

NAME (Print): _____

Chemistry 310N
Dr. Brent Iverson
1st Midterm
Feb. 16, 2012

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	(20)
3	(19)
4	(18)
5	(16)
6	(24)
7	(20)
8	(24)
9	(21)
10	(13)
11	(13)
12	(19)
13	(14)
14	(4)
15	(12)
Total	(261)
%	
T Score	
HW	
(HW score + Exam Grade) \implies	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)

1. (4 points) What is the most important question in organic 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.

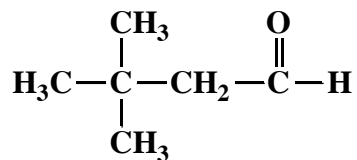
The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely **the flipping (i.e. resonance) of nuclear spins of protons by radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field gradients**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

2 (cont.). (1 pt each) Fill in each blank with the word that best completes the following sentences about NMR.

In the so-called "FT" approach to NMR, all the nuclear _____ **spins** _____ are flipped instantaneously with a multi-frequency pulse, then the rate at which the _____ **spins** "relax" back to the **+1/2 (or lower energy)** state is monitored. This latter approach uses a mathematical algorithm called _____ **Fourier** _____ **transform** (FT) to reconstruct individual resonance signals for the different equivalent sets of hydrogen atoms so the spectra can be plotted. The great thing about this technique is that it allows many spectra to be taken quickly then averaged, dramatically increasing the _____ **signal** _____ -to-noise ratio of the averaged spectra.

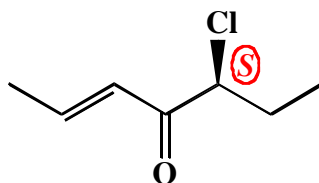
3. (5 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



3,3-Dimethylbutanal

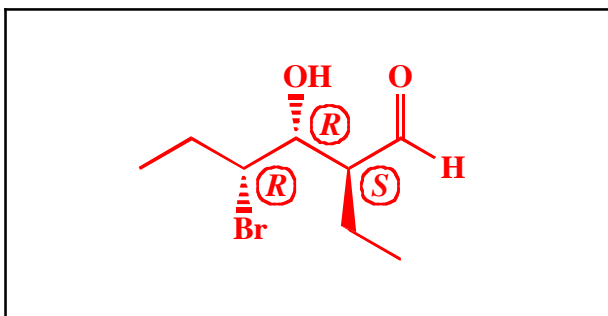
B.



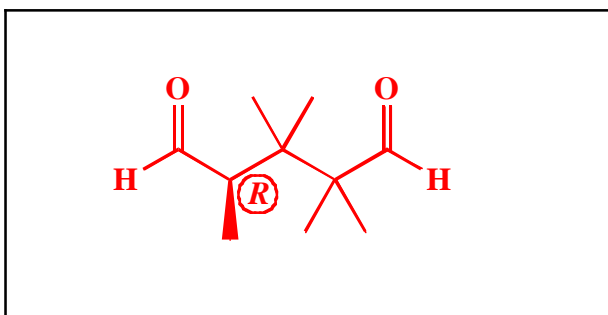
(S,E)-5-Chloro-2-hepten-4-one

It is OK if it says (5S, 2E)

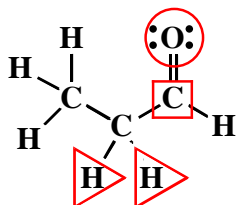
C. **(2S,3R,4R)-4-Bromo-2-ethyl-3-hydroxyhexanal**



D. **(R)-2,2,3,3,4-Pentamethylpentanedial**



6. (8 pts) An important part of chemical understanding is being able to recognize the chemical reactivity of different functional groups. On the aldehyde below, DRAW A BOX around the atom that will be attacked by nucleophiles, DRAW A CIRCLE around the atom that will be protonated in acid, and DRAW TRIANGLES around the most acidic H atom(s).

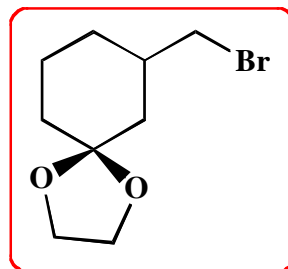
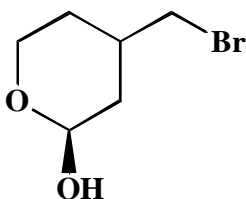
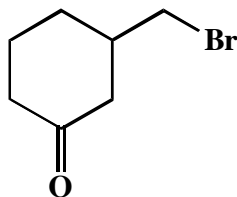
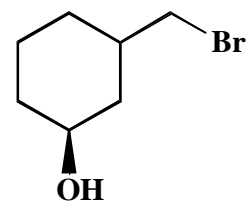
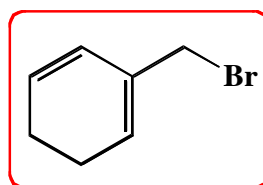
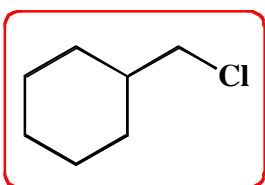
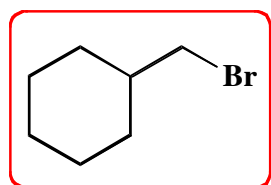


7. (4 pts) Given your answer to all the parts of the last question, what might go "wrong" if you use an organolithium reagent with the same aldehyde (propanal) intending to make a new carbon-carbon bond? Please use no more than two sentences, but be specific in your answer. (EXACTLY what might go wrong in the reaction with propanal?)

Organolithium reagents are **very strong bases**, and they could **deprotonate** the α -hydrogens (triangles) instead of reacting with the carbonyl carbon to make a new carbon-carbon bond.

Note that in the near future we will learn that the enolate is actually an incredibly useful species so that its formation will not be considered the "wrong" result.

