CHEM 234, Spring 2008 First Midterm Ian R. Gould

*PRINTED* **FIRST** NAME _____ *PRINTED* **LAST** NAME _____ *ASU ID or Posting ID* _____

*Person on your **LEFT** (or **Aisle**)* _____ *Person on your **RIGHT** (or **Aisle**)* _____

- ***PRINT YOUR NAME ON EACH PAGE!***
- ***READ THE DIRECTIONS CAREFULLY!***
- ***USE BLANK PAGES AS SCRATCH PAPER***
  ***work on blank pages will not be graded...***
- ***WRITE CLEARLY!***
- ***MOLECULAR MODELS ARE ALLOWED***
- ***DO NOT USE RED INK***
- ***DON'T CHEAT, USE COMMON SENSE!***

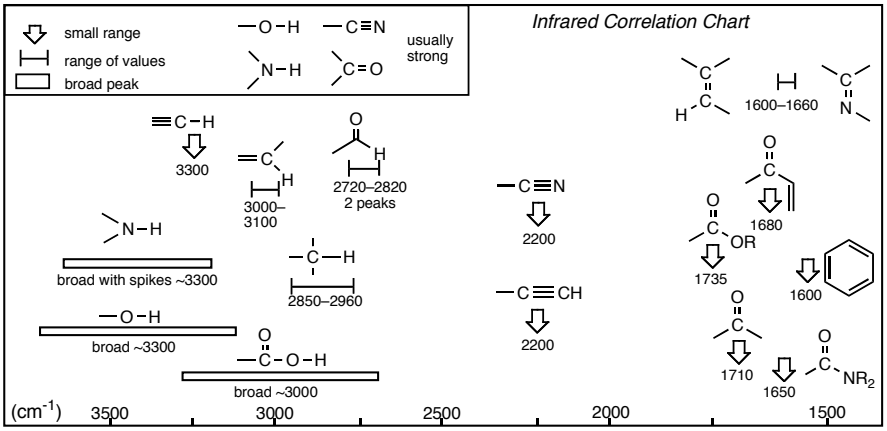
| | | | |
|---|---|---|---|
| 1 nomenclature | /10 | 9 | /10 |
| 2 hydride | /10 | 10 | /10 |
| 3 reactions | /30 | 11 | /10 |
| 4 C-C bonds | /24 | 12 | /10 |
| 5 Retro | /38 | 13 | /10 |
| 6 mechanisms | /34 | 14 | /10 |
| 7 acidity 1 | /12 | 15 | /10 |
| 8 acidity 2 | /12 | 16 | /10 |

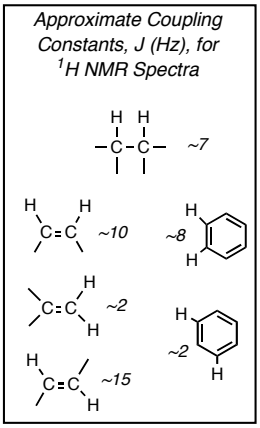
**Extra Credit** _____/5 **Total (incl Extra)** _____/175+5

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | Lu | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |

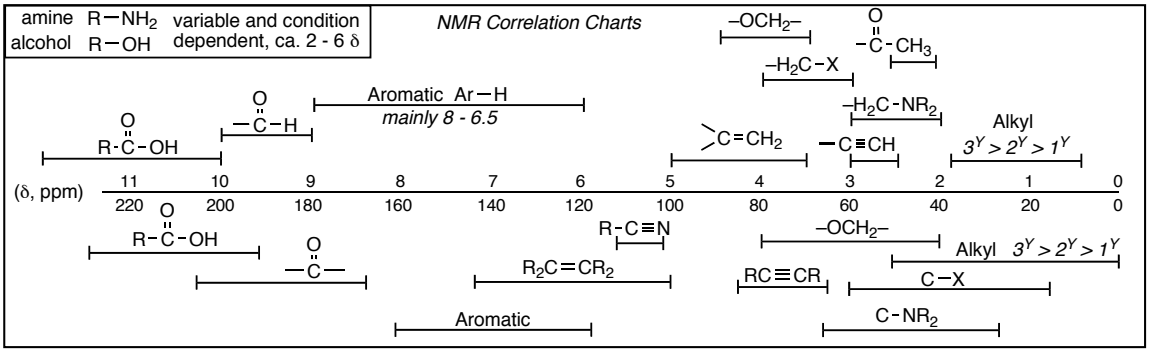
**Interaction Energies, kcal/mol**

| Eclipsing | | Gauche | |
|---|---|---|---|
| H/H | ~1.0 | Me/Me | ~0.9 |
| H/Me | ~1.4 | Et/Me | ~0.95 |
| Me/Me | ~2.6 | i-Pr/Me | ~1.1 |
| Me/Et | ~2.9 | t-Bu/Me | ~2.7 |

