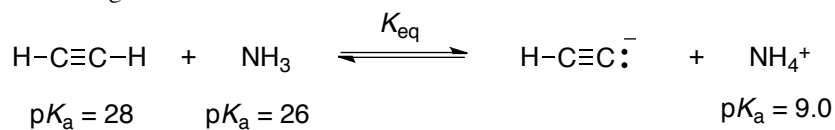
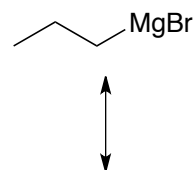
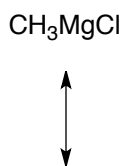
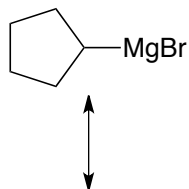


Completion (6 pts)		Name	
Random Sample(s) (4 pts)		BID	
Total (10 pts)		Section-CRN	
Additional Recommended Problems from McMurray (8 th Ed.)		17.25, 17.30, 17.31, 17.32, 17.33, 17.34, 17.35, 17.36, 17.37, 17.38, 17.39, 17.50, 17.52, 17.54, 18.25	

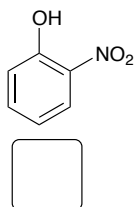
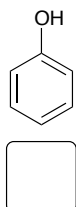
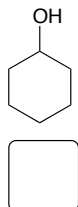
1. Determine whether ammonia is a strong enough base to fully deprotonate acetylene by calculating the K_{eq} for the reaction. Show all work. Write the equation being used.



2. Draw no-bond resonance structures for each of the following Grignard reagents. Include all electron lone-pairs and all formal charges.



3. First, rank the compounds in order of increasing C–O bond length (1 = shortest; 3=longest). Second, explain your ranking. Discuss hybridization and draw resonance structures to support your conclusions.



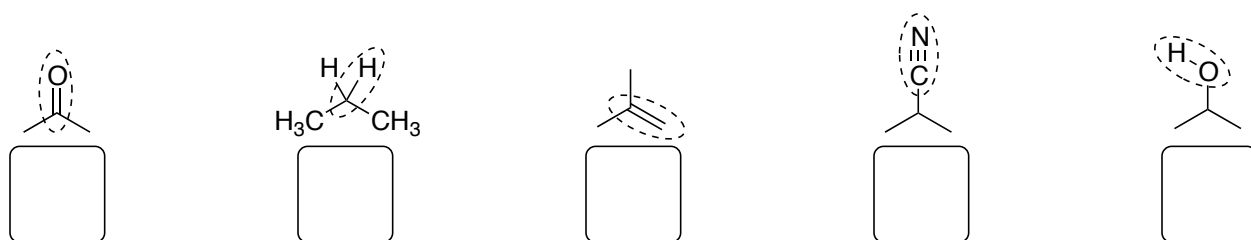
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4. Rank the molecules in each set below according to the trends observed for the physical and chemical properties indicated.

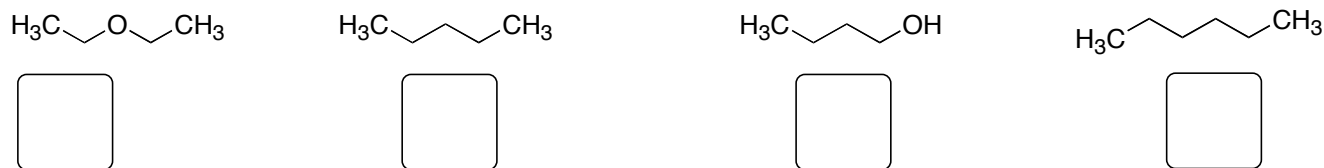
A. (2 pts) Rank in order of *increasing* nucleophilicity. (1 = least nucleophilic; 4 = most nucleophilic).



