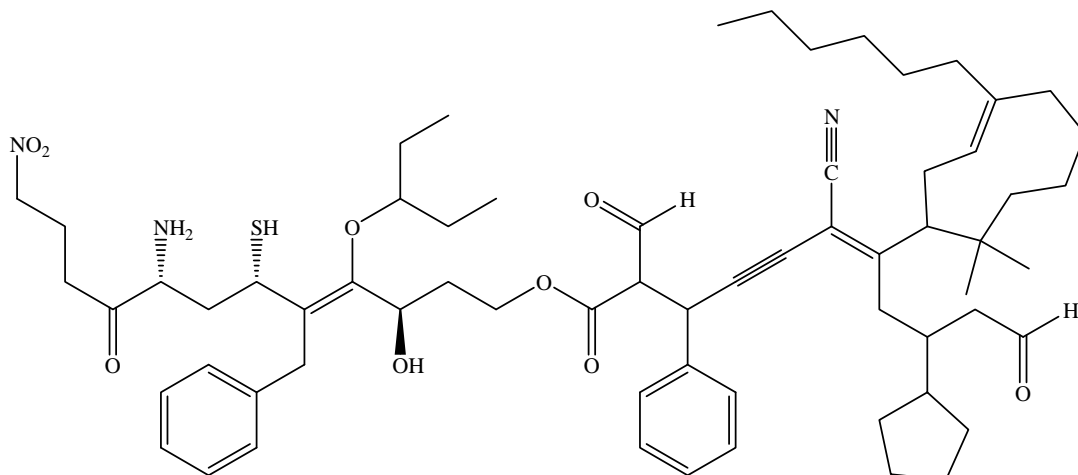


Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	X	
2. Various possibilities: Types of Isomers, Degrees of Unsaturation, common nomenclature, polarity, logic arguments of organic chemistry	X	
3. Cyclohexane Conformations, 2 substituents, Newman Projections	X	
4. Newman Projections, Conformational Energies	X	
5. Stereochemical Analysis	X	
6. 3D Structure, Hybridization, Angles, Shapes	X	
7. Forces of Interaction and Physical Properties, Inductive and Resonance Effects	X	
8. Acid / Base Chemistry, Explanation, Curved Arrows, Formal Charge	X	
9. S _N /E Mechanisms, with all of the details	X	
10. Various Reactions, predict the products (20 reactions)	X	
11. Fill in all mechanistic details, curved arrows, lone pairs, formal charge, 3 examples in acid or base	X	
12. S _N /E Chemistry, Carbocations	X	
13. Free Radical Chemistry	X	
Total	X	

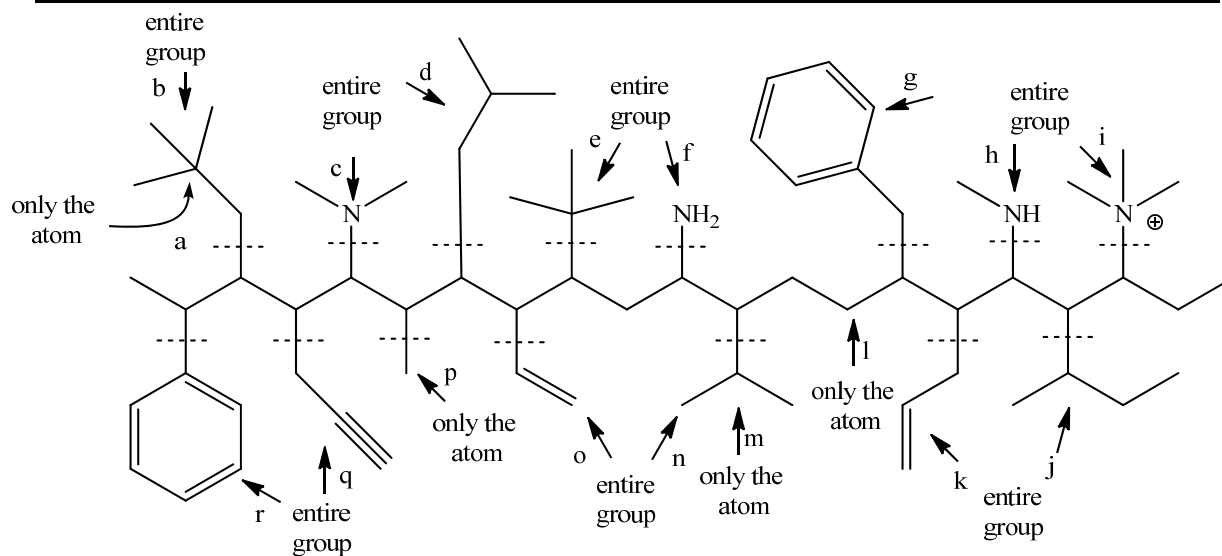
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Do your best to show me what you know in the time available.

1. Provide an acceptable name for the following molecule. (X pts)



2. Match the arrows with the terms. Some arrows may be associated with more than one term. (X pts)

- | | | | |
|------------------------|----------------------|---------------------|-----------------------------------|
| 1. vinyl _____ | 7. sec-butyl _____ | 13. methyl _____ | 19. quaternary ammonium ion _____ |
| 2. allyl _____ | 8. t-butyl _____ | 14. methylene _____ | 20. tertiary amine _____ |
| 3. propargyl _____ | 9. neopentyl _____ | 15. methine _____ | 21. secondary amine _____ |
| 4. phenyl _____ | 10. quaternary _____ | 16. primary _____ | |
| 5. benzyl _____ | 11. isopropyl _____ | 17. secondary _____ | |
| 6. primary amine _____ | 12. isobutyl _____ | 18. tertiary _____ | |



3. Draw all possible chair conformations of trans-1-ethynyl-2-phenylcyclohexane. Draw C1 as the left-most carbon and number towards the front. Show all axial and equatorial groups. Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw a Newman projections of the more stable conformation using the $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ bonds to sight along. Point out any gauche interactions shown in your Newman projection. If the axial energy of a ethynyl group is 0.5 kcal/mole and 2.9 kcal for a phenyl group and a ethynyl/phenyl gauche interaction is 1.0 kcal/mole, what is the difference in energy between the chair conformations? What is the ratio of the more stable conformation to the less stable conformation? Sketch an energy diagram that shows how the energy changes with the conformational changes. (X pts)

a.
$$K = 10^{\frac{-\Delta G}{2.3RT}}$$

$$R = 2 \text{ cal/mol-K}$$

$$T = 300 \text{ K}$$



(15 pts)

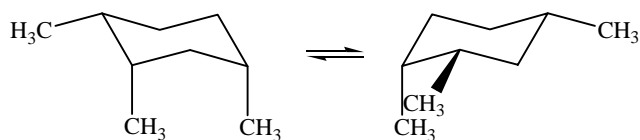
chair 1

chair 2

- b. Newman projection ($C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$) – most stable, point out any gauche interactions with the substituent(s)

- c. Energy diagram (lower to higher) and relative percents ($K_{eq} = ?$) (5 pts)

- d. Calculate an approximate ΔH difference between the two conformations. Use that value to estimate a K_{eq} . (Assume $R = 2 \text{ cal/mol-K}$ and $T = 300 \text{ K}$.) Use energy values provided in the box. Show your work. (5 pts)



One axial methyl group = +1.7 kcal/mole,
 Two axial methyl groups, on the same side (cis) = +5.5 kcal/mole,
 Three axial methyl groups, on the same side = +12.9 kcal/mole and
 1,2 gauche methyl groups = 0.8 kcal/mole.

$\Delta H \approx$

$K_{eq} \approx$

4. Use a Newman projection of the C1→C2 bond of 2-methyl-1-phenylbutane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight. (X pts)

2D structure

Approximate Eclipsing Energy Values (kcal/mole) Some were estimated by me.							
	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	1.0	1.4	1.5	1.6	3.0	1.7	1.6
Me	1.4	2.5	2.7	3.0	8.5	3.3	2.8
Et	1.5	2.7	3.3	4.0	10.0	3.8	3.1
i-Pr	1.6	3.0	4.0	7.8	13.0	8.1	3.6
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5	9.1
Ph	1.7	3.3	3.8	8.1	13.5	8.3	4.2
Br	1.6	2.8	3.1	3.6	9.1	4.2	3.0

$$\Delta G \approx \Delta H$$

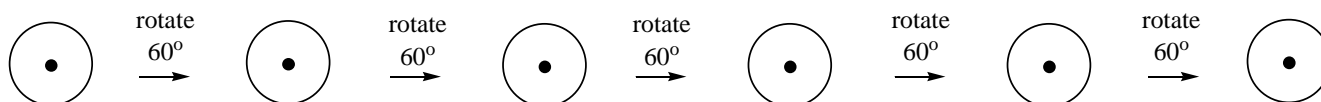
$$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$$

Approximate Gauche Energy Values (kcal/mole) Some were estimated by me.							
	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	0	0	0.1	0.2	0.5	0.2	0.1
Me	0	0.8	0.9	1.1	2.7	1.4	1.0
Et	0.1	0.9	1.1	1.6	3.0	1.5	1.3
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1	1.6
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9	3.3
Ph	0.2	1.4	1.5	2.1	3.9	2.3	1.9
Br	0.1	1.0	1.3	1.6	3.3	1.9	1.1

most stable
conformation



(14 pts)



$\Delta H^\circ =$

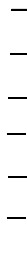
$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

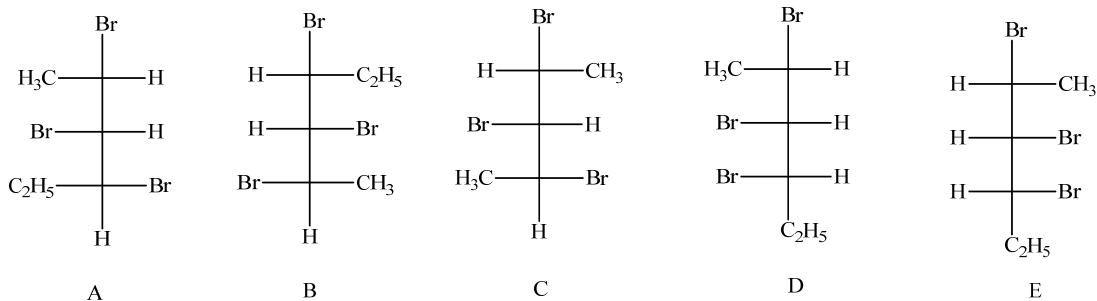
$\Delta H^\circ =$



(4 pts)

$K_{\text{calculation}}$ (4 pts)

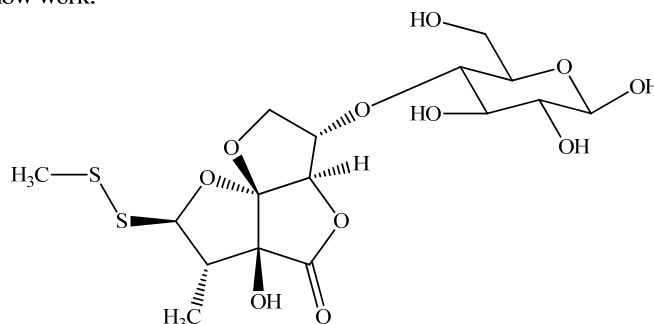
5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (X pts)



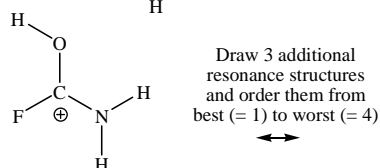
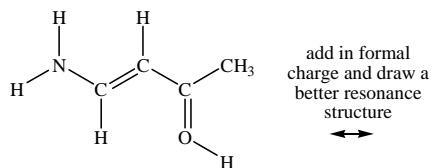
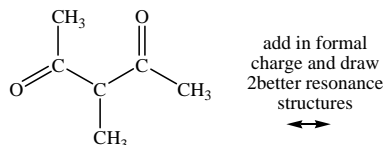
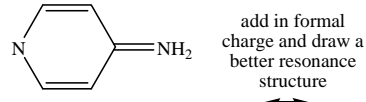
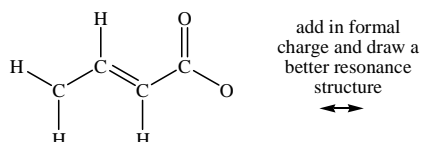
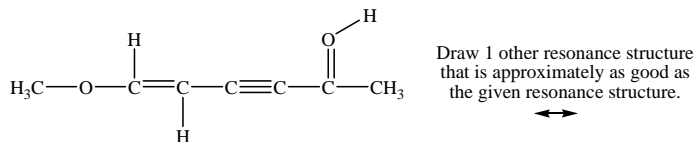
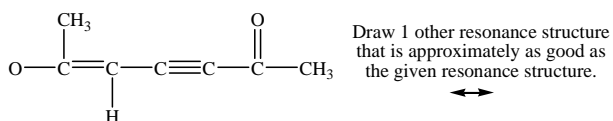
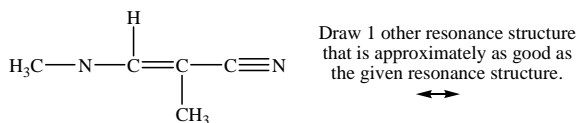
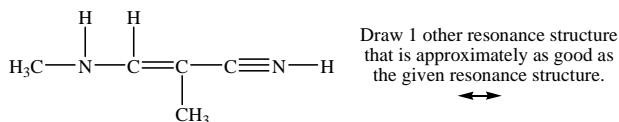
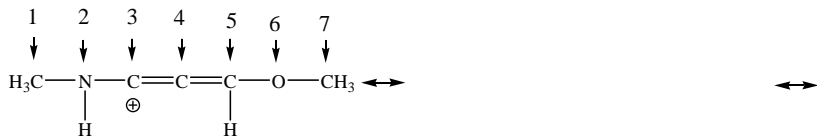
- | | |
|---|---|
| a. Which are optically active? | A B C D E |
| b. Which are meso? | A B C D E |
| c. Which is not an isomer with the others? | A B C D E |
| d. Which pairs are enantiomers? | AB AC AD AE BC BD BE CD CE DE |
| e. Which pairs are identical? | AB AC AD AE BC BD BE CD CE DE |
| f. Which pairs are diastereomers? | AB AC AD AE BC BD BE CD CE DE |
| g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? | AB AC AD AE BC BD BE CD CE DE |
| h. Draw any stereoisomers, which are not shown above, as Fischer projections. If there are none, indicate this. | |

- i. In the most recent Organic Letters, 2018, 20, 28-31, three new sulfur compounds were isolated from welsh onion plant grown in Kyoto, Japan (only Kujounin A₁ is shown). Circle all of the chiral centers. How many stereoisomers are possible? Show work.

