CHEM 234, Spring 2012 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!***

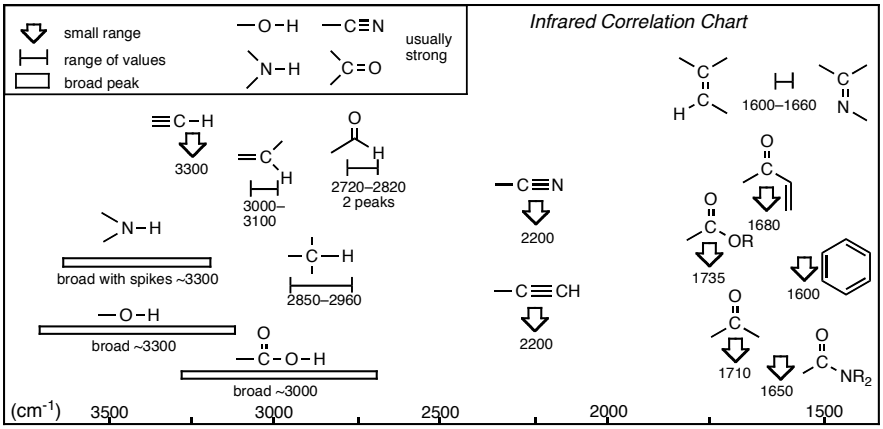
1 acidity /25
2 reactions /42
3 C-C bonds /14
4 Grignard /7
5 nomen /10
6 concept /5 <everybody got 5 pts
7 retro /36
8 mechn. /36

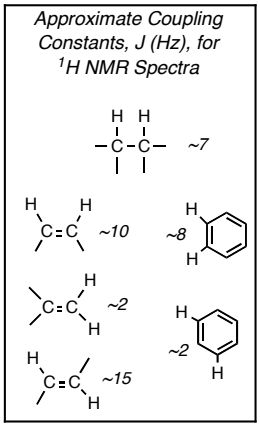
Extra Credit_____/5 **Total (incl Extra)**_____/175+5

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

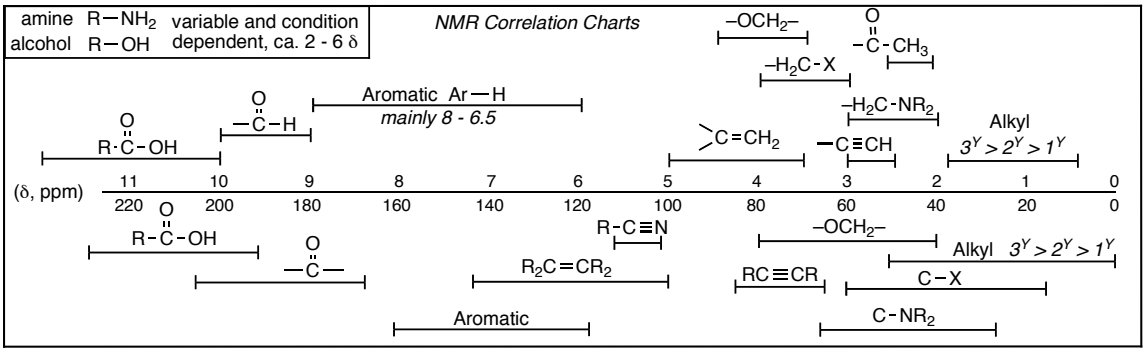
Interaction Energies, kcal/mol

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

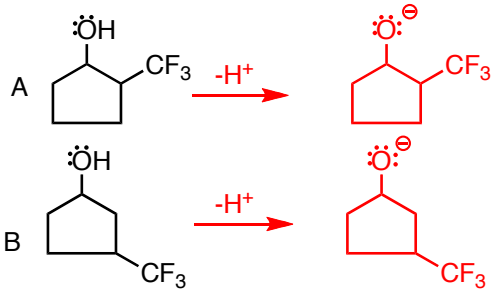


Question 1 (25 pts.) In each case give the STRONGER Bronsted acid of the two structures A and B and give a BRIEF explanation for your choice.

