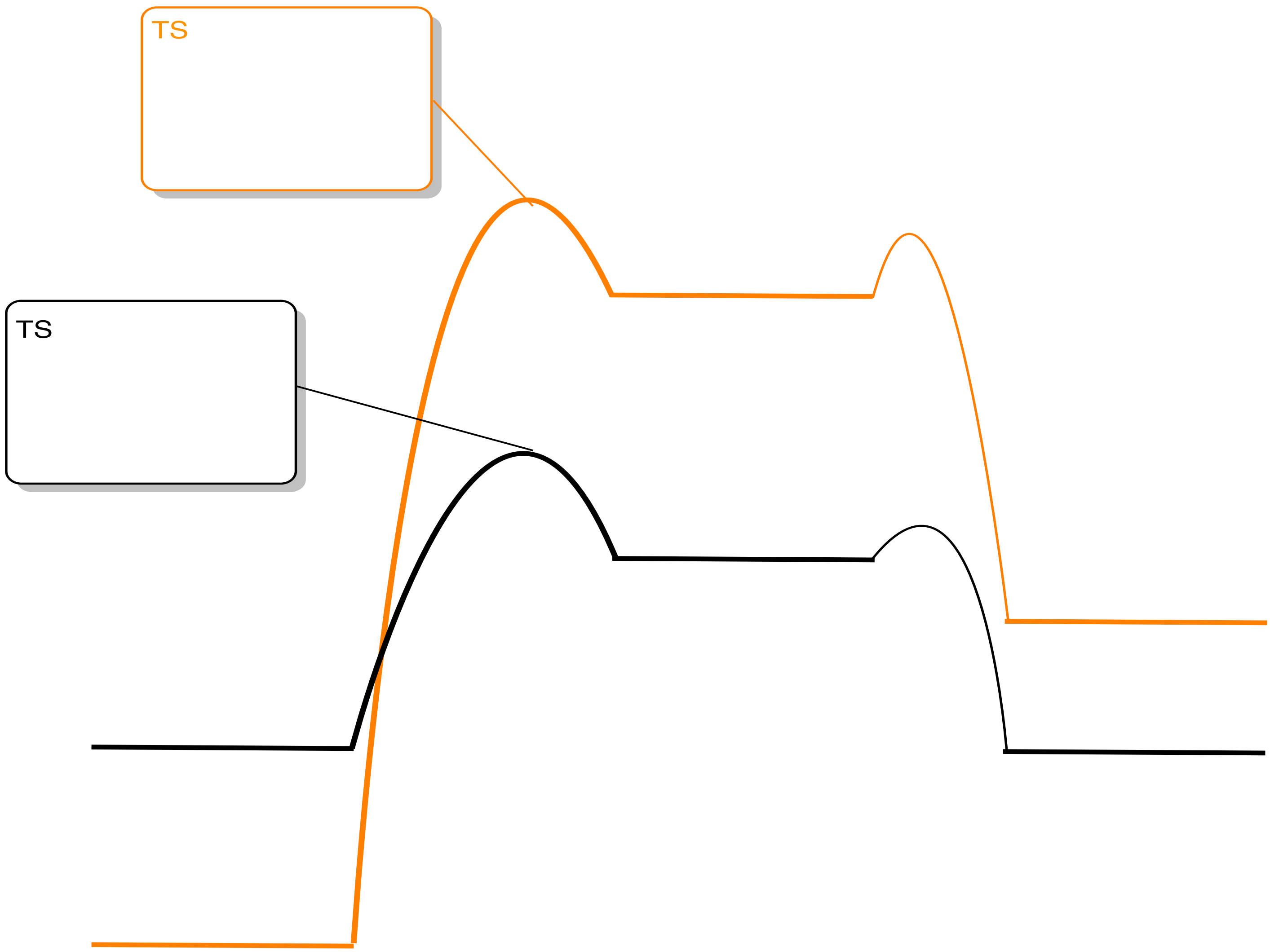
Oakton Community College	**Homework Three** Organic Chemistry II (224) • Prof. Chad Landrie Spring 2013

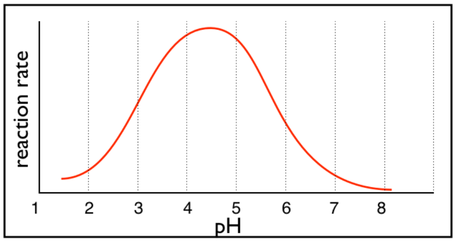
Completion (6 pts)			**Name**	
Random Sample(s) (4 pts)			**BID**	
Total (10 pts)			**Section-CRN**	

Additional Recommended Problems from McMurray (8th Ed.)	