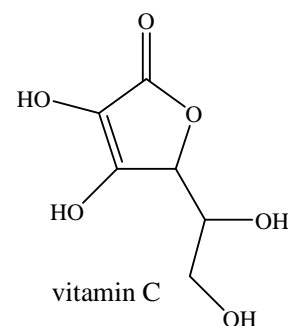
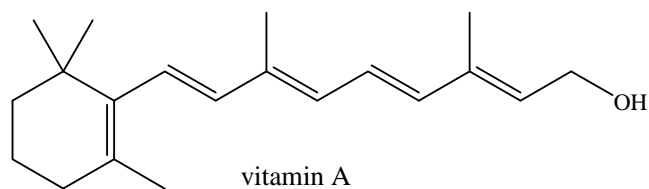
Kujounin A₁ has anti-cancer activity.



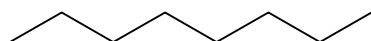
6. Draw additional 2D resonance structures of the given structure as indicated. Which structure(s) is (are) best and why? Draw a 3D structure for the best resonance structure. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Be able to identify the hybridization, bond angles and descriptive shape for all non-hydrogen atoms. (X pts)



7. a. The structures of vitamin A and vitamin C are shown below. If they are taken in large daily amounts one is toxic and one is not. Explain why this observation is reasonable? (X pts)

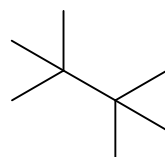


- b. The melting points and boiling points for the following two compounds are: -57°C , 101°C , 106°C and 126°C . Match those temperatures with the structures below and provide a possible explanation for the differences. (X pts)



$T_{\text{bp}} =$

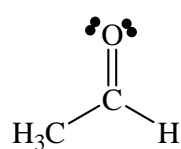
$T_{\text{mp}} =$



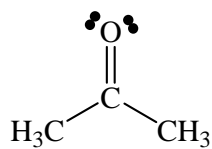
$T_{\text{bp}} =$

$T_{\text{mp}} =$

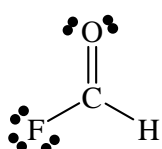
- c. Explain what the following dipole moments suggest about inductive effects and resonance effects in organic and biochemistry. You may need to draw additional structures to help your explanation. (X pts)



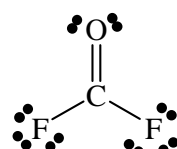
$\mu = 2.68$



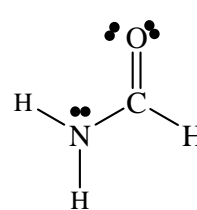
$\mu = 2.91 \text{ D}$



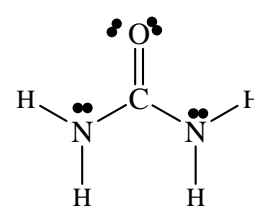
$\mu = 2.02$



$\mu = 0.95$

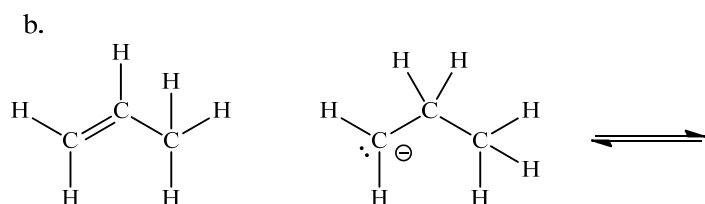
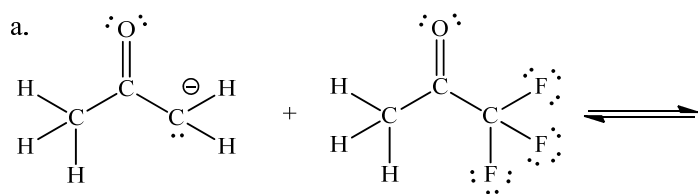


$\mu = 3.71$

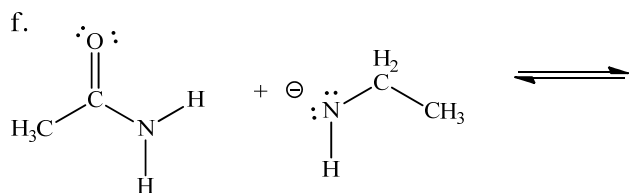
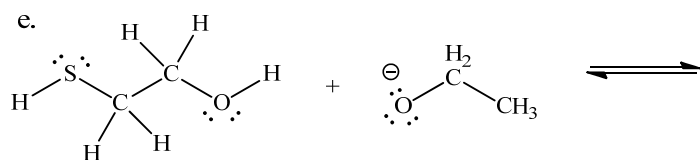
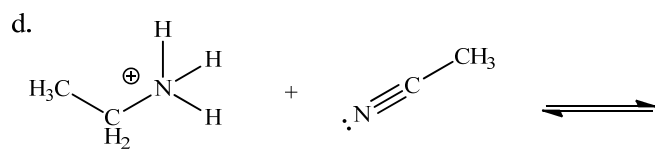
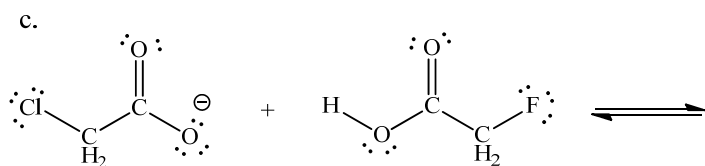


$\mu = 4.56$

8. Using arrow-pushing mechanisms, write the expected products from the following reactions and indicate whether the equilibrium lies to the “right” or to the “left”. Also, very briefly explain your reasoning. (X pts)

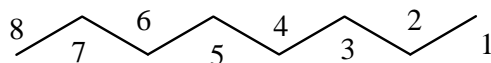


The two acids have K_a 's of 10^{-50} and 10^{-42} . Calculate an equilibrium constant for this reaction.



9. 5. Use 4S-bromo-5R-deuteriooctane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants are not drawn in the proper orientation to show how the reaction must proceed, then redraw them in a more informative way that shows this. **Do not** consider carbocation rearrangement possibilities. (40 pts)

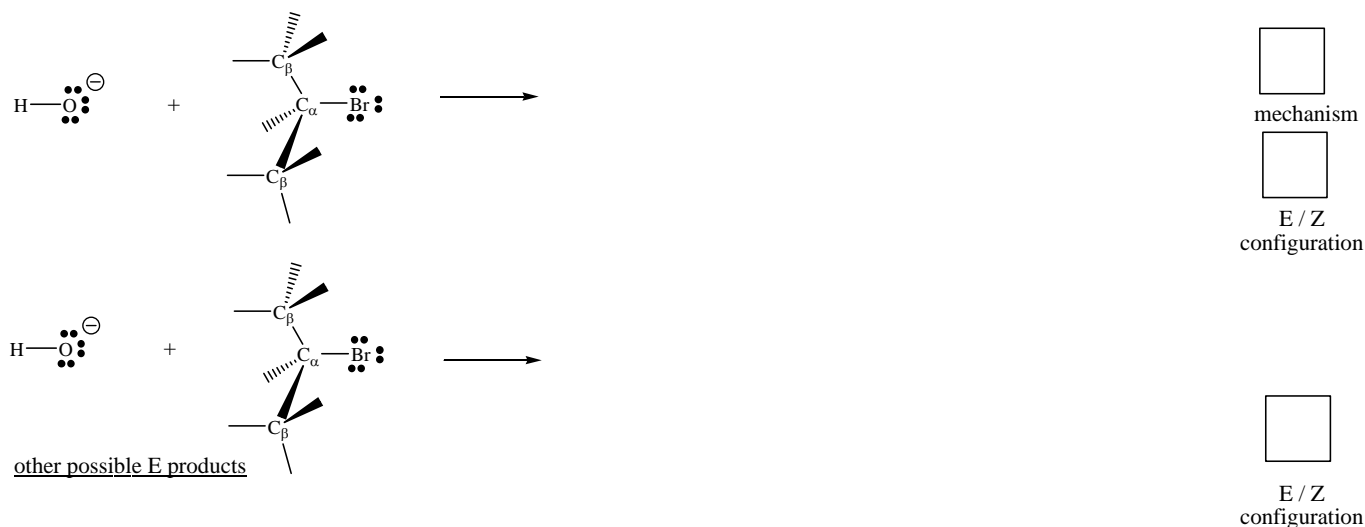
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)



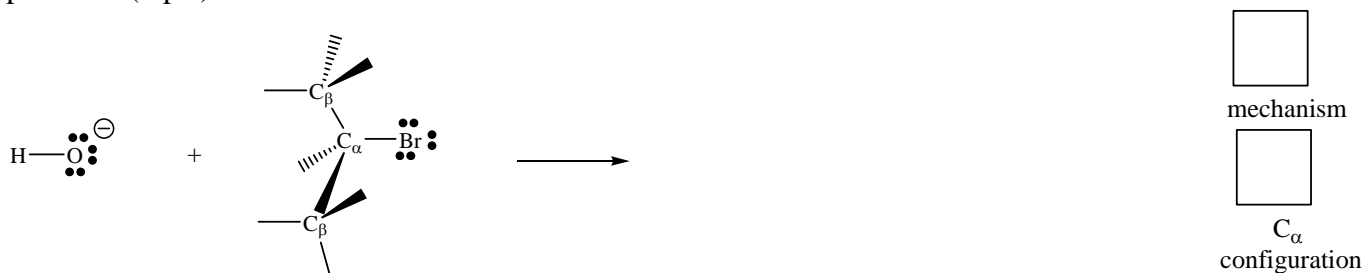
2D structure

3D structure of (4S,5R)-5-deuterio-4-bromooctane

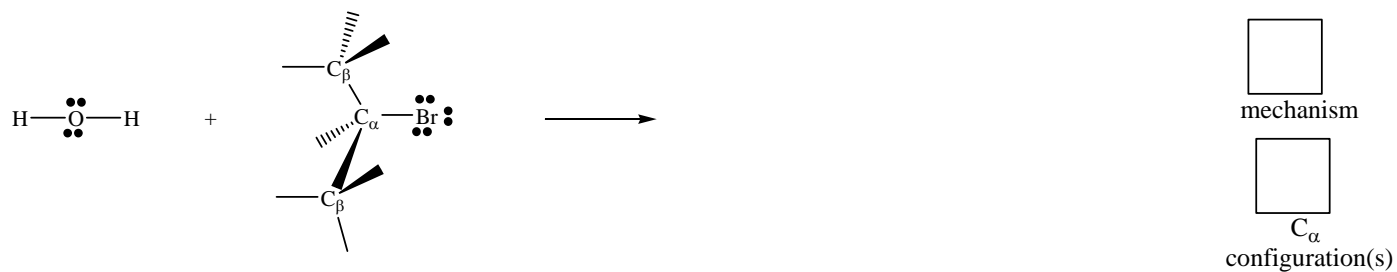
b. Show a mechanism for each C_β position and simply draw all other possible E reaction products (what kind?). Indicate if E, Z or neither. You can abbreviate common branch names if they are not part of your mechanism. There may or may not be fewer products than there are numbers. (10 pts)



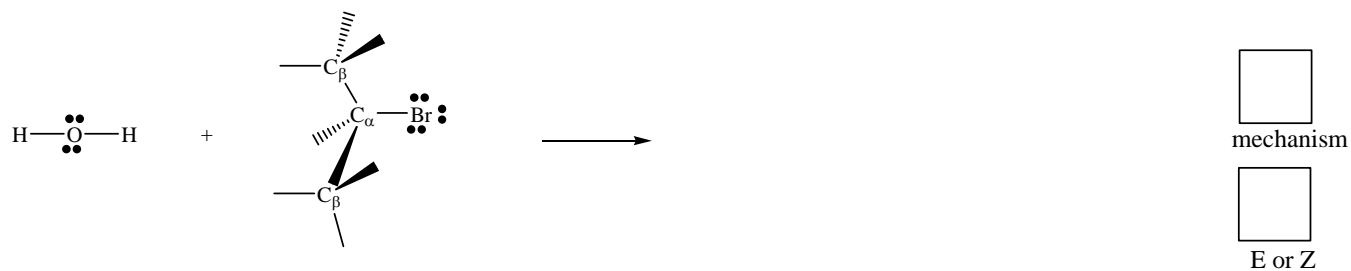
c. Show the S_N reaction (what kind?), indicate the absolute configuration(s) of the C_α center in the product. (6 pts)



d. Show all steps of the S_N reaction (what kind?). You can use one intermediate to show all possible S_N possibilities. Indicate the absolute configuration(s) of the C_α center in the product. You can abbreviate common branch names if they are not part of your mechanism (9 pts)



e. Show a mechanism for two E products and simply draw all other possible E reaction products (you can use the same intermediate for your two mechanisms). Indicate if E, Z or neither. There may or may not be fewer products than numbers. (12 pts)



