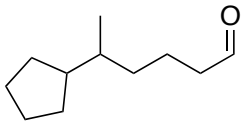
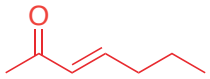
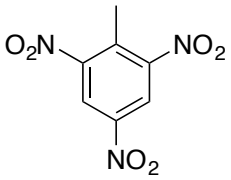
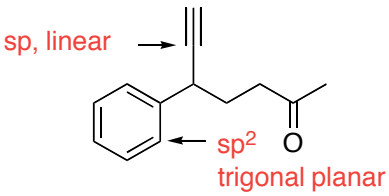
Part A

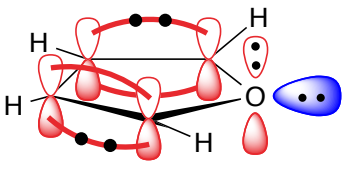
1. (3 pts) In the following table, provide the missing IUPAC name or molecular line structure.

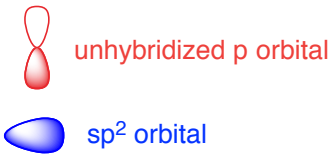
Name or description	Structure
5-cyclopentyl hexanal	
E-hept-3-ene-2-one	
2,4,6-trinitrotoluene (a.k.a. TNT!)	

2. (2 pts) For the following compound, show the hybridization and geometry of the indicated atoms.

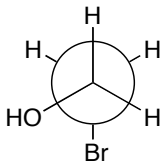
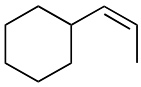
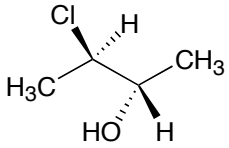
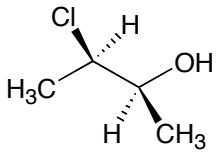


3. (3 pts) From the following molecules, circle the aromatic compound. In the space below, draw the LCAO orbital diagram of the π system of the molecule you've chosen.

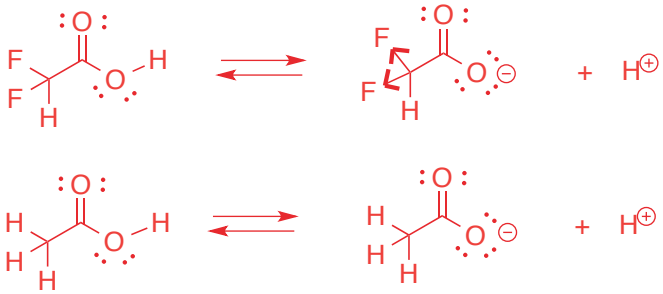




4. (3 pts) Identify the relationship between the following pairs of molecules (conformers, enantiomers, identical molecules, etc.)

	2-bromoethanol	**same molecule**
(E)-1-cyclohexylpropene		**diastereomers (geometric isomers)**
		**conformers**

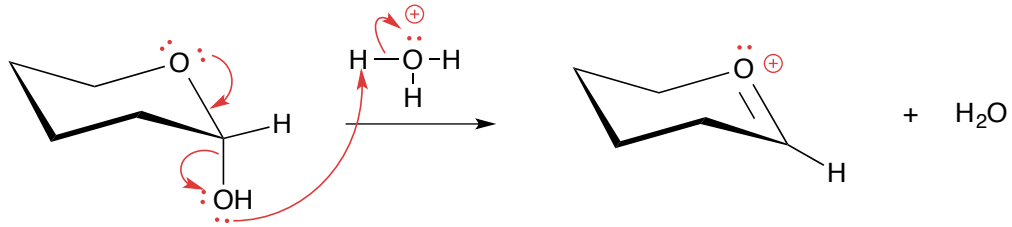
5. (2 pts) Which is the stronger acid: 2,2-difluoroethanoic acid or ethanoic acid? Explain.



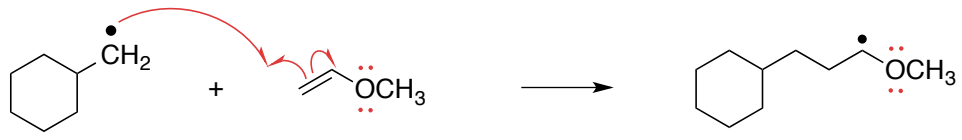
2,2-difluoroethanoic acid is the stronger acid. We can determine this by looking at the stability of the resulting conjugate bases: any factor that increases the stability of the anion correspondingly results in a stronger original acid (i.e., it is a better proton donor). In this case, the two very electronegative fluorine atoms help stabilize the negative charge of the conjugate base via the inductive effect. Delocalizing negative charge in this manner leads to a more stable anion, which means it is the stronger acid.

