indicated product. All carbon atoms in the 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)

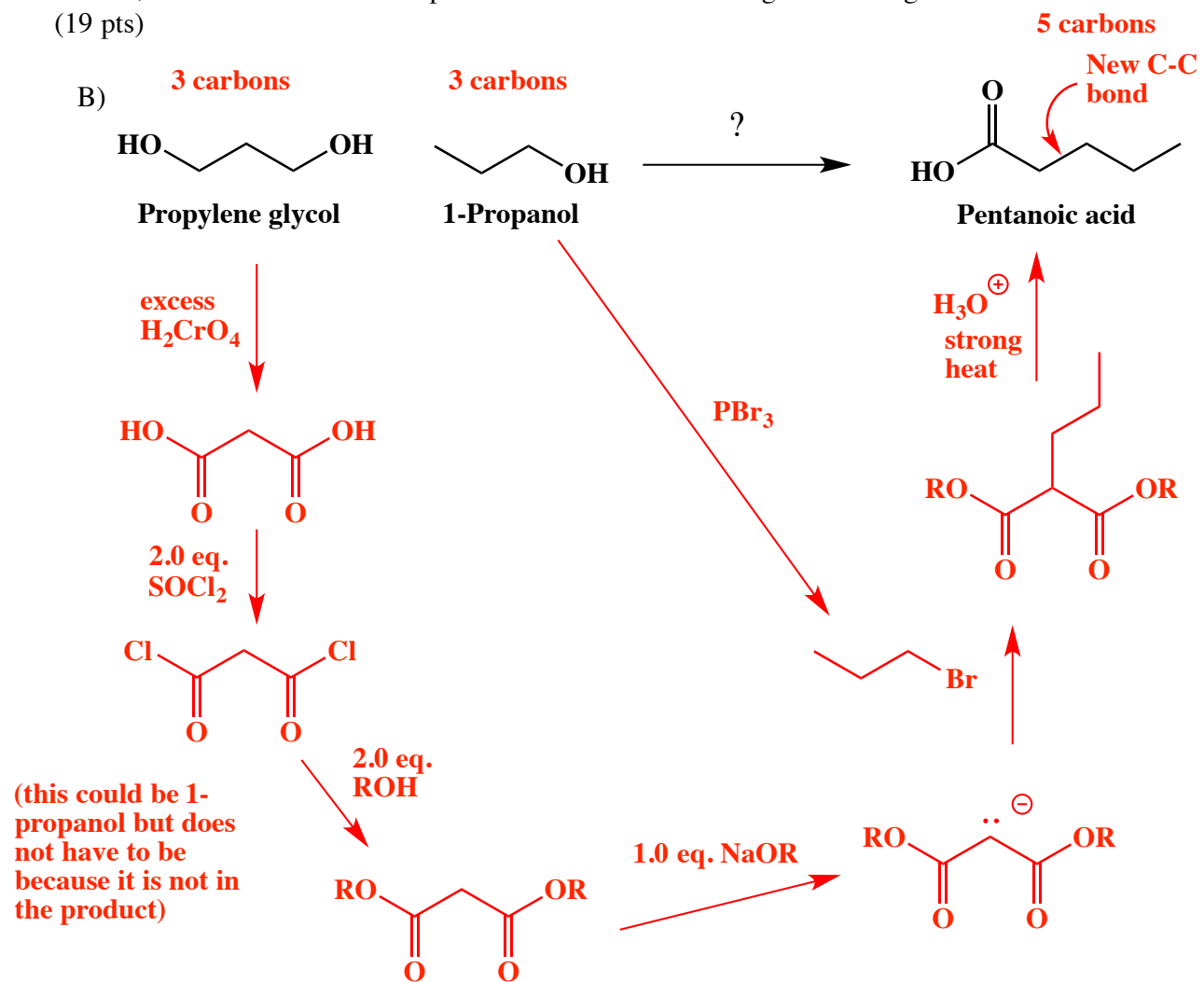


Recognize there are 6 carbons in the product, but 3 carbons in the starting material so 2 molecules of starting material must be assembled into the product. **Recognize** further the final product as an α,β -unsaturated aldehyde, the KRE of an aldol reaction followed by dehydration. **Recognize** the required aldehyde as being derived from the starting propene via non-Markovnikov hydroboration followed by PCC.