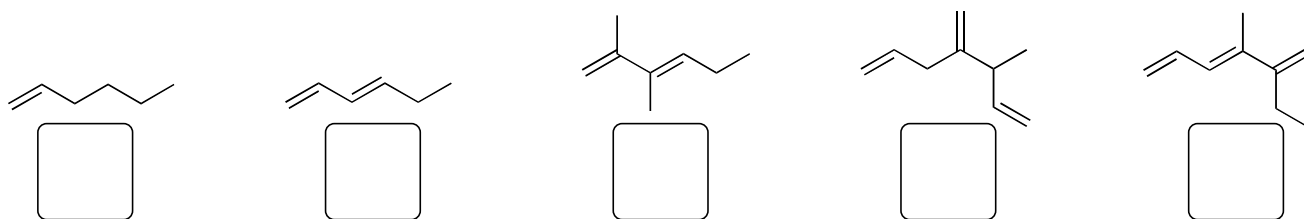
B. (2 pts) Rank in order of increasing infrared stretching frequency for each circled bond. (1 = lowest frequency; 5 = highest frequency).



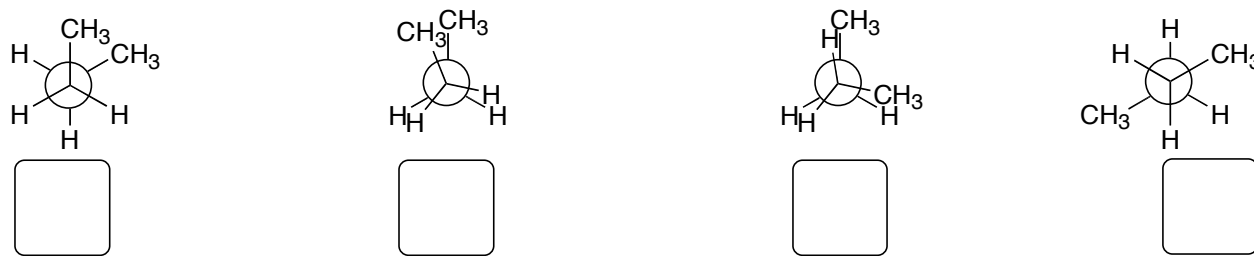
C. (2 pts) Rank in order of increasing solubility in water (1 = least soluble; 4 = most soluble).



D. (2 pts) Rank in order of increasing heat of hydrogenation (ΔH_{hydrog}) (1 = lowest ΔH_{hydrog} , least exothermic; 5 = highest (ΔH_{hydrog} , most exothermic).

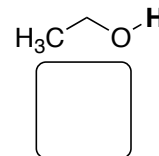
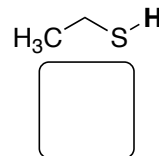
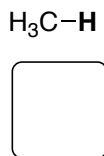
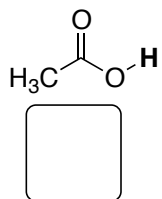
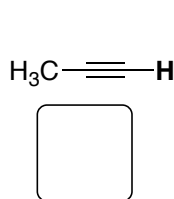


E. (2 pts) Rank in order increasing stability (1 = least stable, highest energy; 4 = most stable, lowest energy).

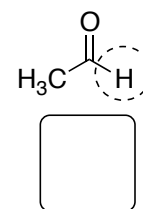
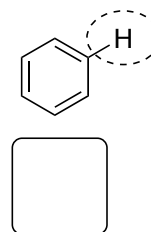
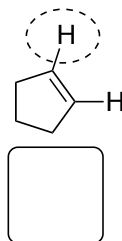
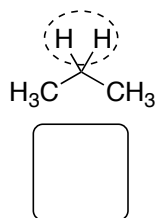
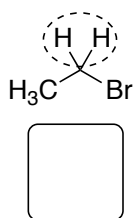


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	Section CRN (-1 pt)	

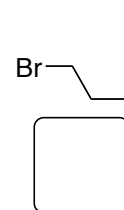
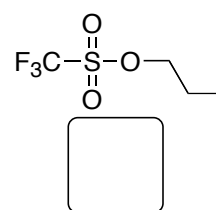
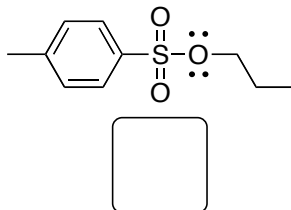
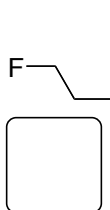
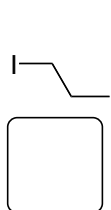
- F. (2 pts) Considering only the most acidic proton in each molecule (bold), rank in order of increasing acidity. (1 = least acidic, highest pK_a ; 5 = most acidic, lowest pK_a).