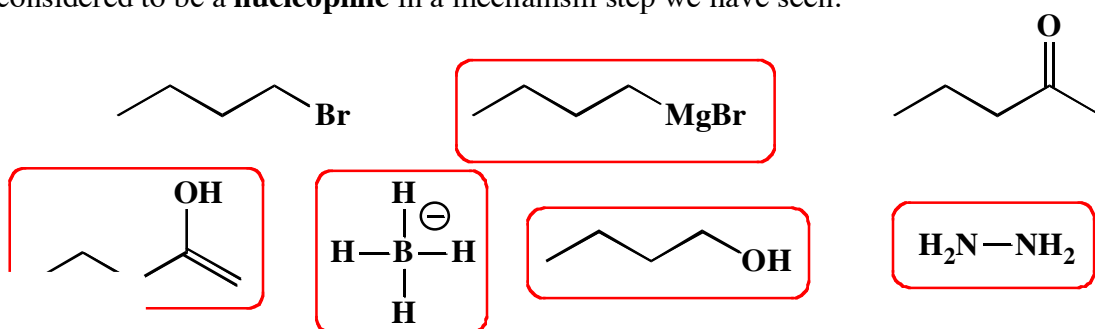
8. (7 pts) Of the list below, circle those molecules that could be used to make a Grignard reagent as shown. No protecting groups allowed for this one!!!



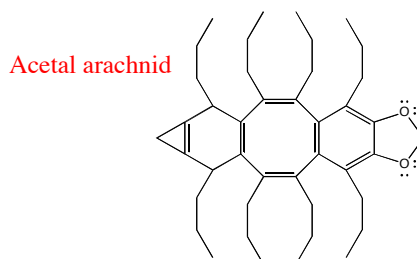
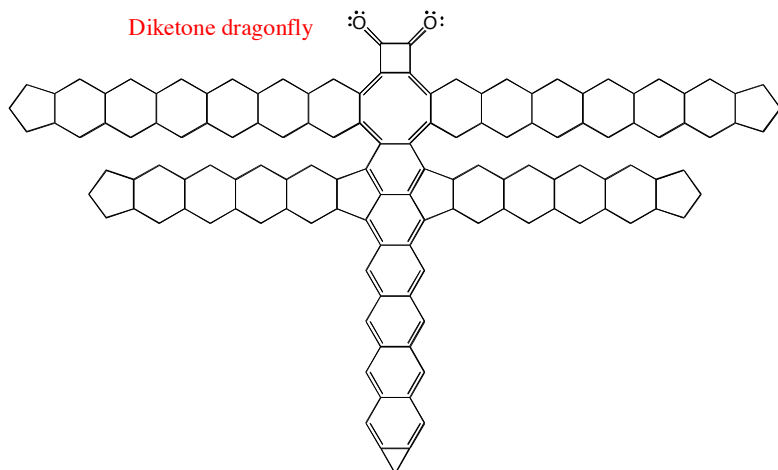
9. (4 pts) List the four mechanistic elements we talked about that together make up the large majority of the mechanism steps we will encounter this semester.

1. **Make a bond** between a nucleophile and an electrophile
2. **Break a bond** to give stable molecules or ions
3. **Add a proton**
4. **Take a proton away**

10. (14 pts) Of the list below, draw a circle around those molecules/reagents that could be considered to be a **nucleophile** in a mechanism step we have seen.

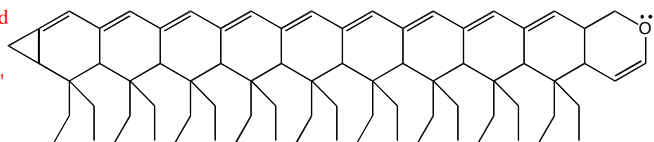


No question here, I just wanted to show you some newly discovered molecular insects. Notice one is a diketone, one is an acetal and the other is an ether.



A highly conjugated ether caterpillar.

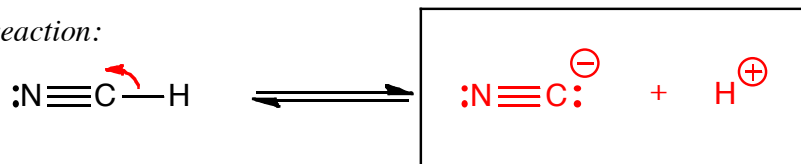
Notice the "pi-way" running along its back.



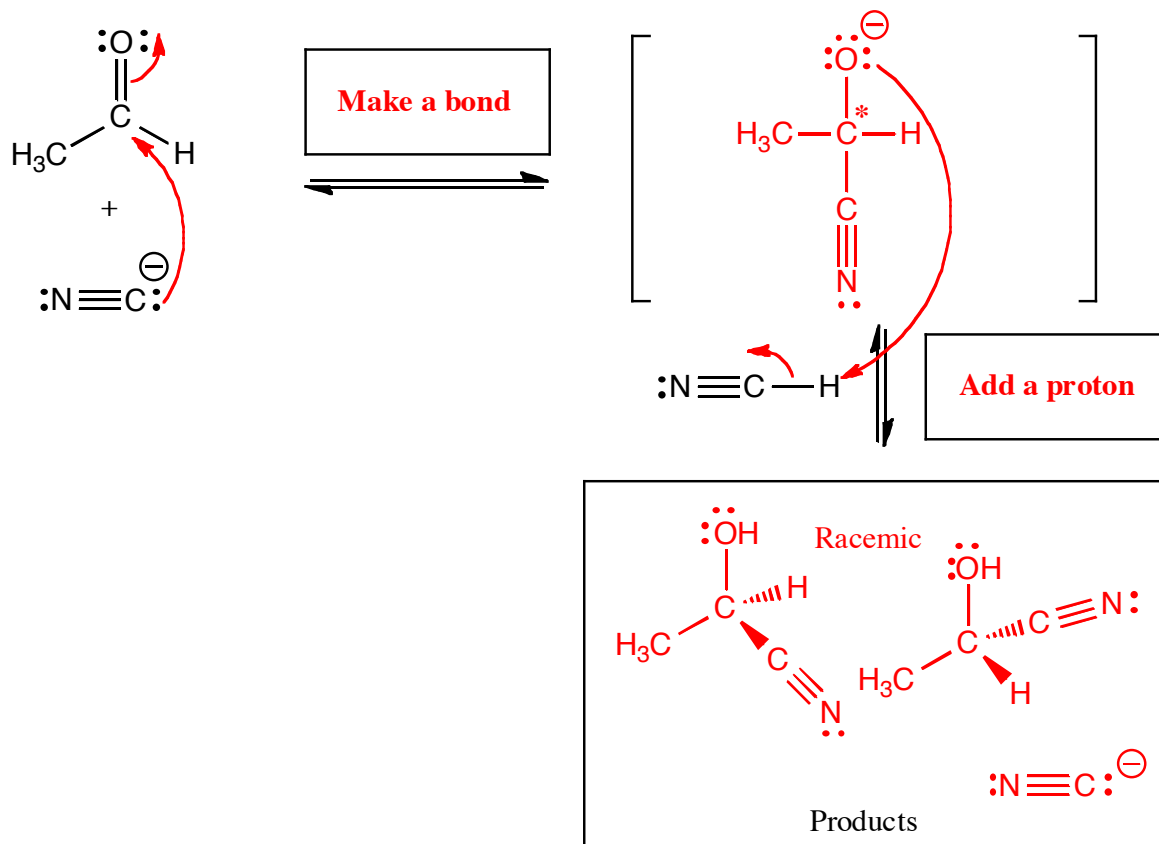
11. (14 pts.) Complete the mechanism for the following reaction of an aldehyde with HCN. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIOMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF RELEVANT.** I realize these directions are complex, so please read them again to make sure you know what we want.