other possible E products

1

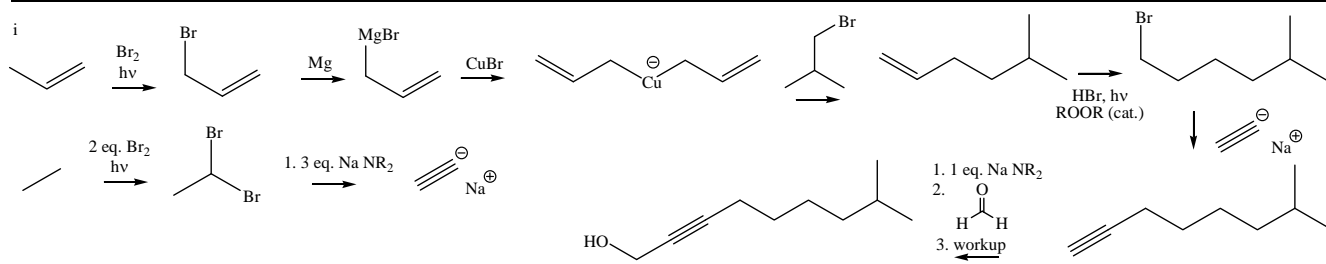
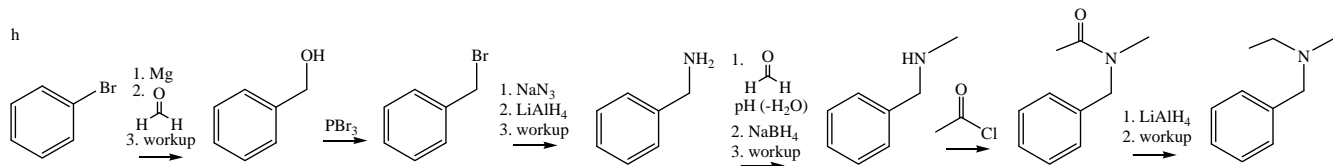
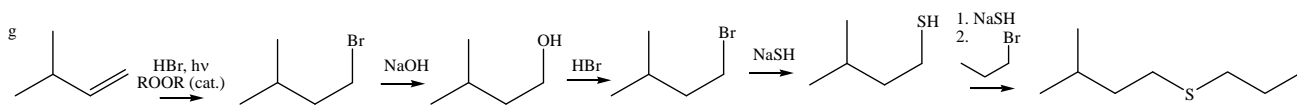
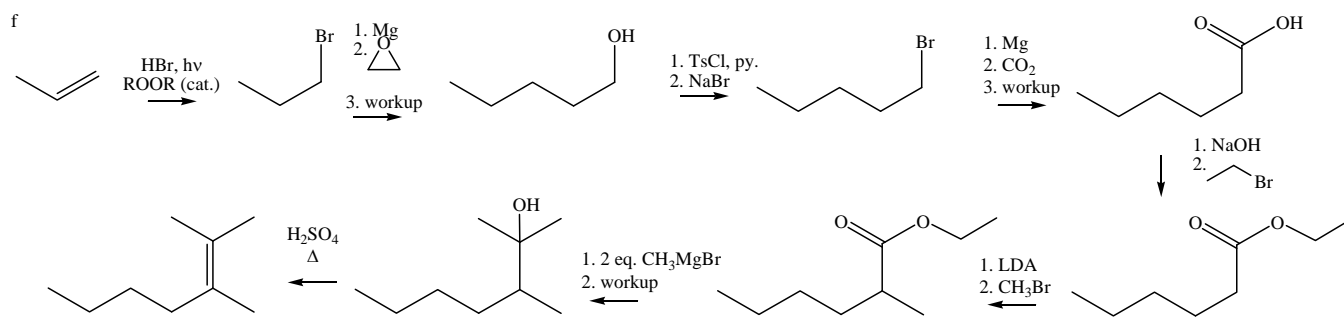
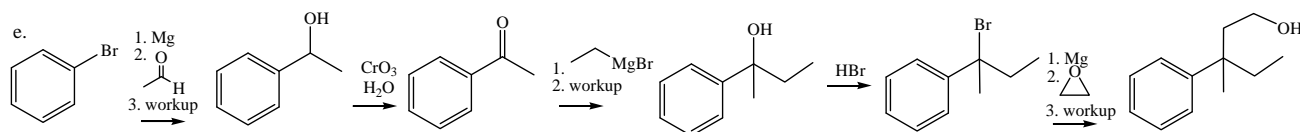
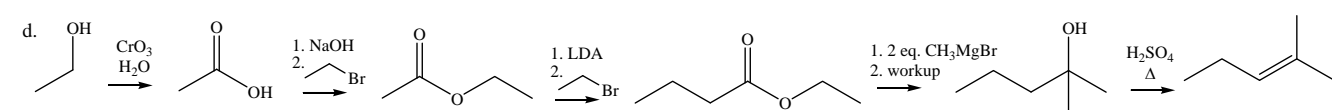
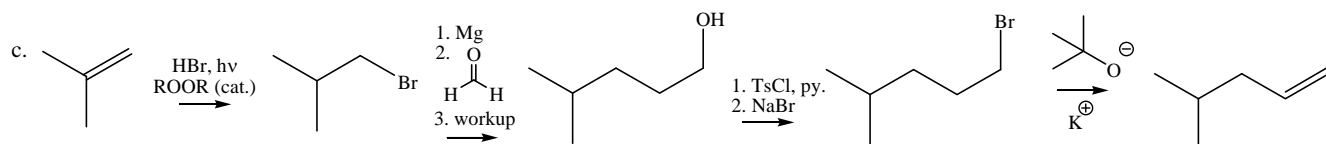
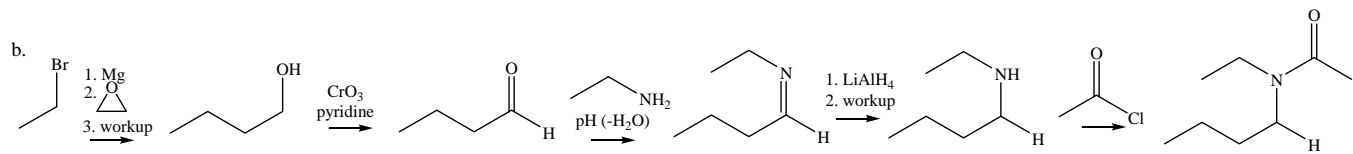
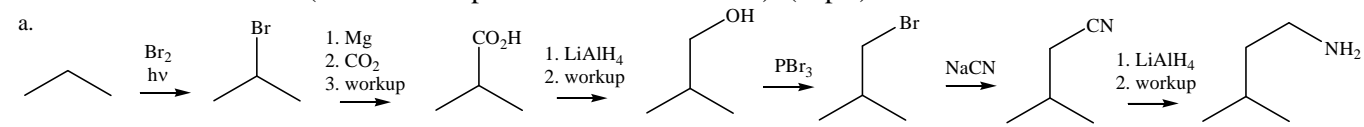
2

3

4

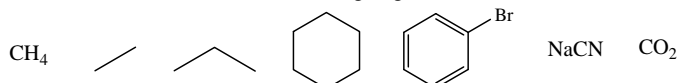
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








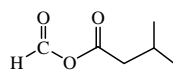
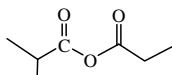
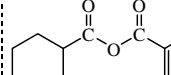
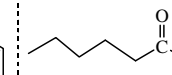















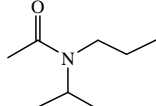
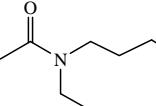
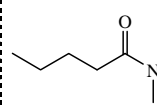
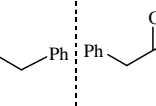
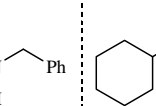




















































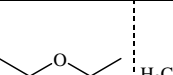
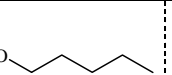
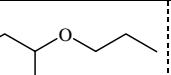
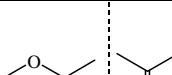
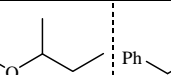
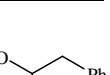
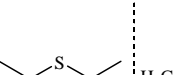
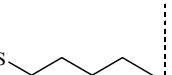
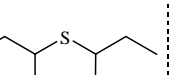
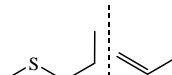
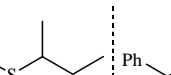
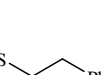
10. Indicate the **major** product in the following reactions. Indicate stereochemistry if part of the reaction. Do NOT show mechanisms. (WK = workup = neutralize conditions) (X pts)
















































11. Propose syntheses for any of the following molecules from the given starting structures.

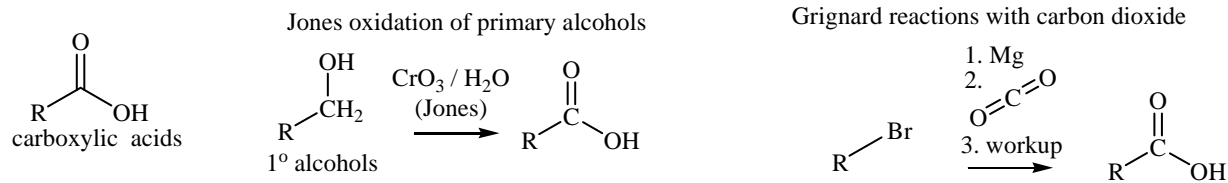
Allowed carbon structures for the following target molecules (TM).



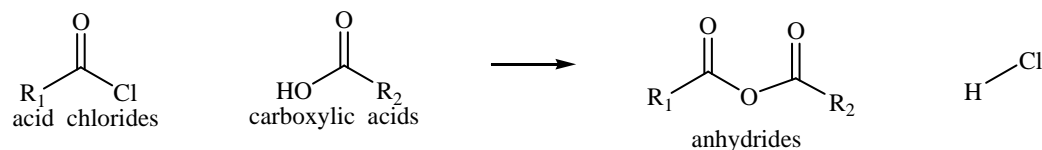
$\text{R}-\text{C}(=\text{O})-\text{OH}$ carboxylic acids	        
$\text{R}_1-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{R}_2$ carboxylic acids	   
$\text{R}_1-\text{C}(=\text{O})-\text{O}-\text{R}_2$ esters	     
$\text{R}-\text{C}(=\text{O})-\text{Cl}$ acid chlorides	        
$\text{R} = \text{H or C}$ $\text{R}_1-\text{C}(=\text{O})-\text{N}(\text{R}_2)(\text{R}_3)$ 1°, 2°, 3° amides	    
$\text{R}-\text{C}\equiv\text{N}$ nitriles	       
$\text{R}-\text{C}(=\text{O})-\text{H}$ aldehydes	        
$\text{R}_1-\text{C}(=\text{O})-\text{R}_2$ ketones	        
$\text{R}-\text{O}-\text{H}$ alcohols	        
$\text{R}-\text{S}-\text{H}$ thiols	        
$\text{R} = \text{H or C}$ $\text{R}_1-\text{N}(\text{R}_2)(\text{R}_3)$ 1°, 2°, 3° amines	       
$\text{R}_1-\text{O}-\text{R}_2$ ethers	     
$\text{R}_1-\text{S}-\text{R}_2$ thioethers / sulfides	     

$\text{R}-\text{Br}$ bromohydrocarbons	$\text{H}_3\text{C}-\text{Br}$         
$\text{R} = \text{H or C}$ $\text{R}_1-\text{C}(\text{R}_2)=\text{C}(\text{R}_3)-\text{R}_4$ alkenes	        
$\text{R} = \text{H or C}$ $\text{R}_1-\text{C}\equiv\text{C}-\text{R}_2$ alkynes	      
$\text{R} = \text{H or C}$ $\text{R}-\text{C}_2\text{H}_4-\text{O}-\text{C}_2\text{H}_4-\text{R}$ epoxides	      
R_1-R_2 alkanes	      
R X aromatics	     

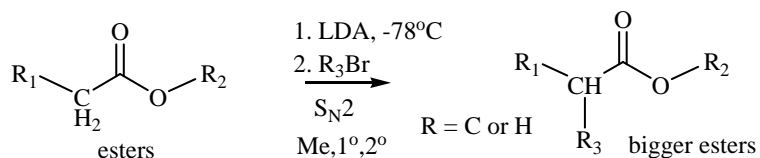
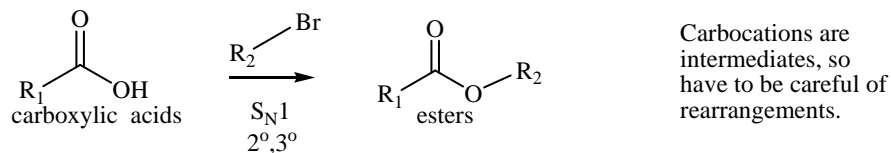
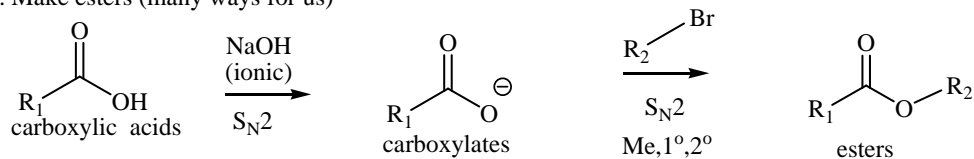
1. Make carboxylic acids (2 ways for us)



2. Make anhydrides (1 way for us)

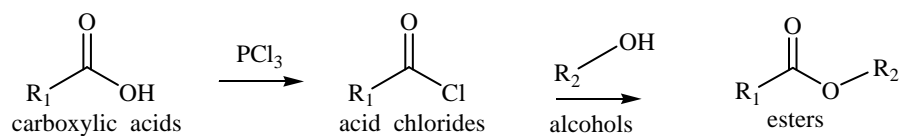


3. Make esters (many ways for us)

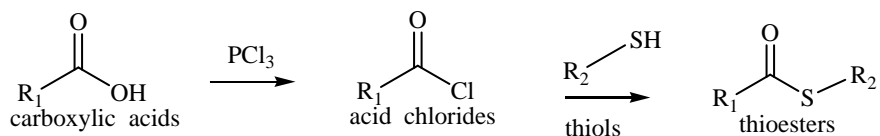


ester enolate chemistry

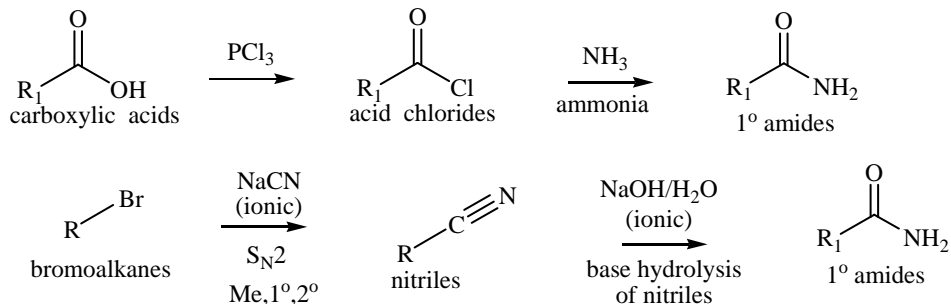
LDA = lithium diisopropyl amide
 sterically bulky, very strong base



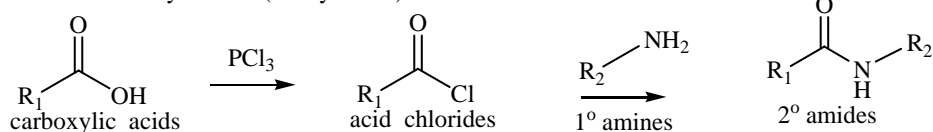
4. Make thioesters (1 way for us)



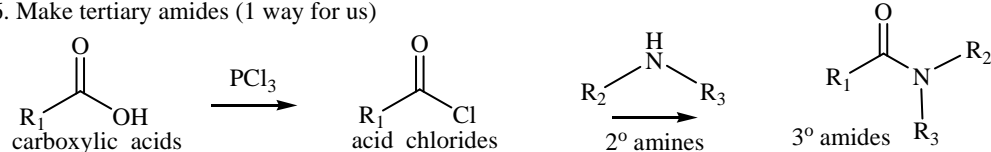
4. Make primary amides (2 ways for us)



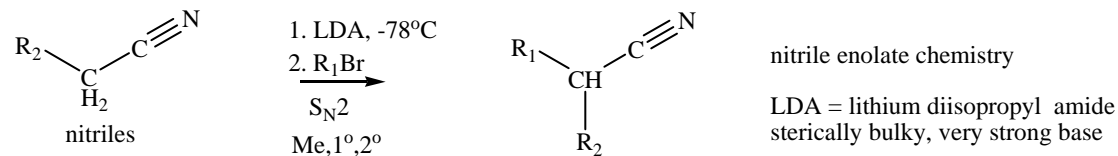
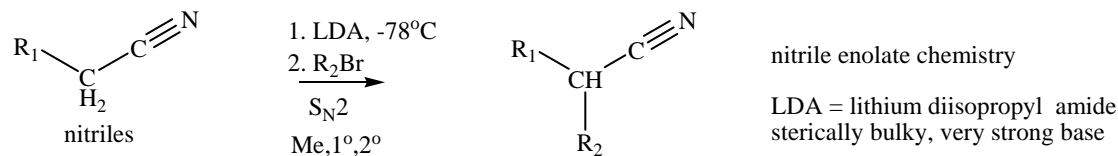
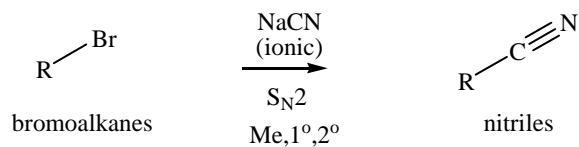
5. Make secondary amides (1 way for us)



