CHEM 233, Fall 2018 Final Exam Ian R. Gould

COMPLETE THIS SECTION : Up to TWO POINTS will be removed for incorrect/missing information!

PRINTED **FIRST** NAME answer key PRINTED **LAST** NAME _____

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

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

Class you are REGISTERED FOR (onground or hybrid) _____

The room where most students will take the test for your class, i.e. LS A-191 for onground and PS H-152 for hybrid) _____

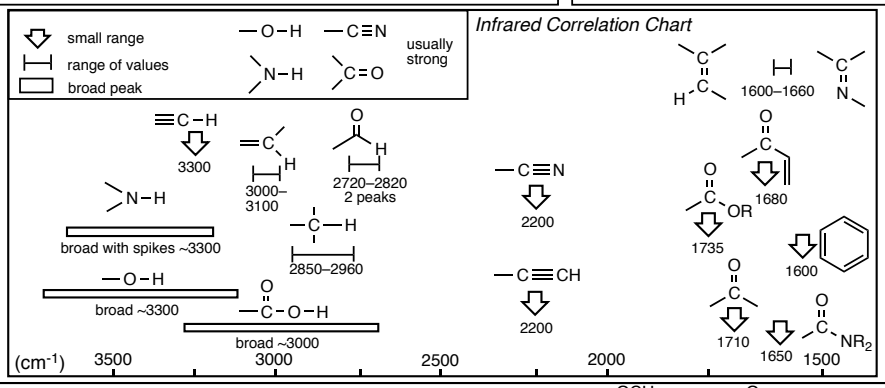
*****YOU ARE NOT ALLOWED TO TAKE SPARE COPIES OF THIS EXAM FROM THE TESTING ROOM*****

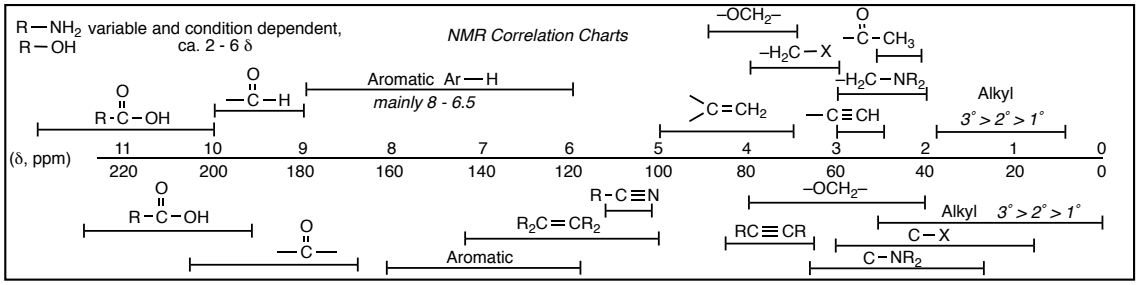
- *PRINT YOUR NAME ON EACH PAGE!*
- *READ THE DIRECTIONS CAREFULLY!*
- *USE BLANK PAGES AS SCRATCH PAPER*
  work on blank pages will not be graded...
- *WRITE CLEARLY!*
- *MOLECULAR MODELS ARE ALLOWED*
- *DO NOT USE RED INK*
- *DON'T CHEAT, USE COMMON SENSE!*