HCN Reacting with an Aldehyde

Equilibrium present in reaction:



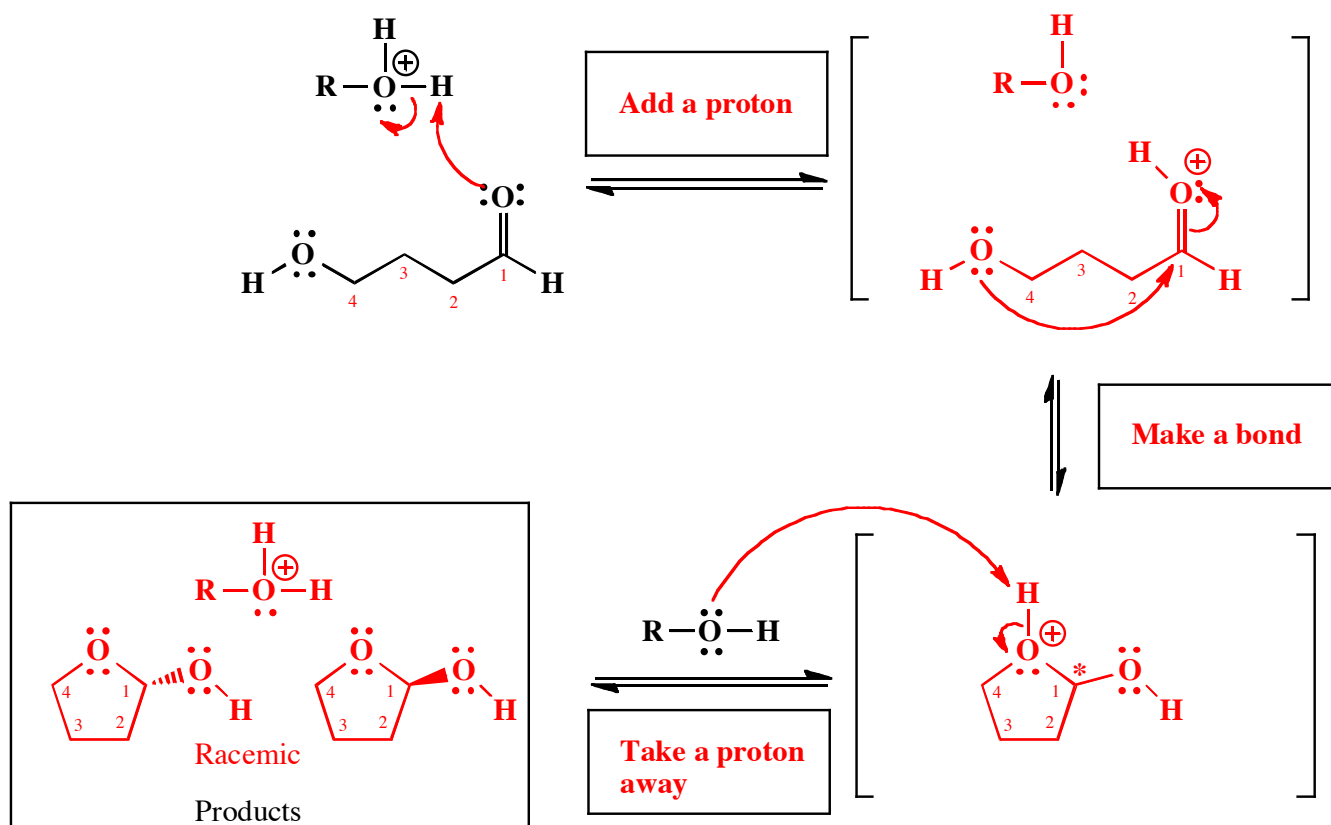
Actual reaction:



(2 pts) In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.

↑↑
NOTICE THIS

12. (17 pts.) Complete the mechanism for the following 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, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIOMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF RELEVANT.** I realize these directions are complex, so please read them again to make sure you know what we want.