6. Make tertiary amides (1 way for us)

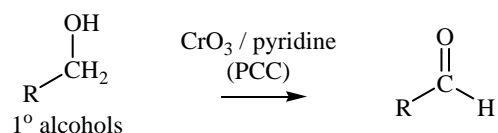


7. Make nitriles (2 ways for us)



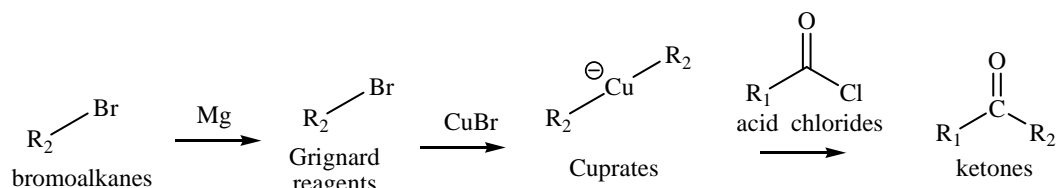
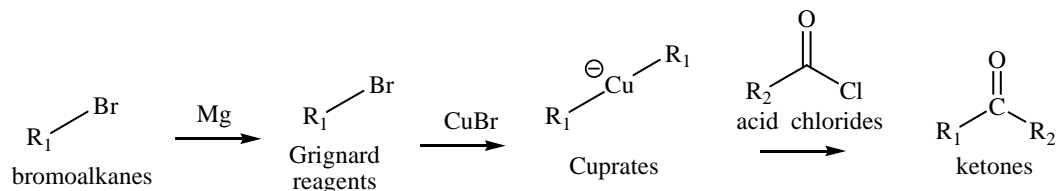
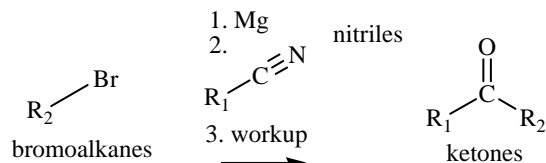
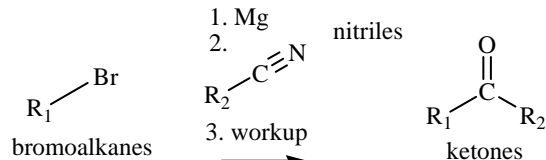
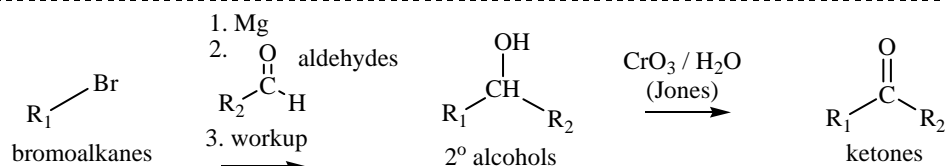
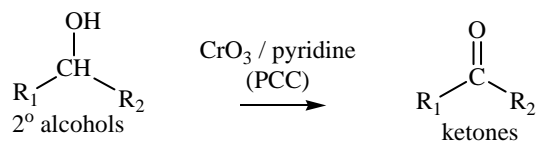
8. Make aldehydes (1 way for us)

Jones oxidation of primary alcohols

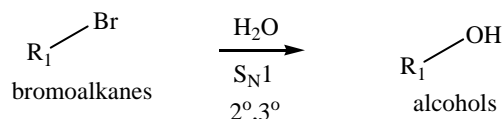
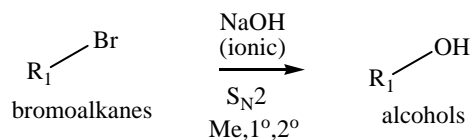


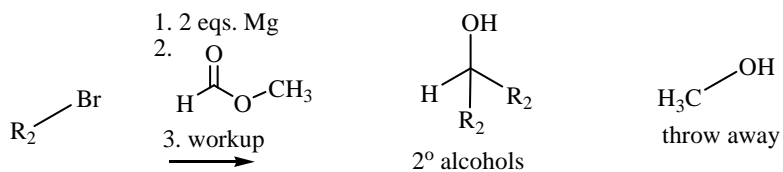
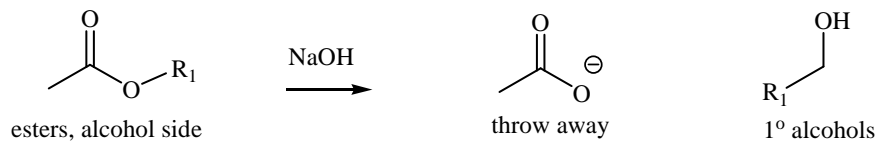
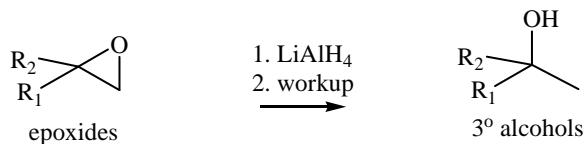
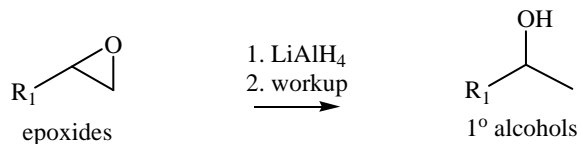
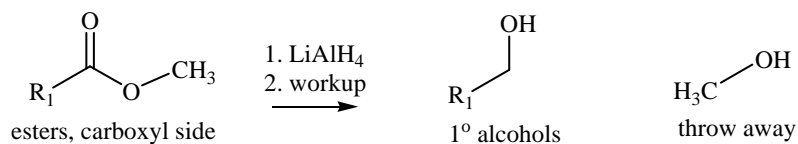
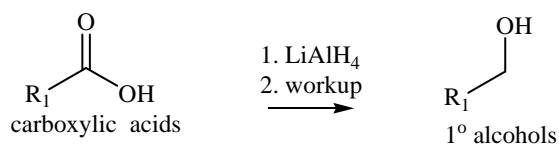
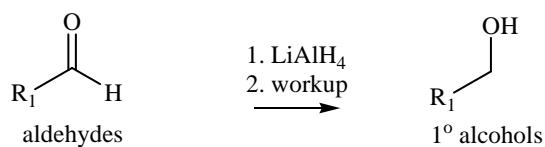
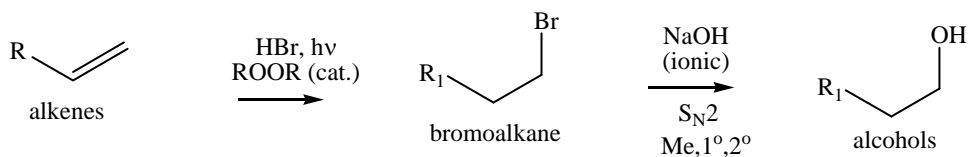
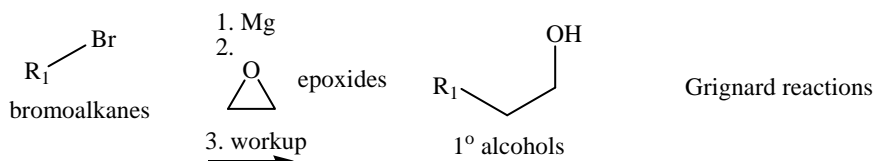
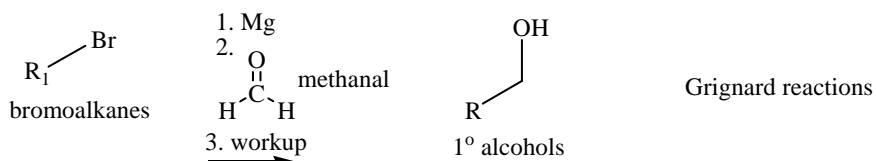
9. Make ketones (many ways for us)

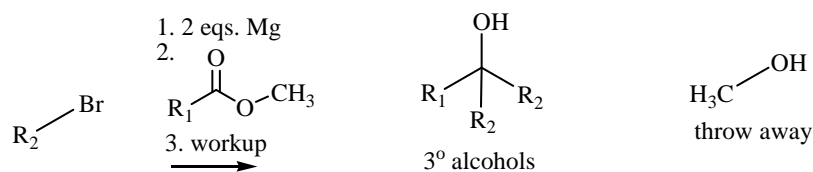
Jones oxidation of primary alcohols



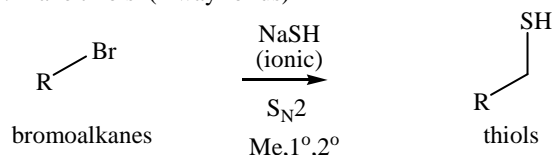
10. Make alcohols (many ways for us)



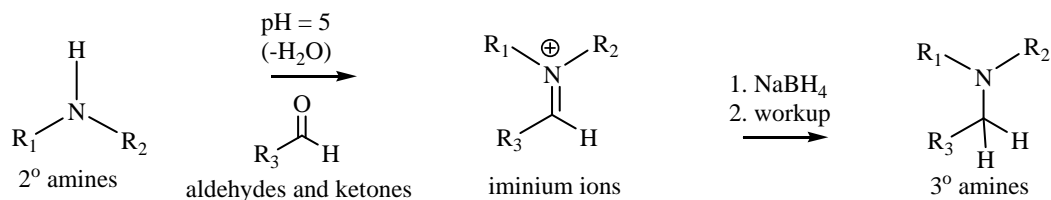
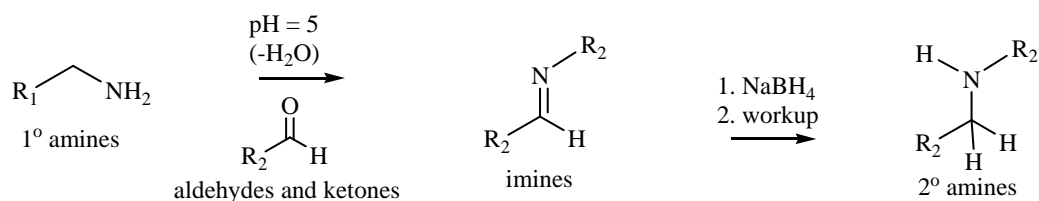
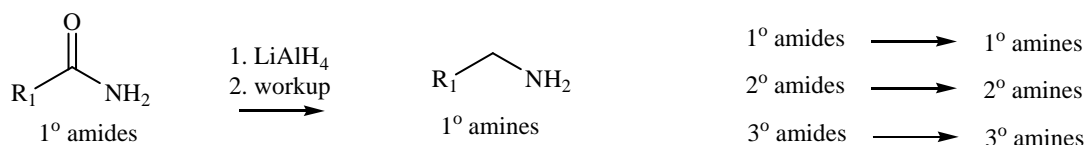
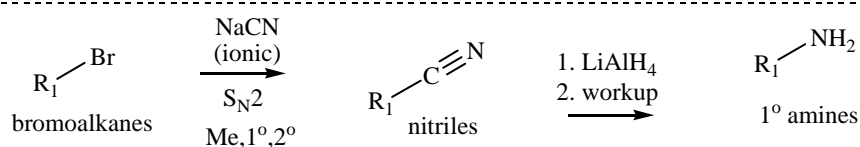
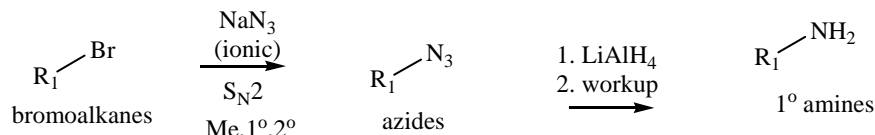




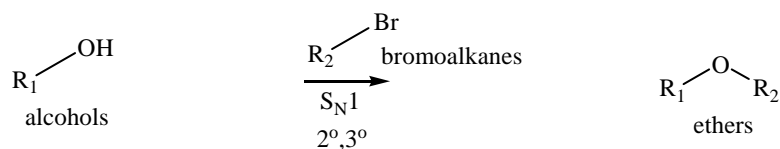
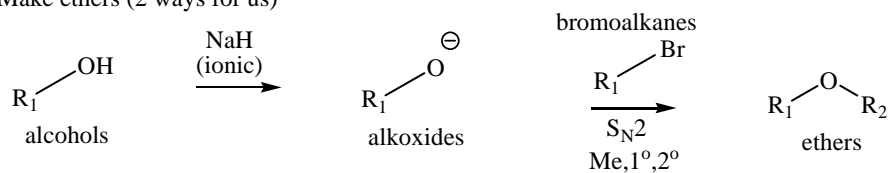
11. Make thiols (1 way for us)



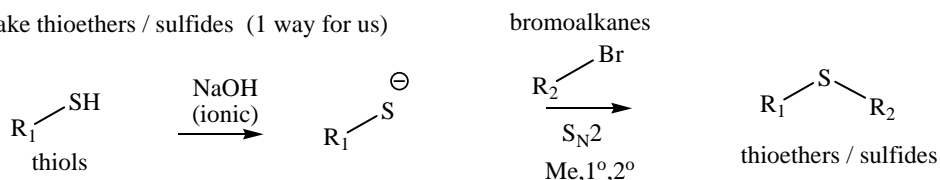
12. Make amines (3 ways for us)



