CHEM 234, Spring 2009 | Second 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!***

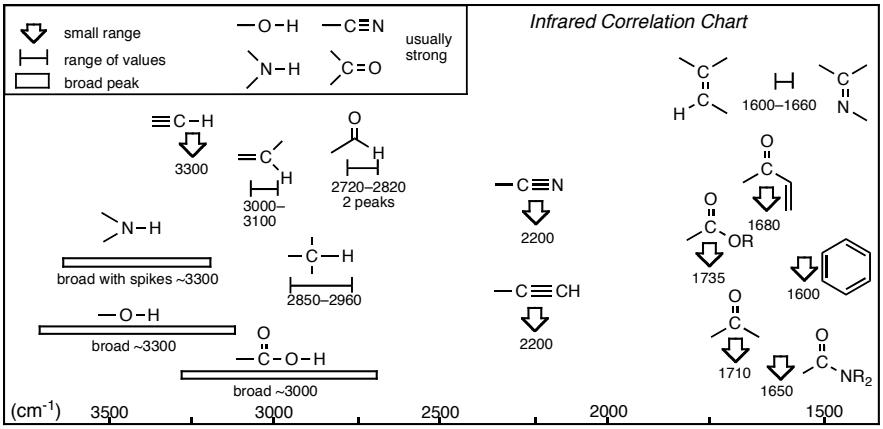
1 nomen	/10	9 peri2	/8
2 arom	/10	10 peri3	/12
3 D/A	/9	11 peri4	/12
4 reverse D/A	/9	12 spectrum	/25
5 prods	/18		
6 k vs Th	/25		
7 retro	/25		
8 peri1	/12		

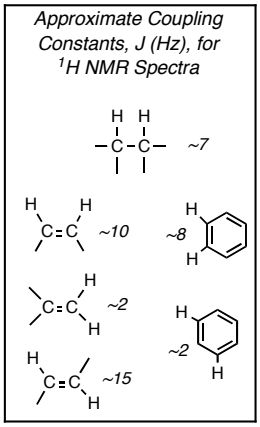
Extra Credit_____/5 **Total (incl Extra)**_____/175+5

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

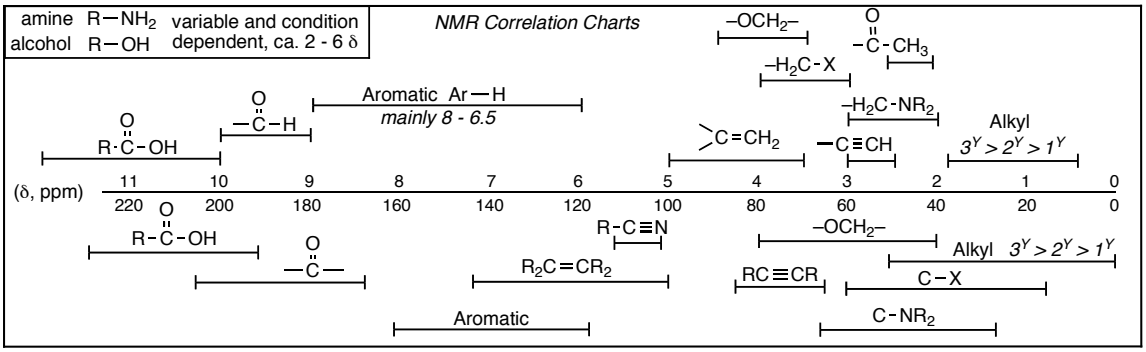
Interaction Energies, kcal/mol

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

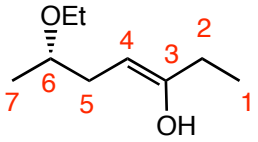




amine R–NH2 variable and condition
alcohol R–OH dependent, ca. 2 - 6 δ

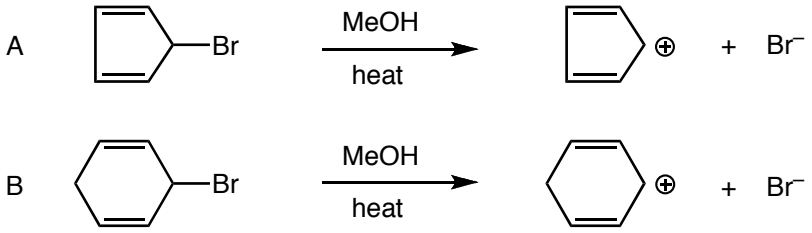


Question 1 (10 pts.) Give the IUPAC name for the following compound. Be sure to use cis/trans, E/Z or R/S where appropriate.