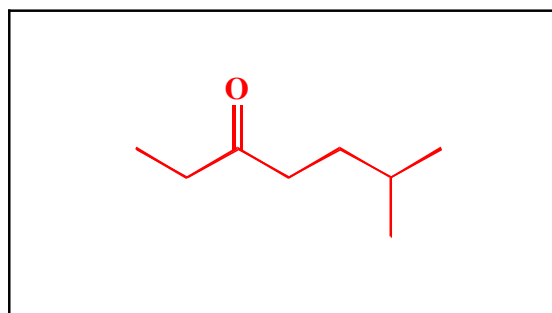
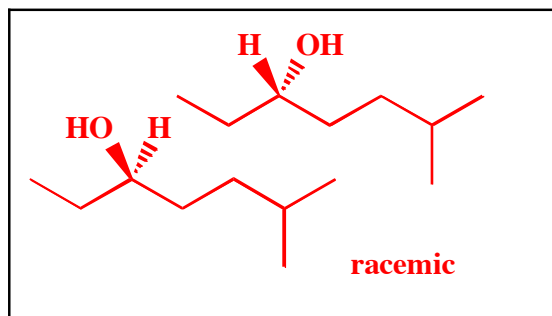
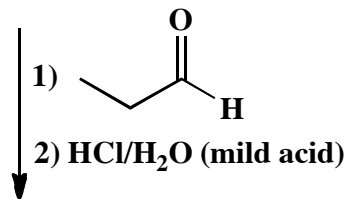
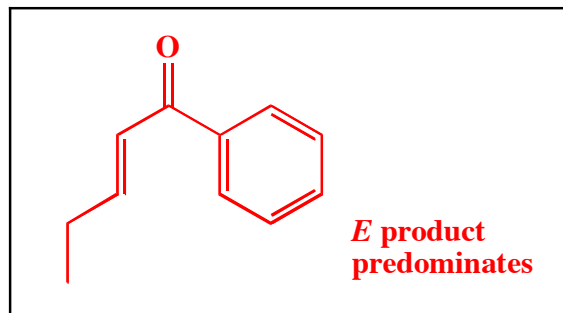
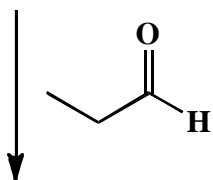
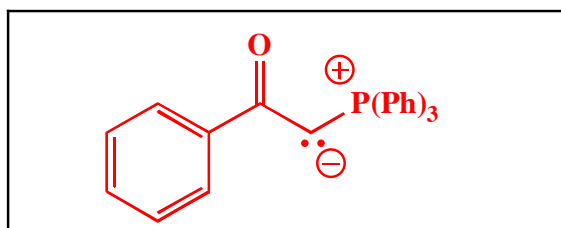
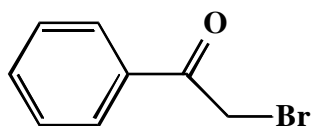
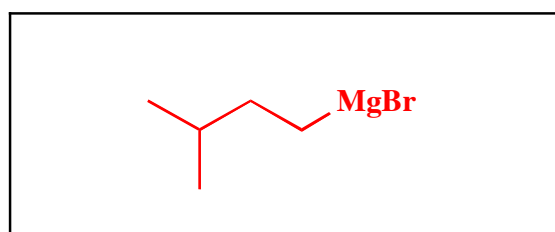
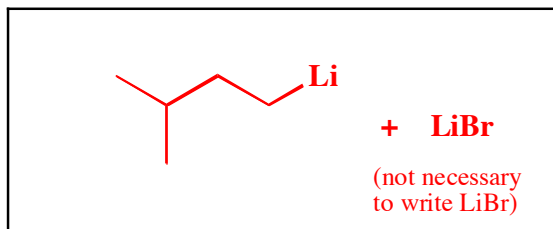
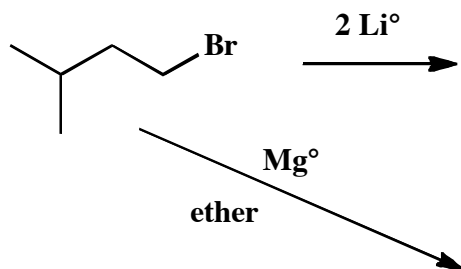
(3 pts) In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc).

↑↑ ↑↑ ↑↑ ↑↑
 NOTICE THIS NOTICE THIS NOTICE THIS NOTICE THIS
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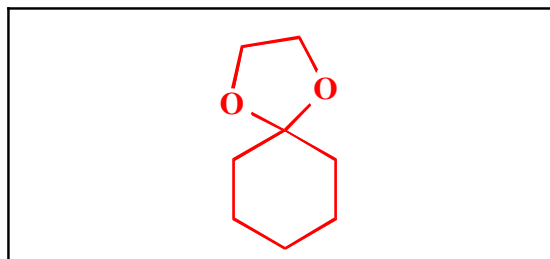
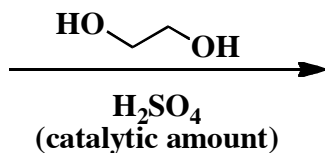
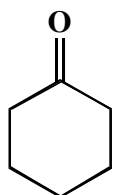
(4 pts) In one sentence, state whether the pH changes during this reaction, and why or why not that is the case.

The pH DOES NOT CHANGE during the reaction because there is no net change in the concentration of protons (i.e. it is catalytic in acid).

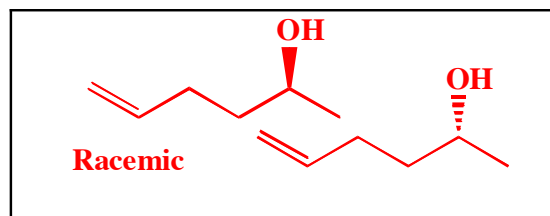
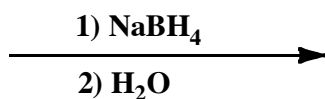
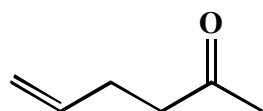
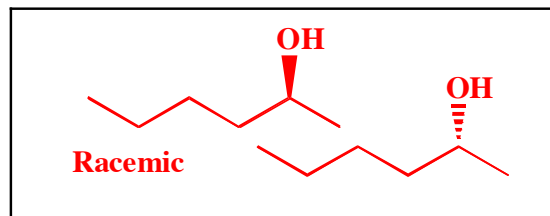
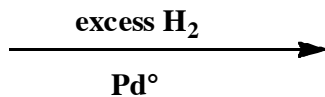
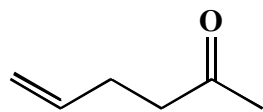
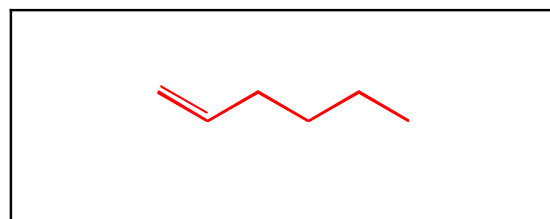
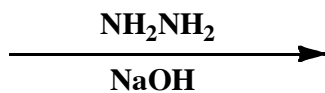
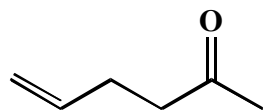
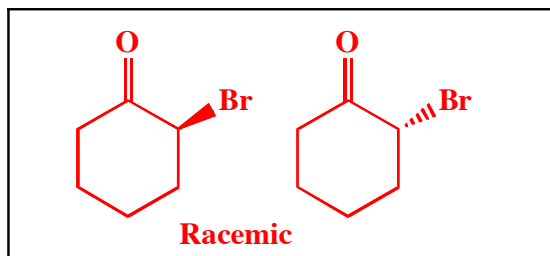
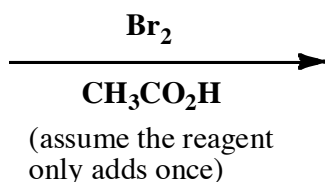
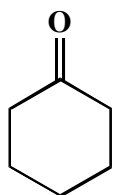
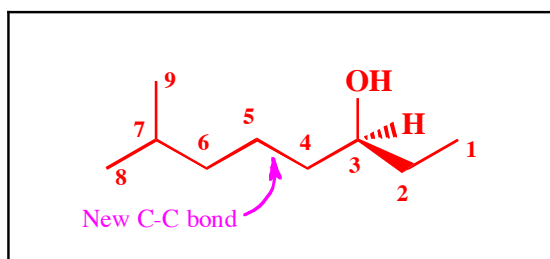
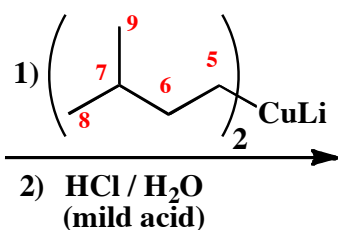
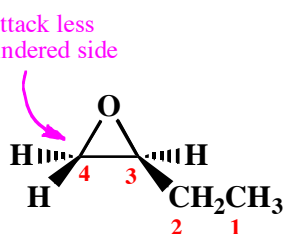
14. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (▲) and dashes (▼) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.