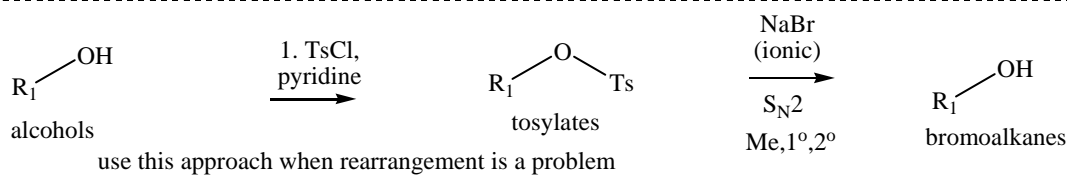
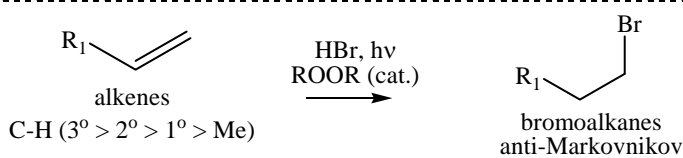
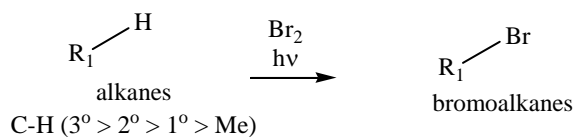
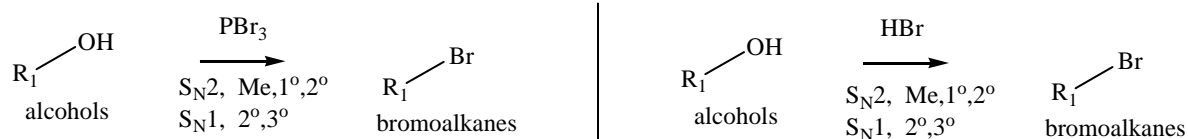
13. Make ethers (2 ways for us)



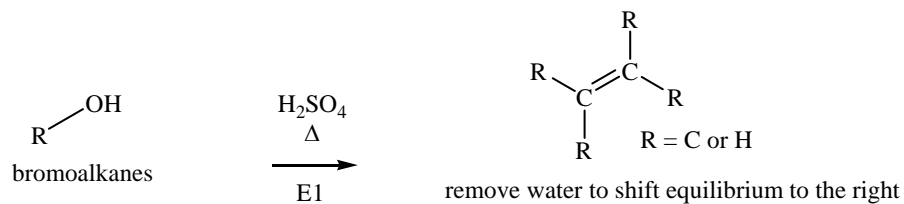
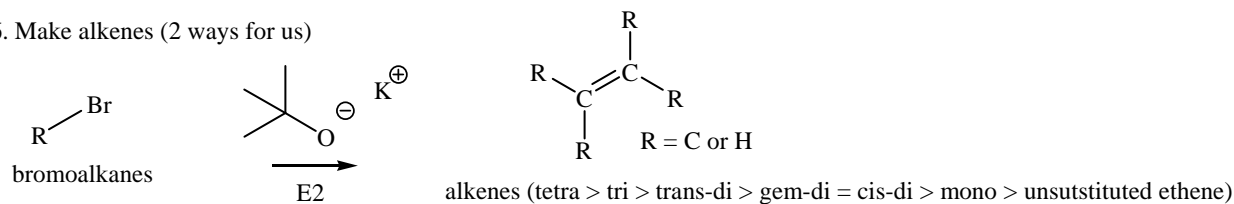
14. Make thioethers / sulfides (1 way for us)



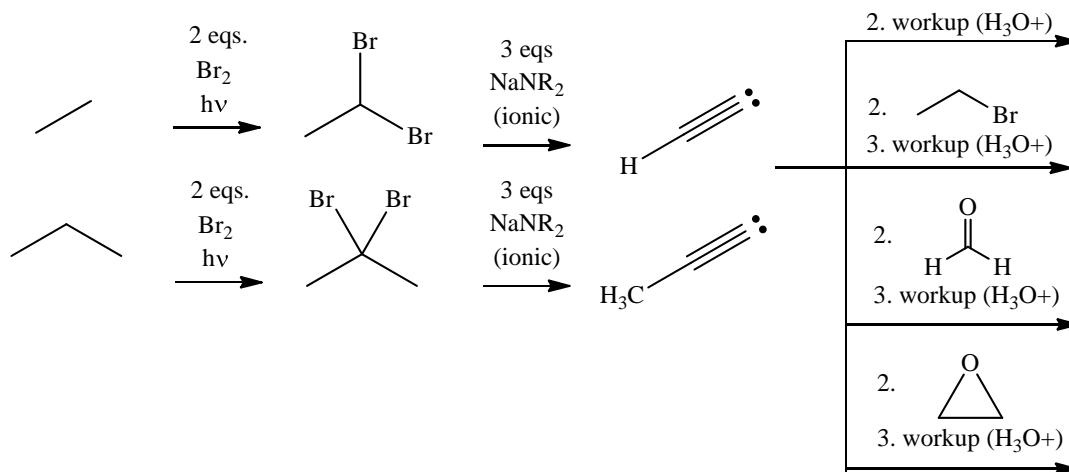
15. Make bromohydrocarbons (many ways for us)



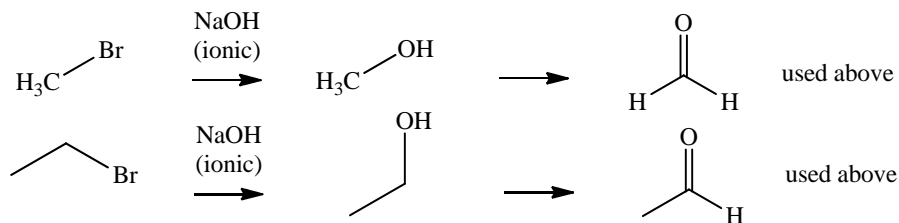
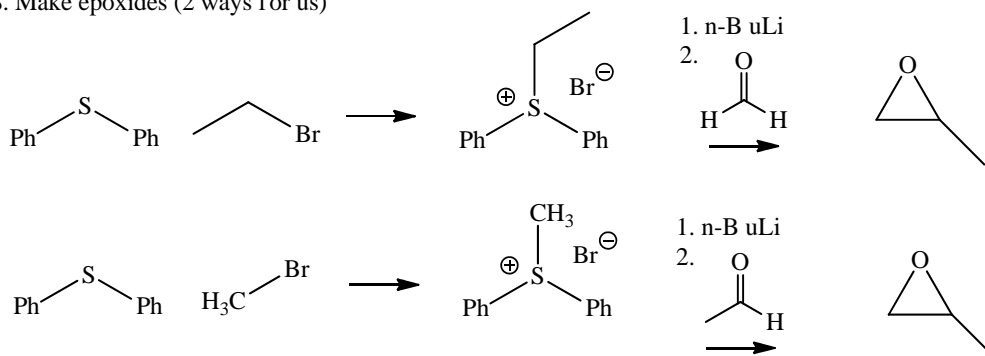
16. Make alkenes (2 ways for us)



17. Make alkynes (many ways for us)

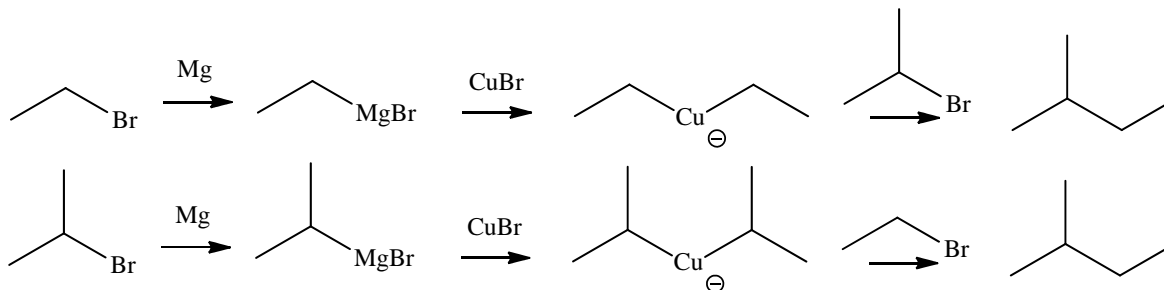


18. Make epoxides (2 ways for us)



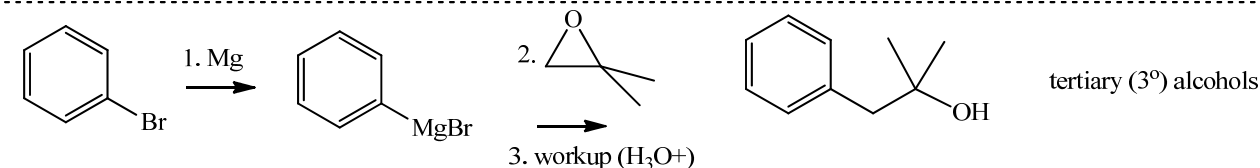
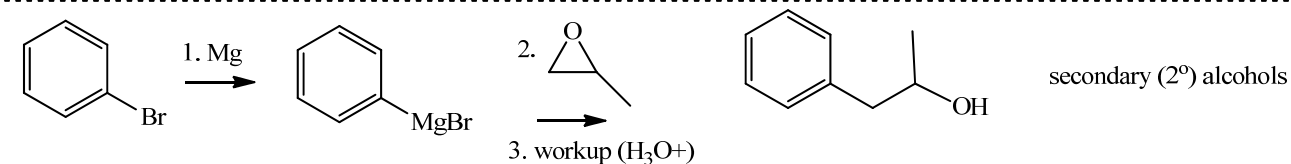
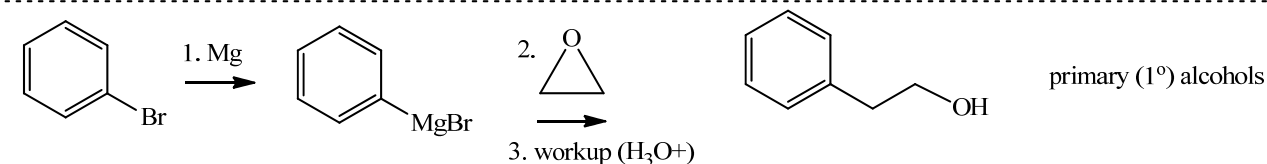
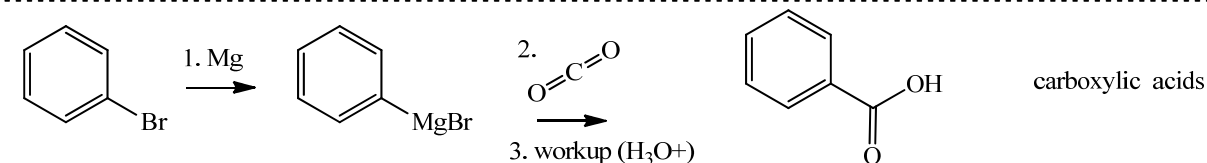
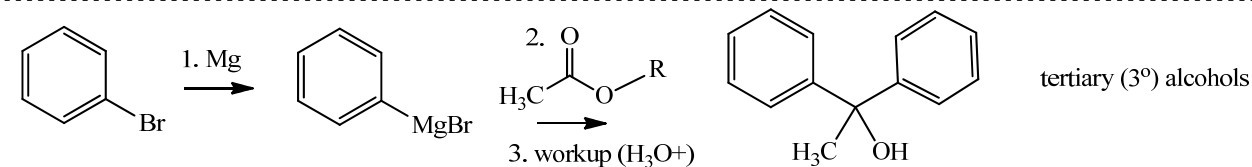
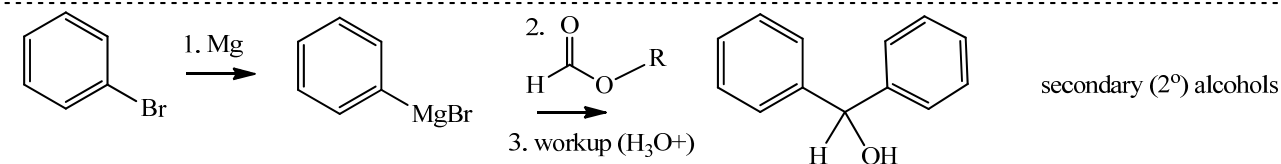
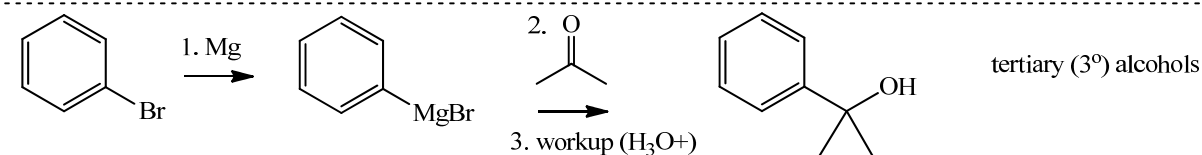
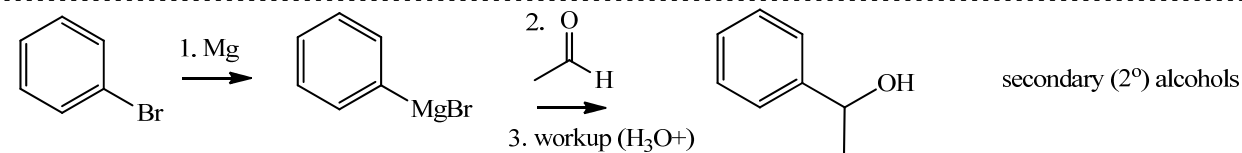
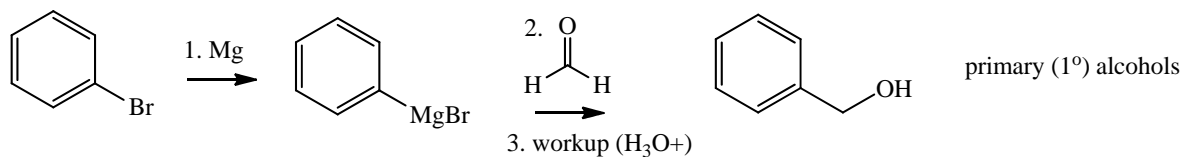
18. Make alkanes (2 ways for us)

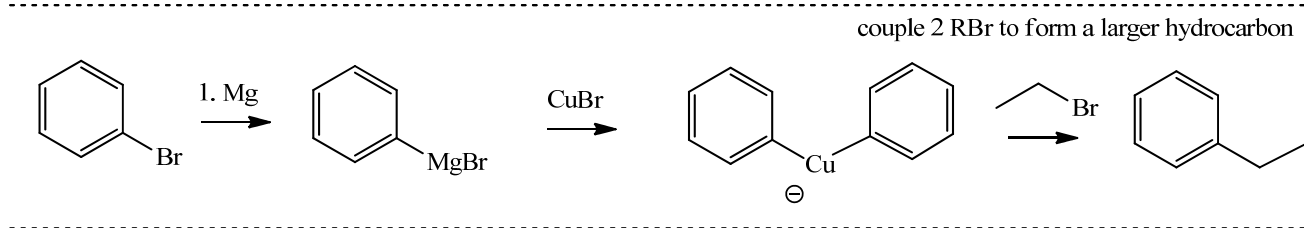
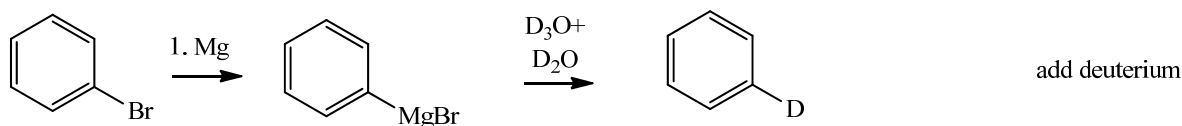
Cuprate coupling of two different RBr compounds, one as the cuprate nucleophile and one as the RBr electrophile