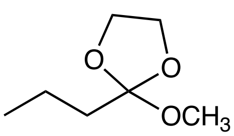
1. The potential energy diagram below represents the hydration equilibria for propanal (K = 1) and 3-pentanone (K = 0.001). Draw the structure of the reactants, transition states, intermediates and products in the correct locations. Transition states should have dashed lines (----) to indicate partial bonds and show partial charges (δ^+ or δ^-) where necessary. Intermediates should include all electron lone-pairs and all formal charges.



2. The rate of imine formation is greatest when the pH of the solution is 4.5. **First**, draw the mechanism for the condensation of acetone with methyl amine to give an imine. **Second,** use your mechanism to explain why the rate decreases when the pH fall below 4.5. Explain why the rate decreases when the pH rises above 4.5.



3. A chemist was attempting to make the compound below. They dissolved the required carbonyl reactant in methanol, added the solution to a round-bottom flask and then added acetic acid. A Dean-Stark trap with a reflux condenser was fitted onto the round-bottom flask and the solution was brought to boiling. The chemist, however, did not observe an aqueous layer in the Dean-Stark trap. Additionally, analysis of the mixture indicated that no reaction had taken place and the carbonyl reactant was recovered. **First**, list the reasons this reaction would not be successful (at least 5). **Second**, explain why each error would impede the reaction. **Third**, suggest **specific** modifications that the chemist should make to correct each error.



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4. Draw the structure for each compound. Include all electron lone-pairs on heteroatoms and all formal charges where appropriate.

triethylamine (TEA)	oxalyl chloride	dimethyl sulfoxide (DMSO)
Dess-Martin periodinane (DMP)	chromic acid ($H_2Cr_2O_7$)	potassium hexamethyldisilazide (KHMDS)
n-butyl lithium (BuLi)	*p*-toluene sulfonic acid (PTSA)	sodium acetate (NaOAc)
potassium *tert*-butoxide ($KOC(CH_3)_3$)	hydrazine	methyltriphenylphosphonium bromide
lithium diisopropyl amide (LDA)	*N*-bromosuccinamide (NBS)	benzyl bromide
trimethylsilyl chloride (TMSCl)	pyridinium chlorochromate	tetrahydrofuran (THF)
succinic anhydride	*m*-chloroperbenzoic acid (mCPBA)	pentyl magnesium bromide