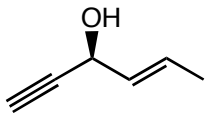



amine R–$NH_2$ variable and condition
alcohol R–OH dependent, ca. 2 - 6 δ



Question 1 (10 pts.) Give an unambiguous IUPAC or common name for the following compound. Be sure to use cis/trans, E/Z or R/S where appropriate.




hex-(4E)-en-1-yn-(3S)-ol

Question 2 (10 pts.). Sodium borohydride ($NaBH_4$) reduces only aldehydes and ketones. Lithium aluminum hydride ($LiAlH_4$) will reduce aldehydes and ketones and also esters and carboxlic acids. Do you think that sodium hydride (NaH) will also reduce esters and acids? Give a BRIEF explanation for your asnwer.

Yes. $LiAlH_4$ is more reactive than $NaBH_4$ because the electrons in the Al-H bonds are higher in energy than those in the B-H bond, since Al is larger than B. Since the electrons in NaH are in a very weak bond to a metal (mainly ionic), they must be even more reactive than in $LiAlH_4$, so yes, NaH should reduce esters and acids.

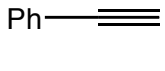
5 pts Extra Credit. organic metals can be made by polymerizing.....

epoxides alkenes alcohols alkynes

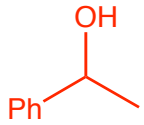
from "O-Chem in Real Life" page : organic Metals, week #2

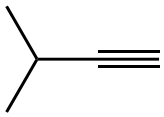
Question 3 ( 35 pts.)

Provide the missing **major organic product, the reagents and conditions, or the reactant** for the following reactions, as appropriate. Ignore sterochemistry.

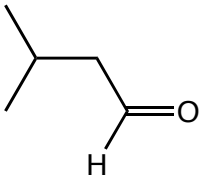
a) 

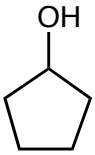

1. $HgSO_4/H_2SO_4/H_2O$
2. $NaBH_4/EtOH$



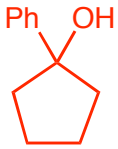

b) 

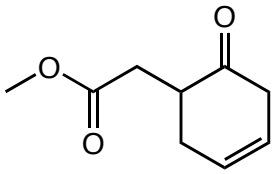
1. $Sia_2BH.THF$
2. $^{-}OH/H_2O_2$



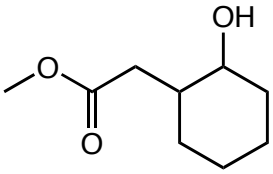

c) 

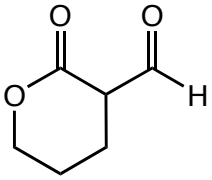

1. PCC
2. PhMgBr
3. $H_3O^+$



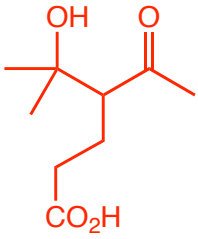

d) 