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

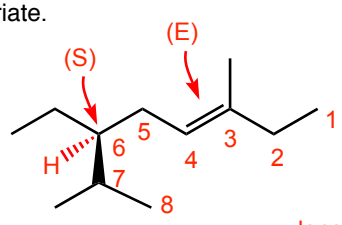
Interaction Energies, kcal/mol

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
Et/Et	~3.1	t-Bu/Me	~2.7





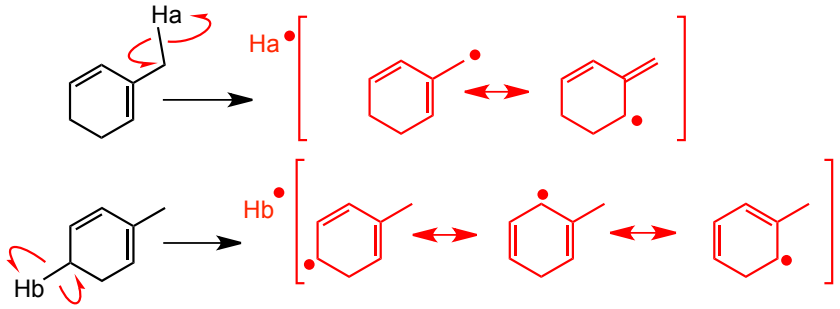
Question 1 (15 pts.) Give the IUPAC name for the following. Specify stereochemistry as appropriate.

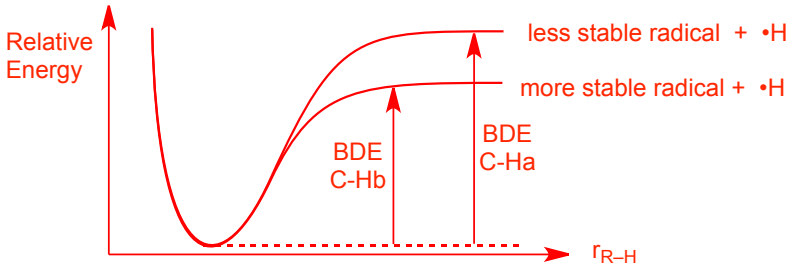


(6S)-ethyl-3,7-dimethyl-(3E)-octene

longest chain that contains the most substituents and functional groups

Question 2 (30 pts.) For each of the two C-H bonds indicated below as C-**Ha** and C-**Hb**:
a) Draw the curved arrow pushing for bond cleavage and show the products, including all reasonable resonance contributors as appropriate.
b) Indicate which has the larger bond dissociation energy.
c) Draw an energy diagram for homolytic cleavage of the two C-H bonds
d) Give a BRIEF explanation for the difference in bond dissociation energies that includes:
• The energies of the electrons in the bonds
• The energies of the electrons in the radicals



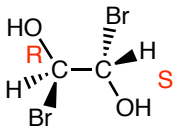


The energies of the electrons IN the BONDS are identical, the difference is the electron energy of the non-bonding electron in the radicals AFTER the bond breaks

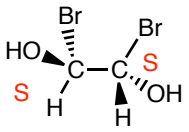
the more stable the radical, the lower the energy of the electron in the radical, the less energy it takes to form that radical, the lower the BDE

the radical from cleavage of C-Hb is more resonance stabilized has lower energy electrons than that from cleavage of C-Ha

Question 3 (18 pts.)
1. Determine whether the following structures are identical, enantiomers or diastereomers
2. Identify any meso compounds.
3. Give the absolute configuration at each chiral (asymmetric) center