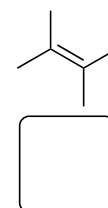
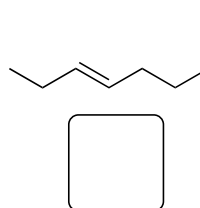
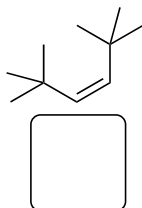
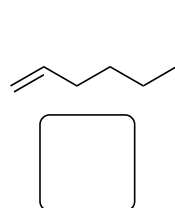
- G. (2 pts) Rank in order of increasing $^1\text{H-NMR}$ chemical shift for each circled set of protons (1 = lowest chemical shift, most shielded; 5 = highest chemical shift, least shielded/most deshielded).



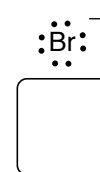
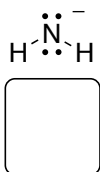
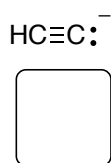
- H. (2 pts) Rank in order of increasing rate of $\text{S}_{\text{N}}2$ substitution (1 = slowest rate; 5 = fastest rate). *Hint: better leaving group = faster rate of $\text{S}_{\text{N}}2$.*



- I. (2 pts) Rank in order of increasing heat of hydrogenation (ΔH_{hydrog}) (1 = lowest ΔH_{hydrog} , least exothermic; 5 = highest (ΔH_{hydrog} , most exothermic).

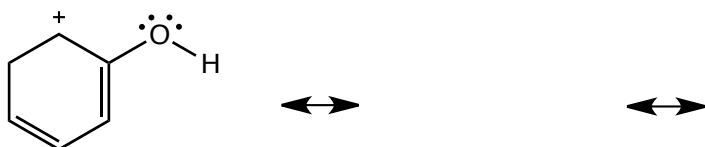
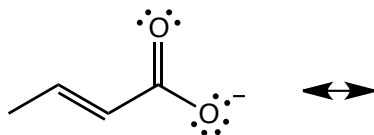


- J. (2 pts) Rank in order of increasing basicity (1 = weakest base; 4 = strongest base). *Hint: The stronger the conjugate acid, the weaker the conjugate base.*

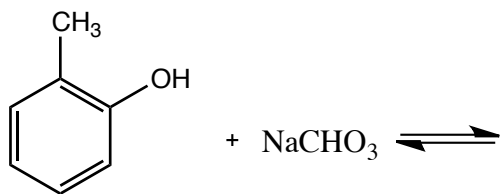


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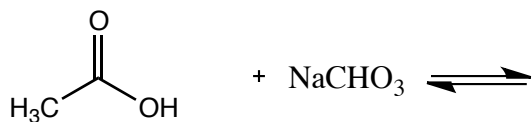
5. **First**, draw resonance structures for each compound, depending on how many resonance arrows are present. **Second**, draw a mechanism using curved-arrow notation to show how the resonance structure on the right is formed from the one on the left. **Third**, circle the major contributor for each series. If two or more are equally the major contributor, circle both. **Fourth**, explain your choice of major contributor in the box below each series.



1. Sodium bicarbonate (NaHCO_3) is the conjugate base of carbonic acid (H_2CO_3 , $\text{pK}_a = 6.37$). **First**, draw the products of the reaction of sodium bicarbonate with phenol and acetic acid. **Second**, use your book to determine the pK_a values of a phenol and a carboxylic acid. **Third**, determine which of these substances will react significantly (i.e., $K_{\text{eq}} > 1$) with sodium bicarbonate. Explain your reasoning.