Give drawings of the conjugate base anions including ALL resonance contributors as appropriate

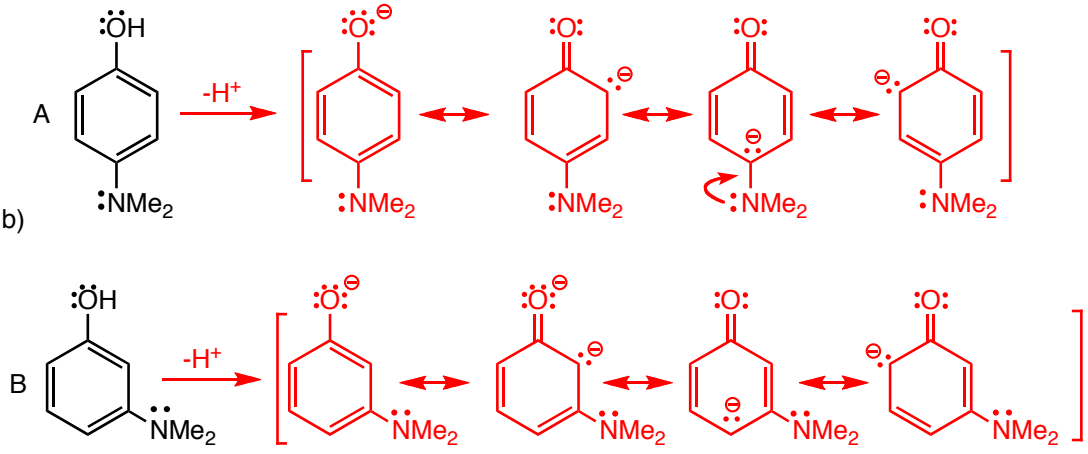
Each of your explanations MUST mention the possible roles of RESONANCE and the INDUCTIVE EFFECT, even if there is none in these particular cases

a)



A is the stronger acid, the conjugate base anion in A is more stabilized by the inductive effect of the electronegative fluorines, the inductive effect is greater in A than B because the fluorines are closer to the non-bonding electrons of the base, the non-bonding electrons are not stabilized by resonance and the -CF3 substituent does not donate electrons by resonance

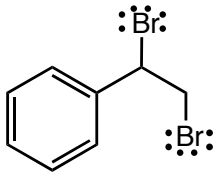
b)



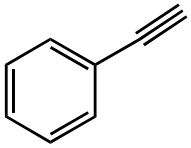
B is the stronger acid, the conjugate base anion in A is directly DEstabilized by the resonance donation effect of the -NMe2 substituent, which is more important than the inductive effect of the nitrogen, in B the anion is not directly destabilized since there is no partial negative charge on the carbon with the -NMe2 substituent

Question 2 (first part, 21 pts.) For each reaction
1) Provide the missing **reagents/conditions**
2) **State** whether each reaction is an Addition, Elimination, Substitution or Rearrangement
3) **State** whether each reaction is Reduction, Oxidation or Neither

a)

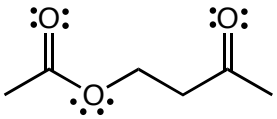


1. Excess $NaNH_2$/heat
2. H_2O

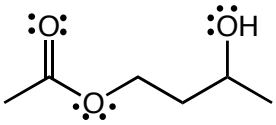


elimination
neither

b)



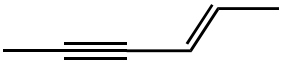
$NaBH_4$ / EtOH



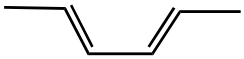
(±)

addition
reduction

b)