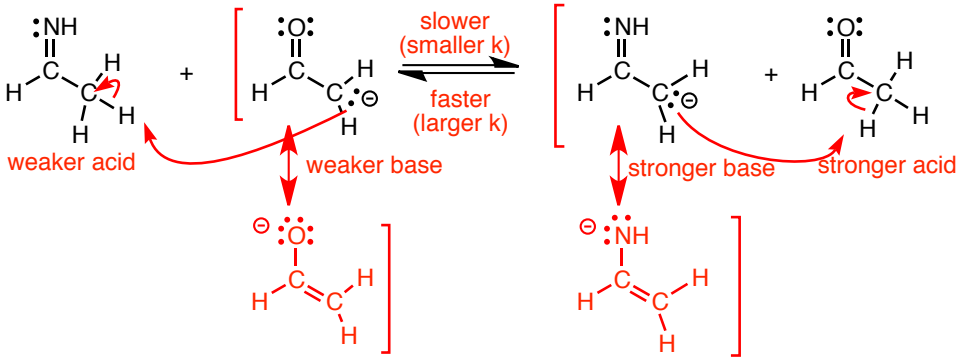
meso



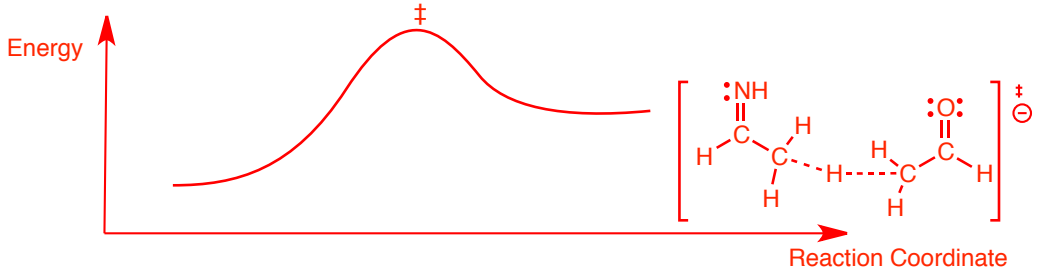
diastereomers

Question 4 (32 pts) For the acid/base reaction shown below
a) add the curved arrow pushing that shows bond making/breaking **IN BOTH DIRECTIONS**
b) identify the stronger and weaker acids and stronger and weaker bases, **and give a brief explanation for your choice**
c) state which reaction would have the larger rate constant (be faster) left to right or right to left
d) identify on which side the equilibrium would lie
e) draw a reaction energy diagram that includes a drawing of the transition state

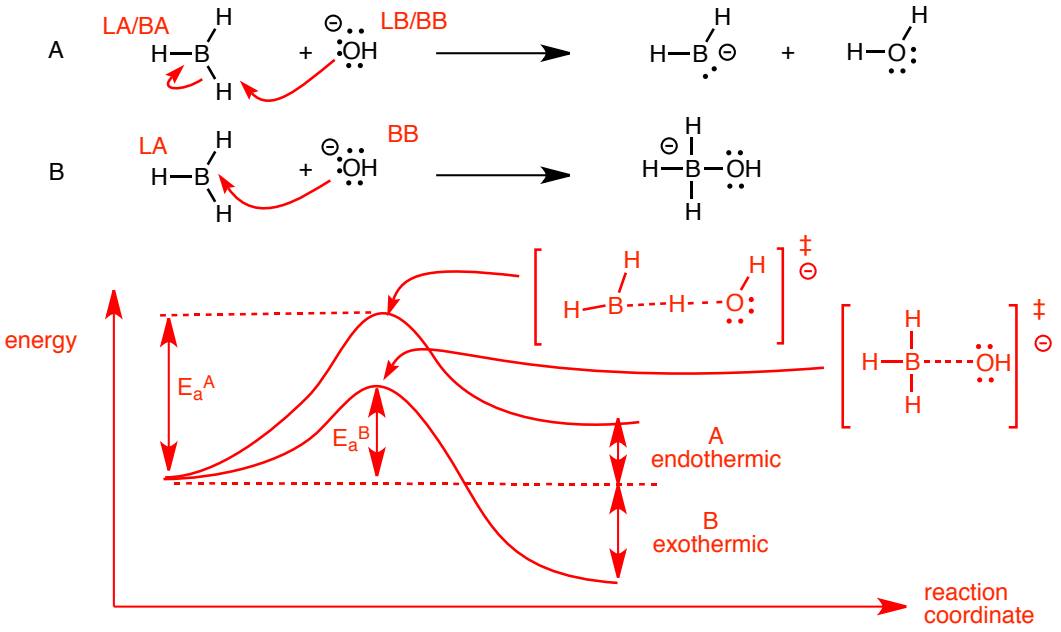
if your explanation uses resonance arguments, draw all important resonance contributors



equilibrium lies on the left, reaction right to left is faster, the weaker base has lower energy less reactive electrons, both bases are resonance stabilized but the weaker base can put the negative charge on the more electronegative oxygen compared to nitrogen in the case of the stronger base