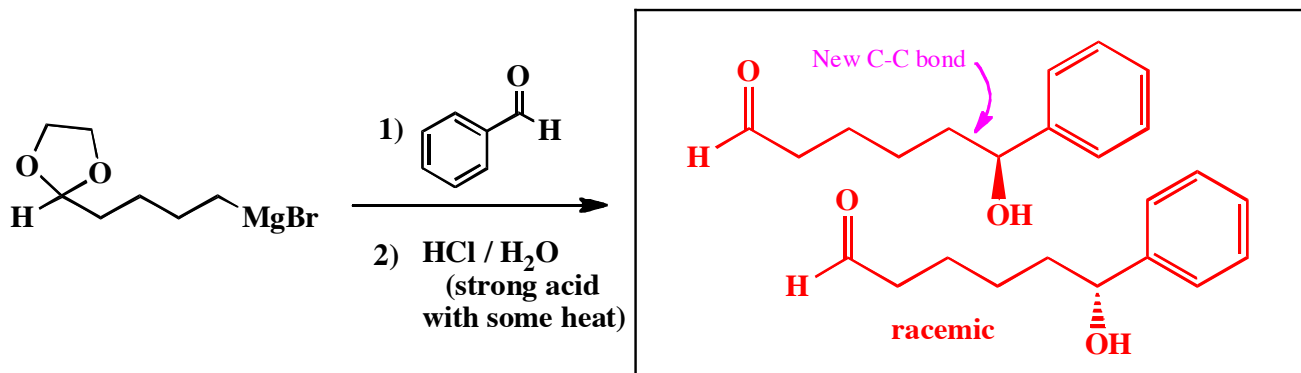
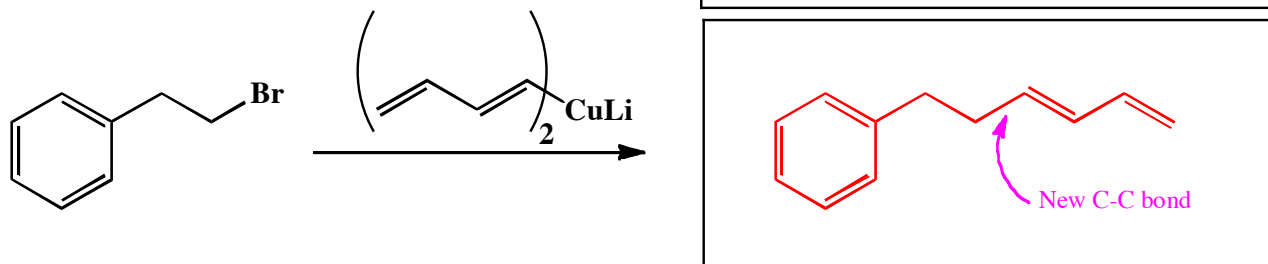
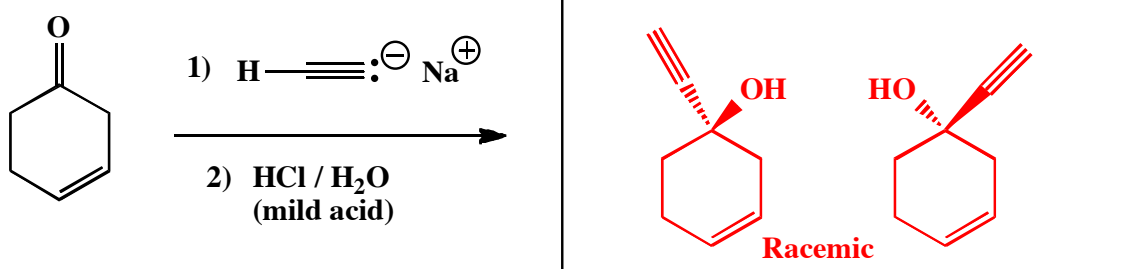
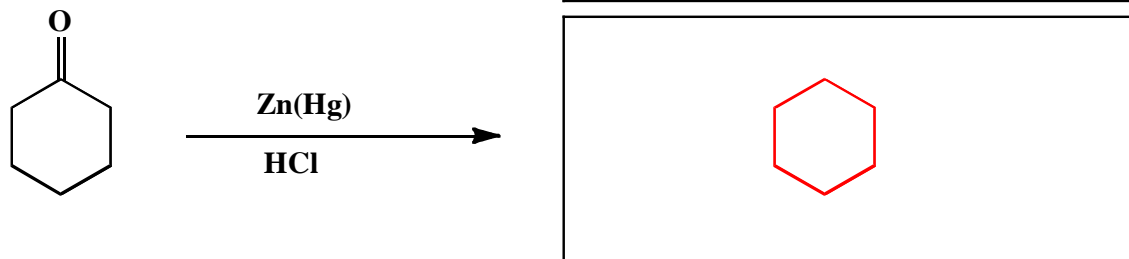
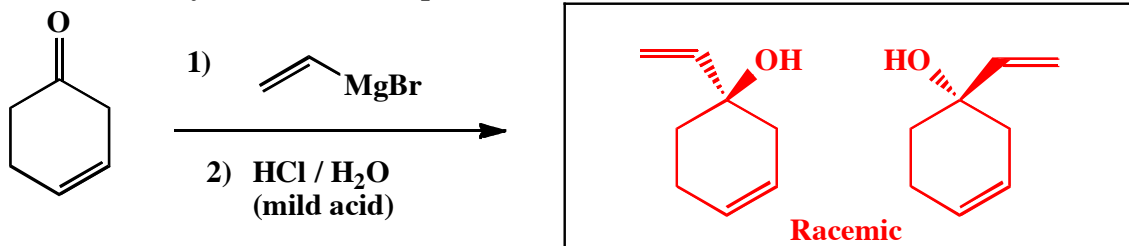
15. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (\blacktriangleleft) and dashes (\dashv) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.