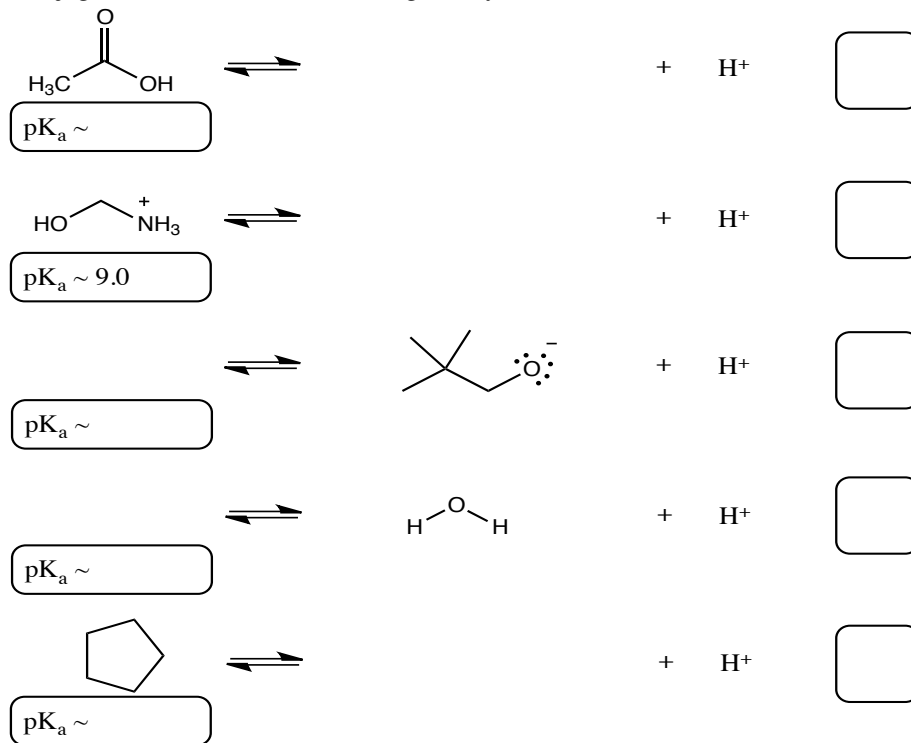
2-methylphenol
a phenol



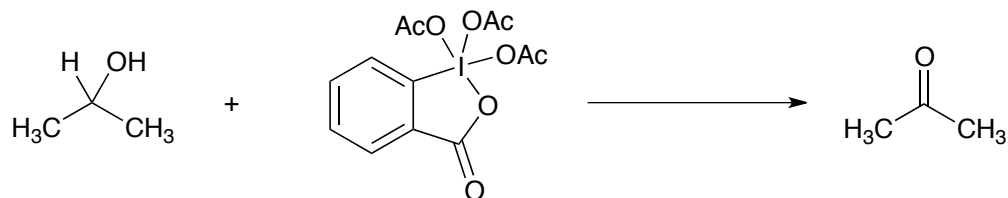
acetic acid
a carboxylic acid

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2. **First**, draw the missing conjugate acid or conjugate base in each dissociation reaction. For acids that have more than one type of H, you should only consider the most acidic H. Be sure to include all formal charges and all lone-pairs on charged atoms. **Second**, write the approximate pK_a under each conjugate acid. Use the table of pK_a 's in your textbook (Appendix B). **Third**, using those pK_a values, rank the conjugate acids in order of increasing acidity (1 = least acidic, 5 = most acidic).