6. (4 pts) Include *all* lone pairs of electrons and formal charges and add electron-pushing arrows as needed to complete the following reactions:

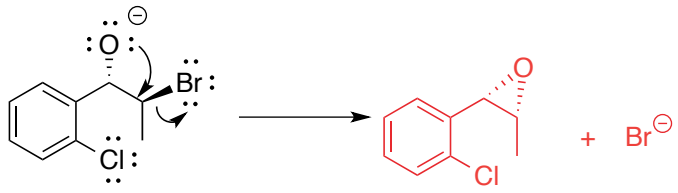
a.

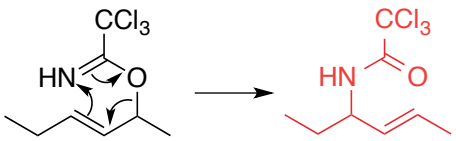


b.

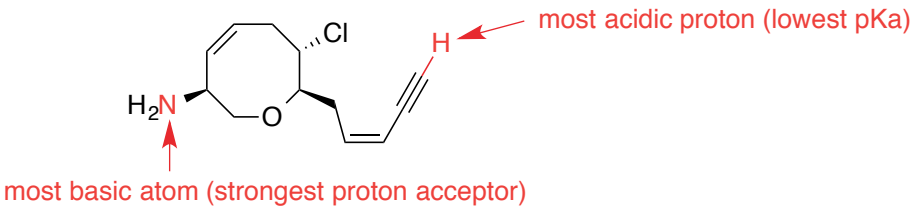


7. (2 pts) Using the electron-pushing arrows as a guide, draw the expected product of the following reactions.

a. 

b. 

8. (2 pts) Indicate the most basic atom and the most acidic proton in the following molecule.

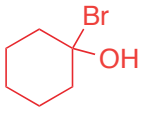


9. (2 pts) What is the number of stereoisomers of the following compounds?

$CH_3CHClCHOHCH_3$ _____**4**_____ $CH_3CHClCHClCH_3$ ___**3 (one is a meso compound)**___

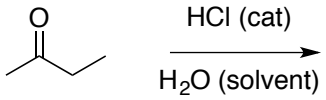
10. (2 pts) Clearly draw the structure of *R*-1-bromo-cyclohexanol.

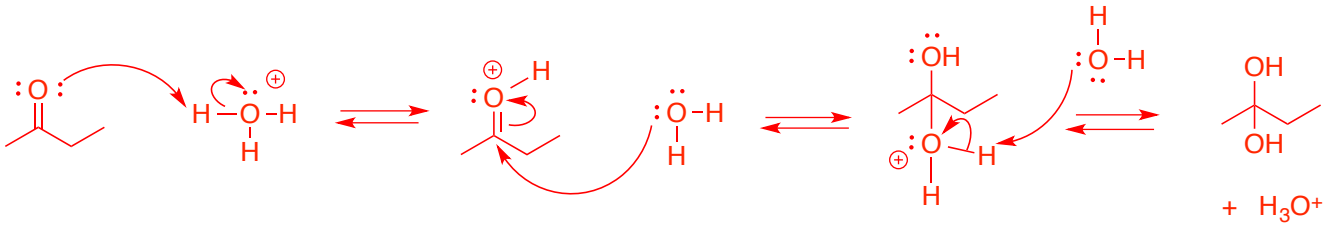
Trick Question! This is not a chiral compound: it has a plane of symmetry (i.e. there aren't 4 different groups around the relevant carbon atom). So, you can just draw the molecule without stereospecificity:



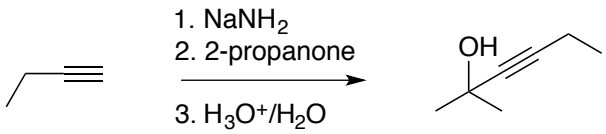
Part B

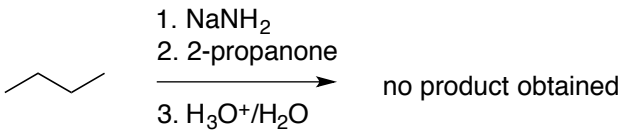
11. (6 pts) Draw the full mechanism and show the final product of the following reaction. Clearly indicate any stereochemistry, if necessary.



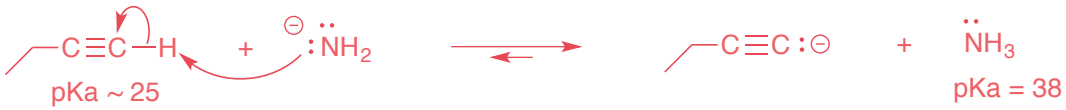


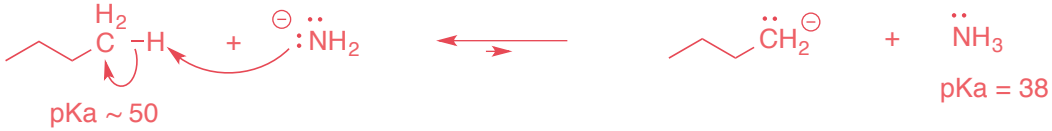
12. (3 pts) Explain, in a few sentences and/or using chemical reactions, why the first reaction below yields product while the second does not work at all.