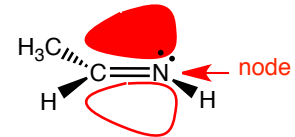


Question 5 (32 pts.) For the following reactions A and B
a) Add the curved arrows that indicated bond breaking/making and indicate the Lewis acid/base and whether they are also Brønsted acids/bases
b) Draw a reaction energy diagram for both ON THE SAME DIAGRAM, clearly indicating which is which, and draw the TRANSITION SATES for each reaction and indicate their positions on the diagrams
c) One of tehse reactions is EXOTHERMIC, the other is ENDO thermic. On the diagram, indicate the activation energy and the endo- or exothermicity as appropriate for each reaction and give a brief explanation for your choice of endothermic or exothermic reaction

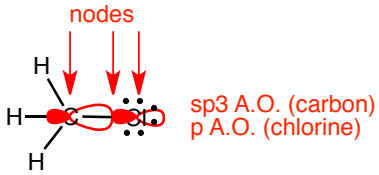


A is endothermic because the products have the same number of bonds and the negative charge is on the less electronegative boron
B is exothermic since the products have one more bond

Question 6 (22 pts.) For the orbitals indicated
a) Draw a picture of the Ψ for the molecular orbital requested ON TOP of the structures
b) Indicate the atomic orbital or orbitals that you used to construct the requested orbitals
c) Indicate the positions of any nodes in the moelcular orbitals

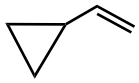
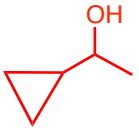


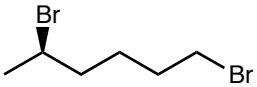
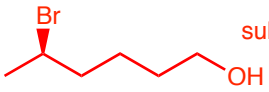
Ψ for the C-N π M.O.
p A.O. (carbon)
p A.O. (nitrogen)

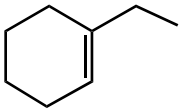
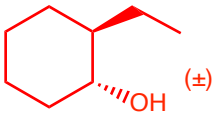


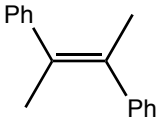
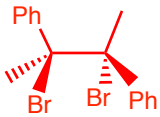
Ψ for the C-Cl σ* M.O.

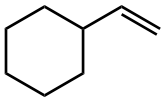
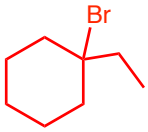
Question 7 (63 pts.) Give the missing major **ORGANIC PRODUCT** for each reaction
a) **Show all stereochemistry** as appropriate**, identify any MESO compounds**
b) **Briefly explain whether and why a solution of the product would be optically active or not**
c) assign each reaction as addition, elimination, substitution or rearrangement

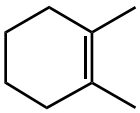
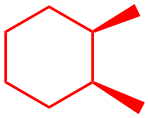
a) 
1. $Hg(OAc)_2/H_2O$
2. $NaBH_4$

(±) addition
not optically active, racemc

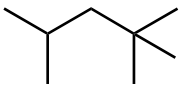
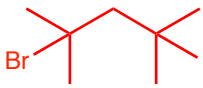
b) 
1 Equiv. $Na^+ {}^-OH$
DMSO