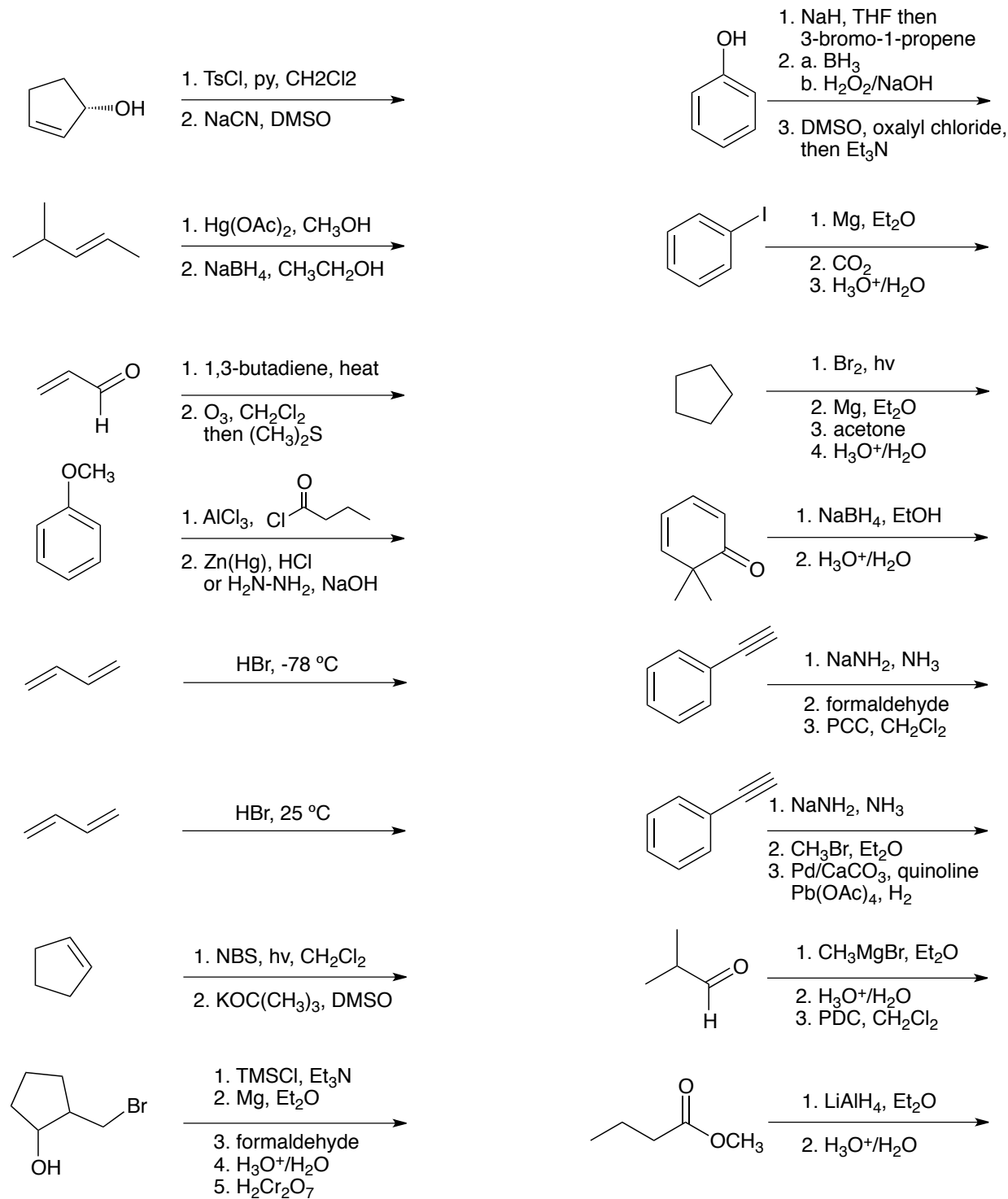


6. The Dess-Martin periodinane oxidation is another common mild method for oxidizing primary alcohols to carbonyls. Draw a mechanism for the reaction below. Hint: Acetate groups (-OAc; -OCOCH₃) are good leaving groups and the first step is substitution of an acetate group by the alcohol.



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7. Draw the major product. If more than one regioisomer or stereoisomer exists, draw the major.



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8. A chemist reacted phenyl magnesium bromide with acetone. After acidic workup, the GC chromatogram showed a mixture of only benzene and acetone and none of the expected product. **First**, draw the expected product. **Second**, explain what might have gone wrong in the experiment and suggest some techniques that may solve the problem.
9. Unlike aldehydes and ketones, esters cannot be reduced by NaBH_4 , but are readily reduced by LiAlH_4 . Explain this observation. Your reasoning should include a discussion of the ground state energies of NaBH_4 vs. LiAlH_4 and for ketones vs. esters. Draw resonance structures where appropriate to support your logic.
10. A chemist attempted to protect the primary alcohol in 3-bromo-2-butanol by treating it with trimethylsilyl chloride in dry methylene chloride (solvent). Even after several days, no reaction was observed by TLC. Explain the likely reason for no reaction then suggest a solution. Be specific.
11. A chemist attempted to make methyl magnesium bromide by adding strips of magnesium metal to a solution of methyl bromide in diethyl ether. Despite gentle heating, no reaction was observed (i.e., the magnesium metal was not disappearing) so the chemist added more magnesium strips that were freshly cut into small pieces. This time the reaction proceeded quickly and all the magnesium was consumed. Explain.

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12. Design a synthesis for each of the following molecules. I highly recommend that you begin with a retrosynthesis (i.e., think backwards, not forwards). There are likely several ways to construct each; try to use an organometallic reaction in all.