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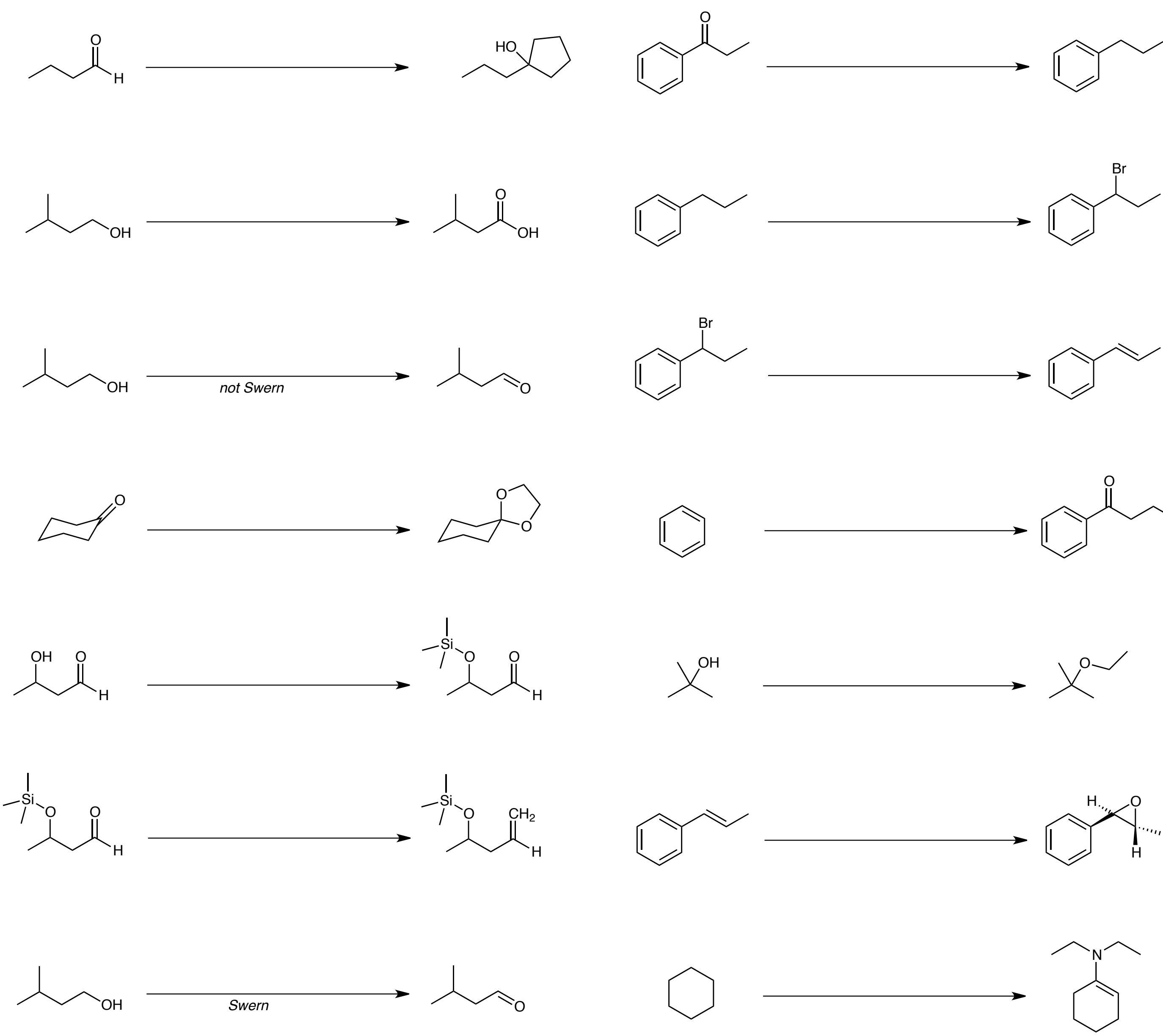
5. Write all of the required reagents and solvents for each transformation above and below the reaction arrows. Each uses at least one of the compounds in the previous table, but is not limited to those compounds.



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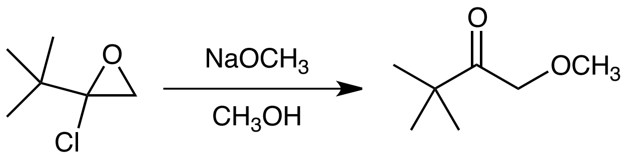
6. Draw a specific example of each of the following reactions. Include the reactant(s), all necessary reagents and the major organic product(s).

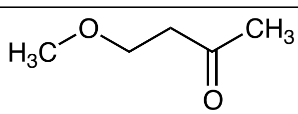
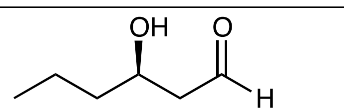
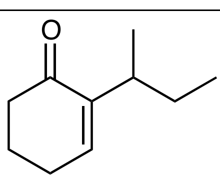
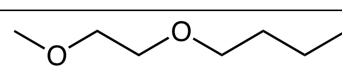
Williamson ether synthesis	reductive amination
Swern oxidation	Dess-Martin periodinane oxidation
Wittig reaction	imine formation
enamine formation	Grignard reaction
acetal formation	epoxidation

7. Suggest a reasonable mechanism for the following reaction.



8. The reaction above is regioselective. Draw the transition state for the rate determining step above and then use that to explain why nucleophilic addition takes place at the least substituted carbon of the epoxide. Transition states should include partial charges and dashed lines (----) to indicate partial bond formation or cleavage.