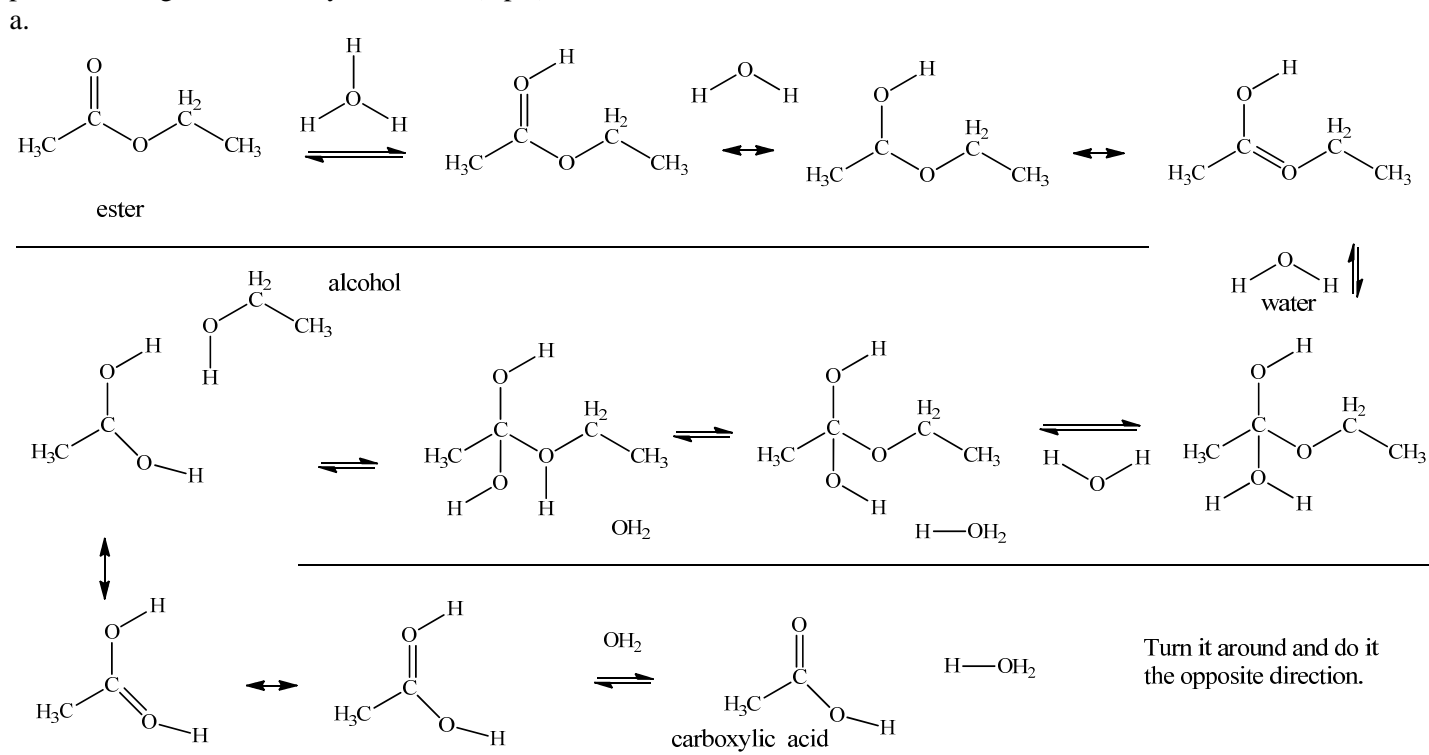
19. Make aromatic compounds using Grignard reaction and bromobenzene (several possibilities)

Grignard reagents react as nucleophiles with various electrophiles. Usually there needs to be a final workup step (neutralization)

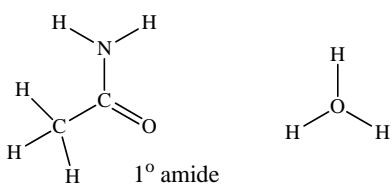
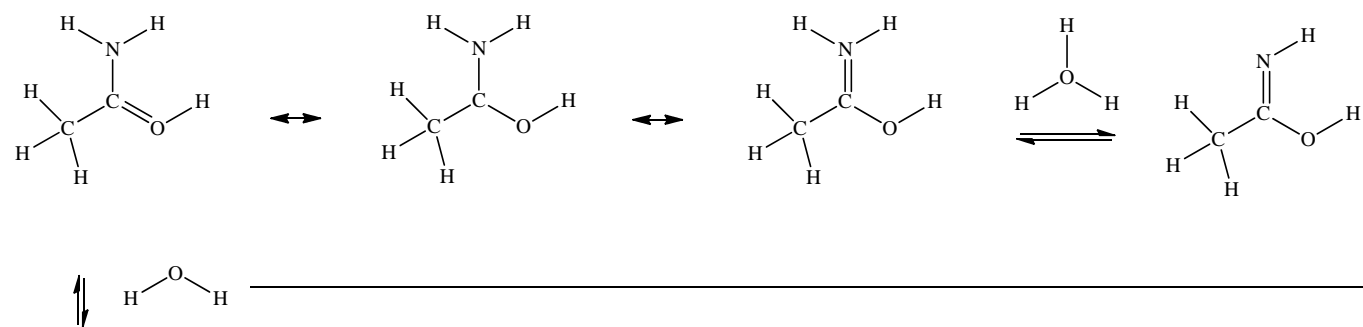
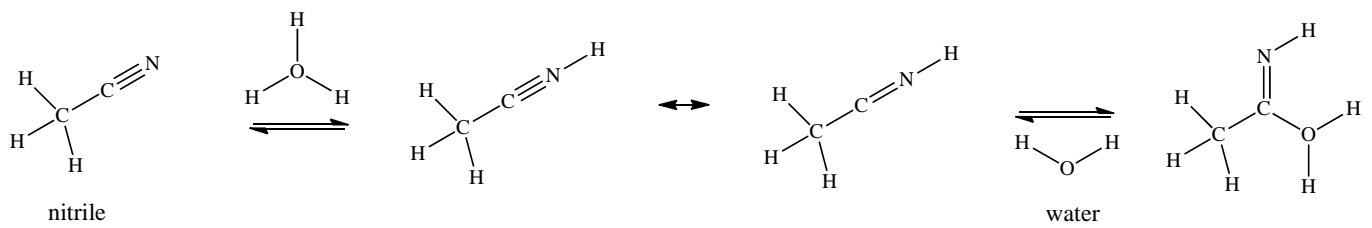




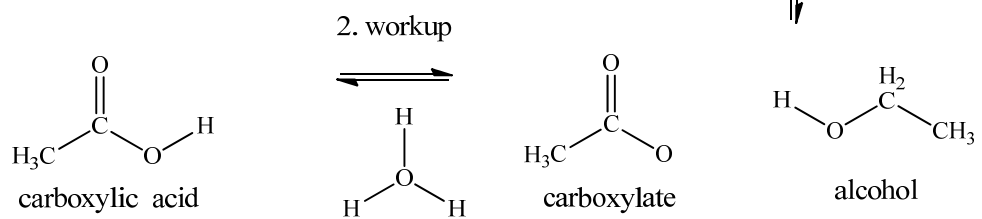
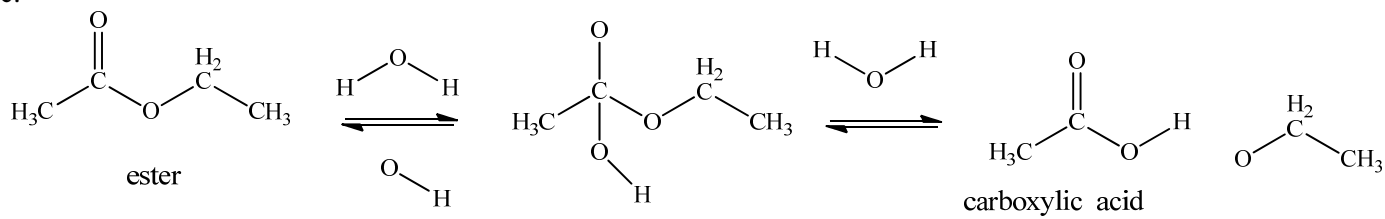
12. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformations, one in acid and one in base. Assume all nonhydrogen atoms have full octets unless a positive charge is written by the atom. (Xpts)

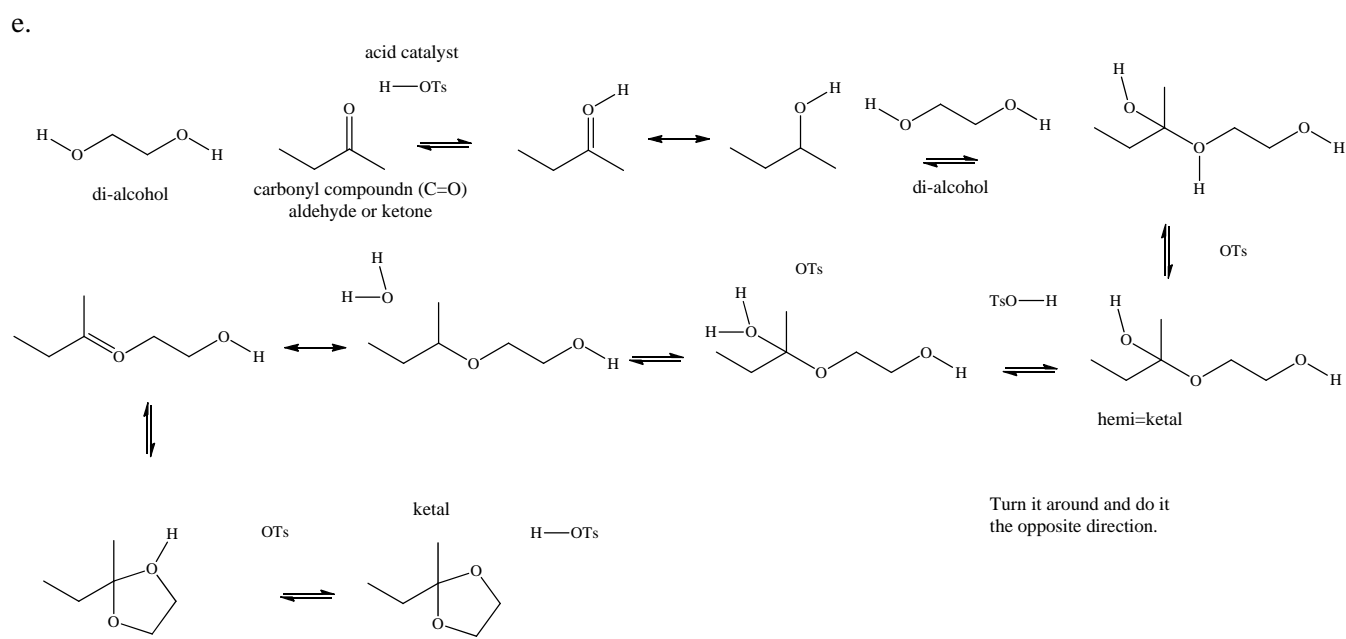
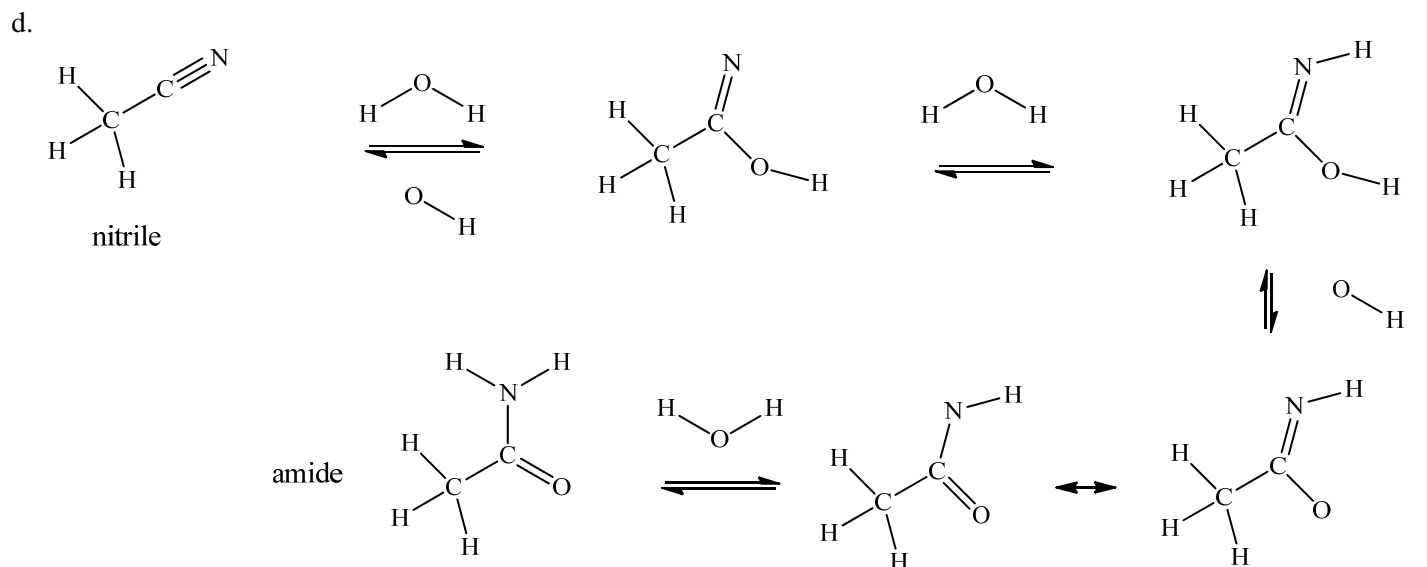


b.

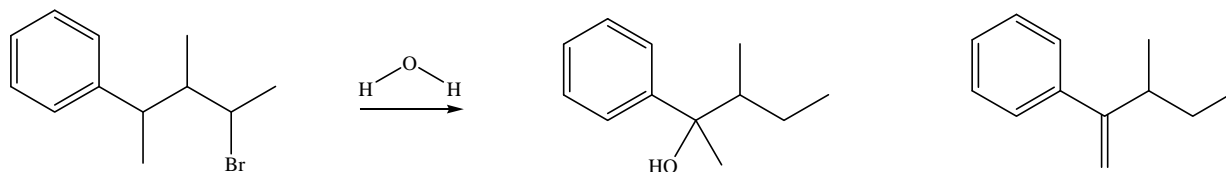


c.