14. Using any reagents turn the starting material into the indicated product. All carbon atoms in the 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.

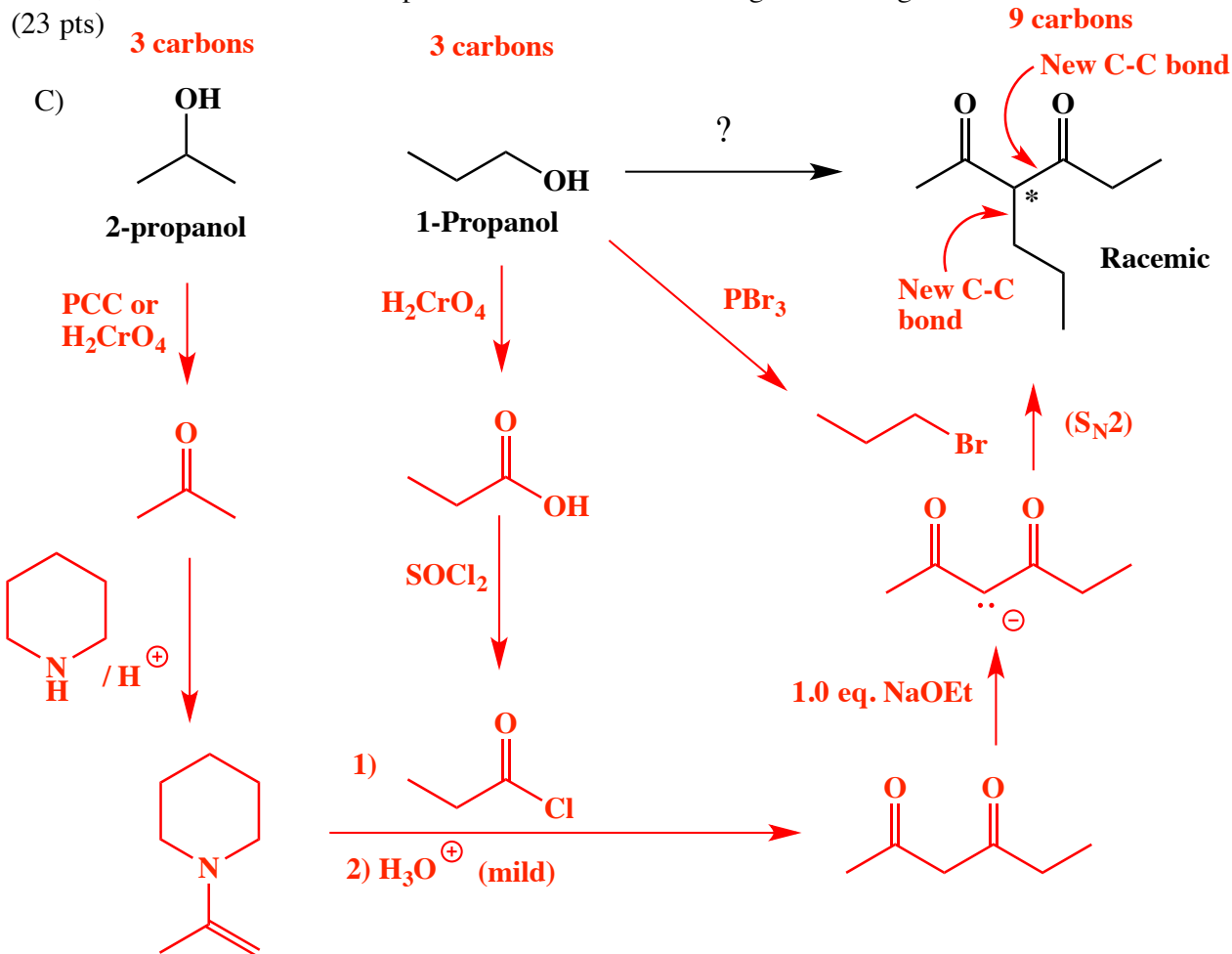
(19 pts)



