

NAME (Print): _____

Chemistry 320N
Dr. Brent Iverson
3rd Midterm
April 17, 2014

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	(24)
2	(18)
3	(30)
4	(14)
5	(18)
6	(26)
7	(23)
8	(26)
9	(21)
10	(20)
11	(16)
12	(19)
13	(13)
14	(13)
15	(12)
16	(4)
Total	(297)

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	$\text{RCH}_2\text{OH}_2^{\oplus}$	-2
Hydronium ion	$\text{H}_3\text{O}^{\oplus}$	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Ammonium ion	$\text{H}_4\text{N}^{\oplus}$	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	$\text{H}_3\text{N}^{\oplus}\text{CH}_2\text{CH}_3$	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

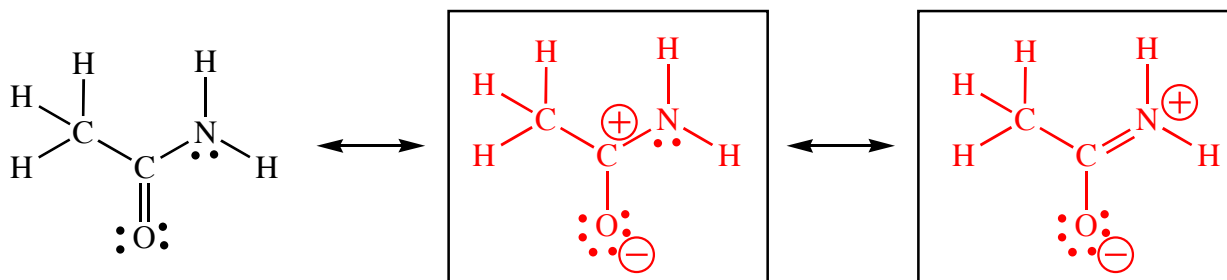
1. (2 pts) What is the most important question in chemistry?

Where are the electrons?

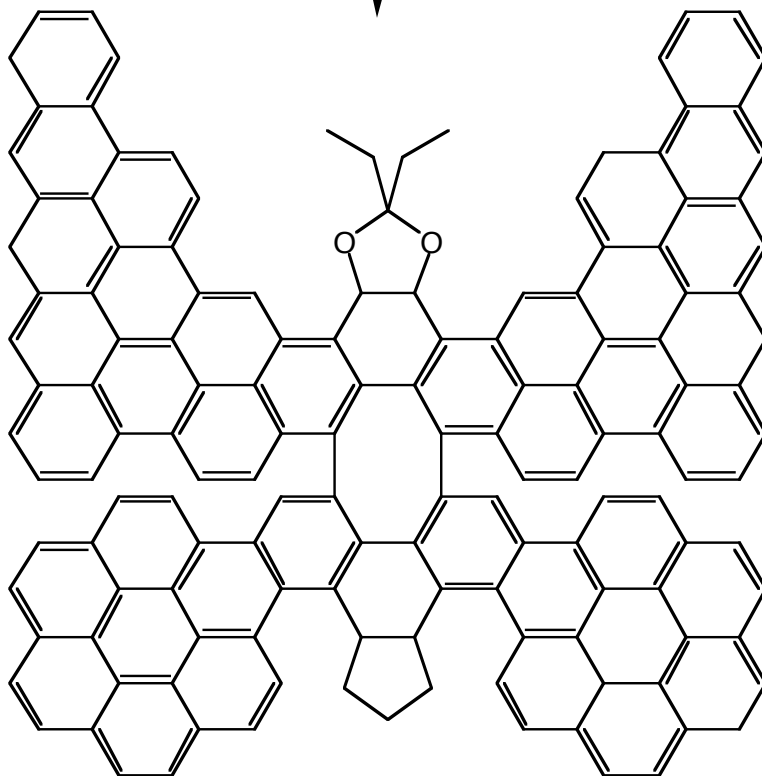
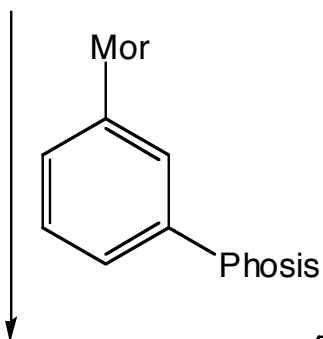
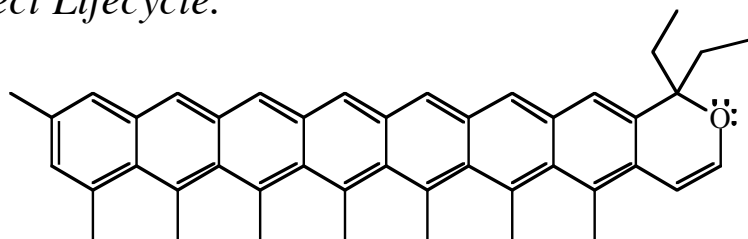
2. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

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.

3. (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.



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.)

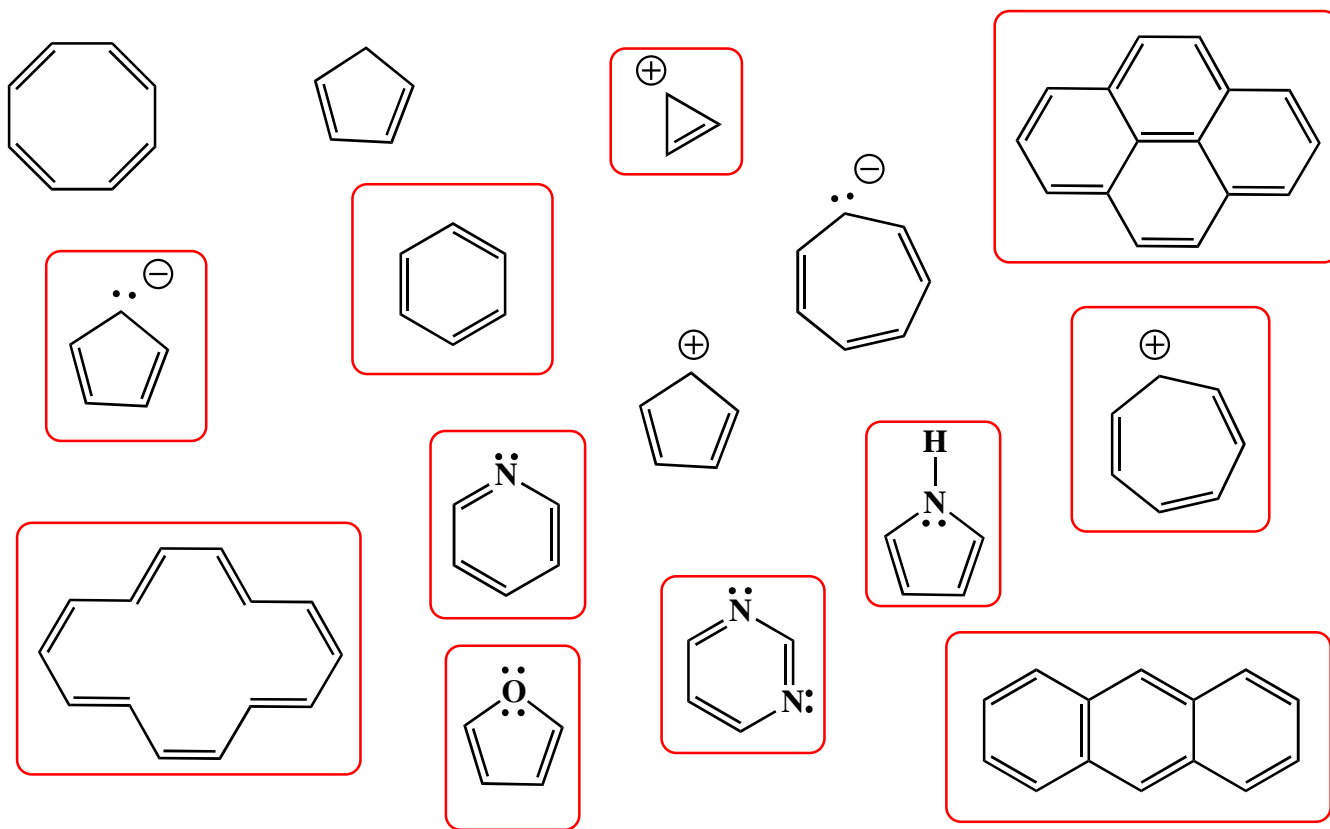
4. (1 pt. each) Here are a number of statements regarding conjugation and light absorption/emission. Do not second guess yourself, this is not meant to be tricky! Check the appropriate box to indicate whether the statement is true or false.