substitution
optically active
single enantiomer formed

c) 
1. BH_3 . THF
2. ^-OH, H_2O_2

(±) addition
not optically active, racemc

d) 
Br_2
CCl_4

addition
not optically active, meso

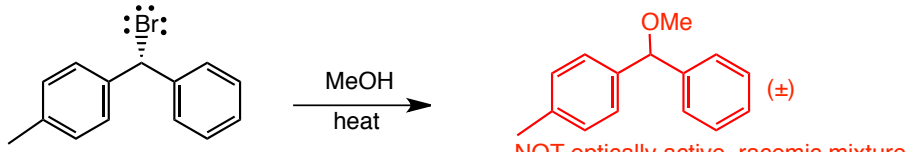
e) 
HBr
CCl_4

addition
not optically active, achiral

f) 
H_2
Pd/C

not optically active, meso
addition

g) 
Br_2
hν

not optically active, achiral
substitution

Question 8 (24 pts.) Give the missing major organic product for each reaction
a) **Show all stereochemistry** as appropriate
b) Briefly explain whether and why a solution of the product would be optically active or not
c) Assign each reaction as SN1 or SN2 and give a very brief explanation for your choice

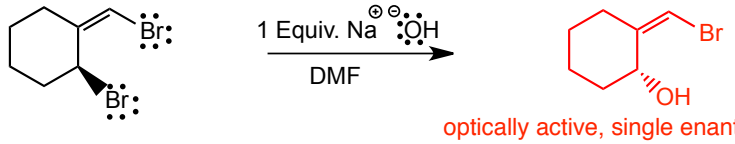
a)



weak nucleophile, polar protic solvent, must be SN1

NOT optically active, racemic mixture

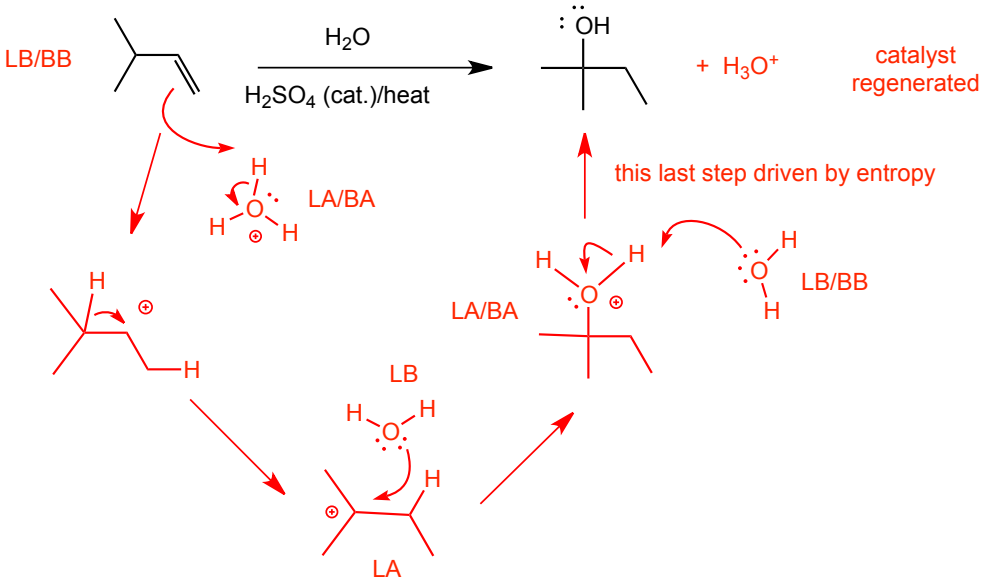
b)



optically active, single enantiomer formed

strong nucleophile, polar aprotic solvent, must be SN2

Question 9 (30 pts.) Provide a curved-arrow pushing mechanism for the following reaction, indicate the Lewis acid and base at each step as appropriate, and whether they are also Bronsted acids and bases. Indicate the number of steps and the number of sets of intermediates.