9. Write the IUPAC name for each molecule.

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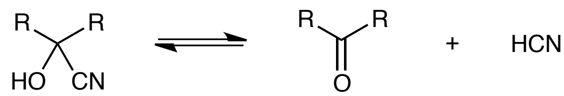
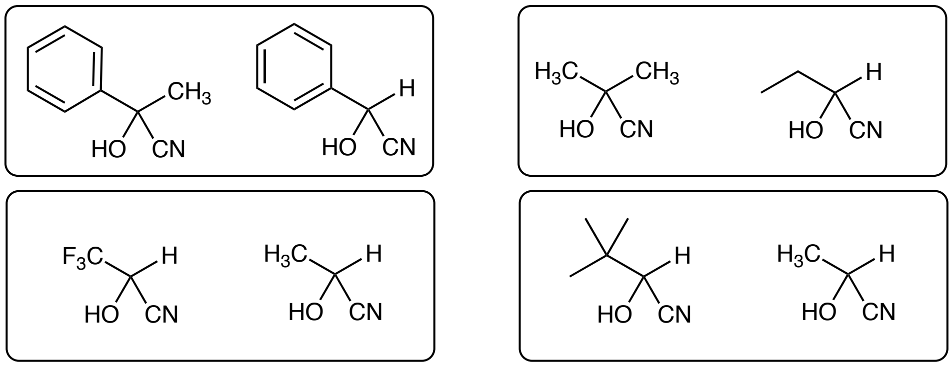
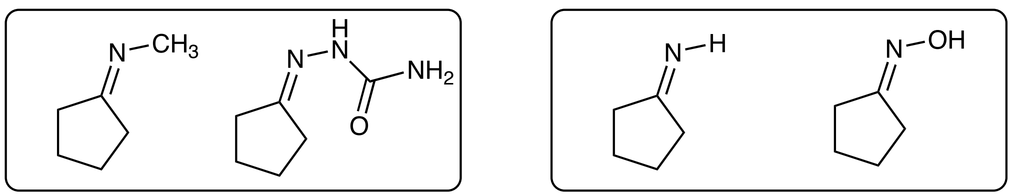
10. Circle the cyanohydrin in each pair with the largest equilibrium constant for dissociation as shown in the reaction below.

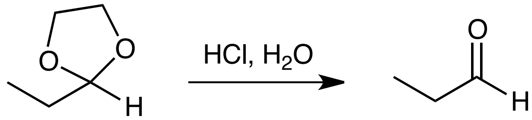




11. **First**, circle the most stable (lowest potential energy) imine in each pair. **Second**, explain your reasoning.



12. Draw the mechanism for the hydrolysis of the acetal shown.



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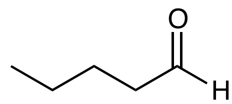
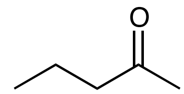
13. Draw the major product of when each set of reaction conditions is applied to pentan**al** and 2-pentan

Conditions	 pentanal	 2-pentanone
a. lithium aluminum hydride then water		
b. sodium borohydride, methanol		
c. methylmagnesium iodide then dilute acid		
d. sodium acetylide then dilute acid		
e. phenylmagnesium bromide then dilute acid		
f. methanol containing dissolved hydrogen chloride		
g. ethylene glycol, *p*-toluenesulfonic acid, benzene		
h. water		

i. dimethylamine, *p*-toluenesulfonic acid, benzene		
j. hydroxylamine		
k. hydrazine		
l. hydrazine, sodium hydroxide, heat		
m. *p*-nitrophenylhydrazine		
n. semicarbazide		
o. ethyltriphenylphosphonium bromide, butyl lithium		
p. sodium cyanide then dilute sulfuric acid		
q. chromic acid		
r. ammonia, dilute acid then sodium cyanoborohydride		