	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.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
B. When molecules absorb light, electrons are excited from a bonding to an antibonding molecular orbital.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
C. If a substance absorbs blue light, it will appear blue to our eyes.	<input type="checkbox"/>	<input checked="" type="checkbox"/>
D. The larger the number of pi bonds involved in a conjugated molecule (a "pi-way") the smaller the energy gap between the highest occupied pi molecular orbital and the lowest unoccupied molecular orbital.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
E. A reaction is said to be under kinetic control if the ratio of products is dependent on the relative energies of the products.	<input type="checkbox"/>	<input checked="" type="checkbox"/>
F. A reaction is said to be under thermodynamic control if the ratio of products is dependent on the relative energies of the products.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
G. Fluorescence occurs when a photon is emitted as an electron relaxes from an antibonding molecular orbital back to a bonding molecular orbital in a molecule that has absorbed light.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
H. Phosphorescence occurs when a chemical reaction generates a product in an excited state.	<input type="checkbox"/>	<input checked="" type="checkbox"/>
I. Phosphorescence occurs when an electron must flip its spin before relaxing back to a bonding molecular orbital while emitting a photon.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
J. The light from a green laser will go through your finger, while the light from a red laser is absorbed.	<input type="checkbox"/>	<input checked="" type="checkbox"/>

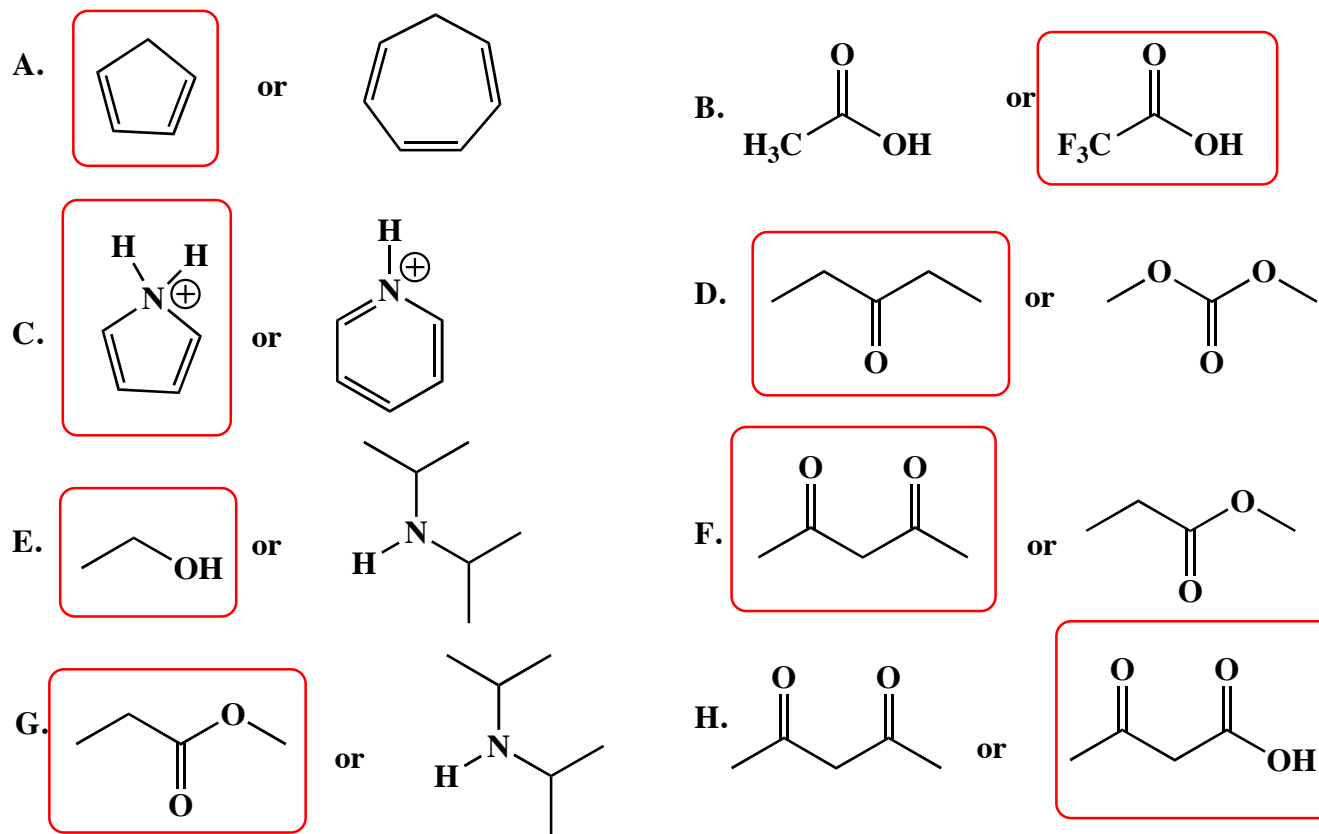
5. (8 points) Aromaticity is a term that refers to molecules with characteristic pi systems. A theorist named Hückel helped to derive several criteria that can be used to determine if a molecule is aromatic. List all four of these criteria:

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 $n = 0, 1, 2, 3, 4, 5, \dots$

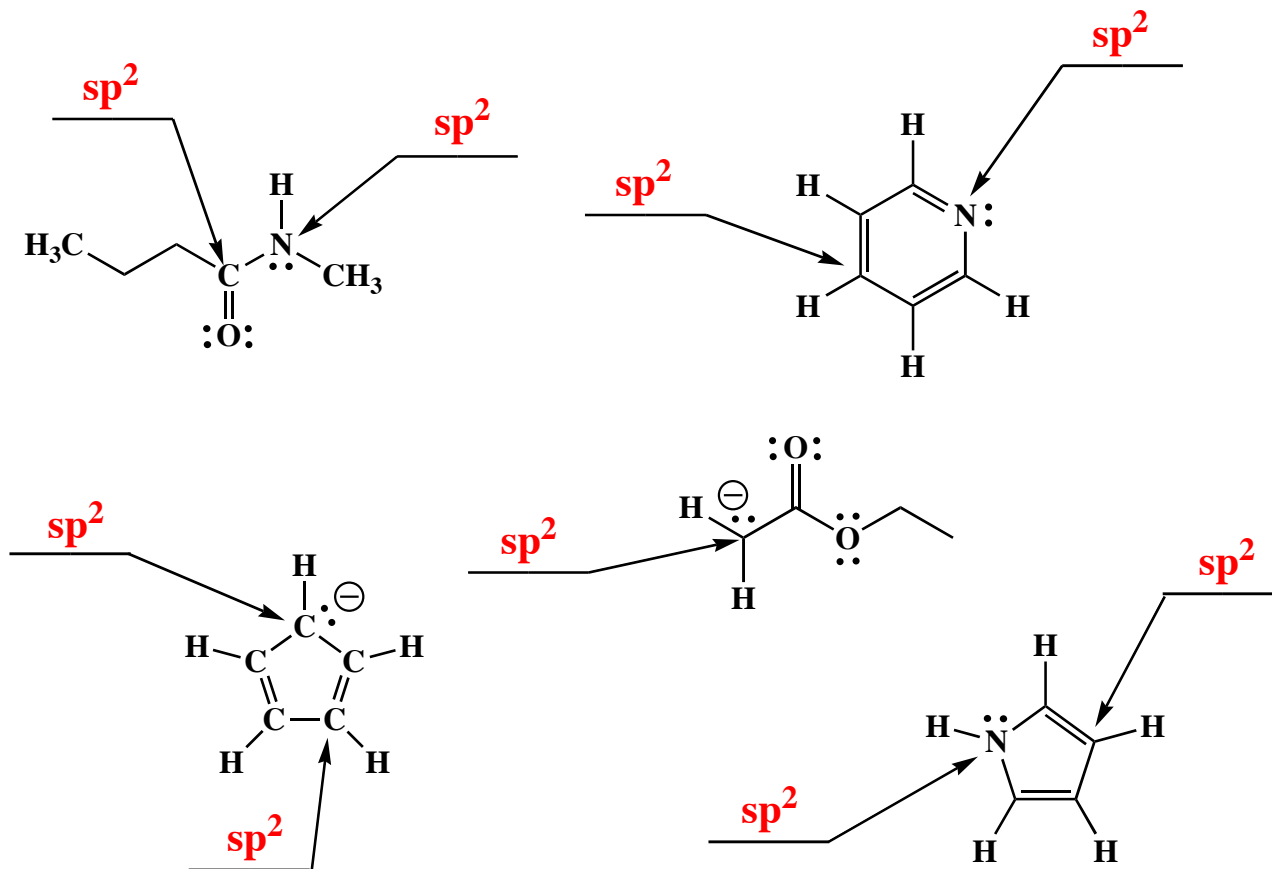
6. (15 points) Draw a circle around all of the molecules below that can be considered aromatic.



