CHEM 233, Fall 2016 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) _____

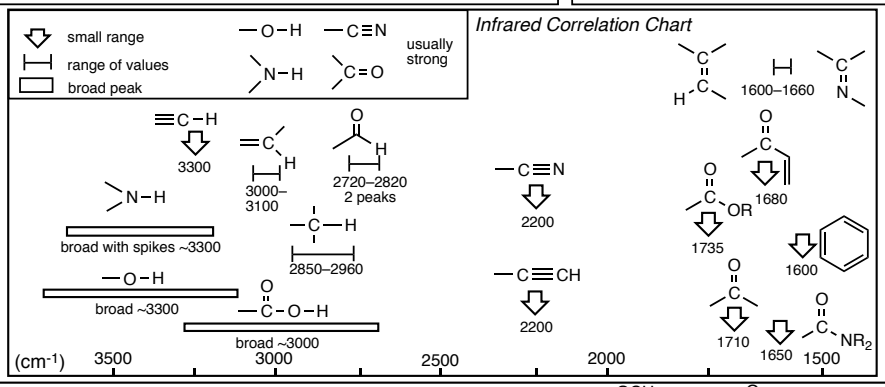
*****YOU ARE NOT ALLOWED TO TAKE SPARE COPIES OF THIS EXAM FROM THE TESTING ROOM*****

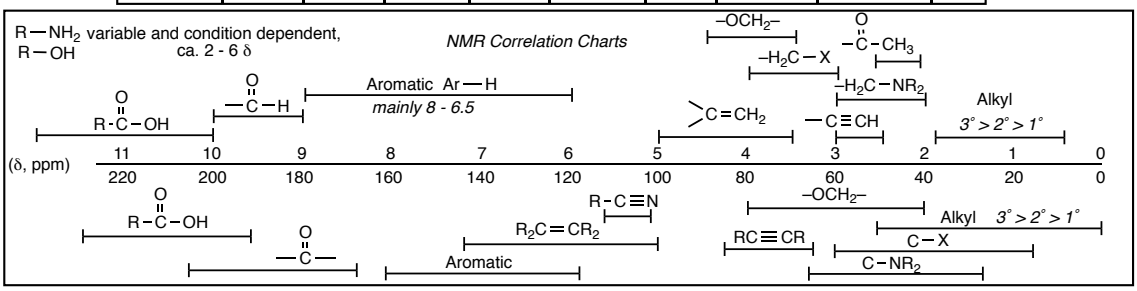
- *PRINT YOUR NAME ON EACH PAGE!*
- *READ THE DIRECTIONS CAREFULLY!*
- *USE BLANK PAGES AS SCRATCH PAPER*
  work on blank pages will not be graded...
- *WRITE CLEARLY!*
- *MOLECULAR MODELS ARE ALLOWED*
- *DO NOT USE RED INK*
- *DON'T CHEAT, USE COMMON SENSE!*

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





YOU MUST COMPLETE THIS PAGE WITH YOUR NAME
(EVEN THOUGH YOU ALREADY DID THIS ON THE COVER PAGE)
AND ALSO GIVE YOUR ASU OR POSTING ID NUMBER
WE NEED THIS NUMBER BECAUSE YOU WOULDN'T BELIEVE THE NUMBER OF STUDENTS WHOSE NAMES WE CAN'T READ!

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

Points by question

1	nomen	/13
2	E2 a	/24
3	MOs	/20
4	E2 b	/42
5	acid/base	/24
6	S vs E	/18
7	E1	/18
8	reacts	/70
9	mxns 1	/40
10	t-BuO	/8
11	LAB	/22
12	bases	/18
13	mxn 2	/34
14	spec	/24

Points Removed for cover errors ____/2

Extra Credit_____/5

Total (incl Extra)_____/175+5

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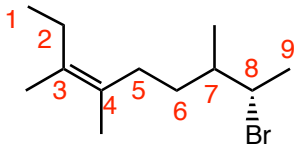
Question 1 (13 pts.) Give the IUPAC name for the following structure. Specify stereochemistry as appropriate.