Recognize there are 5 carbons in the product, but 3 carbons in each starting material so you should assume that the two starting materials are somehow assembled into the product. **Recognize** further the final product as a carboxylic acid, the KRE of a malonic ester synthesis. Therefore assume the new C-C bond is between the α and β carbons as shown. **Recognize** the required malonate diester has a three-carbon addition that could easily be derived from the enolate of a malonate diester reacting with 1-bromopropane, which in turn can be made via reaction of the starting 1-propanol with PBr₃. **Recognize** that the malonate diester can be prepared via oxidation of propylene glycol with excess chromic acid, followed by conversion to the diacid chloride with 2.0 eq. SOCl₂ then reaction with 2.0 eq. alcohol. These last two steps could be accomplished using the Fischer esterification as an alternative.

14. Using any reagents turn the starting material into the indicated product. All carbon atoms in the 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.



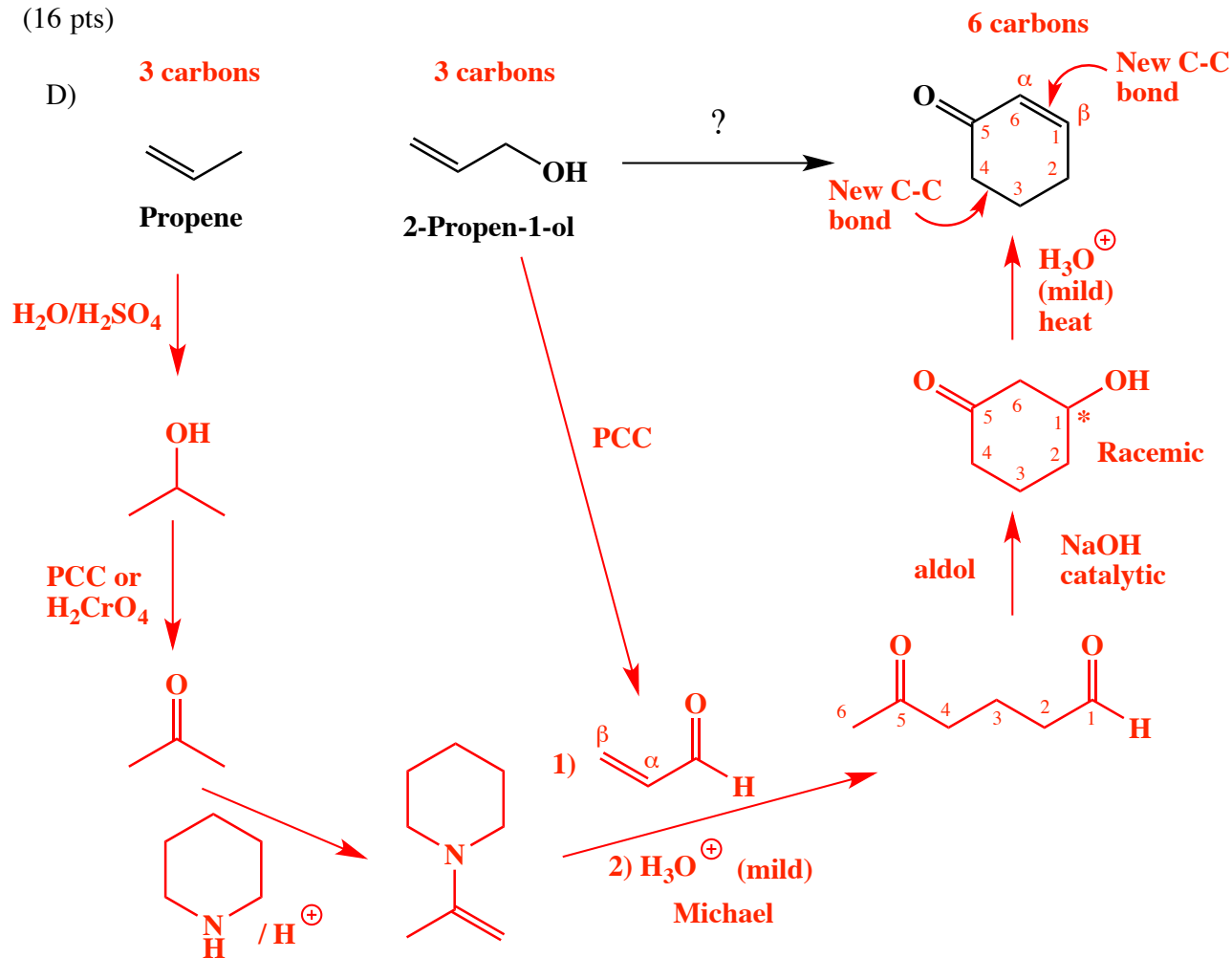
Recognize there are 9 carbons in the product, but 3 carbons in the starting materials so 3 molecules of starting material must be assembled into the product. There must be two new C-C bonds as shown.

