CHEM 234, Spring 2010 | Second Midterm | Ian R. Gould

PRINTED **FIRST** NAME **ANSWER** *PRINTED* **LAST** NAME **KEY** *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!***

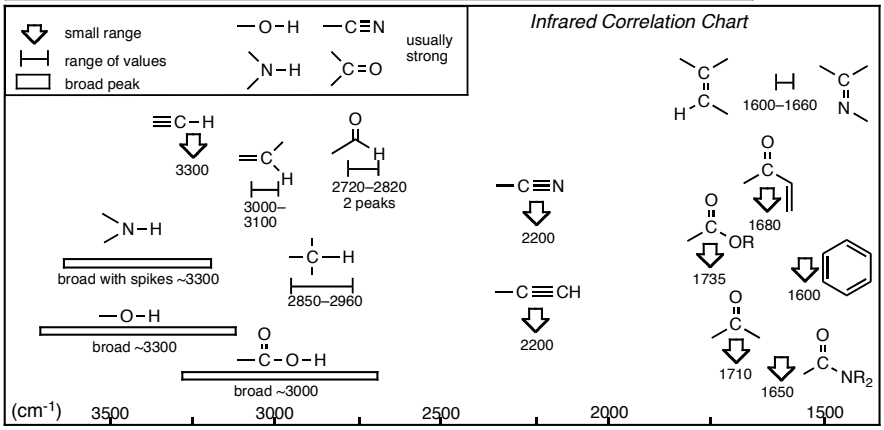
1	nomen /10	9	peri3 /18
2	mxn 1 /20		
3	D/A /16		
4	reactions /16		
5	k vs Th /34		
6	retro /25		
7	peri1 /18		
8	peri2 /18		

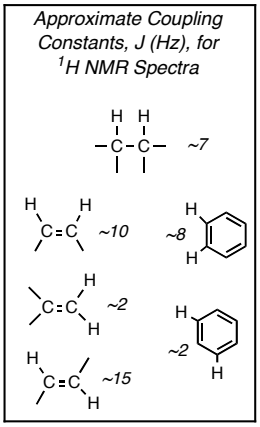
Extra Credit_____/5 **Total (incl Extra)**_____/175+5