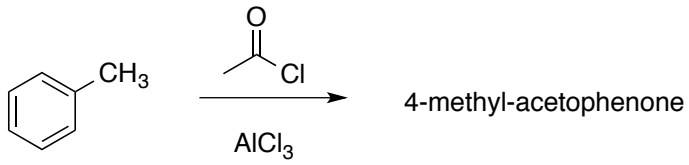


These reactions are both attempting a nucleophilic carbanion addition to 2-propanone (a.k.a. acetone). The key here is step one, in which the nucleophile is prepared: a strong base, $NaNH_2$, is used to deprotonate the starting material and produce the corresponding carbanion. Using pKa's, we can see that this will work in the first reaction, but not in the second:



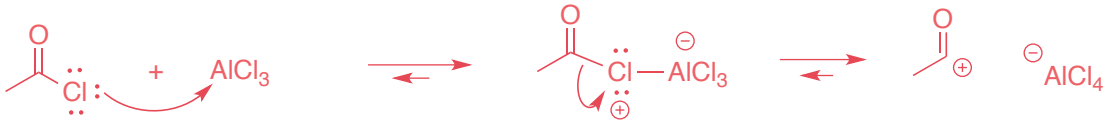


13. A student performs the following reaction and observes the formation of 4-methyl-acetophenone.



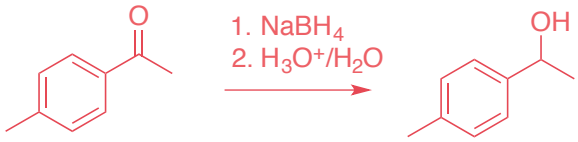
a. (2 pts) What is the function of the $AlCl_3$? Explain, using a sentence and a chemical reaction.
b. (2 pts) Why is 2-methyl-acetophenone only a minor product?
c. (2 pts) Show how you could transform the major product into 1-(p-methylphenyl) ethanol.

a. The $AlCl_3$ is a LEWIS ACID, its function is to ACTIVATE THE ELECTROPHILE by producing the ACYLIUM ION:



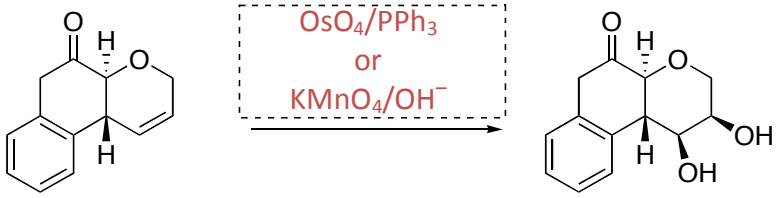
b. The methyl group on the aromatic ring is a WEAKLY ACTIVATING GROUP and it is an ORTHO/PARA DIRECTOR, meaning that the addition of the acyl group should occur at the ortho and para positions. However, due to STERIC HINDRANCE between the methyl group and the acyl group, addition to the para position is preferred, meaning the 2-methyl-acetophenone isomer is less favoured and formed in minor amounts.

c.

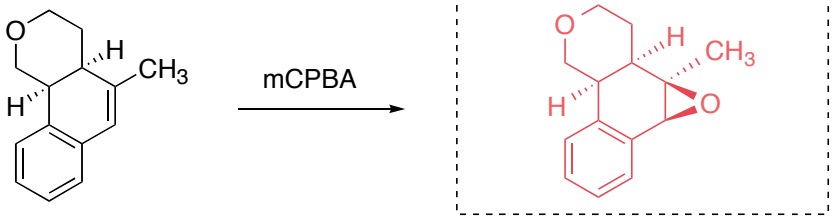


14. (6 pts) For each of the following, provide the missing product or reagents (no mechanisms).

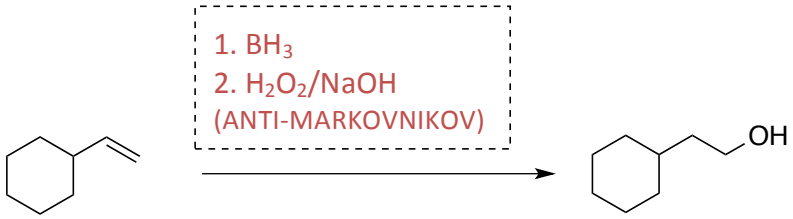
a.