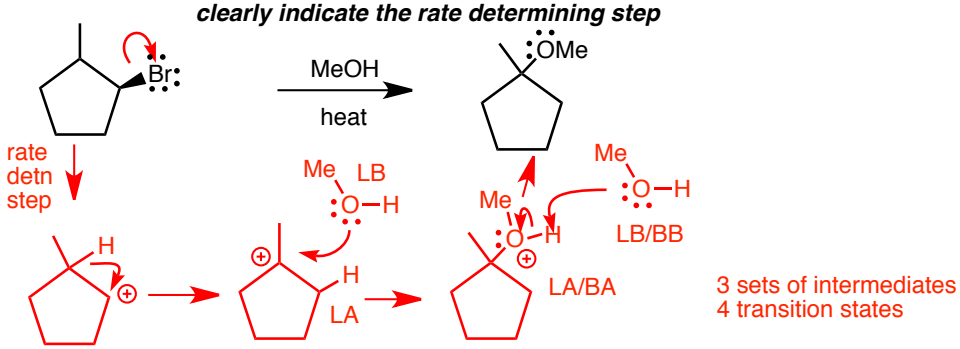


number of steps 4 number of sets of intermediates 3

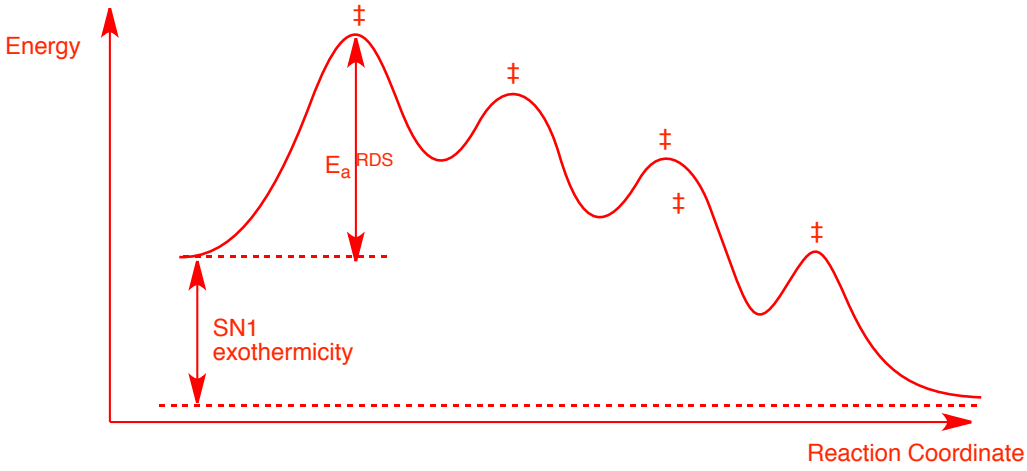
Question 10 (42 pts.)

a) Give a curved arrow mechanism for the provided bromide in hot methanol. Label the Lewis acid and Lewis base in each step as appropriate, and whether they are also Brønsted acids and bases. Indicate the number of sets of intermediates and transition states for each mechanism

clearly indicate the rate determining step



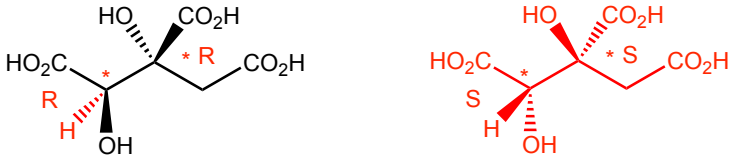
b) Draw a properly labelled reaction energy diagram the reaction. **Assume that the reaction is exothermic under the conditions**, do not draw any transition states, but **INDICATE THEIR POSITIONS Clearly indicate the activation energy for the rate determining step and the exothermicity for the reaction.**