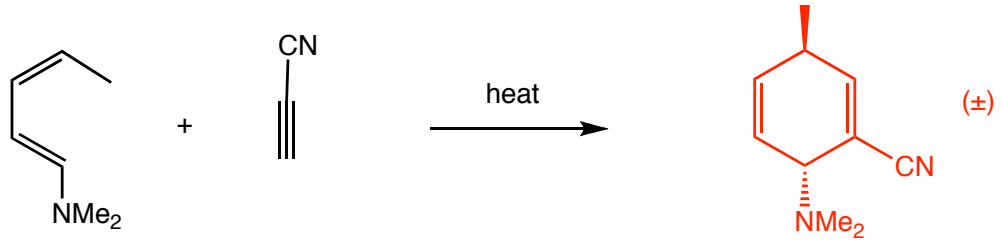
(6S)-ethoxyhept-(3Z)-en-3-ol

Question 2 (10 pts) Indicate which of the following two reactions, A or B would be faster. **GIVE AN EXPLANATION THAT INCLUDES A DISCUSSION OF THE EXOTHERMICITY OR ENDOTHERMICITIES OF THE REACTIONS** (only 1 point for the correct answer, 9 pts for the explanation)

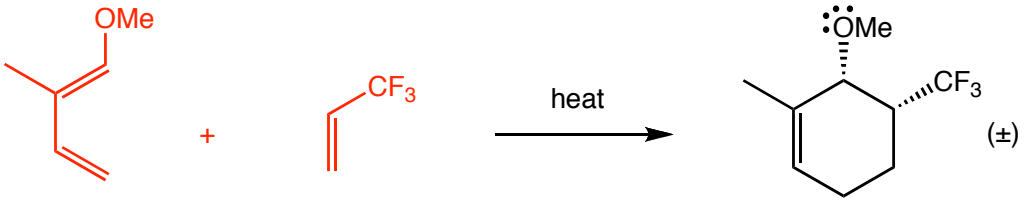


both reactions are endothermic, but reaction A is more endothermic since it makes a less stable ANTI-AROMATIC cation, reaction B is less endothermic since it makes a conjugated but NONAROMATIC cation, reactiuon B is thus faster

Question 3 (9 pts) Give the product of the following Diels-Alder reaction. Indicate both the relative and the absolute stereochemistry



Qestion 4 (9 pts) Give the diene and dienophile that react to give the provided structure in a Diels-Alder reaction



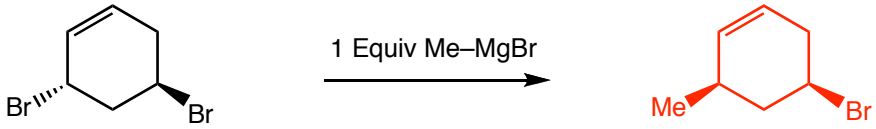
Extra Credit Question (5 pts.) In which kind of biomolecule can a photochemical 2 + 2 cycloaddition reaction take place

DNA phospholipid carbohydrate protein

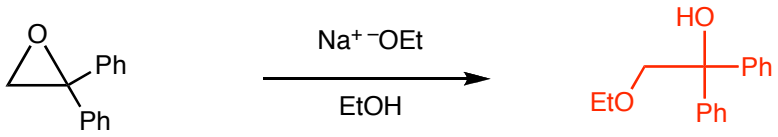
from weekly work # 7

Question 5 (18 pts.) For the following reactions, provide the missing **MAJOR REACTION PRODUCT**. **Indicate stereochemistry where appropriate**.

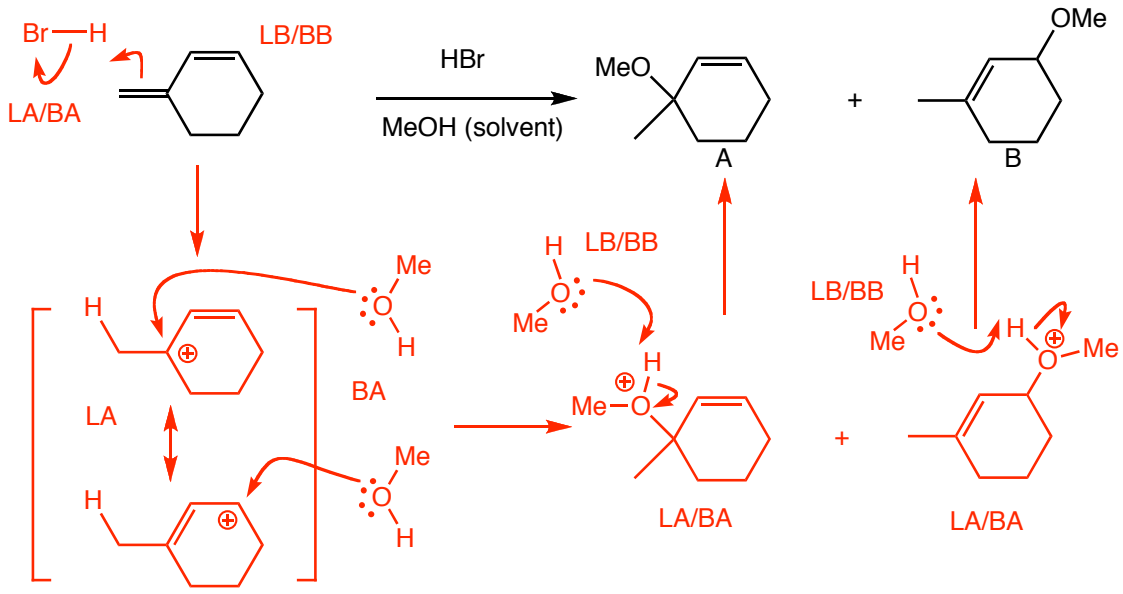
a)