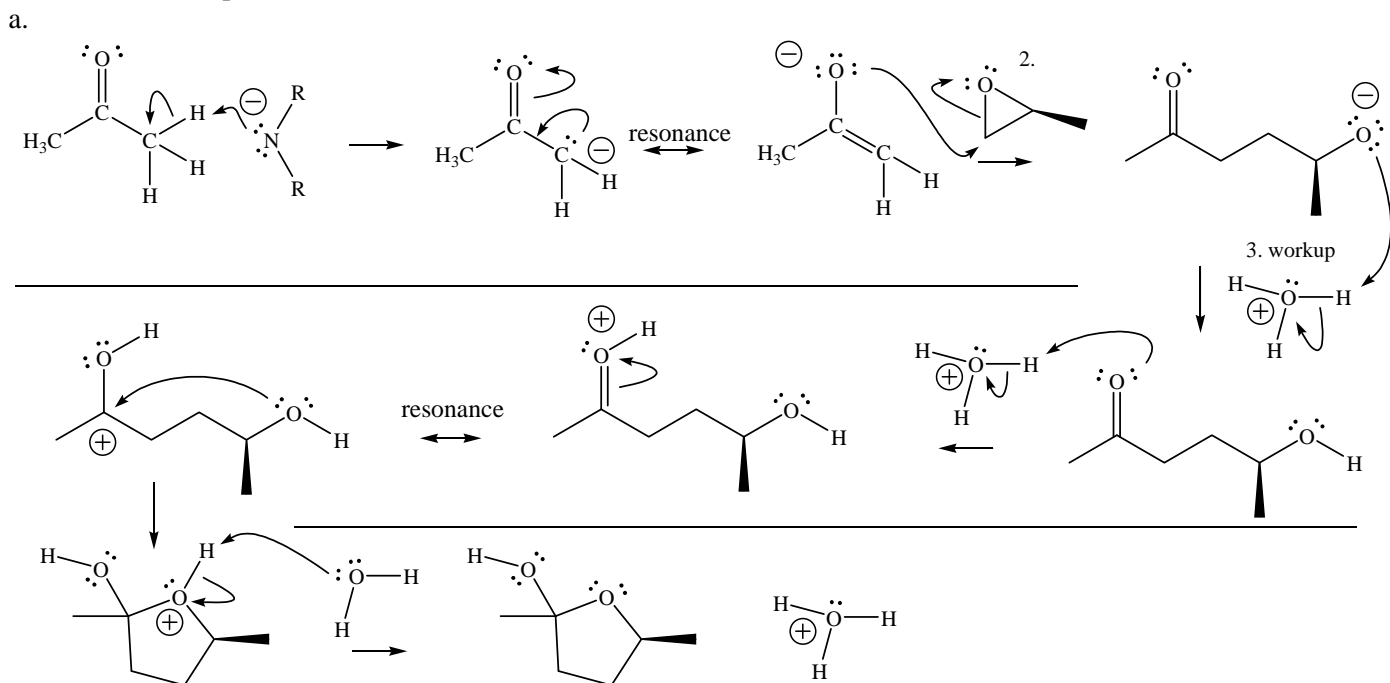




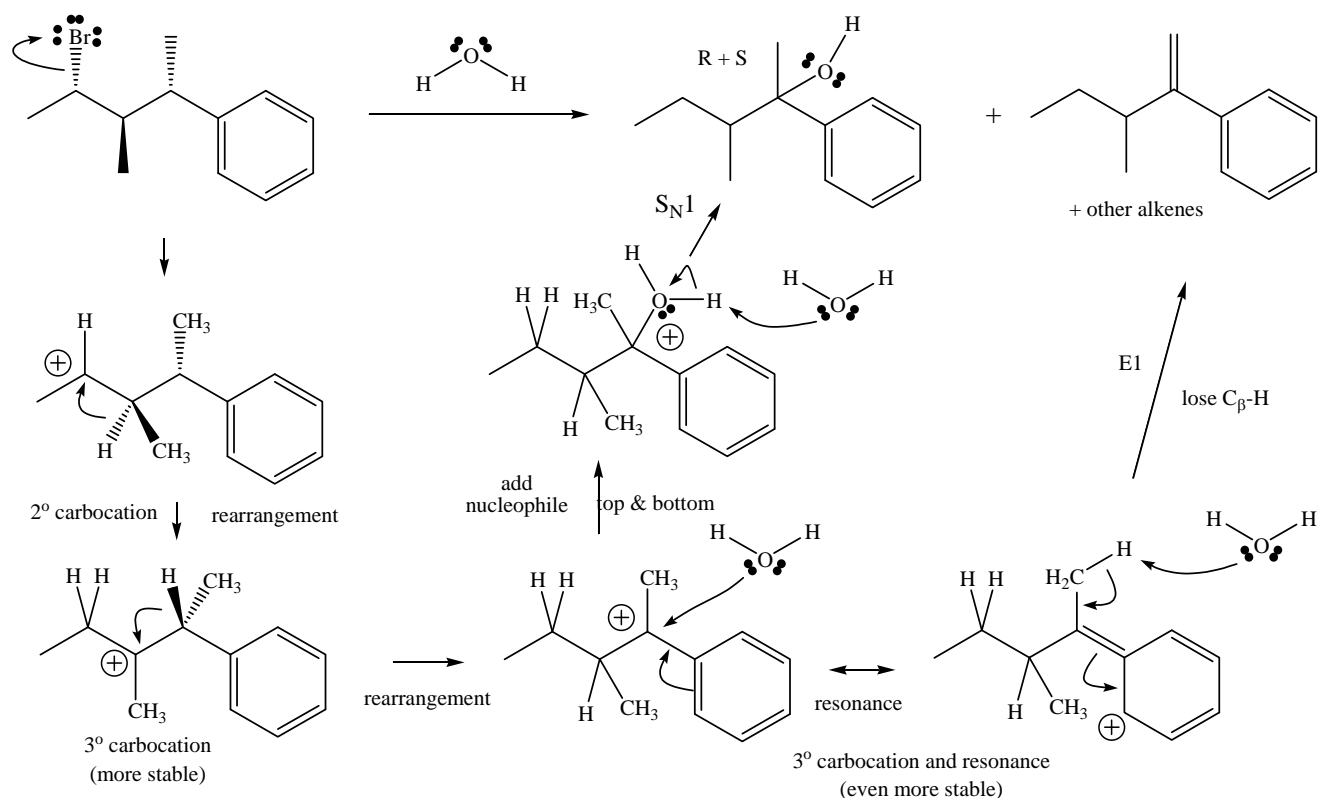
13. Provide a complete arrow-pushing mechanism for the following transformations. (X pts)



14. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformation. Assume all nonhydrogen atoms have full octets unless a positive charge is written by a carbon atom. (20 pts)



15. Provide a complete arrow-pushing mechanism for the following transformations (lone pairs, formal charge and curved arrows). (15 pts)



16. a. Show all possible products when 2-methylpentane is brominated with $\text{Br}_2/h\nu$? Indicate the approximate relative amounts of each product formed if the relative rates of reaction of a bromine atom with an sp^3 C-H bond are: primary = 1, secondary = 80 and tertiary = 1600. (X pts)

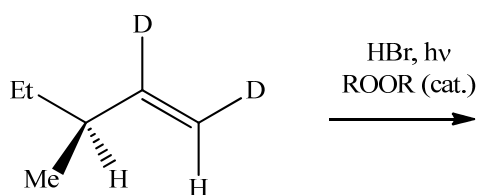
b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrows, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall ΔH for each step of your mechanism using the given bond energies. To make a bond is positive energy and to make a bond is negative bond energy. (X pts)

Br—Br	46
H—Br	87

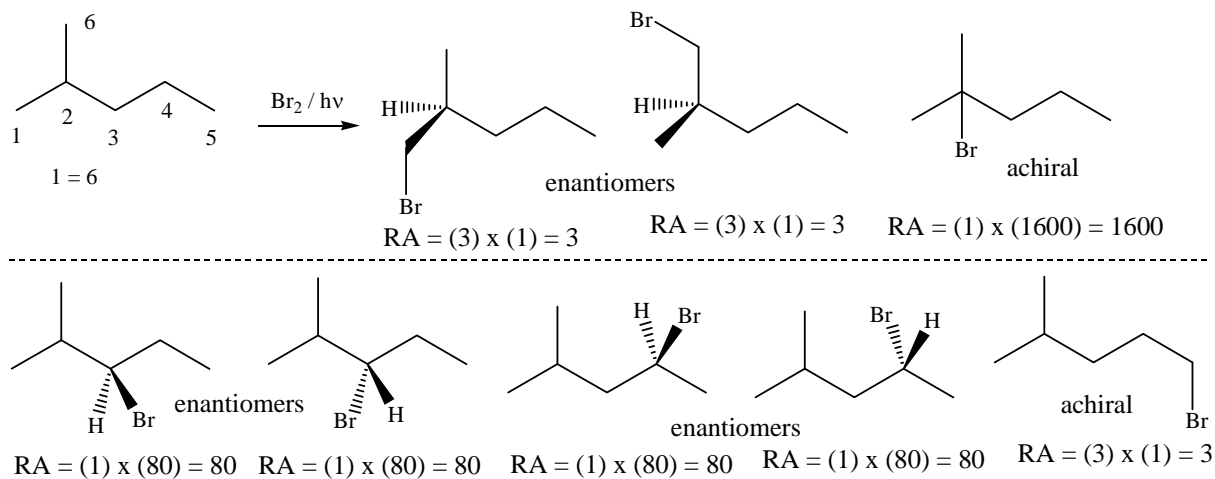
Me C-H	105
1° C-H	98
2° C-H	95
3° C-H	92

Me C-Br	70
1° C-Br	68
2° C-Br	68
3° C-Br	67

17. Show all possible products when the following compounds react. Identify what kinds of isomers are present.



17. (possible answer) a. Show all possible products when 2-methylpentane is brominated with $\text{Br}_2/h\nu$? Indicate the approximate relative amounts of each product formed if the relative rates of reaction of a bromine atom with an sp^3 C-H bond are: primary = 1, secondary = 80 and tertiary = 1600. (X pts)



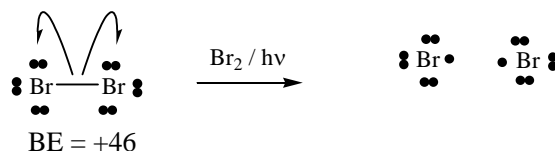
b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrows, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall ΔH for each step of your mechanism using the given bond energies. To make a bond is positive energy and to make a bond is negative bond energy. (X pts)

Br—Br	46
H—Br	87

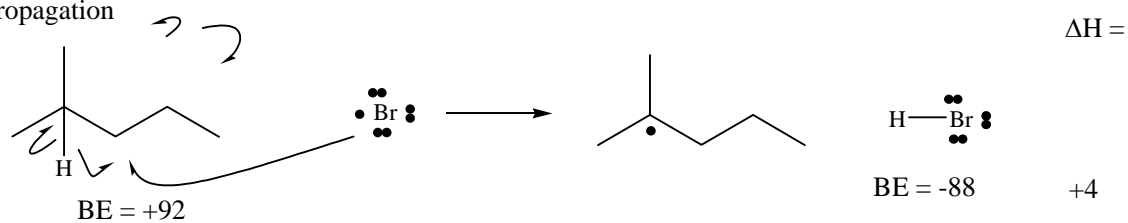
Me C-H	105
1° C-H	98
2° C-H	95
3° C-H	92

Me C-Br	70
1° C-Br	68
2° C-Br	68
3° C-Br	67

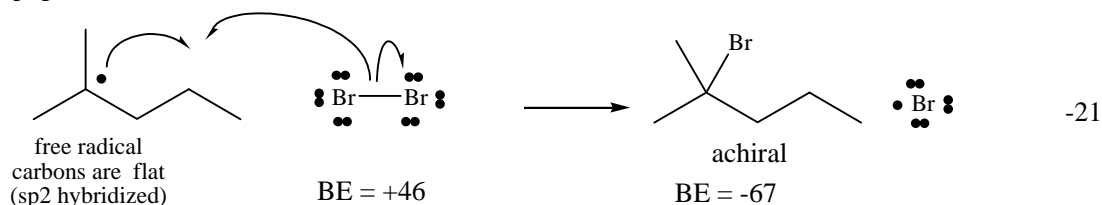
1. initiation



2a. propagation

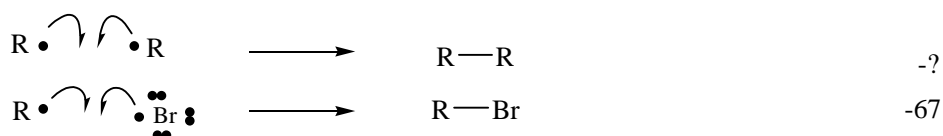


2b. propagation



$\Delta H_{\text{overall}} = -19$

3. termination = combination of 2 radicals to shut down chain reaction



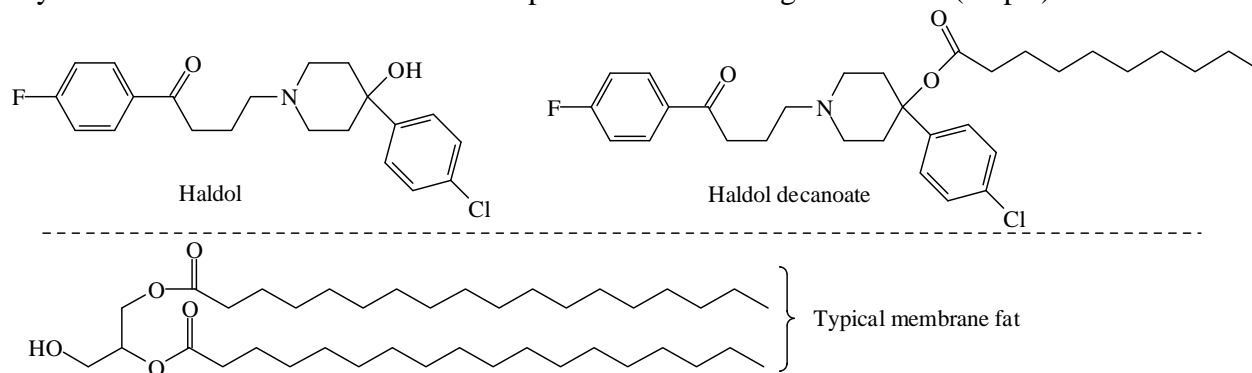
18. Draw a 2D structure that includes the listed functional groups. Write the functional group name by its appearance in your 2D structure. Calculate the degree of unsaturation for the given formula. (25 pts)

alkyne, alkene, 1° amine, ester, alcohol
ether, thiol, ketone, acid, 2° amide, nitrile

degree of unsaturation calculation



19. a. Haldol is a potent orally active central nervous system tranquilizer used in the treatment of psychoses. Peak plasma levels, when taken orally, are 2-6 hours (in the aqueous blood). Cell membranes, on the other hand, are composed largely of alkane-like fatty acid chains. A decanoate ester prodrug was prepared to increase Haldol's lifetime in the body. When injected intramuscularly its anti-psychotic activity lasted about 1 month. Provide an explanation for its longer lifetime. (12 pts)