$H_2/Pd/C$



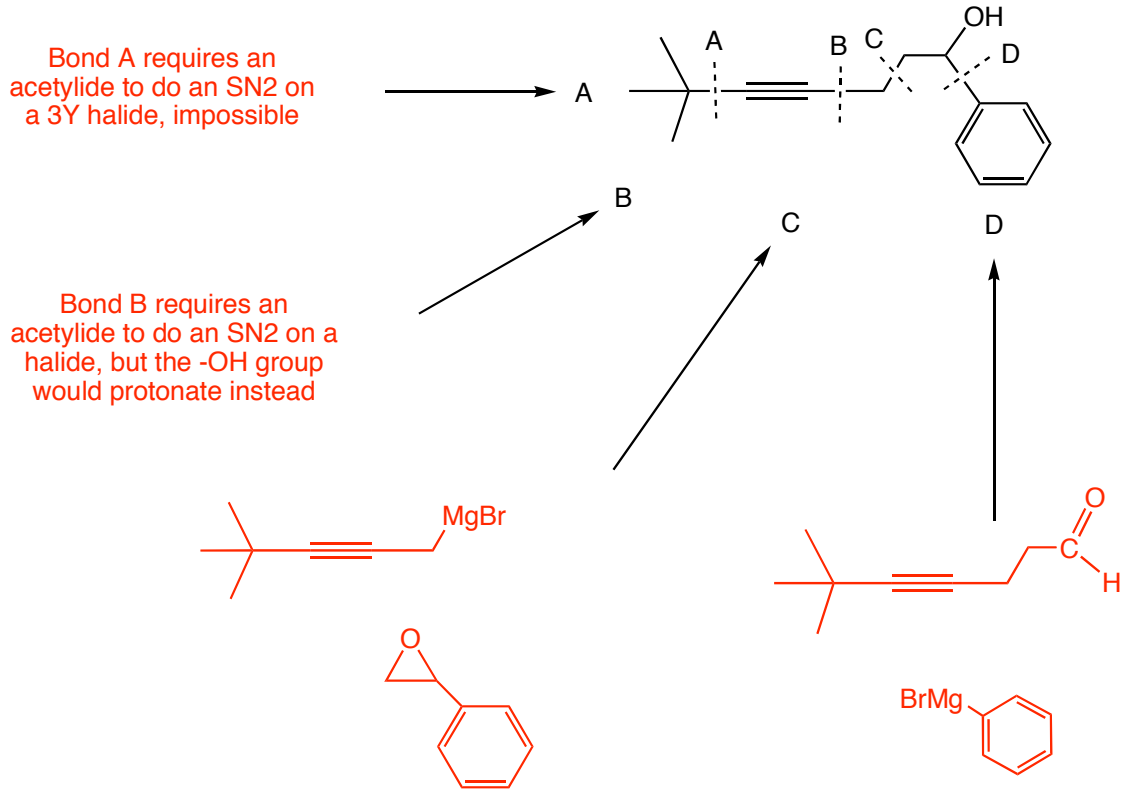

e) 


1. Excess $CH_3MgBr$
2. $Na_2Cr_2O_7/H_2SO_4/H_2O$



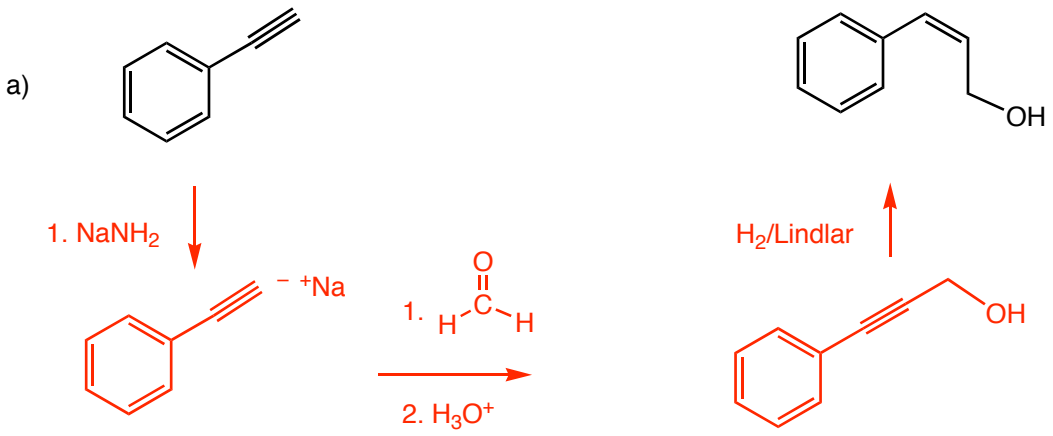
Question 4 (24 pts.) For **EACH of the bonds labelled A, B, C and D**, draw the **structure of the the acetylide anion or the Grignard reagent** AND the **other structure it would react with** perform the reaction and give the product shown (you do not need to specify any follow-up hydrolysis steps using $H_3O^+$, they are assumed)

**IF IT IS NOT POSSIBLE TO MAKE THE BOND using an actetylide or Grignard reaction**, give a **BRIEF explantion why not.**