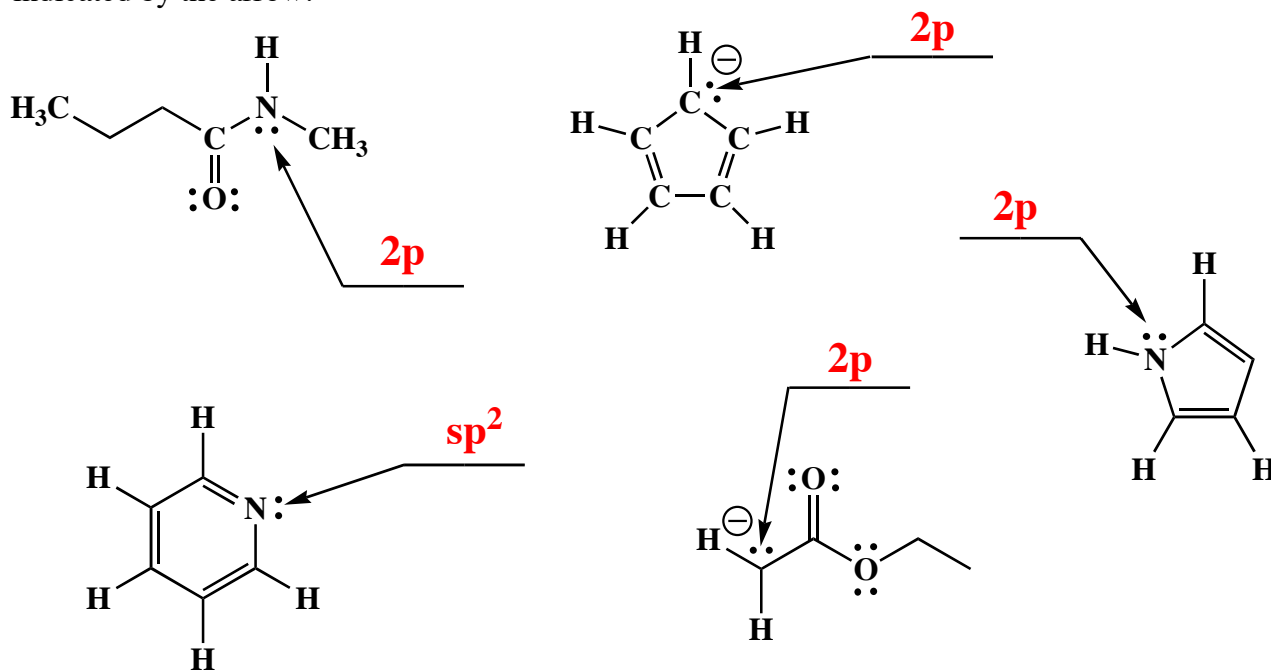
7. (16 points) For each pair of molecules, circle the one that is more acidic.



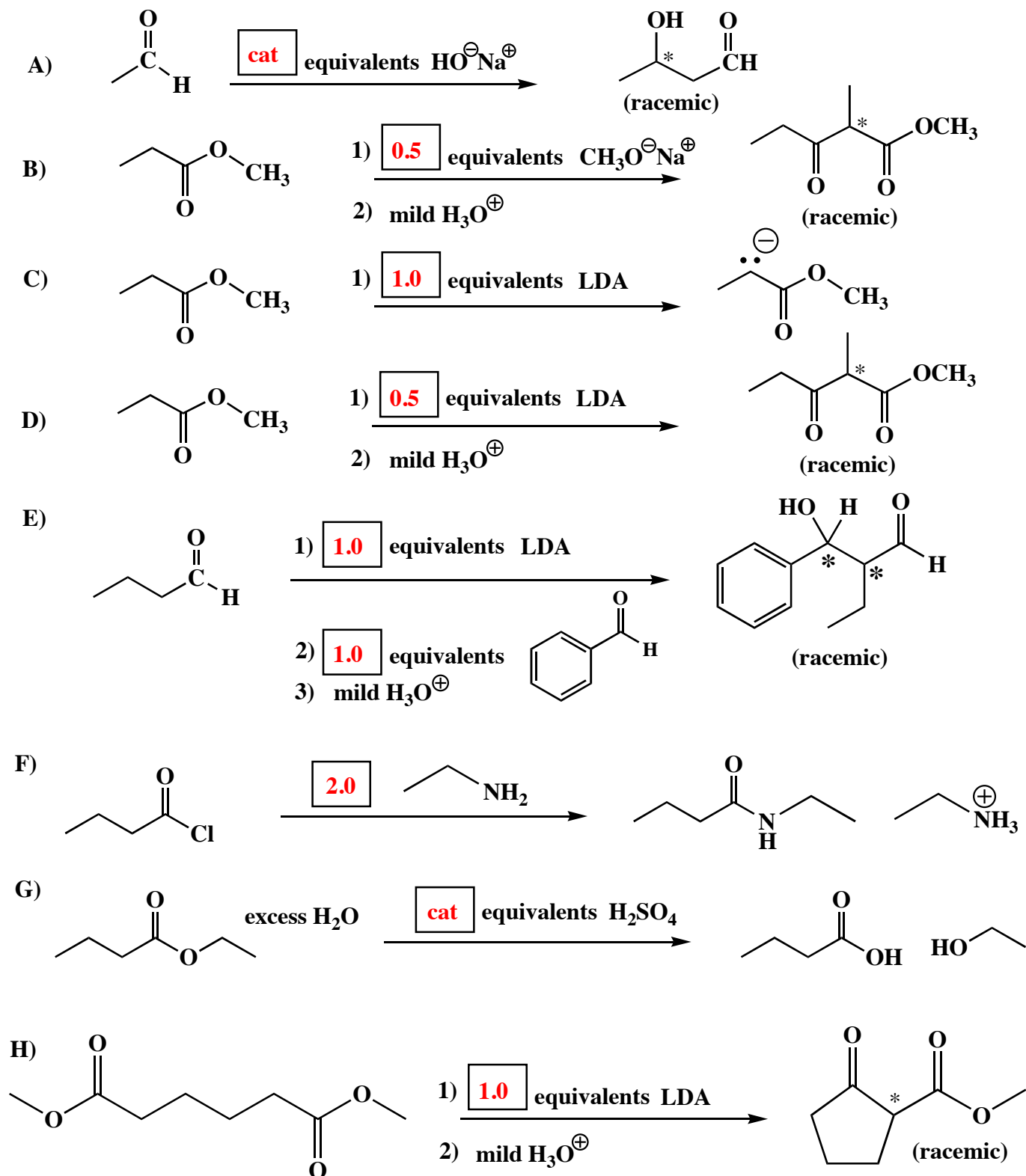
8. (9 points) On the lines provided, state the **hybridization state of the atom** indicated by the arrow.