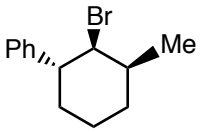
(8S)-bromo-3,4,7-trimethyl-(3Z)-nonene

OR

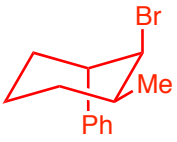
(S,E)-8-bromo-3,4,7-trimethyl-3-nonene

etc.

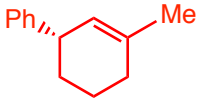
Question 2 (24 pts). For the cyclohexane structure shown below, draw....
1. The **lowest energy chair conformation**
2. The **chair conformation** required for an **E2 elimination reaction**
3. The **product of an E2 elimination reaction**



lowest energy chair

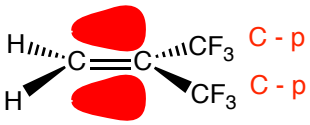


chair for E2 elimination

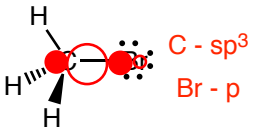


E2 elimination product

Question 3 (20 pts.)
a) Draw a picture of the wavefunction, **OR** the wavefunction squared **AS REQUESTED**, of the molecular orbitals requested, *on the molecules*. In each case **indicate the A.O.'s used to make the M.O.'s.**



Ψ^2 for the C–C π orbital



Ψ for the C-Br σ^* orbital

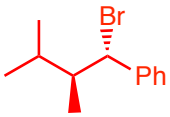
Extra Credit (5 pts) The hole in the ozone layer has been attributed to the atmospheric chemistry of which kind of molecule?

halides alkanes alkanes alcohols

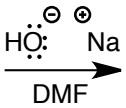
Question 4 (42 pts). For (1S)-bromo-(2S,3)-dimethyl-1-phenylbutane.....
a) Draw a line-angle structure showing stereochemistry using wedged/dashed bonds
b) Draw a 3-D (sawhorse) structure AND a Newman projection for the lowest energy conformation for rotation around the C1-C2 bond
c) Draw a 3-D (sawhorse) structure AND a Newman projection for the conformation that is required for E2 elimination
d) Draw the E2 elimination product

(1S)-bromo-(2S,3)-dimethyl-1-phenylbutane

a)

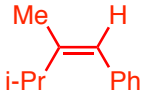


line-angle structure, wedged/dashed bonds



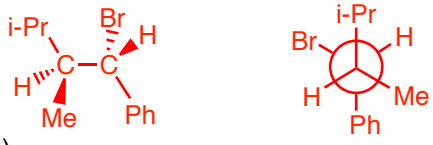
E2 product

d)



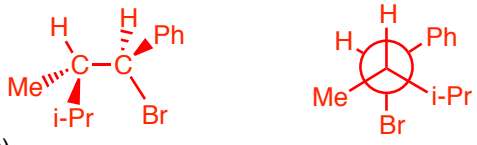
line-angle structure

b)



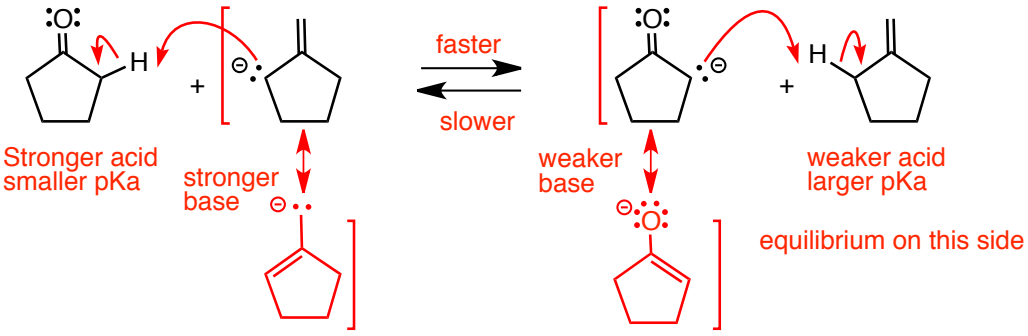
3D (sawhorse) AND Newman projection for lowest energy conformation

c)



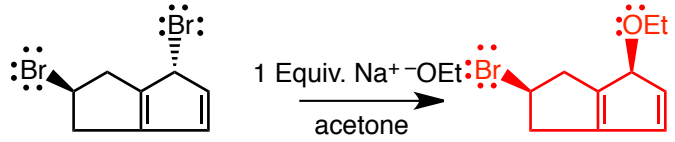
3D (sawhorse) AND Newman projection for E2 reactive conformation