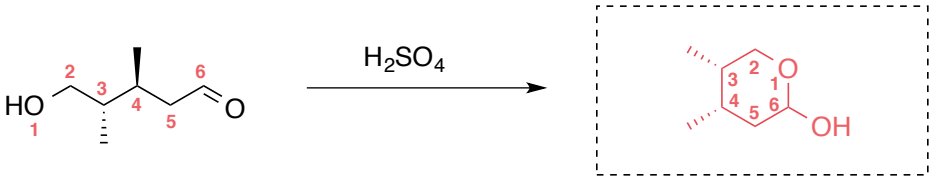
b.



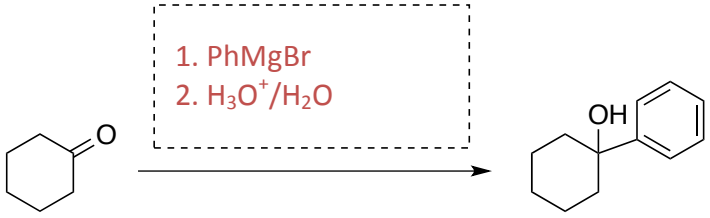
c.



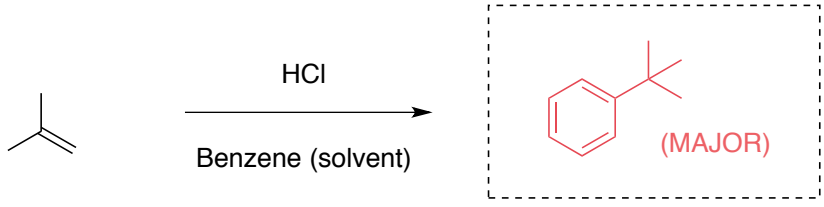
d.



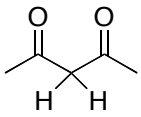
e.



f.

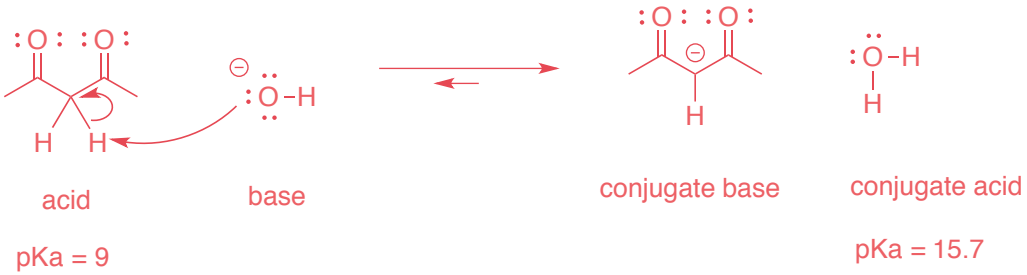


15. (6 pts) For the following molecule:



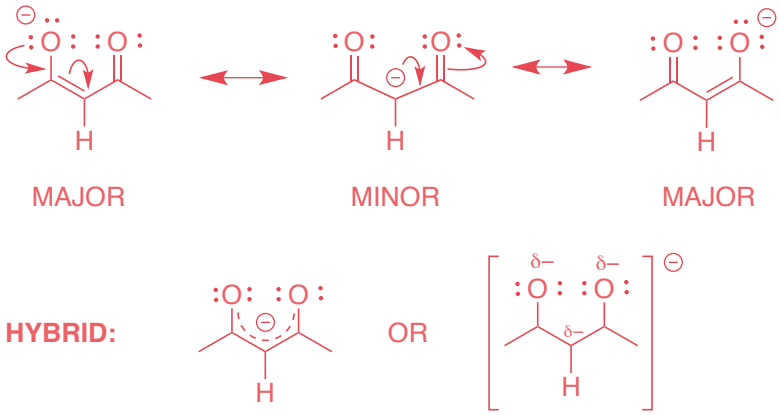
a. Draw the mechanism of the acid-base reaction of this molecule with OH^-.
b. Are the reactants or products favoured? Justify your answer.
c. Draw all the possible resonance forms of the anionic product, indicating the major and minor resonance forms. Include all lone pairs of electrons. Finally, draw the overall resonance hybrid.

a.

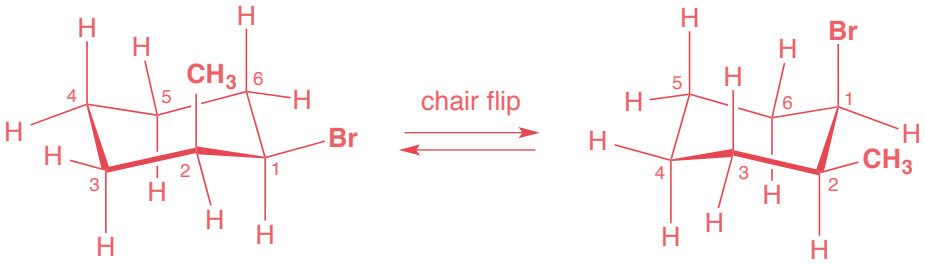


b. Using the pKa's we can see that the starting material is the stronger acid. Therefore, the reaction is product favoured.

c.