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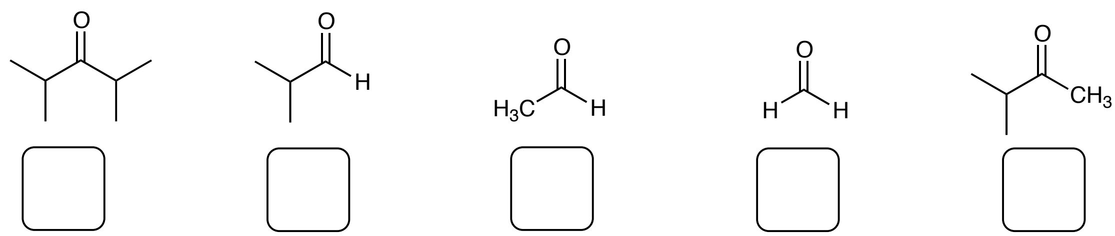
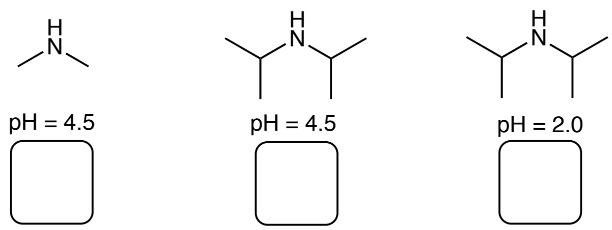
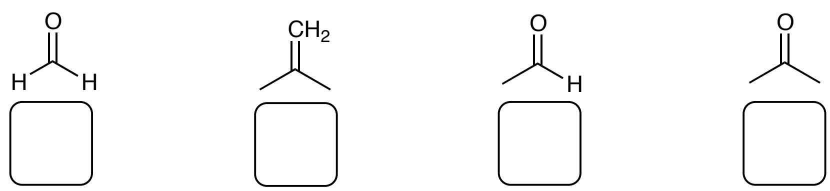
14. Rank in order of increase Keq for hydration (1 = smallest Keq, least % hydrate; 5 = largest Keq, greatest % hydrate).



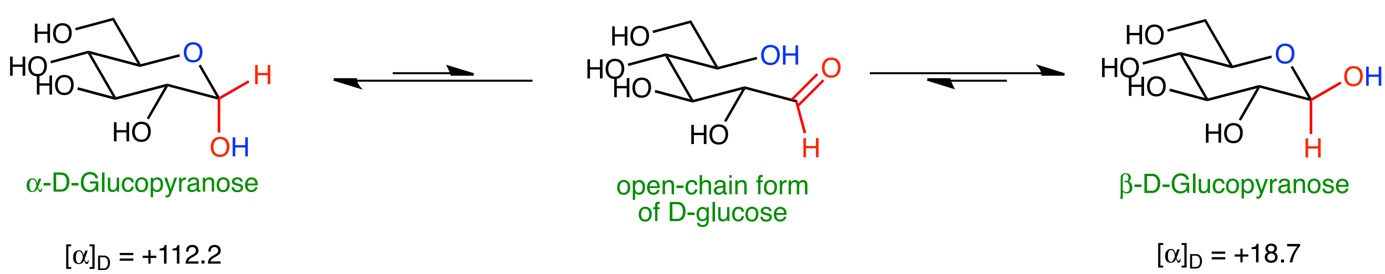
15. Rank in order of increasing nucleophilicity of each amine at the pH given (1 = least nucleophilic; 3 = most nucleophilic).



16. Rank in order of increasing strength of the pi-bond in each compound (1 = weakest pi-bond; 4 = strongest pi-bond).



17. If you dissolve solid α-D-glucopyronose in water, the $[\alpha]_D$ slowly changes from +112.2 to +52.5. If you dissolve solid β-D-glucopyranose in water, the specific optical rotation ($[\alpha]_D$) slowly changes from +18.7 to +52.5. Determine the percentage of α- and β-D-glucopyranose in an aqueous solution. Hint: Use a weighted average.



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18. Design a synthesis for each of the following molecules. Where stereochemistry is shown, your synthesis must be stereoselective.