Question 5 (24 pts.) For the following Bronsted acid/base reaction (not all H atoms are included in the provided structures
a) Draw the curved-arrows that describes the bond making and breaking in BOTH directions
b) Label the **STRONGER** acid/base and the **WEAKER** acid/base on EACH side
c) Indicate which reaction would be faster, left to right or right to left
d) Indicate on which side the equilibrium will lie
e) Indicate which acid has the smaller and which the larger pKa
f) Give a BRIEF explanation for your choice of stronger/weaker Bronsted acids/bases that includes drawings of ALL relevant resonance contributors



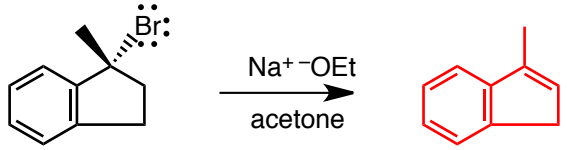
the stronger base has higher energy electrons, both bases are resonance stabilized but the weaker base has a partial negative charge on the more electronegative oxygen compared to only carbons on the stronger base

Question 6 (18 pts.) For each reaction, decide whether the mechanism would be SN1/SN2/E1 or E2 and give a brief explanation. Draw the product and **show stereochemistry** where appropriate and **state whether a solution of the product would be optically active** or not **AND give a BRIEF explanation.**

a) 

optically active single enantiomer formed

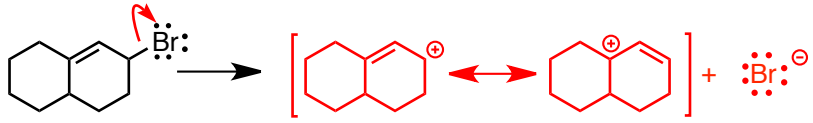
allylic halide more reactive, strong nucleophile and strong base, but E2 not possible at the allylic position, polar aprotic solvent, must be SN2

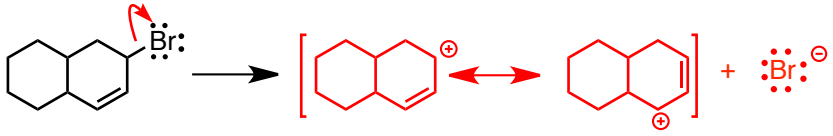
b) 

not optically active, achiral

tertiary halide, SN2 not possible, strong base, polar aprotic solvent, must be E2, non-bulky base therefore Sayetzeff alkene product formed

Question 7 (18 pts.) For E1 elimination in the following two structures (assume a polar protic solvent and heat), give the curved arrow pushing and the intermediates forme**d for FIRST STEP of the mechanism ONLY**, include resonance contributors as appropriate. Which E1 elimination reaction would you expect to be faster, A or B, give a **BRIEF** explanation.

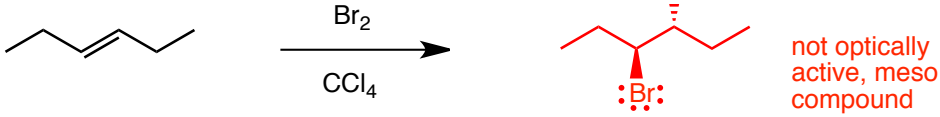
A 

B 

The rate determining step is formation of a carbocation intermediate. Both cati9ons are resonance stabilized, but that from A has a formal 2° and 3° cation as contributors whereas that from C has 2° and 2°, thus the cation from A is most stable and forms fastest

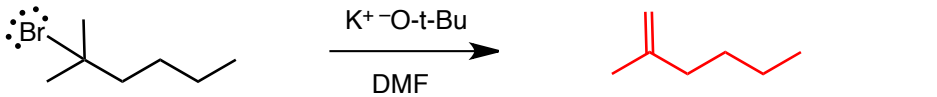
Question 8 (70 pts.) Give the missing major **ORGANIC PRODUCT** for each reaction
a) **Show all stereochemistry** as appropriate**, identify any MESO compounds**
b) **Briefly explain whether and why a solution of the product would be optically active or not**
c) assign each reaction as addition, elimination, substitution or rearrangement

a)