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

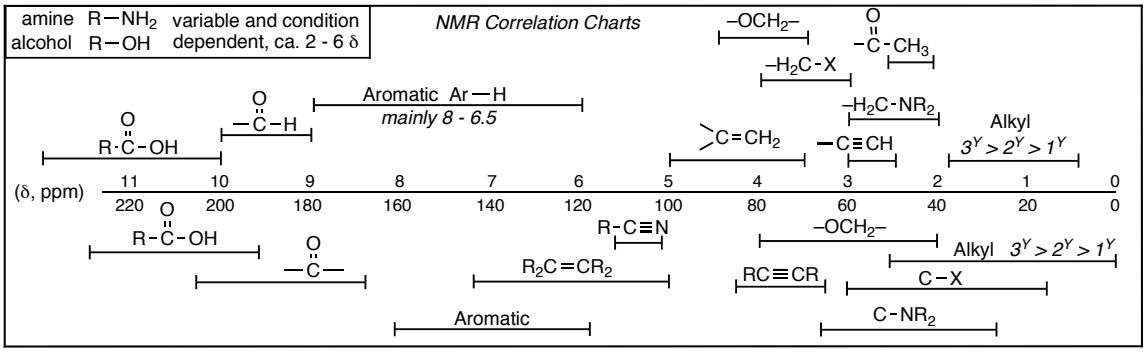
Interaction Energies, kcal/mol

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

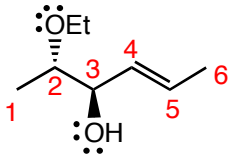




amine R—NH_2 variable and condition
alcohol R—OH dependent, ca. 2 - 6 δ



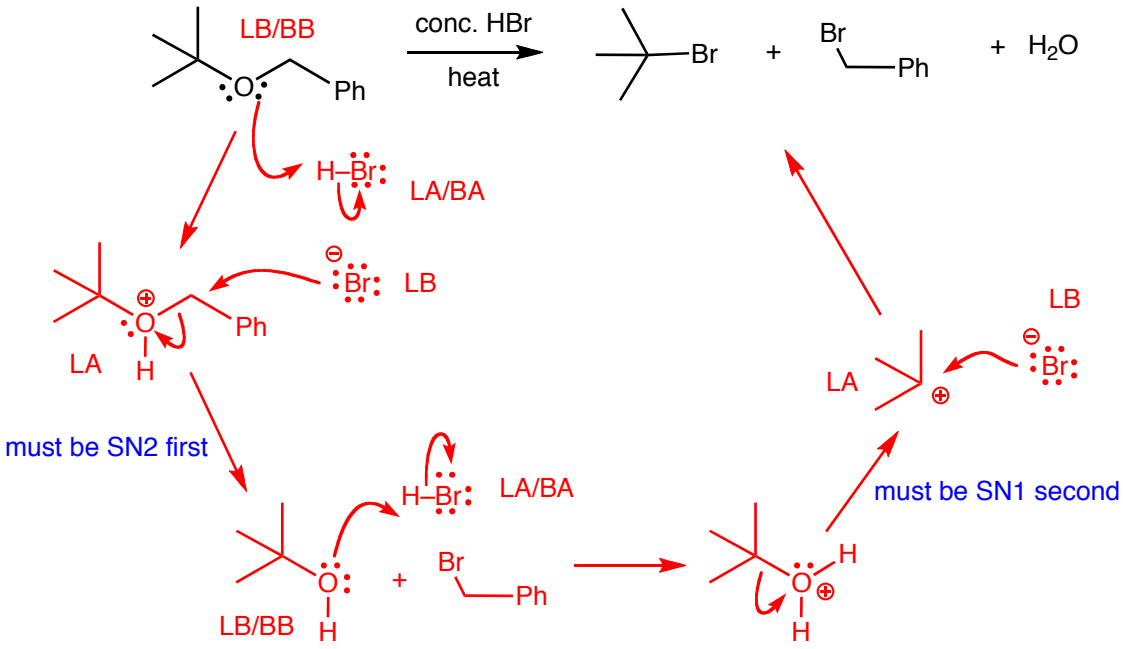
Question 1 (10 pts.) Give the IUPAC name for the following compound. Be sure to use cis/trans, E/Z or R/S where appropriate.



(2S)-ethoxyhept-(4E)-en-(3R)-ol

grading -2pts each error

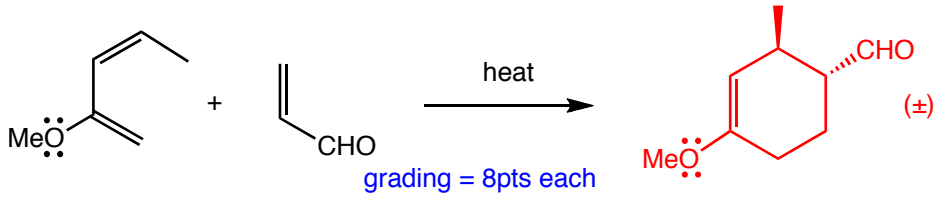
Question 2 (20 pts) GIve a curved-arrow pushing mechanism for the following reaction. Be sure to indicate the Lewis acids/bases (LA/LB) and Bronsted acids/bases (BA/BB) as appropriate



grading: mainly half right = half points etc
1 pts if SN1 first then SN2 second
18 pts if SN2 in second step
18 pts if SN1 in first step
no LA/BA and LB/BB then -5 pts
only LA/BA and LB/BB 4 pts

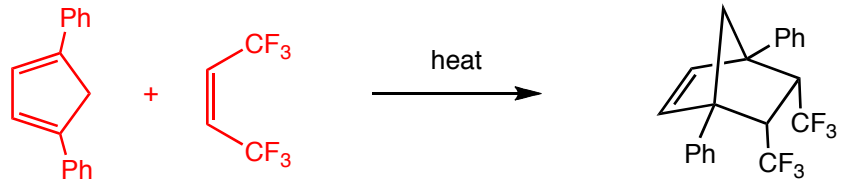
Question 3 (16 pts) Give the missing products or reactants in the following Diels-Alder reactions. In the missing product, indicate both the **relative** and the **absolute** stereochemistry.