b)



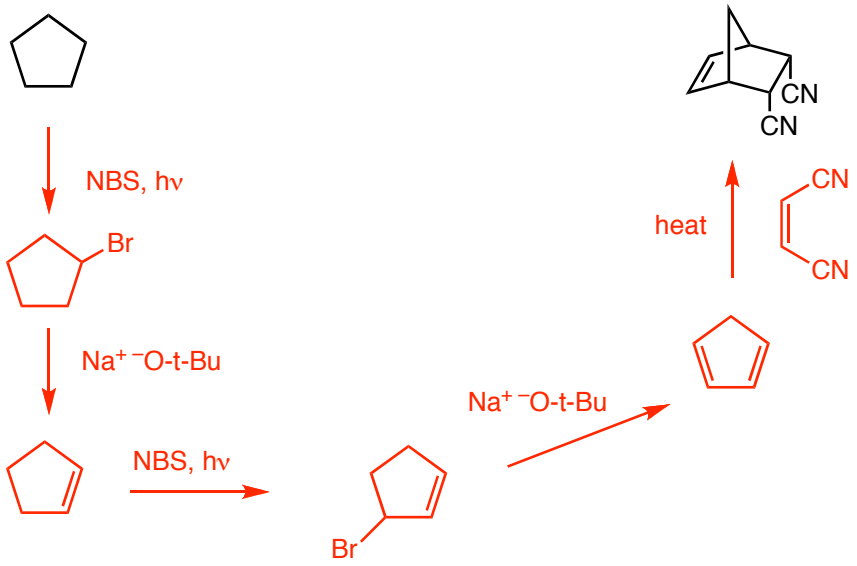
Question 6 (25 pts.) For the following reaction, give a full curved-arrow pushing mechanism for formation of BOTH products and **indicate the Lewis acid and base at each step (LA or LB) and whether they are also Bronsted acids and bases (BA or BB).**
Include all reasonable resonance contributors for any intermediates



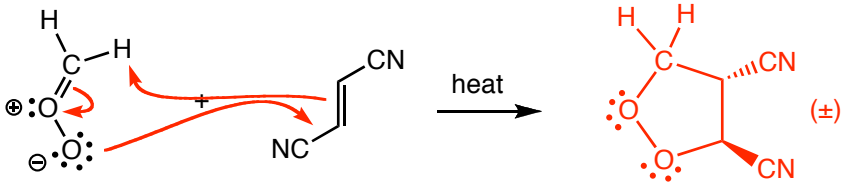
b) Indicate which product would be formed under thermodynamically controlled conditions and which would be formed under kinetically controlled conditions and state which would be more likely to be formed at HIGHER temperature and give a BRIEF explanation

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

Question 7 (25 pts.) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



Question 8 (12 pts)
a) Give the curved arrow-pushing and the allowed product for the following cycloaddition reaction. Be sure to indicate both relative and absolute stereochemistry.



b) How many π-electrons are involved in the reaction that you drew? 6

c) For the number of electrons that are involved in YOUR reaction, is a Huckel or a Mobius transition state allowed? 4 = Mobius, 6 = Huckel etc.

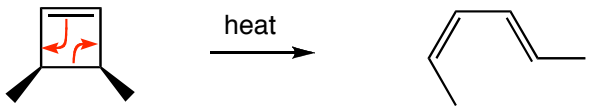
d) Explain WHY a Huckel/Mobius transition state (as appropriate) is allowed in YOUR reaction. Include a discussion of the energies of the electrons in the transition state in your explanation.