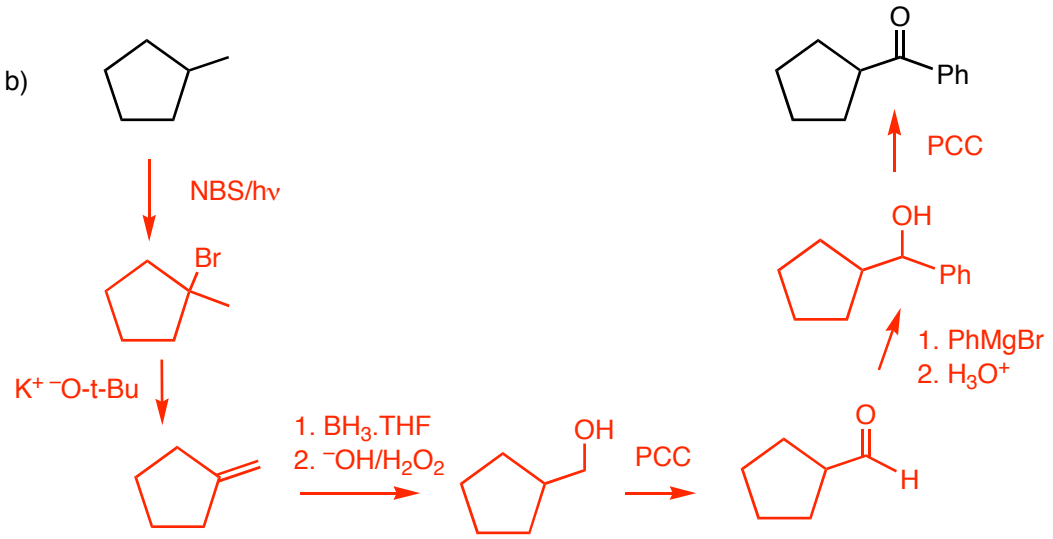


Question 5 (38 pts.) Show how you would synthesize the target compounds on the right from the starting compounds on the left. Show reagents and conditions, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

a)

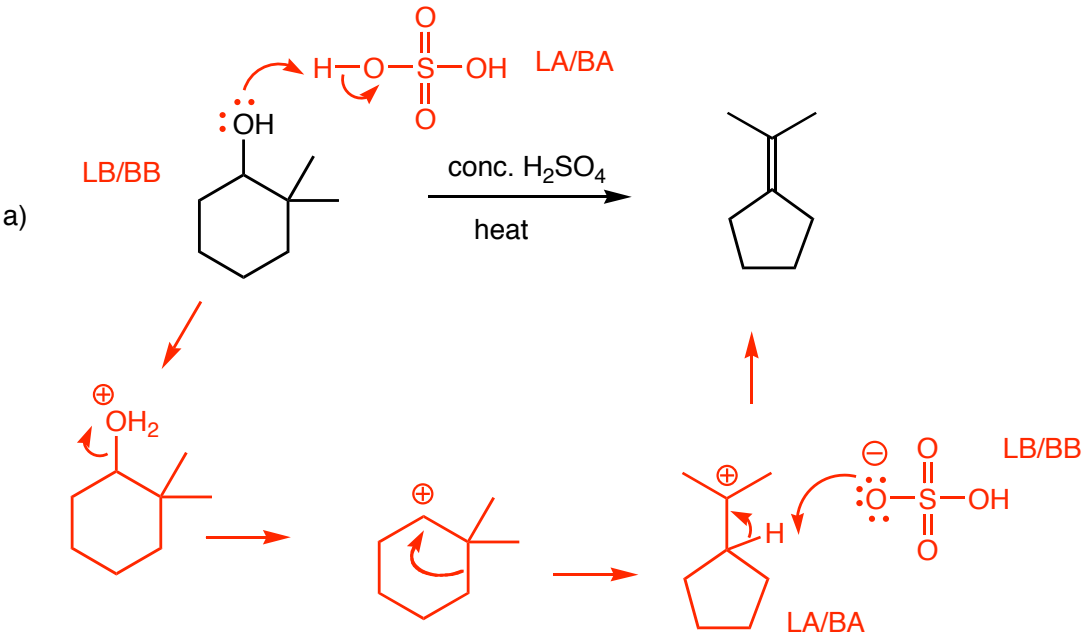



b)