a)



grading = 8pts each

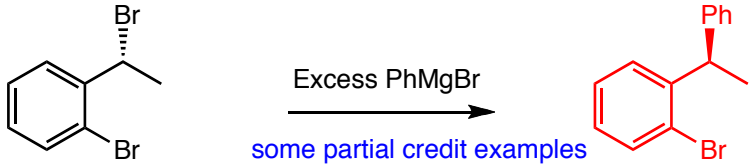
b)

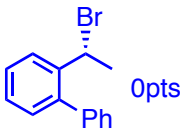


Question 4 (16 pts.) For the following reactions, provide the missing **MAJOR REACTION PRODUCT**. **Indicate stereochemistry where appropriate**.

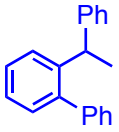
grading = 8pts each

a)

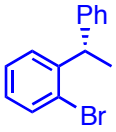




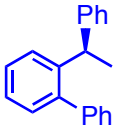
0pts



4pts

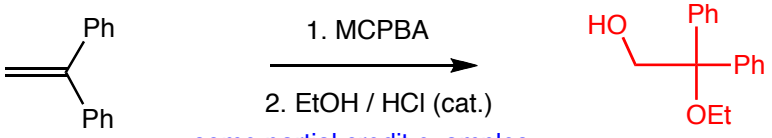


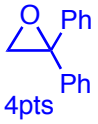
4pts



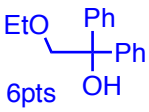
6pts

b)

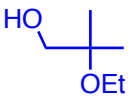




4pts

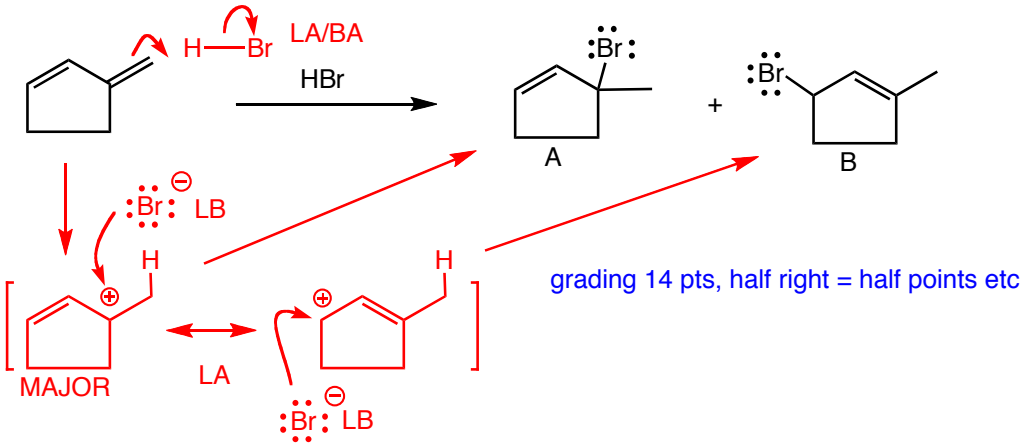


6pts



6pts

Question 5 (34 pts.) For the following reaction, give a full curved-arrow pushing mechanism for formation of BOTH products and **indicate the Lewis acid and base at each step (LA or LB) and whether they are also Bronsted acids and bases (BA or BB).**
Include all reasonable resonance contributors for any intermediates
AND INDICATE THE MAJOR RESONANCE CONTRIBUTOR IF APPROPRIATE!!