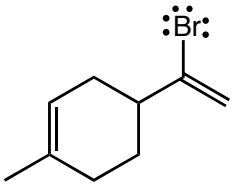
$Na/NH_3(l)$



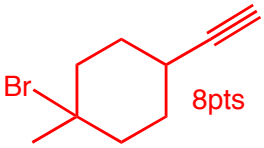
addition
reduction

Question 2 (second part, 21 pts.) GIve the major organic product of the following reactions
DO NOT STATE whether the reaction is Addition/Eimination/Substitution/Rearrangement
DO NOT STATE whether each reaction is reduction/oxidation/neither

c)

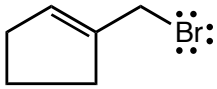


1. Excess $NaNH_2$/ heat
2. H_2O
3. 1 Equiv. HBr

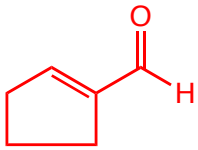


8pts

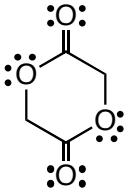
c)



1. $Na^+ {}^-OH$
2. PCC

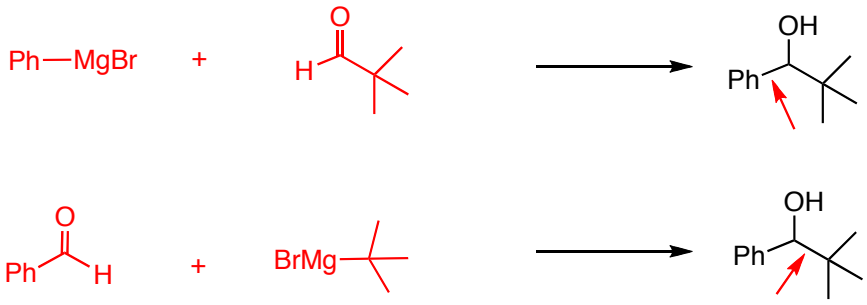


d)

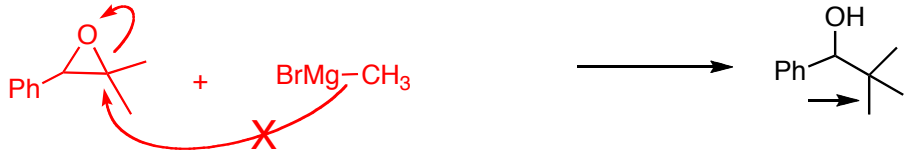


1. Excess $LiAlH_4$
2. H_3O^+

Question 3 (14 pts.) In the provided structure, identify TWO carbon-carbon bonds that can be made using a Grignard reaction, give the structures of the Grignard and moelecule that it reacts with, acid workup steps are assumed you do not need to include them. **CLEARLY indicate the C-C bond you are making in each reaction with an arrow**

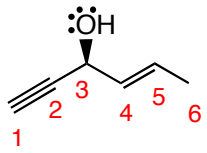


Question 4 (7 pts.) In the provided structure, explain why the bond indicated with the arrow can NOT be made in a Grignard reaction.



this bond would have to have been made by Grignard addition to the most substituted end of an epoxide

Question 5 (10 pts.) Give the IUPAC 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 6 (5 pts.) An alkyne reacts slower than an alkene in an electrophilic addition reaction because....
the electrons in the pi-bonds are lower in energy in the alkyne because the sp hybridization results in a shorter C-C bond and better overlap between the 2 sets of p atomic orbitals