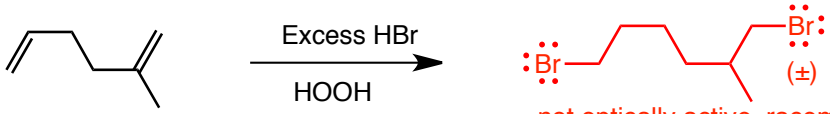
not optically active, meso compound

b)



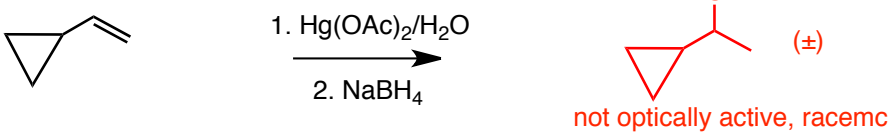
not optically active, achiral

c)



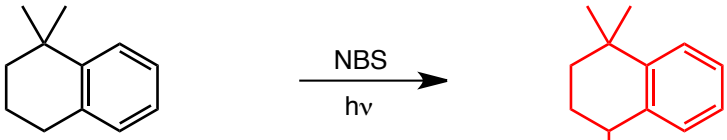
not optically active, racemc

d)



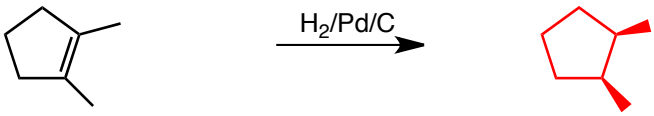
not optically active, racemc

e)



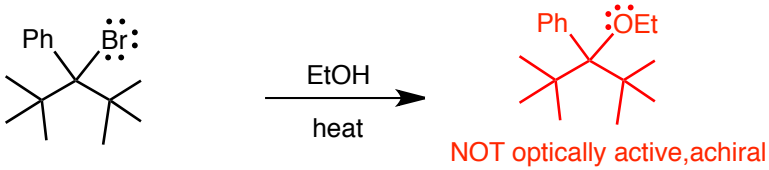
not optically active, racemc

f)



not optically active, meso

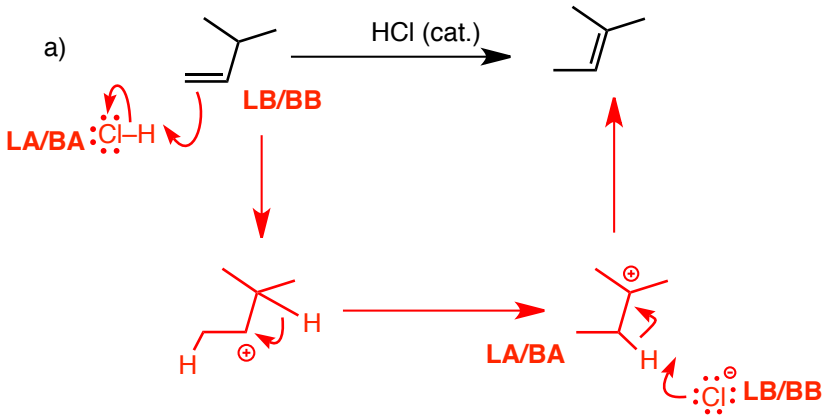
g)



NOT optically active,achiral

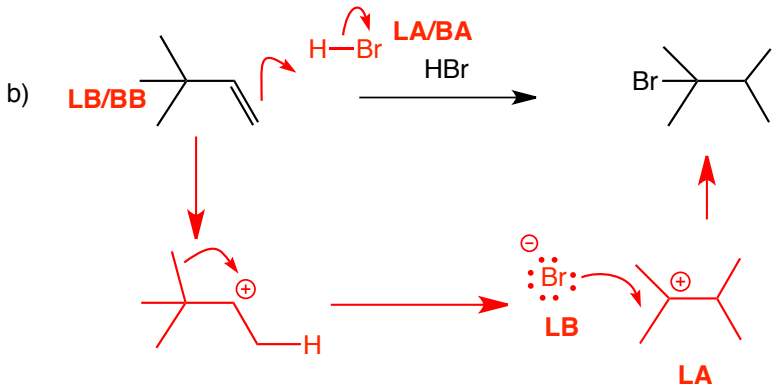
Question 9 (40 pts.) For each of the the following two reactions:
a) Give a curved arrow mechanism, indicate the Lewis acid and Lewis base (LA or LB) for each INTERMOLECULAR step, and whether they are also Brønsted acids and bases (BA or BB).
b) State whether you would expect the reaction to be exothermic or endothermic and give a brief (1 sentence) explanation for your choice.