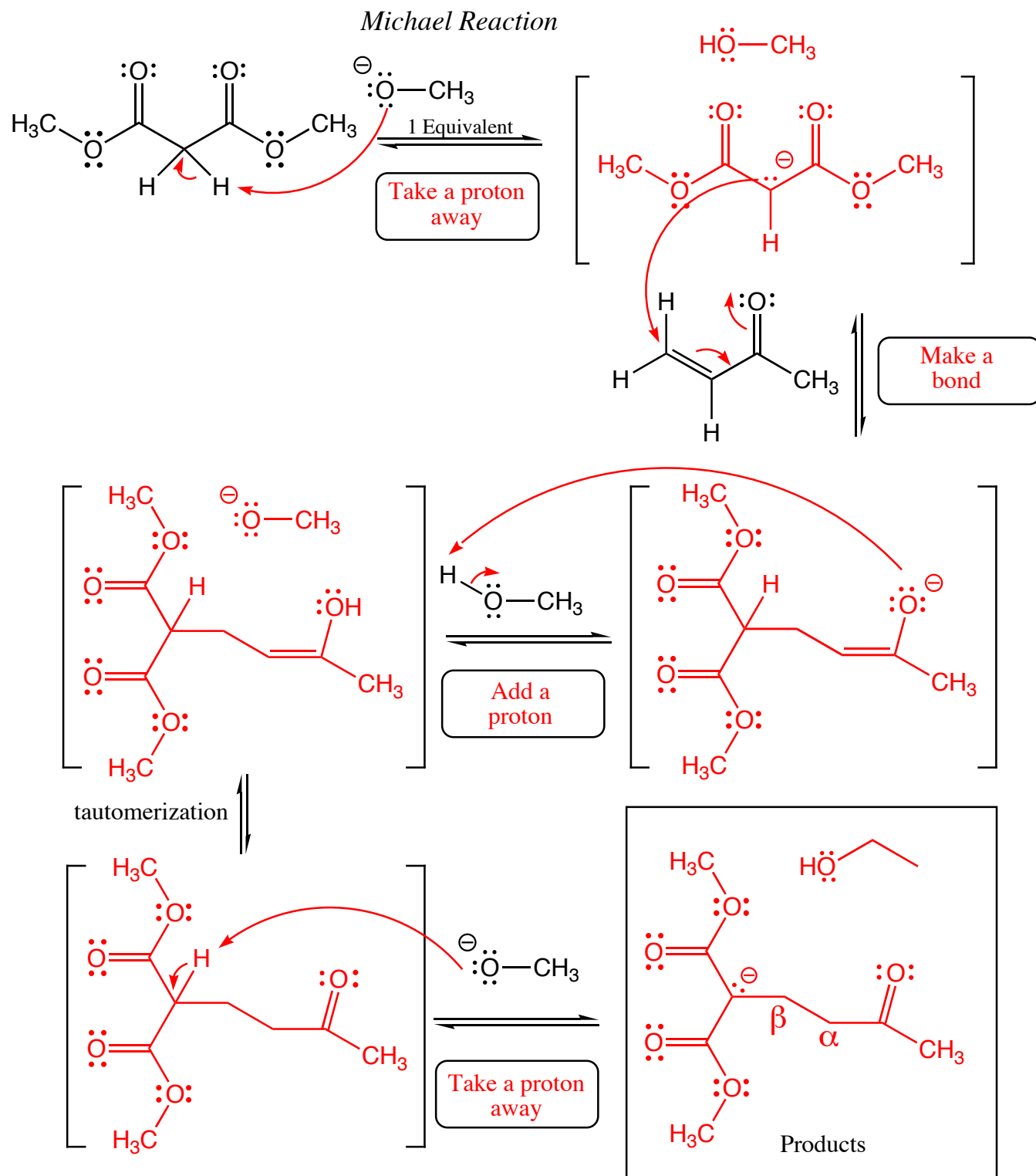
9. (5 points) On the lines provided, state the **atomic orbital that contains the lone pair of electrons** indicated by the arrow.



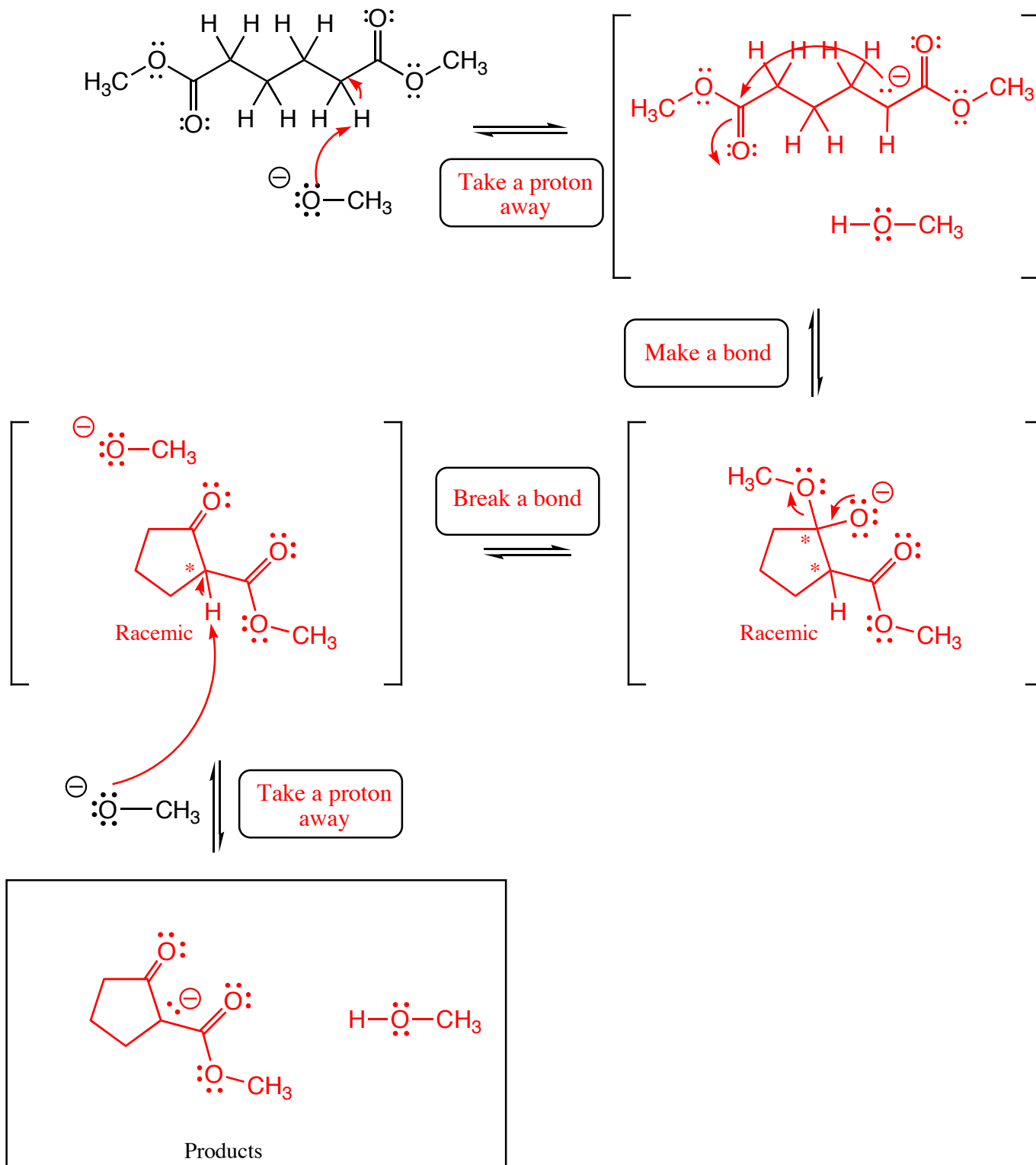
10. (2 pts each) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write "CAT". Note: **You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.**