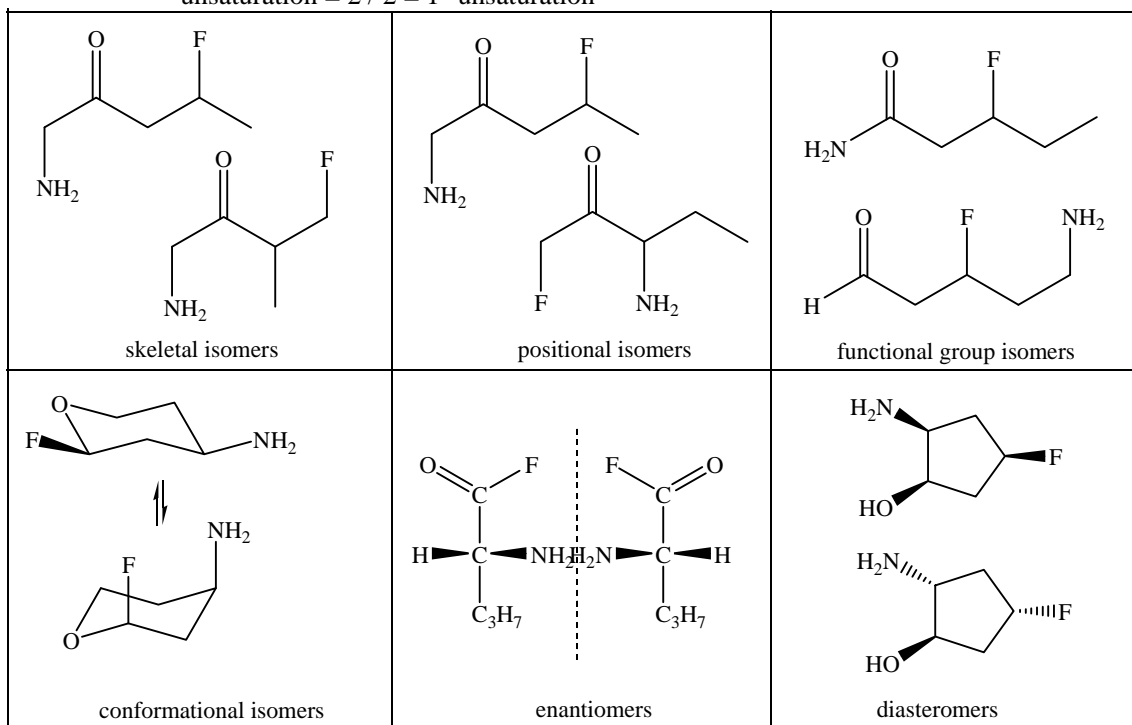
b. Provide an explanation for why NaCl is soluble in water, but not soluble in hexane. Use structures. (8 pts)

20. Use the formula $C_5H_{10}FNO$ to draw examples for each type of isomerism indicated. This will require that you draw at least two structures to show these differences. What is the degree of unsaturation? (25 pts)

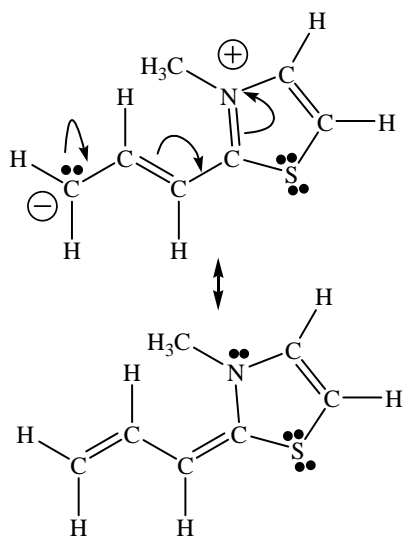
$$C_5H_{10}FNO \quad 2(5) + 2 + 1 = 13 = \text{saturated number}$$

$$-11 = \text{actual number}$$

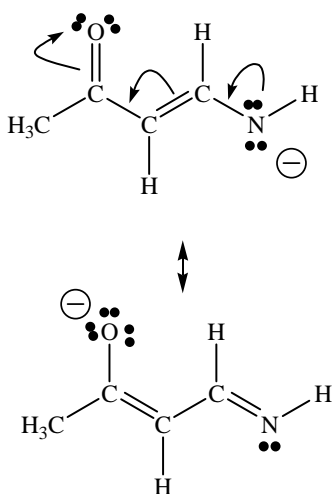
$$\text{unsaturation} = 2 / 2 = 1^\circ \text{ unsaturation}$$



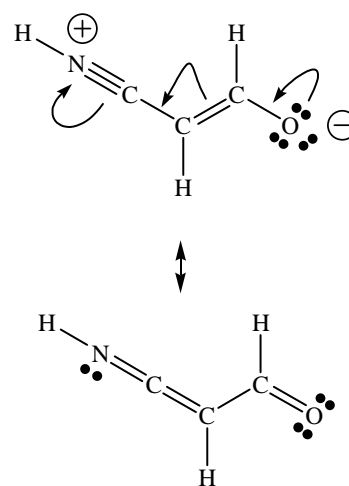
21. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw the best other resonance structure using the proper arrow conventions. Indicate which resonance structure is better or if they are equivalent. (18 pts)



The second resonance structure is better because it has full octets and it quenches formal charge.

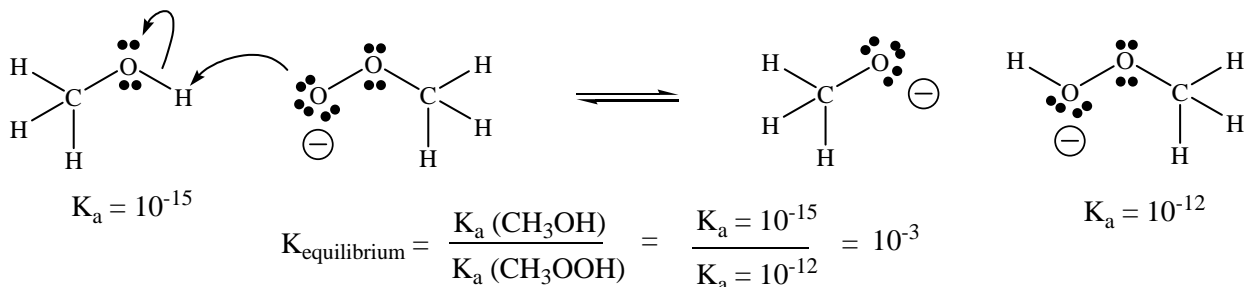


The second resonance structure is better because it moves the negative charge from nitrogen to the more electronegative oxygen.



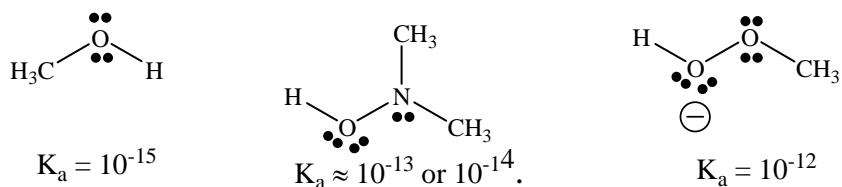
The second resonance structure is better because it has full octets and it quenches formal charge.

22. Only the reactant acid and base are drawn below. Decide which is which and draw a mechanism to show formation of the conjugate base and acid. The two acids have pK_a's of 15 and 12 (K_a values are 10⁻¹⁵ and 10⁻¹²). Match the K_a values with the proper acid, write a K_{equilibrium} expression and calculate a quantitative K_{equilibrium} value for the reaction. Show your work. Provide an explanation for your value of K_{equilibrium}. (15 pts)



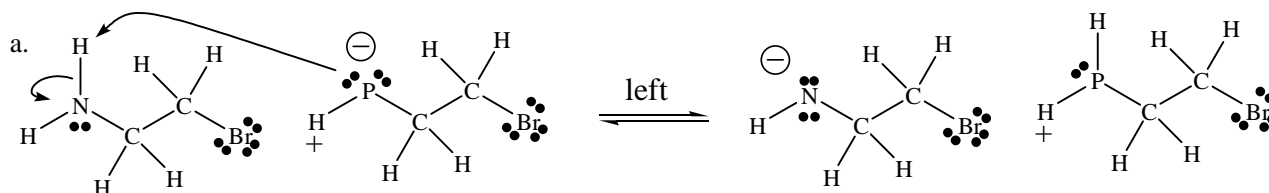
The equilibrium is favored to the left because of the inductive withdrawing effect of the second oxygen atom, which helps to stabilize the negative charge. There is no resonance effect here.

- b. Use the above K_a values to estimate a K_a for the following acid. Very briefly explain your reasoning. (5 pts)

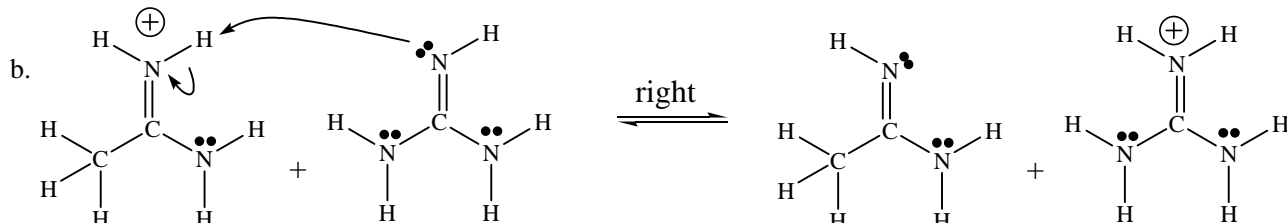


We can estimate a K_a value between the two given acids. N is inductively electron withdrawing relative to carbon, but not as electronegative as oxygen, so the inductive withdrawing effect of N helps stabilize the anion more than carbon but not as much as oxygen.

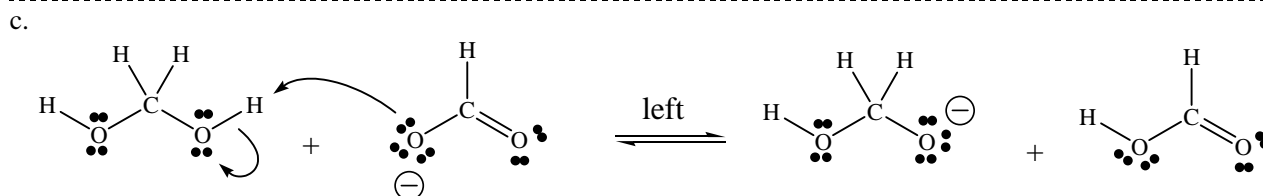
23. Using arrow-pushing mechanisms, write the expected products from the following reactions and indicate whether the equilibrium lies to the “right” or to the “left”. Also, very briefly explain your reasoning. (35 pts)



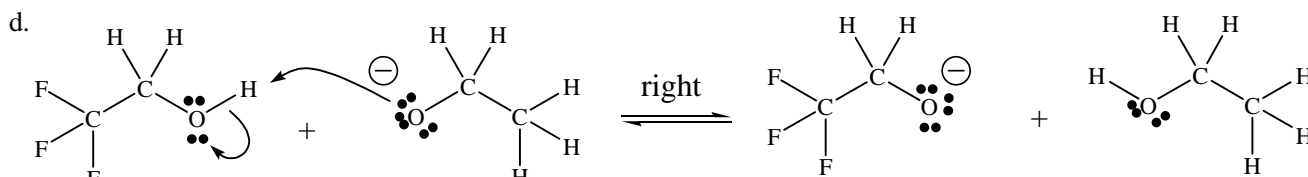
The left side is favored because the anion charge is more delocalized on the larger phosphorous than nitrogen (same Z_{eff}).



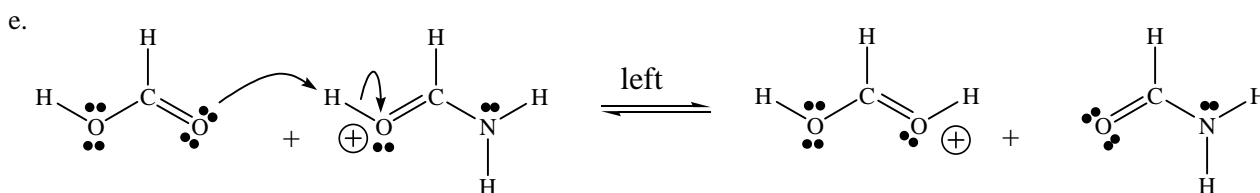
The right side is favored because the cation charge is more delocalized on 3 nitrogen atoms than 2 nitrogen atoms.



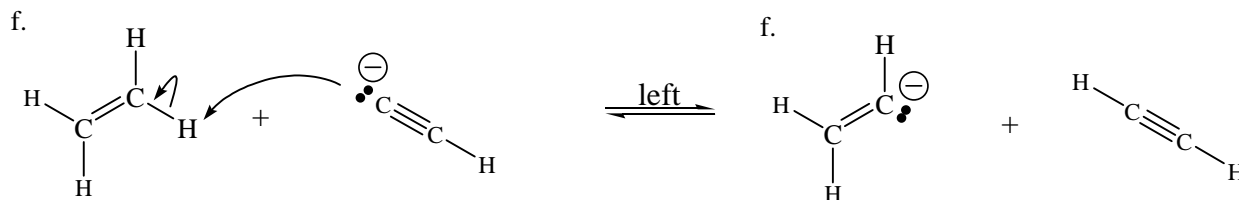
The left side is favored because the anion charge is more delocalized on two oxygen atoms than one oxygen.



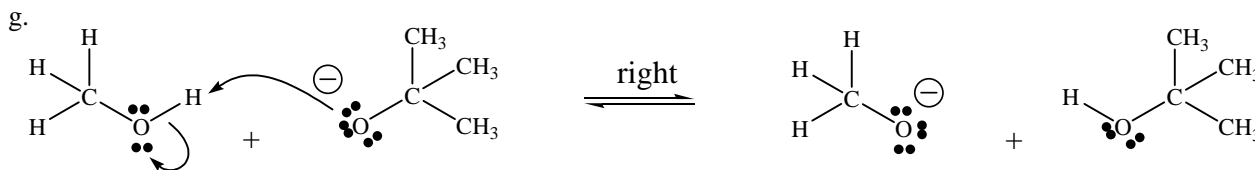
The right side is favored because the anion charge is stabilized by the inductive withdrawing effect of the 3 fluorine atoms.



The left side is favored because the cation charge is more stable with resonance donation from a nitrogen than from an oxygen.



The left side is favored because the anion is more stabilized in a more electronegative sp orbital (50% s) than in an sp^2 orbital (33% s).



The right side is favored because the anion is more stabilized without the inductive donating effect of 3 methyl groups