a)



this reaction converts a less stable less substituted alkene into a more stable more substituted alkene, therefore it should be exothermic

b)

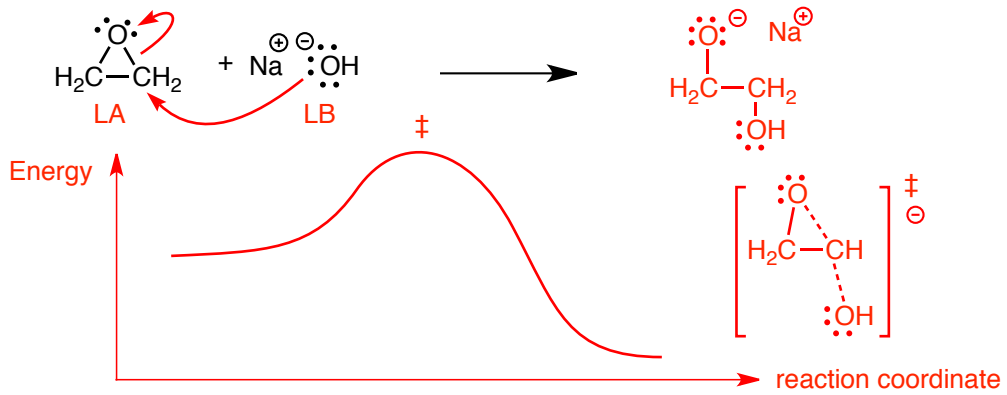


this reaction converts a pi-bond and a sigma-bond into 2 sigma bonds, the energy of the electrons goes down, it is exothermic

Question 10 (8 pts.) The t-butoxide anion (t-BuO$^-$) is a strong base but a weak nucleophile. Give a brief 1 sentence explanation for this.

it is a strong base because it has high energy electrons in the anion
it is a weak nucleophile because of steric hinderance due to the methyl groups

Question 11 (22 pts.)
a) Give the product of the following Lewis acid/base reaction, indicate the Lewis acid and base (LA/LB) and if they are also Bronsted acids bases (BA/BB).
b) Draw a reaction energy diagram for the reaction with properly labelled axes, draw the transition state and indicate its position on the diagram.
c) BRIEFLY explain why your reaction is exothermic or why it is endothermic



exothermic due to relief of ring strain in the 3-membered ring

Question 12 (18 pts)
a) Indicate which of the following two structures is the stronger Bronsted base, and give a brief explanation for your choice.

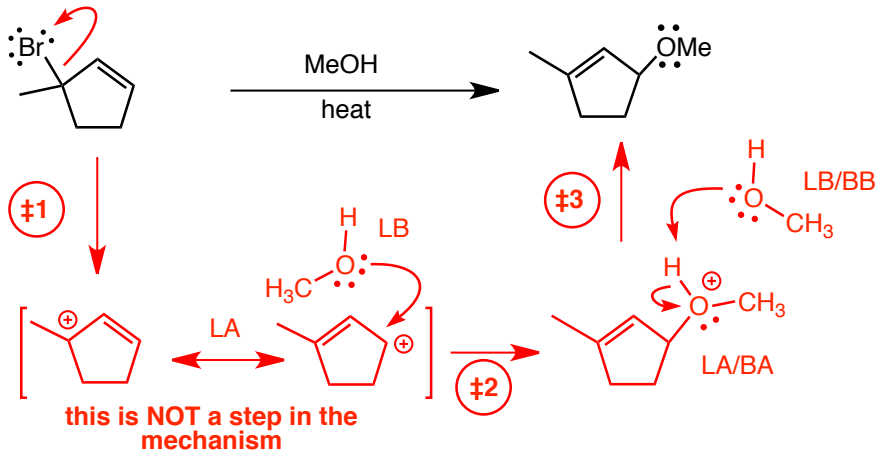
MeO^- is the stronger base because even though O is more electronegative, it makes a stronger bond to a hydrogen atom because it is smaller

b) Indicate which of the following two structures A or B is the stronger Bronsted base, and give a brief explanation for your choice.