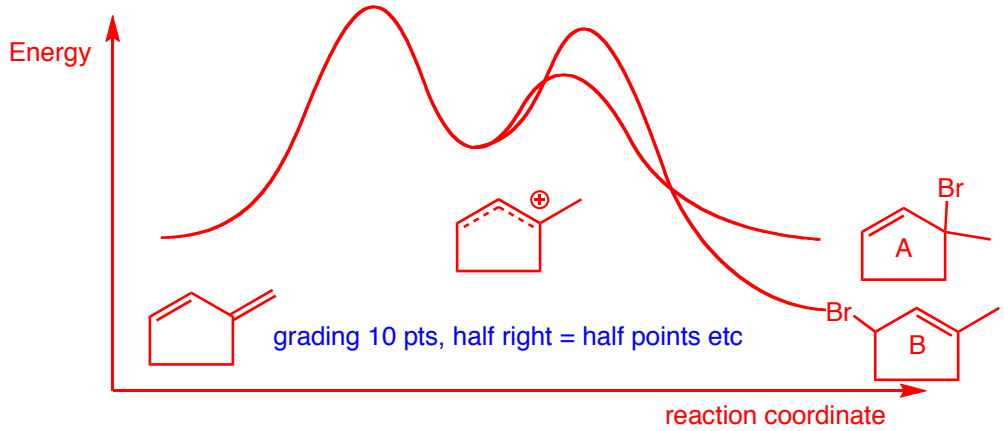
grading 14 pts, half right = half points etc

b) Indicate which product, A or B, would be formed under thermodynamically controlled conditions and which would be formed under kinetically controlled conditions and give a BRIEF explanation of the role of temperature in determining kinetic and thermodynamic control

kinetic = A, thermodynamic = B, B is more likely to be formed at HIGH temperature since higher temperature enables **REVERSIBLE** reactions and allows the reaction to explore the entire reaction energy surface and find the lowest energy product, at low temperatures the reactions are irreversible and the fastest formed product is the major product

grading 10 pts, key words highlighted in blue

c) Draw an energy diagram for formation of both A and B ON THE SAME DIAGRAM, clearly indicate which curve refers to formation of A and which to formation of B



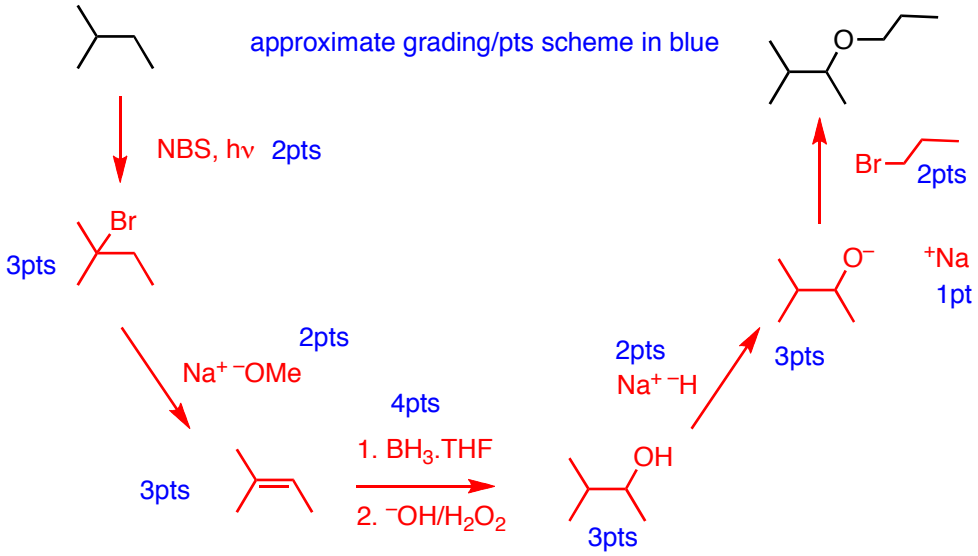
grading 10 pts, half right = half points etc

Extra Credit Question (5 pts.) Which kind of structures were discussed as being carconogenic

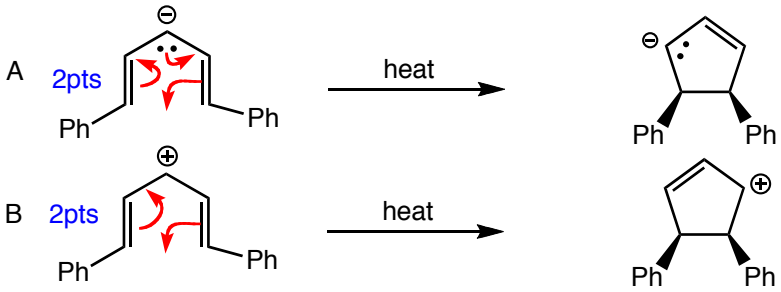
poly-aromatics THF Ethers Dienes

from weekly work # 7

Question 6 (25 pts.) Show how you would make the target compond on the right from the starting compound on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