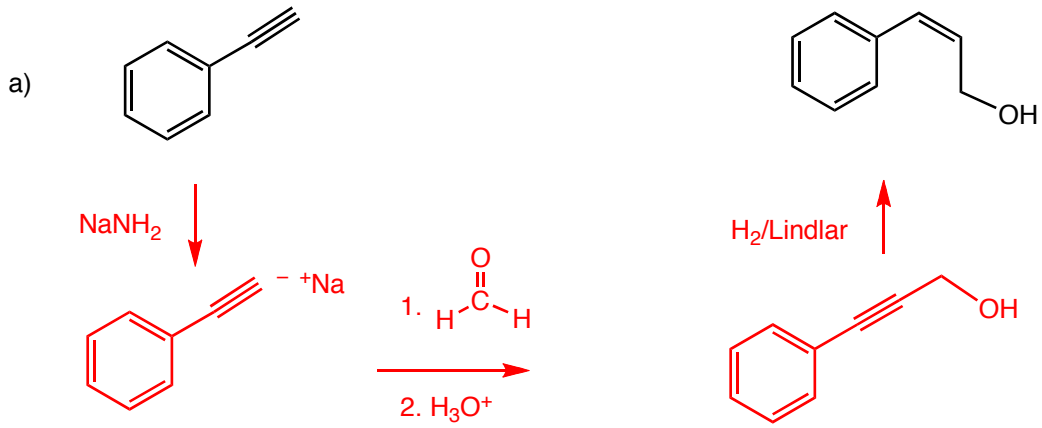
5 pts Extra Credit. organic metals can be made by polymerizing.....

epoxides alkenes alcohols alkynes

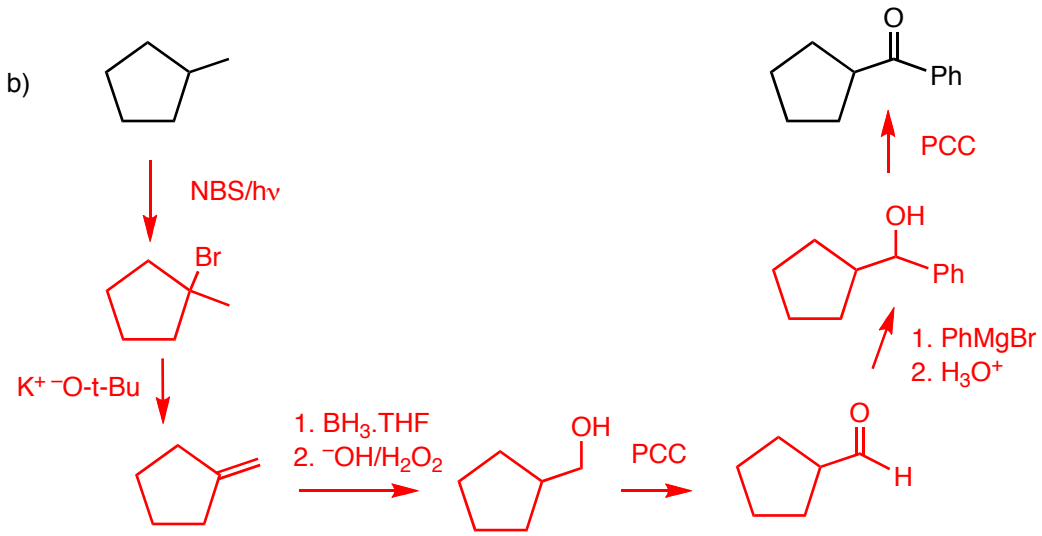
from "O-Chem in Real Life" page : organic Metals, week #3

Question 7 (36 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)