A is the stronger base because the non-bonding electrons are in an sp2 hybridized orbital compared to the sp hybridized orbital in B, the electron energy is higher in A, the electrons are more reactive

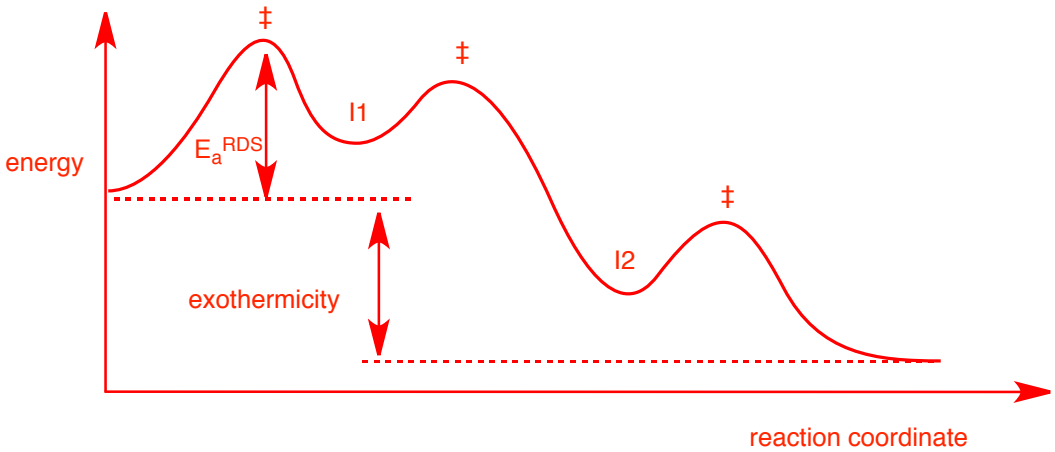
Question 13 (34 pts.)

a) Give a full curved arrow mechanism, indicate the Lewis and Bronsted acids and bases at each step as appropriate. **Give the number of sets of intermediates that are included in your mechanism and also how many transition states are associated with your mechanism**. *(This may not be the only product of this reaction, but you need to show the mechanism for formation of THIS product)*



# of sets of intermediates = **2 sets of intermediates**
# of transition states = **3 transition states**

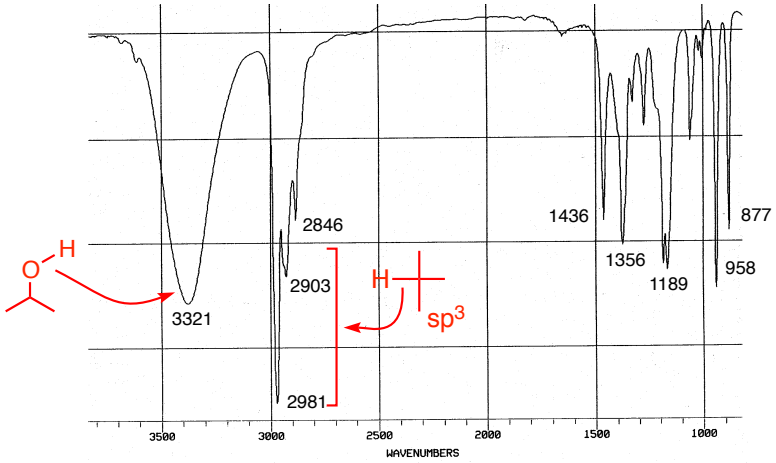
b) Draw a reaction energy diagram for the mechanism you drew, do not draw them but indicate the locations of each of the sets of intermediates and the transition states on your diagram. Indicate also the activation energy for the rate determining step and also the reaction exothermicity.



Question 14 (24 pts) Provided are spectra for a compound with molecular formula **$C_6H_{14}O$**

a) Give the degrees of unsaturation 0 degrees 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)**