Attack less hindered side

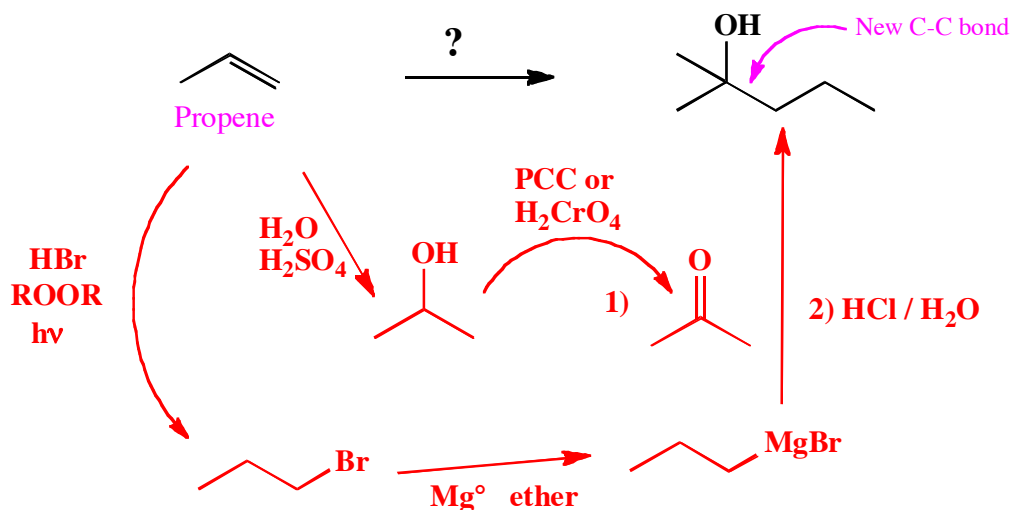


16. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (\blacktriangle) and dashes (\dashv) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.



13. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

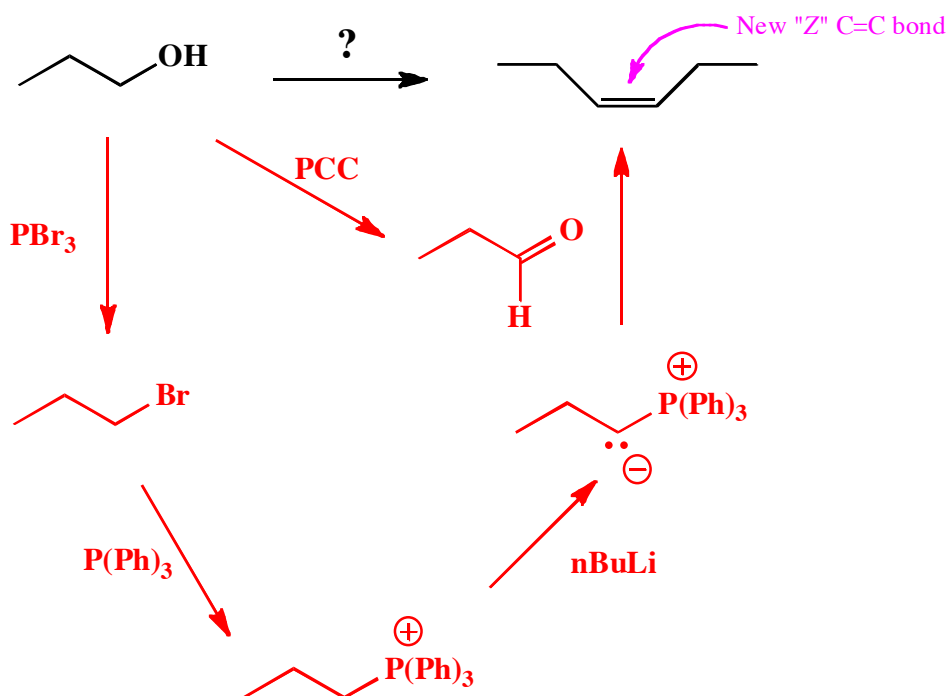
(13 pts) All of the carbon atoms of the products must come from the starting materials for this one!



Recognize that the product has six carbons while the starting material has three. Therefore, predict that two starting material molecules combine in the product. **Predict** further that the new C-C bond created must be as indicated by the arrow. Therefore the product has an -OH group connected to the carbon atom taking part in the new C-C bond, **the KRE of a Grignard reagent reacting with a ketone** (tertiary alcohol product). **Recognize** further that the Grignard reagent must be on the end of propane, and the ketone must be acetone. **Recognize** that the Grignard reagent can be prepared from the corresponding 1-bromopropane, which itself is made from the reaction of HBr with propene in the presence of peroxides and light to insure non-Markovnikov regiochemistry. **Recognize** that acetone can be derived from the Markovnikov addition of H_2O (could have used oxymercuration) to propene followed by oxidation using PCC or H_2CrO_4 .

13. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

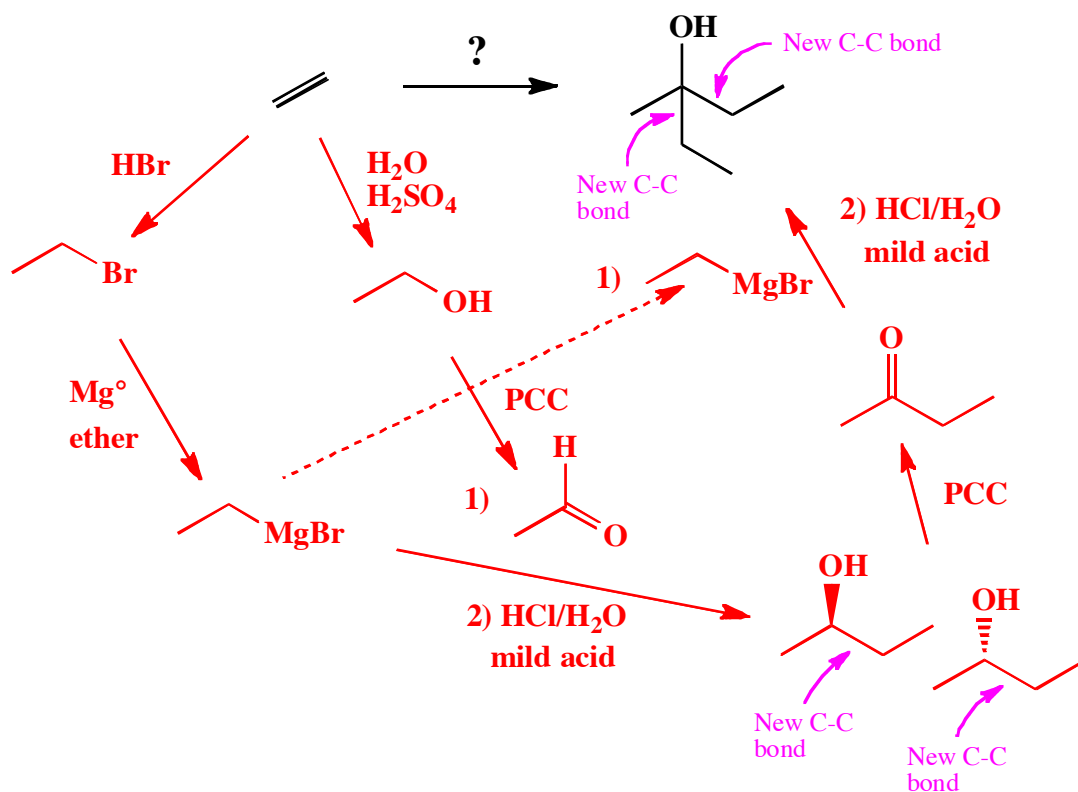
(13 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



Recognize that the product has six carbons while the starting material has three. Therefore, predict that two starting material molecules combine in the product. **Predict** further that the new C=C bond created must be as indicated by the arrow and it is a double bond. Therefore the product has a new "Z" C=C bond, **the KRE of an alkyl Wittig reagent reacting with an aldehyde.. Recognize** that the Wittig reagent can be prepared from the corresponding 1-bromopropane, which itself is made from the reaction of PBr_3 with the 1-propanol starting material. **Recognize** that the required aldehyde, propanaldehyde can be derived from the oxidation of 1-propanol using PCC or H_2CrO_4 .

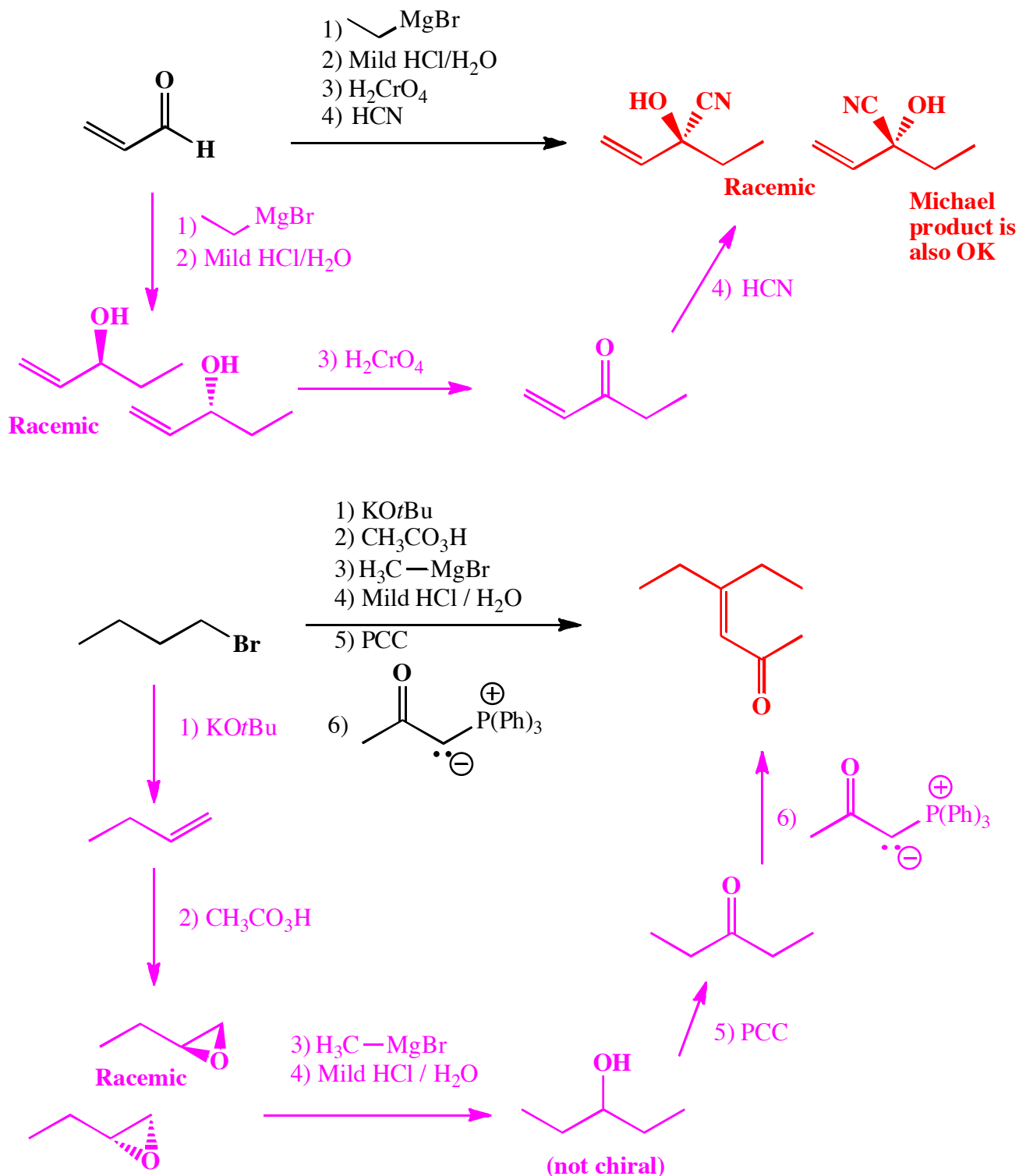
13. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the molecules synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

(19 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



Recognize that the product has six carbons while the starting material has two. Therefore, predict that three starting material molecules combine in the product. **Predict** further that the new C-C bonds created must be as indicated by the arrows. Therefore the product has new C-C bonds connected to the same carbon atom as an -OH group, **the KRE of a alkyl Grignard reagent reacting with a ketone**. **Recognize** that the required ketone can be made from the oxidation of 2-butanol, that in turn can be made from a Grignard reaction between two two-carbon molecules; acetaldehyde reacting with ethyl Grignard. **Recognize** that acetaldehyde can be made from ethene through the two reaction sequence of hydration in acid (or oxymercuration/demercuration) followed by PCC. **Recognize** the ethyl Grignard as coming from ethene via reaction with HBr followed by Mg in ether.