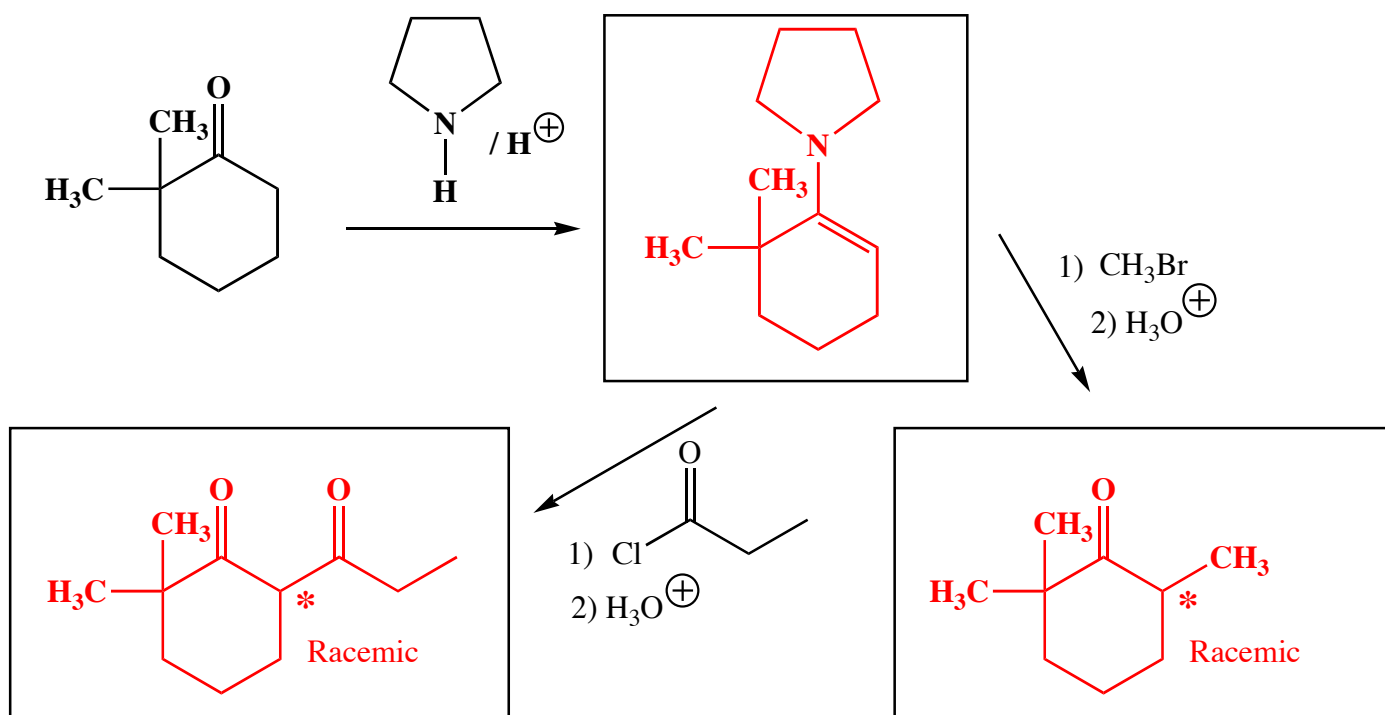
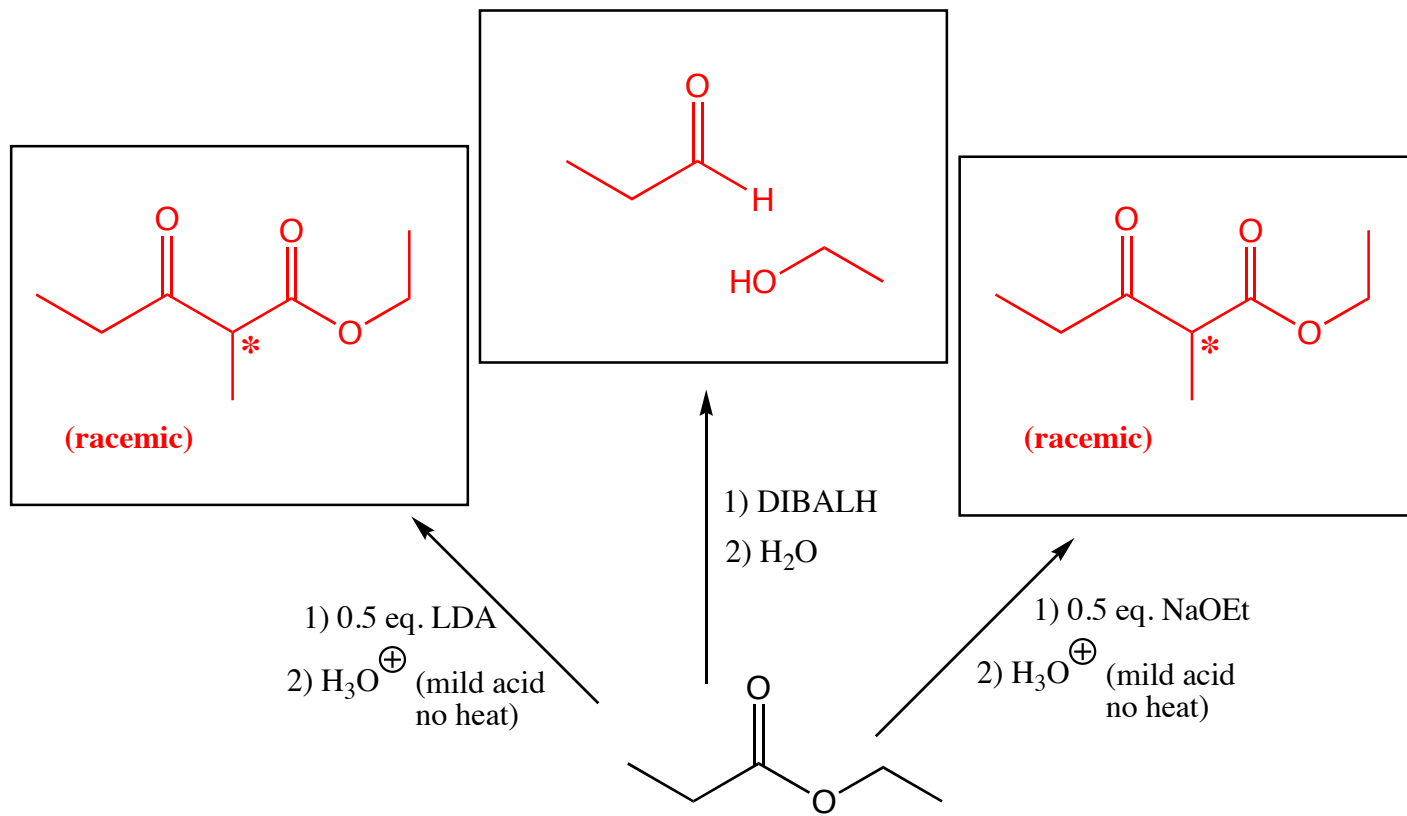
11. (26 pts) Complete the mechanism for the following Michael reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN 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").



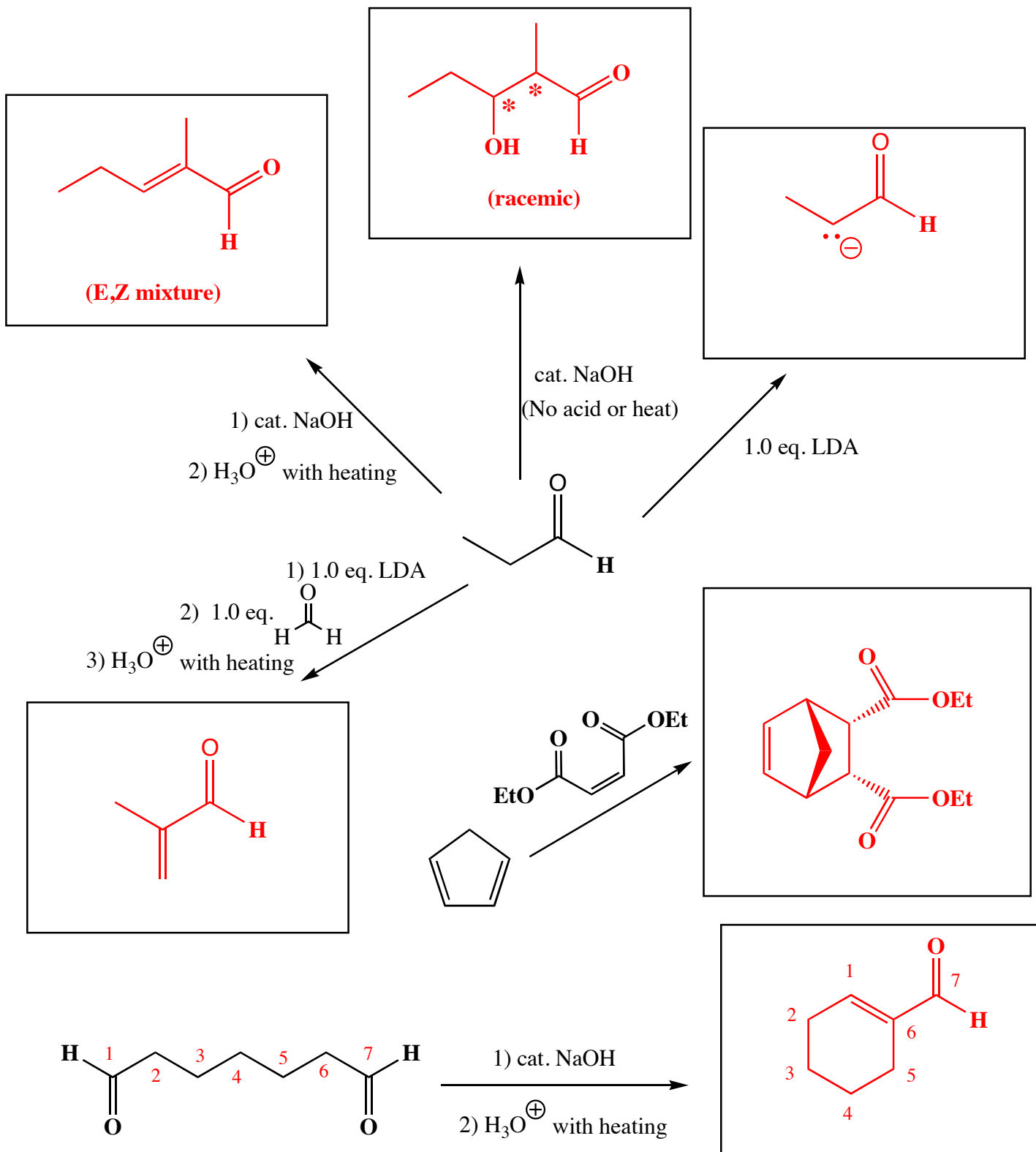
12. (23 pts) Complete the mechanism for the following Dieckmann reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN 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").