6 etc. electrons in a Huckel transition state are aromatic, lowering their energy

4 etc. electrons in a Mobius transition state are nonaromatic, lowering their energy by avoiding the anti-aromatic Huckel transition state

Question 9 (8 pts)

a) Give the curved arrow-pushing for the following electrocyclic ring opening reaction



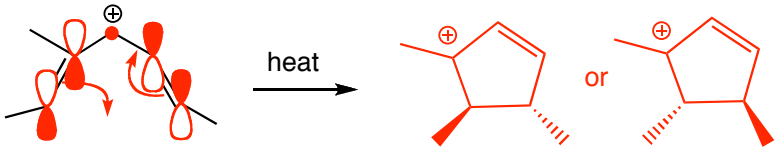
b) Did **THE REACTION SHOWN** (which may or may not be an allowed reaction) proceed via a conrotatory or a disrotatory ring closure? conrotatory

c) Did **THE REACTION SHOWN** (which may or may not be an allowed reaction) proceed via aHuckel or a Mobius transition state? Mobius

d) Is **THE REACTION SHOWN** allowed or forbidden? allowed

Question 10 (12 pts)

a) Give the curved arrow-pushing and the allowed product for the following electrocyclic ring closure reaction

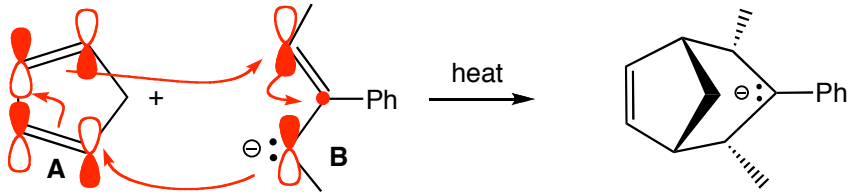


b) ON TOP OF THE STRUCTURE, draw the HOMO of the reactant cation

c) To form YOUR product, did the reaction proceed via a conrotatory or a disrotatory ring opening? conrotatory

Question 11 (12 pts.)

a) Give the curved arrow-pushing for the following cycloaddition reaction



b) On top of the two structures, draw the LUMO for **A** the HOMO for **B**

c) FOR THE PROVIDED PRODUCT (which may or not be the allowed product), was the reaction suprafacial with respect to reactant A? (Y/N) yes

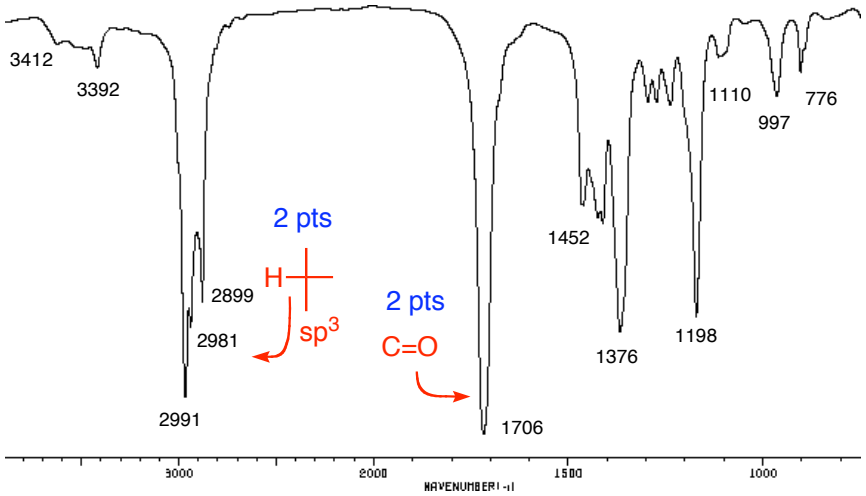
d) FOR THE PROVIDED PRODUCT (which may or not be the allowed product), was the reaction suprafacial with respect to reactant B? (Y/N) yes

e) Is the REACTION SHOWN allowed or forbidden? forbidden

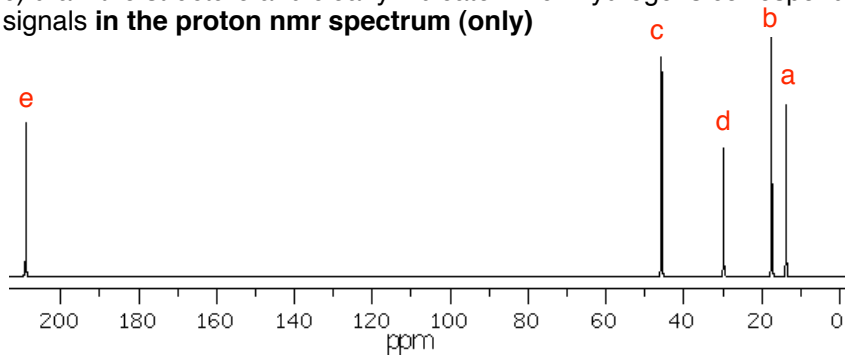
Question 7 (25 pts) Provided are spectra for a compound with molecular formula **$C_5H_{10}O$**

a) Give the degrees of unsaturation 1 degree of unsaturation 2 pts

b) On the infrared spectrum, indicate which peaks correspond to which functional groups



c) draw the structure and clearly indicate which hydrogens correspond to which signals **in the proton nmr spectrum (only)**



19 points, too many variations to list