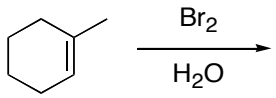
16. (3 pts) Draw the molecule *cis*-1-bromo-2-methylcyclohexane in both chair conformations and indicate which chair is the more stable conformer.



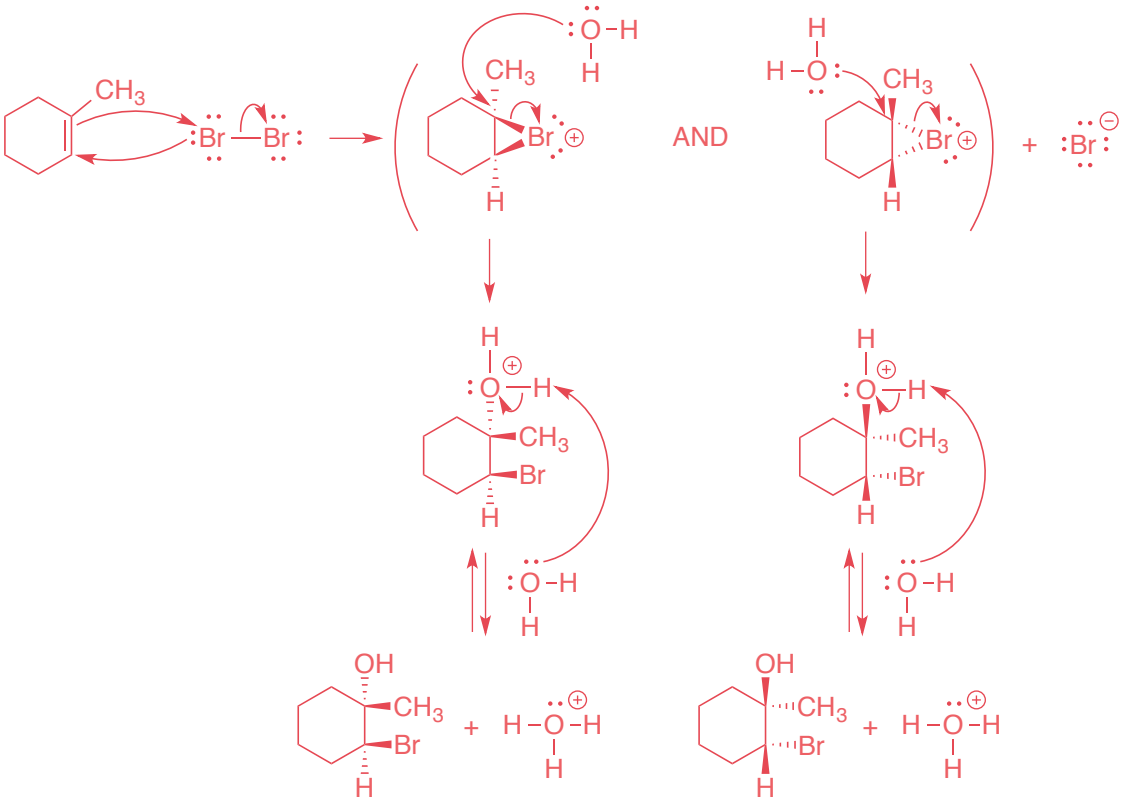
MORE STABLE
(methyl group is in the equatorial position)

Part C

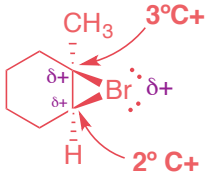
17. Consider the following reaction:



a. (4 pts) Write a detailed mechanism for the reaction.

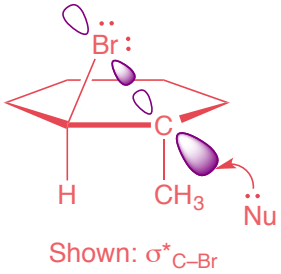


b. (3 pts) Provide a brief explanation for the relative locations of the heteroatoms in the final product (*i.e.* their regiochemistry). You may support your answer by drawing a chemical structure.



This bromonium ion is UNSYMMETRIC: there are two possible carbocation intermediates: a secondary carbocation (2º C+) and a tertiary carbocation (3º C+). Since the 3º C+ is more stable, the nucleophile (H_2O) attacks this electrophilic site, yielding the 1,2-product.