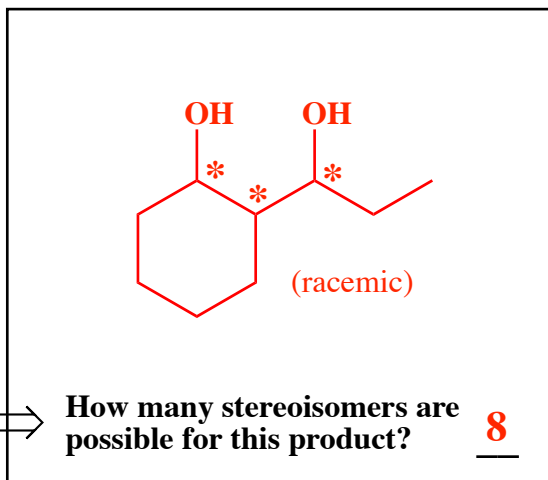
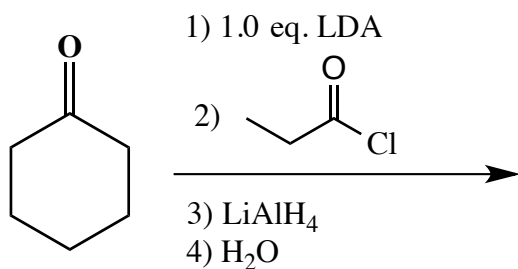
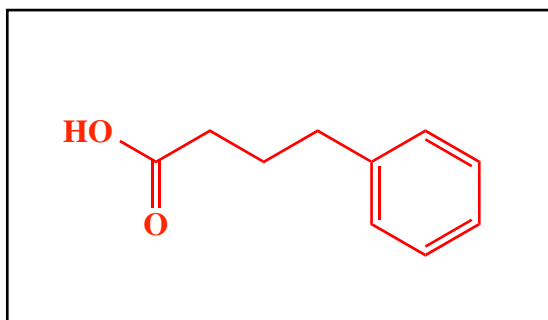
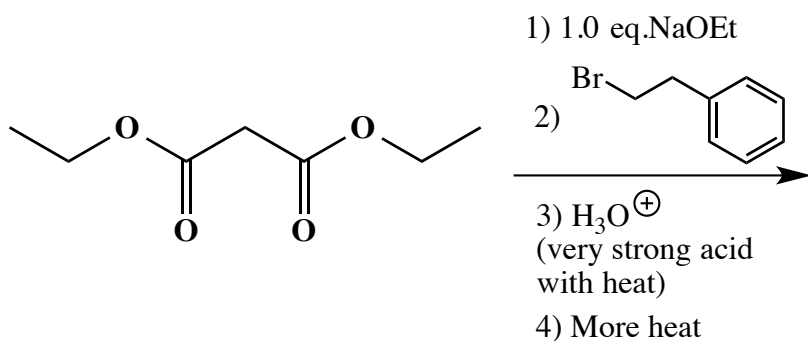
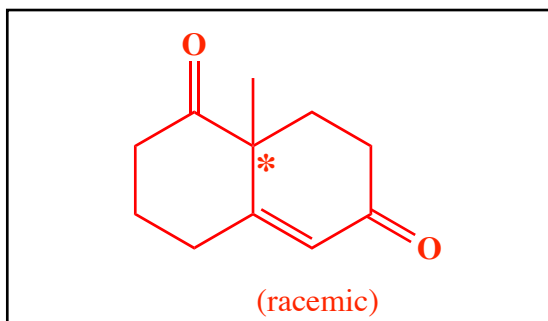
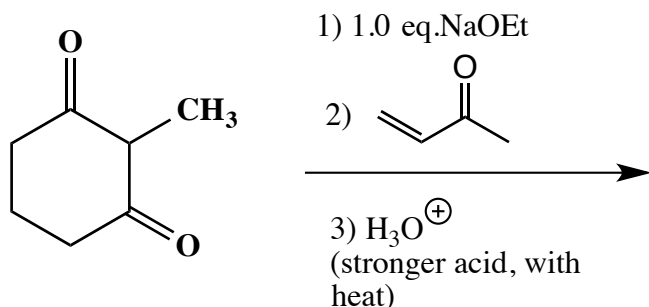
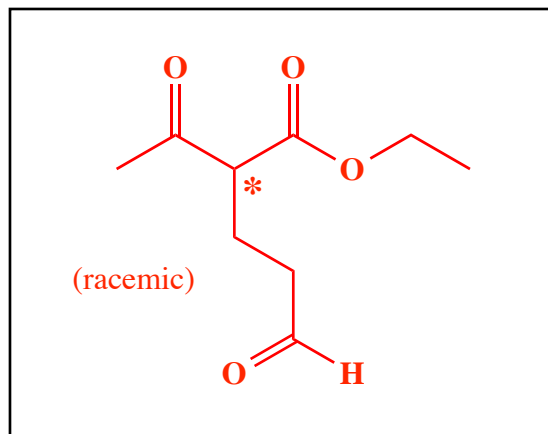
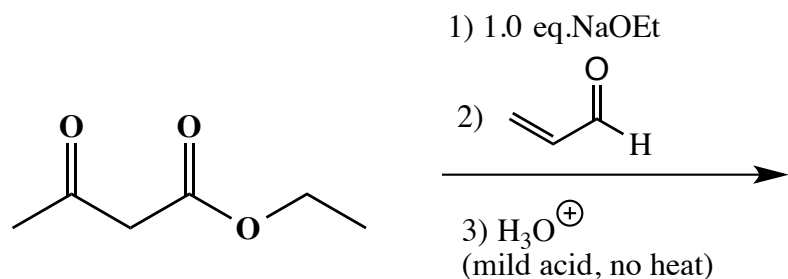
13. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration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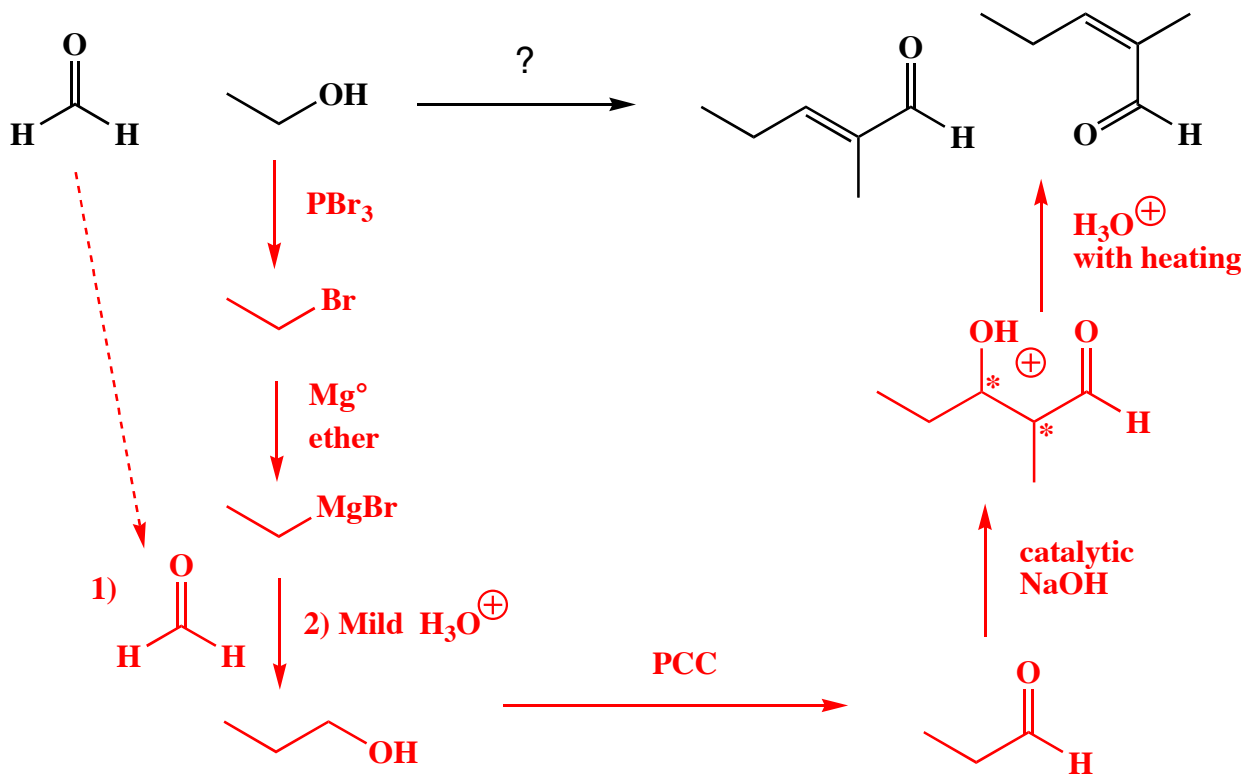