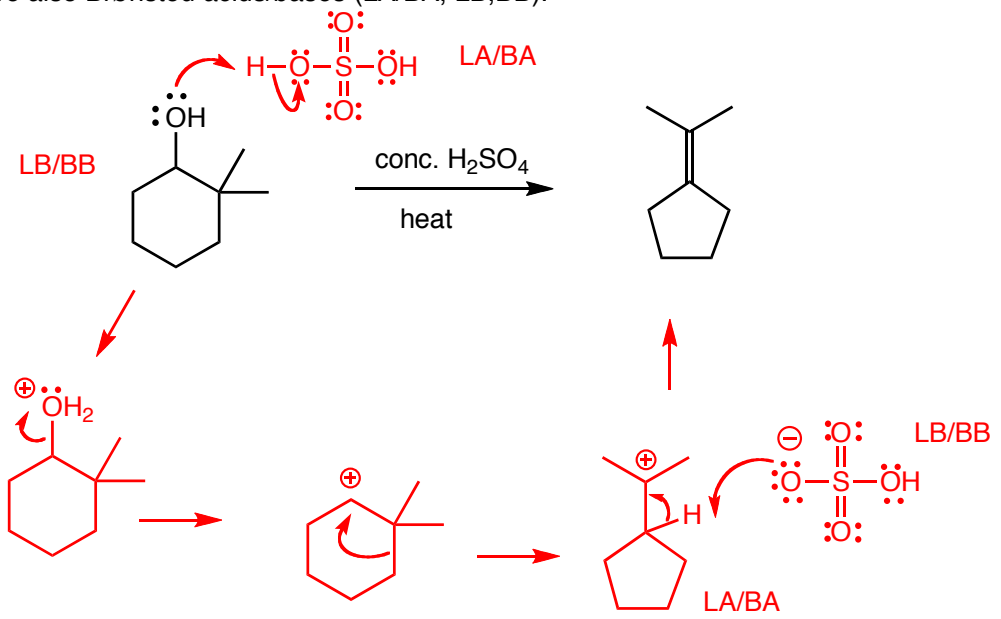


b)

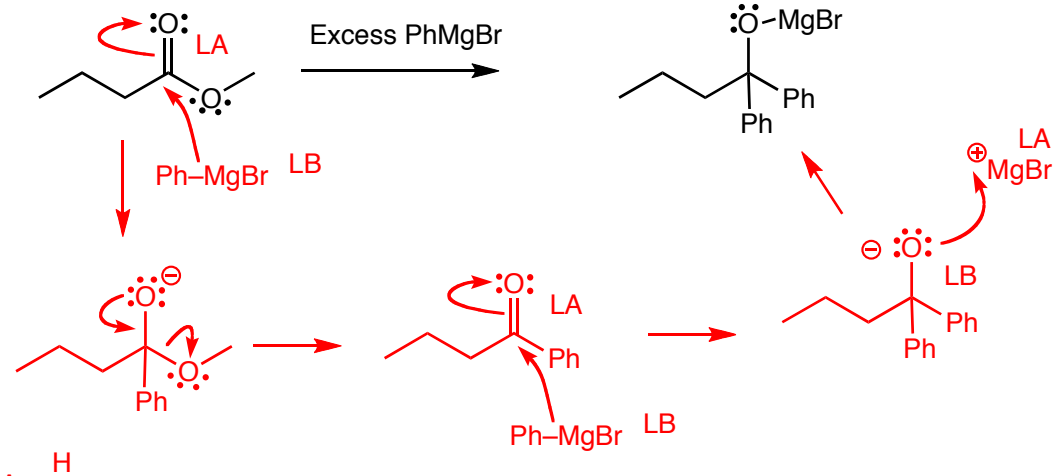


Question 8 (36 pts). For **EACH**, give a complete curved arrow pushing mechanism, and...
1) Show **ALL important resonance contributors for all intermediates.**
2) Add non-bonding electrons and C-H bonds to the line-angle structures as required.
3) Indicate the Lewis acid/Lewis base (LA, LB) at each step as appropriate, and whether they are also Brønsted acids/bases (LA/BA, LB,BB).

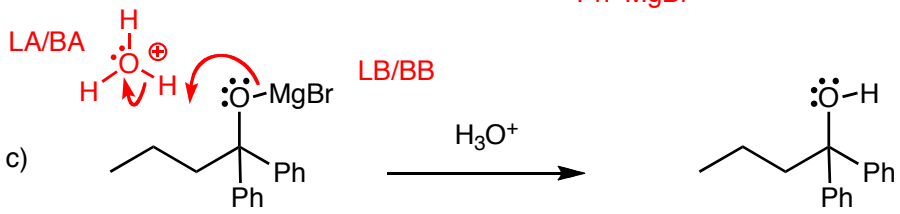
a)



b)



c)



part c) is not a trick, it is a simple 1-step reaction, do the curved arrow-pushing for the one step