Recognize further the final product as a β -diketone with a three carbon chain added at the α -carbon. Therefore predict that the last step is an S_N2 reaction of the β -diketone enolate with 1-bromopropane, which can be made from 1-propanol using PBr_3 . **Recognize** the required β -diketone as being derived from either the acylation (using propanoyl chloride) of the enamine derived from acetone (shown), or alternatively, the enolate made by reacting acetone with 1.0 eq. of LDA (not shown). Either way, the propanoyl chloride is made from propanoic acid, which in turn is made from 1-propanol oxidized by chromic acid. The acetone is made from 2-propanol using either PCC or chromic acid.

14. Using any reagents turn the starting material into the indicated product. All carbon atoms in the 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.

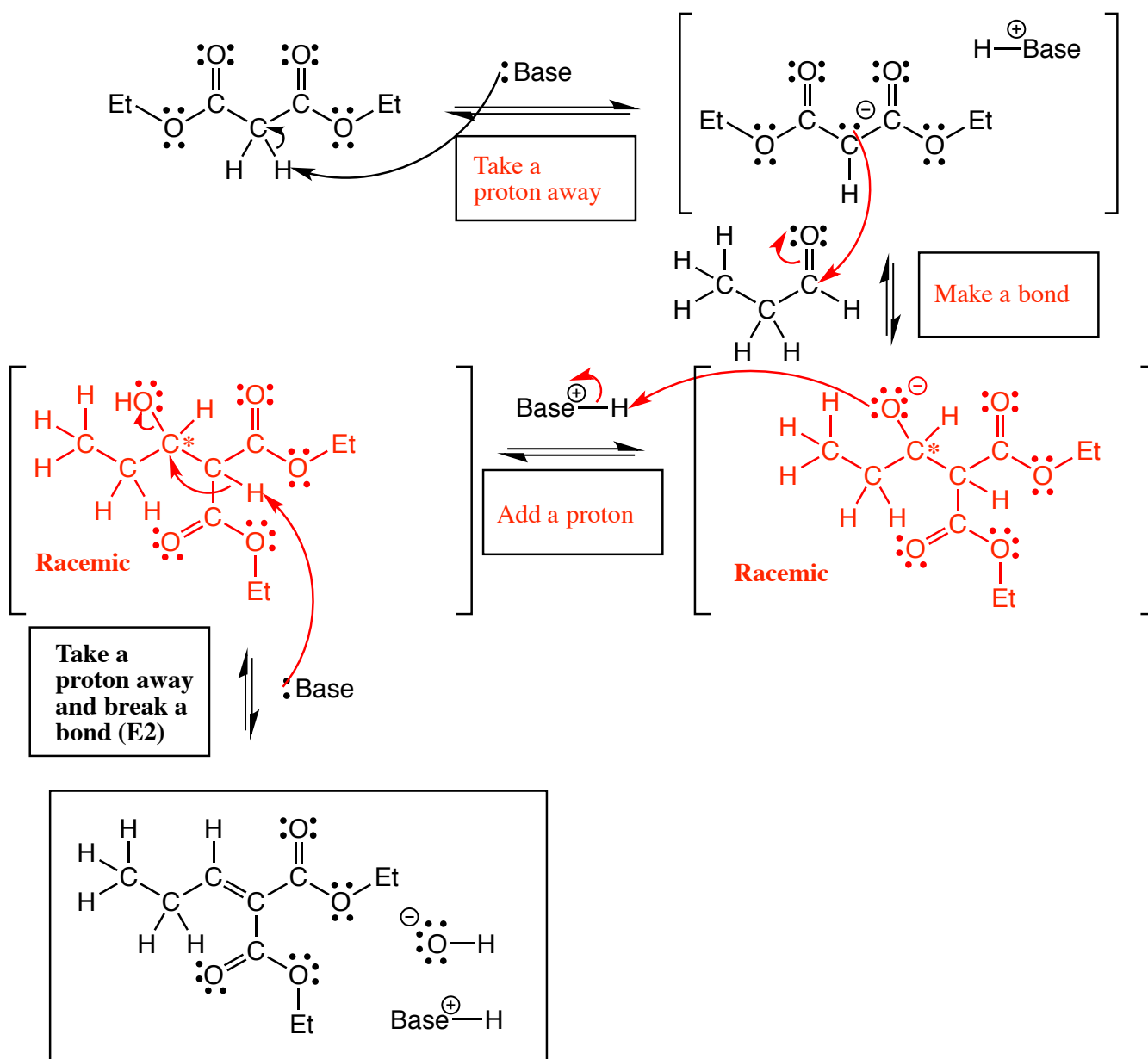
Remember, all of the carbons of the product must come from the given starting material.

(16 pts)



Recognize there are 6 carbons in the product, but 3 carbons in the starting materials so the starting molecules must combine to make the product. Because the product is a six-membered ring there must be two new C-C bonds. **Recognize** the product as an α,β unsaturated ketone, the KRE of a cyclic aldol/dehydration, so predict the two new C-C bonds are as shown. The hard part of this synthesis is realizing that the starting molecule for the cyclic aldol/dehydration is 5-oxopentanal. **Recognize** the 5-oxopentanal as the product of a Michael reaction between the enamine of acetone (shown, or the enolate made using LDA, not shown) reacting with 2-propanal. 2-Propanal can be made via PCC oxidation of the starting 2-propen-1-ol. Acetone can be made by oxidation of 2-propanol, which is derived from propene via the Markovnikov hydration of the starting propene.

15. (18 pts) Here is an “apply what you know” problem. An interesting reaction we did not study is the Knoevenagel Condensation reaction. It involves the reaction of β -dicarbonyl species with aldehydes to give new C=C bonds (cue the trumpet!) in base. The Knoevenagel Condensation provides a rapid way to make very complex molecules from simple starting materials. Use what you know about the reactions we have been studying to fill in the parts of the Knoevenagel condensation reaction mechanism. For the following mechanism, **fill in all the missing arrows, draw the missing intermediates (all charges and lone pairs) and fill in all of the blank boxes with the type of mechanistic element involved (“make a bond”, “add a proton”).** Remember to use asterisks (*) to indicate any chiral centers and write “racemic” if appropriate.



16. (8 pts) You might be surprised to learn that the base used often in the Knoevenagel Condensation is pyridine. Fill in the boxes with the structures that correspond to product of the following Knoevenagel Condensation, followed by what happens when this initial product is heated in strong, aqueous acid. For the following, you only have to draw the main product derived from the starting materials.