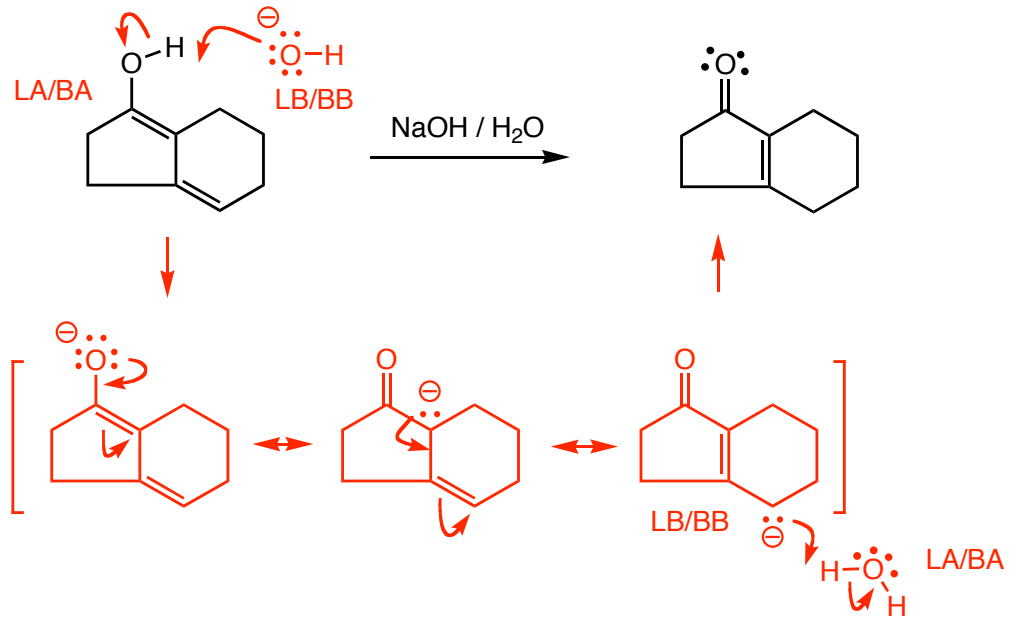


Question 6 (34 pts). **READ THIS QUESTION CAREFULLY**!! For **EACH** reaction, give a complete arrow pushing mechanism, and...
1) Show **ALL** important resonance structures of any intermediates.
2) Add non-bonding electrons and C-H bonds to the line-angle structures as required.
3) Indicate the Lewis acid/Lewis base (LA, LB) at each step as appropriate, and whether they are also Brønsted acids/bases (LA/BA, LB,BB).

a)

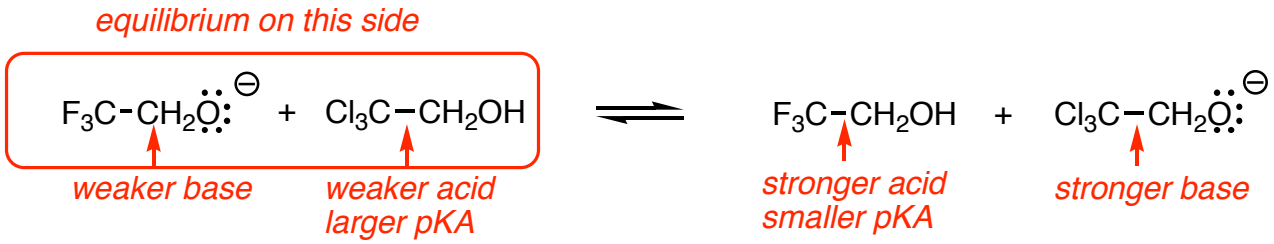



b)



Question 7 (12 pts). For the following acid/base equilibrium

i) Indicate the stronger and weaker **ACID**
ii) Indicate the stronger and weaker **BASE**
ii) indicate which acid has the **LARGER** and which the **SMALLER pKa**
iii) Indicate clearly which side the equilibrium will lie
iii) Give a BRIEF explanation




The $F_3C$– group is more inductively electron withdrawing than the $Cl_3C$– group due to higher electronegativity of F compared to Cl, and thus stabilizes the anion better, stronger acid makes more stable anion, which is thus weker base, equilibrium lies on the side of the weaker acid and base.

Question 8 (12 pts.) Which of the two following alcohols is the stronger Brønsted acid? Give a BRIEF explanation, using drawings of resonance contributors if helpful.