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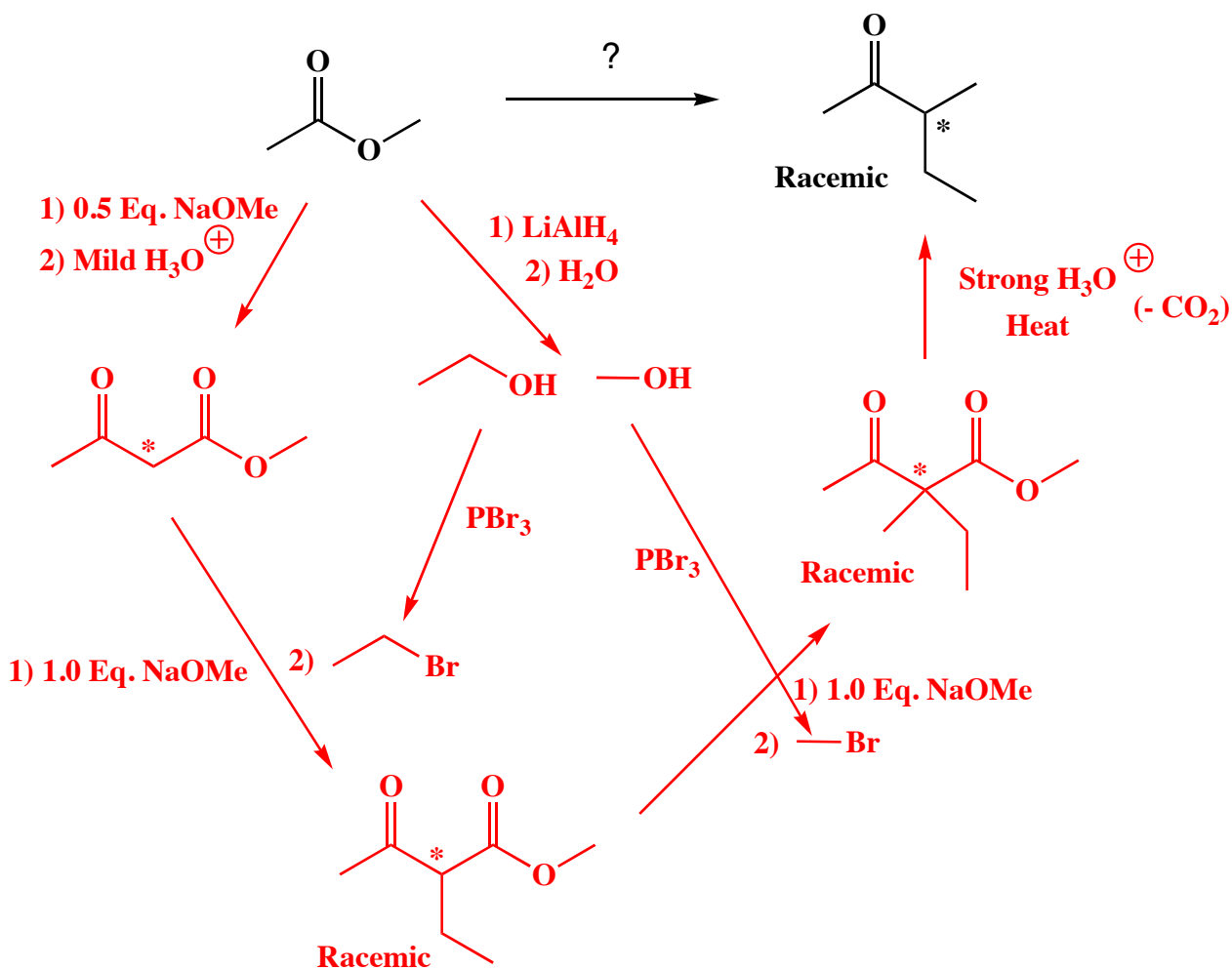
14. (16 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate.

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



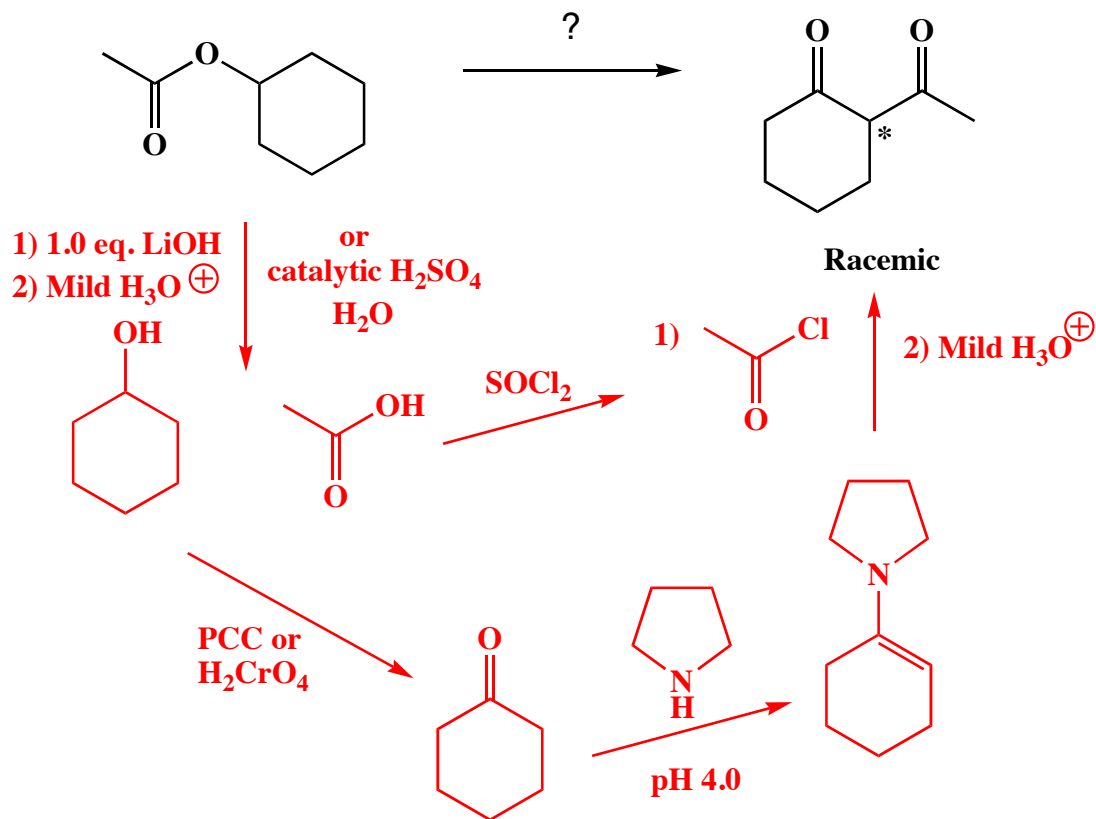
15. (19 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate.