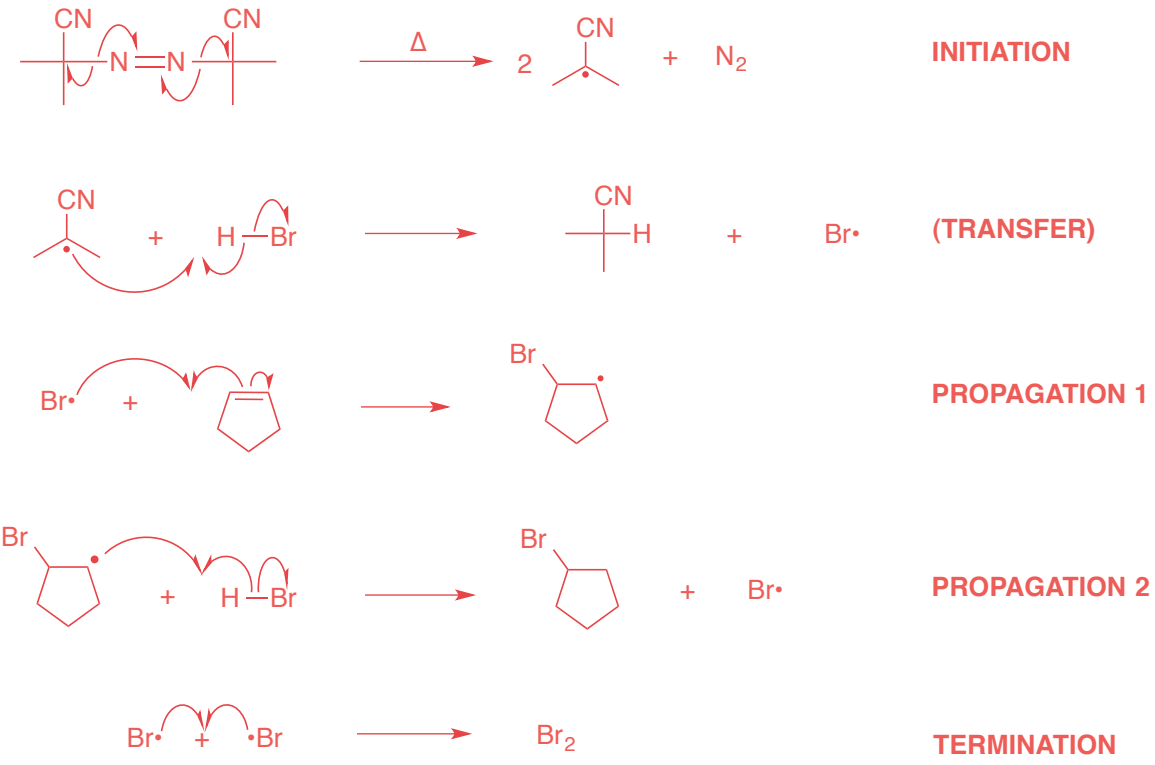
c. (2 pts) Briefly account for the stereochemistry of the final product. Again, you may support your answer by drawing a chemical structure.



Incoming nucleophiles must add to the $\sigma^*_{C\text{-}Br}$ orbital in order to break the C-Br bond. The major lobe of this orbital is located ANTIPERIPLANAR to the C-Br bond → this is why the H_2O attacks from the opposite side to yield the ANTI product.

18. Chain reactions…

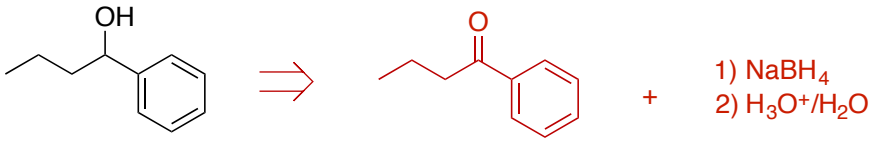
a. (4 pts) Draw the chain reaction mechanism for the reaction of cyclopentene with HBr and AIBN (at about 70°C). Label the initiation, propagation, and termination steps.



b. (1 pt) What is the overall reaction?

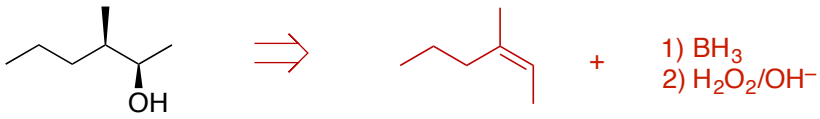
Overall reaction = sum of the propagation steps (there should be no radicals!):

19. (6 pts) Draw one possible set of starting materials that could be used to make each of the following products. There should be a π bond in at least one starting material for each part.

a. 

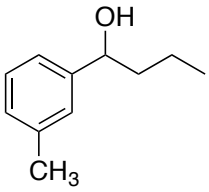
b. 