Question 7 (18 pts)
The product of ONE of the following two reactions A or B is allowed and the other is forbidden
a) draw the curved arrow-pushing that describes the bond making/breaking for both reactions



b) draw a picture of the F.M.O. relevant to these reactions on top of each structure below

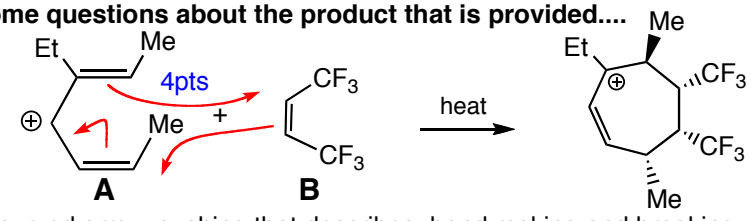
c) Using F.M.O. theory, briefly explain which reaction has the allowed product, A or B, include the terms disrotatory and/or conrotatory as appropriate

both reactions are disrotatory ring closure reactions, disrotatory ring closure in A leads to a bonding situation for the new sigma-bond, disrotatory ring closing in B results in an anti-bonding situation for the new sigma-bond, reaction A is allowed

8pts

Question 8 (18 pts) Shown below is the product of a cycloaddition reaction between two reactants A and B. In this question you are eventually going to determine whether THIS product is allowed or forbidden.

FIRST, some questions about the product that is provided....



a) Do the curved arrow-pushing that describes bond making and breaking 2pts

b) Give the number of electrons that are involved in this reaction 6

c) For the product SHOWN (which may or may not be allowed, remember), was the reaction suprafacial or antarafacial as far as the reactant **A** was concerned? suprafacial 2pts

d) For the product SHOWN (which may or may not be allowed, remember), was the reaction suprafacial or antarafacial as far as the reactant **B** was concerned? suprafacial 2pts

NOW, some questions about the ALLOWED reaction for these reactants

e) Would an ALLOWED reaction between reactants A and B proceed via a Huckel or a Mobius transition state. Give a BRIEF explanation

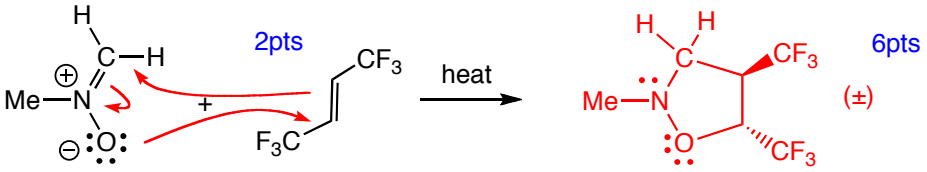
this is a 6-electron reaction, the lowest energy transition state is a cyclic Huckel loop since this is aromatic and relatively stable

6pts, key words highlighted in blue

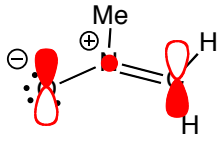
f) Is the product shown above allowed or forbidden? allowed 2pts

Question 9 (18 pts)

a) Give the curved arrow-pushing and the allowed product for the following cycloaddition reaction. Pay attention to stereochemistry



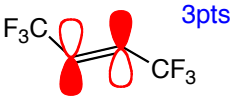
b) ON TOP of the structures as indicated, draw the requested F.M.O.s and give the total number of π-molecular orbitals and electrons associated with the π-system for each structure.



draw the HOMO

total # of π-M.O.s for this structure = 3 1pt

total # of electrons in the π-system for this structure = 4 1pt



draw the LUMO

total # of π-M.O.s for this structure = 2 1pt

total # of electrons in the π-system for this structure = 2 1pt