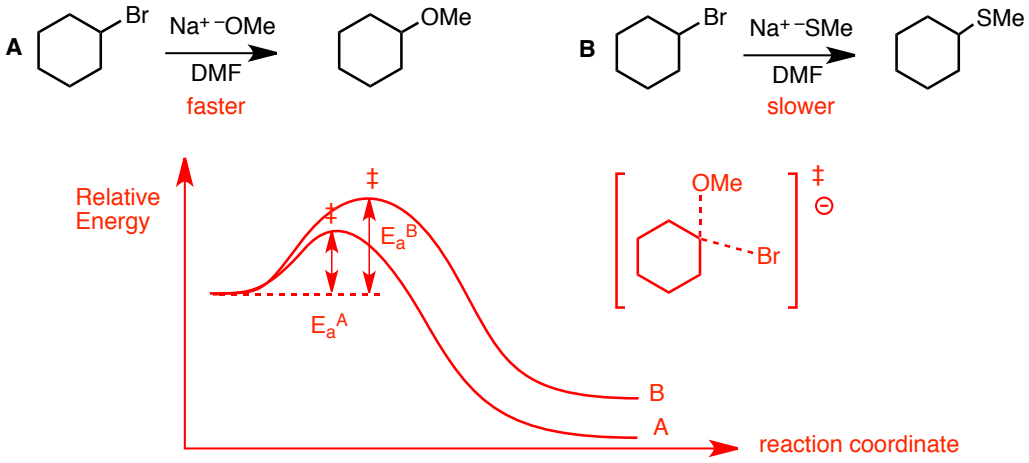
Extra Credit (5 pts) The hole in the ozone layer has been attributed to the atmospheric chemistry of which kind of molecule?

halides alkanes alkanes alcohols

Question 11 (18 pts) The 3D structure of (+)-hydroxycitric acid is shown below (non-bonding electrons omitted for clarity).
a) Indicate the positions of all chiral/asymmetric carbons with the * symbol
b) Give the absolute configuration for all chiral/asymmetric carbons
c) Draw a 3D structure for (–)-hydroxycitric acid and give the absolute configuration for ALL chiral/asymmetric carbons



Question 12 (24 pts.) For the following two reactions:
a) Draw a reaction energy diagram for both on THE SAME DIAGRAM (normalize them at the reactants). **Indicate the positions of the transition states and the activation energies for both reactions and draw the transition state for reaction A only!**
b) Indicate which reaction is faster and give a BRIEF EXPLANATION that ibncludes:
• An indication of the type of mechanism for this reaction(SN1/SN2/E1/E2 etc.).
• An explanation for any differences base strength or nucelophile strength, as appropriate
• You must talk about how the Hammond postulate explains which reaction will be faster

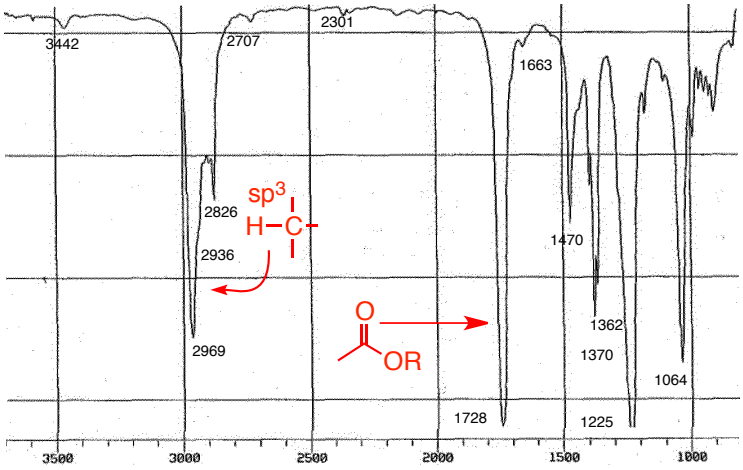


Reaction B is slower
The mechanism is SN2
-OMe is a stronger nucleophile because oxygen is SMALLER than sulfur
The Hammond postulate says that the more exothermic reaction will have the smaller activation energy and therefore the faster rate

Question 13 (25 pts) Provided are spectra for a compound with molecular formula $C_6H_{12}O_2$

a) Give the degrees of unsaturation 1 degree of unsaturation

b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including C(sp^3)-H). Indicate **BOTH the functional group**, and where appropriate, **the specific BOND** in the functional that corresponds to the peak.



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