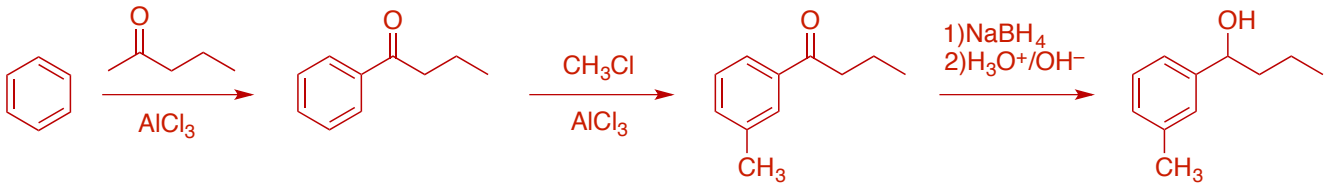
(must be the Z isomer!)

c. 

must be the Z isomer, SYN addition, and ANTI–Markovnikov)

20. (5 pts) Propose a synthesis of the compound below starting from <u>benzene</u> and using any other reagents that you require. Make sure that the compound below is the major product in your synthesis.

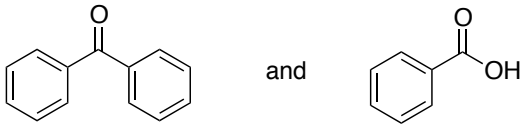




(must be done in this order or the regioselectivity will be incorrect!)

Laboratory Section

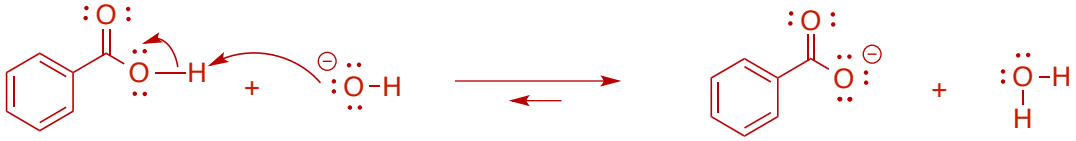
21. Consider a solution of the following compounds in dichloromethane (density = 1.32 g/mL)



Procedure: "Pour the solution into a separatory funnel. Add 10 mL of a 2M aqueous solution of NaOH to the separatory funnel. Shake the funnel."

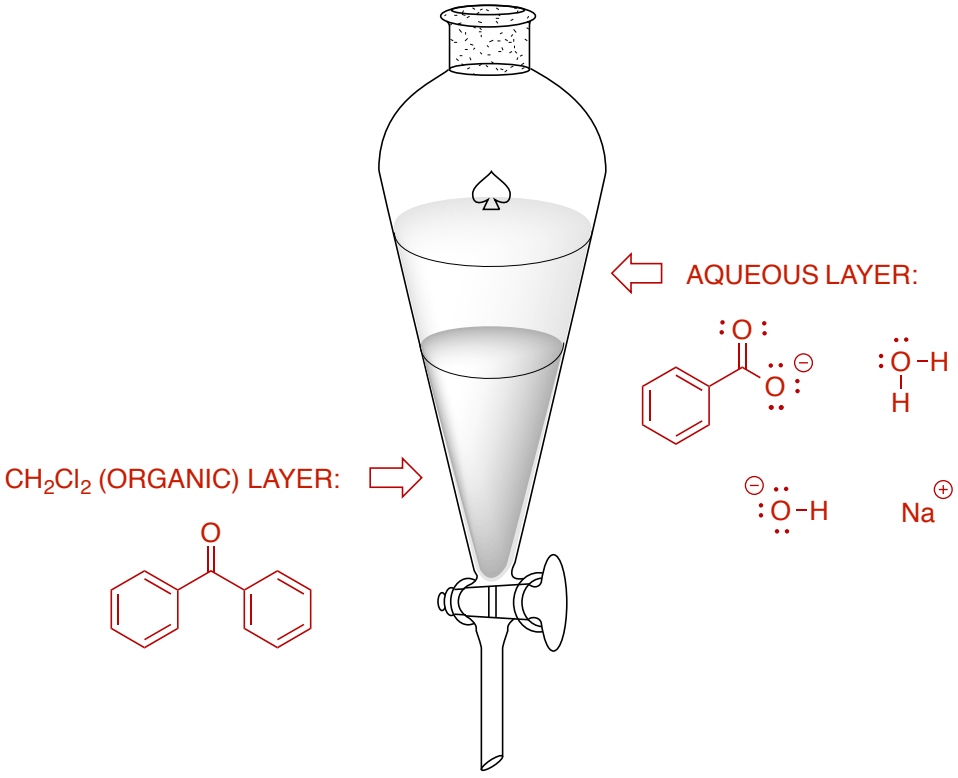
a. (2 pts) Draw the mechanism of the reaction that took place during the procedure above.
b. (4 pts) Draw a diagram of the separatory funnel, clearly labeling the layers and identifying where each species (molecule or ion) is located.

a). Treating the mixture with base will deprotonate the benzoic acid:



Ionizing the acid meaning that the benzoate anion is soluble in the aqueous phase!

b)



22. Consider the following experimental procedure from the Grignard reaction:

"Place 0.80 g of magnesium turnings in a 50 mL round bottom flask. Prepare a solution of 3.0 mL of bromobenzene in about 20 mL of ANHYDROUS diethyl ether. Be sure to keep the flask covered to avoid water contamination. Add the bromobenzene solution to the magnesium solution."