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



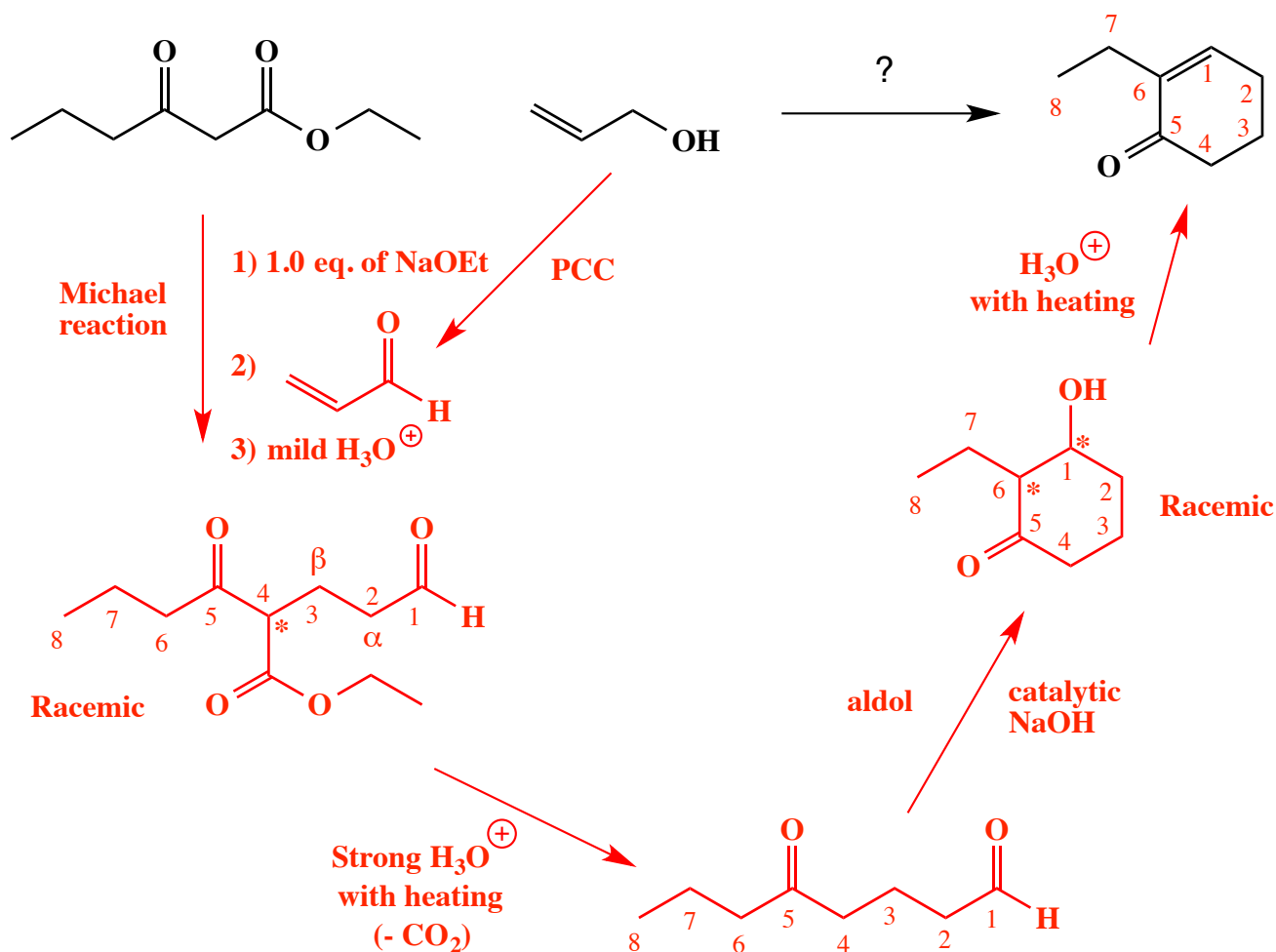
16. (13 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate.

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



17. (13 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting materials. 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.

This is the hardest synthesis problem I have ever put on an exam. SAVE IT UNTIL THE END
Remember, all of the carbons of the product must come from the given starting materials.



Reaction occurs from the enolate at carbon labeled as 6 instead of 2 or 4 because that is the only way a stable ring can be formed (a six-membered ring).

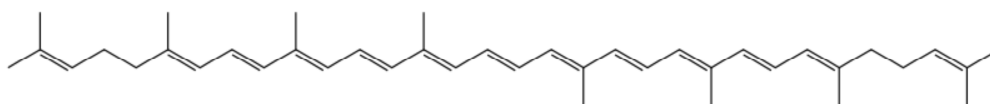
18. Below are listed some key relationships that are useful when analyzing the absorbance and fluorescence properties of molecules.

$$E = hc/\lambda$$

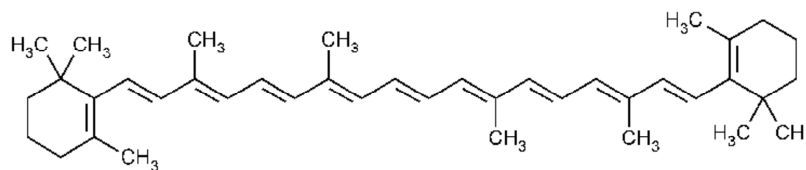
E = energy h = Planck's constant c = the speed of light
 λ = the wavelength of light

Colors of the rainbow, listed with the wavelengths of light corresponding to those colors

Ultraviolet light	Violet	Blue	Green	Yellow	Orange	Red	Infrared light
< 380 nm	380 nm	470 nm	520 nm	585 nm	650 nm	700 nm	> 700 nm



Lycopene



β -Carotene

Select the statement that is true:

- A) Lycopene has 13 pi bonds in conjugation, while β -carotene has 11 pi bonds in conjugation
- B) Lycopene has 11 pi bonds in conjugation, while β -carotene has 11 pi bonds in conjugation**
- C) Lycopene has 11 pi bonds in conjugation, while β -carotene has 9 pi bonds in conjugation
- D) Lycopene has 13 pi bonds in conjugation, while β -carotene has 9 pi bonds in conjugation

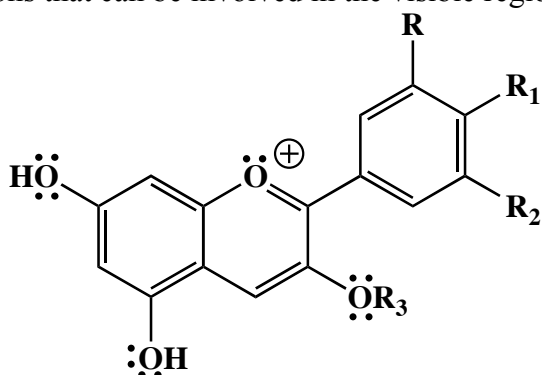
Tomatoes have lycopene and carrots have β -carotene. Tomatoes are red while carrots are orange because:

- A) Lycopene absorbs more violet wavelengths compared to β -carotene
- B) Lycopene absorbs more red wavelengths compared to β -carotene
- C) Lycopene absorbs more yellow wavelengths compared to β -carotene**
- D) Lycopene absorbs more infrared wavelengths compared to β -carotene

Based on your understanding of the light absorbance process, which must be true

- A) The energy difference between the highest occupied pi molecular orbital and the lowest unoccupied pi molecular orbital is larger for lycopene compared with β -carotene.
- B) The energy difference between the highest occupied pi molecular orbital and the lowest unoccupied pi molecular orbital is smaller for lycopene compared with β -carotene.**
- C) The energy difference between the lowest occupied pi molecular orbital and the highest unoccupied pi molecular orbital is larger for lycopene compared with β -carotene.
- D) The energy difference between the lowest occupied pi molecular orbital and the highest unoccupied pi molecular orbital is smaller for lycopene compared with β -carotene.

In addition to molecules with long pi-systems, other types of molecules absorb visible light and are highly colored. For example, many aromatic molecules are used as dyes in our clothes and in nature. For many aromatic molecules, the absorbance of visible wavelengths derives from excitation of an electron in a lone pair on an atom attached to the ring, to the lowest unoccupied pi molecular orbital of the ring. This type of absorbance is often called an “n to π^* ” absorbance in which the “n” refers to the non-bonding lone pair, and the π^* (pronounced “pi-star”) refers to the lowest unoccupied pi molecular orbital, which is an antibonding pi molecular orbital, hence the π^* designation. Below is the parent structure of the so-called anthocyanine molecule responsible for the blue color of blueberries. Notice the O atoms bonding to the aromatic rings, those have lone pairs of electrons that can be involved in the visible region absorbance.



R, R₁, R₂, and R₃ can be various entities including alkyl groups or even carbohydrates

Anthocyanins found in blueberries

The absorbance in molecules such as lycopene or β -carotene is often referred to as “ π to π^* ” because it corresponds to an electron excited from the highest occupied π orbital to an empty antibonding π^* molecular orbital. Based on your understanding of the light absorbance process, which must be true:

- A) The n to π^* energy difference, corresponding to absorbance in the blue and green regions of the spectrum, is larger for blueberry anthocyanins compared with the π to π^* energy difference in lycopene or β -carotene.
- B) The n to π^* energy difference, corresponding to absorbance in the blue and green regions of the spectrum, is smaller for blueberry anthocyanins compared with the π to π^* energy difference in lycopene or β -carotene.
- C) The n to π^* energy difference, corresponding to absorbance in the orange and red regions of the spectrum, is larger for blueberry anthocyanins compared with the π to π^* energy difference in lycopene or β -carotene.
- D) The n to π^* energy difference, corresponding to absorbance in the orange and red regions of the spectrum, is smaller for blueberry anthocyanins compared with the π to π^* energy difference in lycopene or β -carotene.**