14. (7 pts each) For the following sequences of reactions, work through all the different steps and then write the final product(s). Assume only the predominant product is formed at each step. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. **We are only grading your final product(s) here.**



15. (4 pts each) Here are the MCAT passage style questions. Please read the passage and then answer the multiple choice questions at the end by **circling the correct statement**. The passage will provide you with some new information, and combine that with what you already know to decide which is the best answer for each question.

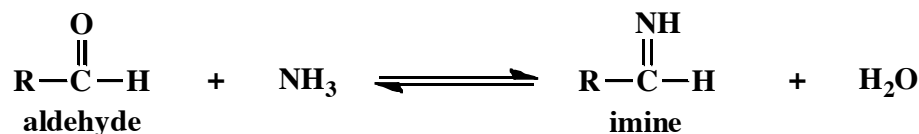
As described along with the Golden Rules of Chemistry, reactions need both "motive" and "opportunity" to occur. The "motive" refers to the requirement for a thermodynamic driving force. Stated another way, a reaction will be favorable if the products are of lower free energy than the starting materials. In a practical sense this usually happens when the bonds being made in the reaction are stronger than the bonds broken. The "opportunity" refers to the reaction mechanism. There can be no unusually high energy barriers if a reaction is proceed quickly. The higher the energy barrier, the slower the reaction. A high energy barrier will be present if there is any unfavorable step in the reaction mechanism, so understanding the mechanism can help you predict relative energy barriers in reactions.

The strength of chemical bonds is usually listed in terms of a table of bond dissociation enthalpies (BDE's) A bond dissociation enthalpy is the energy required to break a bond to give two radicals as shown:



	Bond dissociation enthalpy
H ₂ C=CH ₂ (both bonds together)	147 kcal/mol
H ₂ C=O (both bonds together)	180 kcal/mol
H ₂ C=NR (both bonds together)	148 kcal/mol
H ₃ C-CH ₃	90 kcal/mol
H ₃ C-H	105 kcal/mol
H ₃ C-OH	92 kcal/mol
H ₃ CO-H	105 kcal/mol
H ₂ N-H	93 kcal/mol
HO-H	119 kcal/mol

We learned that aldehydes and ketones will react with amines to give imines according to the following reaction (shown here for an aldehyde):



Use the table of bond dissociation enthalpies to choose the correct statement from among the following:

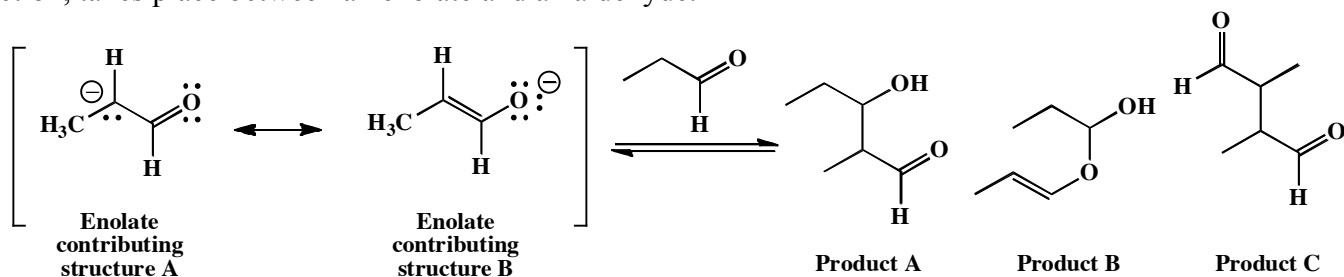
- A. Equilibrium favors imine formation because a C=N bond is significantly stronger than a C=O bond.
- B. Equilibrium favors imine formation because the O-H bond in water is considerably stronger than the N-H bond in ammonia.
- C. Equilibrium favors the aldehyde because a C=O bond is significantly stronger than a C=N bond.
- D. Equilibrium favors the aldehyde because the N-H bond in ammonia is considerably stronger than the O-H bond in water.

15 cont. (4 pts each)

Recall that the order of acidity of water, methanol, ammonia and methane is: water and methanol are roughly tied for being the most acidic, followed by ammonia. Methane being is by far the least acidic. Which of the following statements must therefore be true:

- A. There is a direct correlation between increasing acidity and increasing bond dissociation enthalpy.
- B. There is a direct correlation between increasing acidity and decreasing bond dissociation enthalpy.
- C. There is a rough correlation between increasing acidity and decreasing bond dissociation enthalpy.
- D. There is no correlation between acidity and bond dissociation enthalpy, so relative acidity must be determined by parameters other than relative bond enthalpies.

Last Friday you were introduced to the anion called an enolate that is produced when the α -hydrogen of an aldehyde or ketone is deprotonated. The great thing about enolates is that they can act as nucleophiles when reacting with other carbonyls. For example, the following reaction, called an aldol reaction, takes place between an enolate and an aldehyde.



Enolate contributing structure B is the major contributor because the negative charge is on the more electronegative O atom. The mechanism of the aldol reaction is carbonyl addition mechanism A: “Make a bond” at the carbonyl carbon followed by “Add a proton”.

- A. As written, Product A can be rationalized as coming from attack of the aldehyde carbonyl by the C atom of the enolate followed by the addition of a proton.
- B. As written, Product A can be rationalized as coming from attack of the aldehyde carbonyl by the O atom of the enolate followed by the addition of a proton.
- C. As written, Product B can be rationalized as coming from attack of the aldehyde carbonyl by the C atom of the enolate followed by the addition of a proton.
- D. As written, Product C can be rationalized as coming from attack of the aldehyde carbonyl by the C atom of the enolate followed by the addition of a proton.

Use the information in the BDE table to identify the correct statement about the distribution of the products at equilibrium.

- A. Product A is the predominant product.
- B. Product B is the predominant product.
- C. Product C is the predominant product
- D. Products A, B, and C are formed in roughly equal amounts.