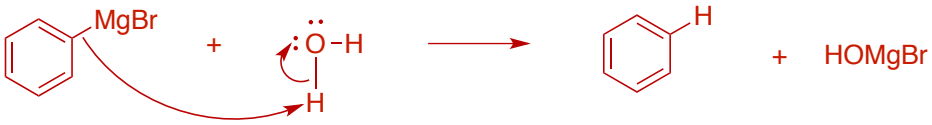
a. (2 pts) Show the reaction that is taking place in this step with an equation.
b. (2 pts) Give a mechanism to show what would happen if water were introduced.
c. (3 pts) Complete the reagent table below:

Compound	Molar mass (g/mol)	Density (g/mL)	Amount (specify units)	Moles (mol)
Magnesium	24.31	N/A	0.80 g	0.033
Bromobenzene	157	1.495	3.0 mL	0.029

d. (2 pts) What is the theoretical yield for this step of the reaction?

a) This is the formation of the Grignard reagent:

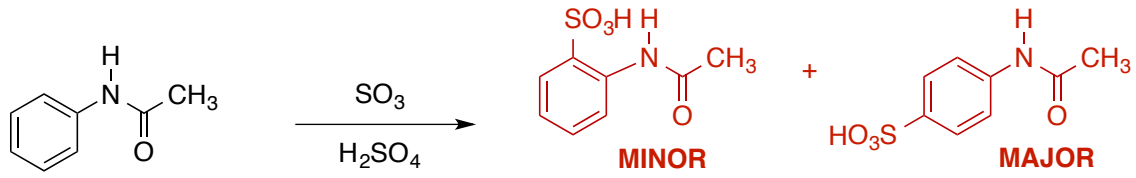
b) If water is introduced, it will destroy the Grignard reagent:



c) See table. Note that the bromobenzene is the limiting reagent.

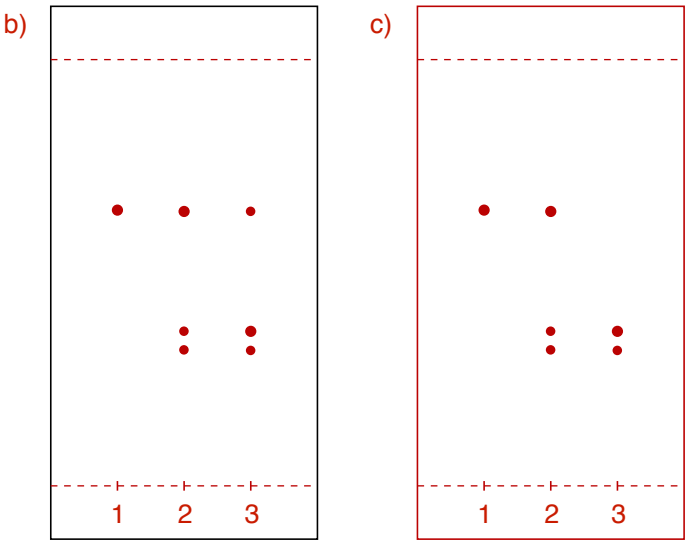
d) If we assume ALL of the limiting reagent (bromobenzene) reacts, we will form 0.029 moles of the product, phenylmagnesiumbromide. Multiplying this quantity by the molar mass of PhMgBr (181.31 g/mol) gives the theoretical yield in grams: 5.2 g.

23. Consider the sulfonation of acetanilide:



a. (1 pt) Draw the expected product(s) in the space above.
b. (2 pts) Draw and label the TLC that would indicate that the reaction was not yet complete (the relative position of the spots is more important than knowing the actual R_f of each component).
c. (2 pts) Draw and label the TLC that would indicate that the reaction was complete (the relative position of the spots is more important than knowing the actual R_f of each component).

For the TLC plates: Lane 1 is the starting material, Lane 3 is the product mixture, and Lane 2 is a co-spot. Note that we expect the products to be MORE POLAR than the starting material, hence the smaller R_f values (but note that it will be tricky to distinguish between the two without reference spots).



24. *Bonus!* Give a mechanism to account for the following transformation: