Chemistry 3351: Organic Chemistry
Thursday: Sept. 23 @ **7:00pm → 9:00/1st Exam**

Name: ~~Hubert~~ Yin (please print)

Page	Possible Points	Score
2	9	
3	9	
4	8	
5	10	
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7	4	
8	9	
9	10	
10	10	
11	10	
12	10	
13	10	
TOTAL	109	

1. (3 pts each) *Clickers* in action:

a) 2,3-Pentadiene, $CH_3CH{=}C{=}CHCH_3$, is a chiral molecule and exists as a pair of enantiomers. It is unique because it does not contain a chiral carbon center. Predict the hybridization of each carbon going from left to right along the carbon chain.

A) sp, sp^2, sp^2, sp^2, sp

B) sp^2, sp, sp, sp, sp^2

C) sp^3, sp^2, sp^2, sp^2, sp^3

D) sp^3, sp, sp, sp, sp^3

(E) sp^3, sp^2, sp, sp^2, sp^3

b) Using MO theory, predict the potential existence of He_2 and/or $He_2^{\oplus}$.

A) He_2 and $He_2^{\oplus}$ may exist.

B) He_2 and $He_2^{\oplus}$ may not exist.

C) He_2 may exist and $He_2^{\oplus}$ may not exist.

(D) He_2 may not exist and $He_2^{\oplus}$ may exist.

c) How many constitutional isomers are there with the molecular formula C_6H_{14}?

A) 4

(B) 5

C) 6

D) 7

d) Predict the magnitude of K_{eq} for the reaction:

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^{\oplus} + CH_3CO_2^{\ominus}$$

A) $K_{eq} = 0$ B) $K_{eq} = 1$ C) $K_{eq} >> 1$ D) $K_{eq} << 1$

Acid	pK_a Value
$H_3O^{\oplus}$	–1.7
CH_3COOH	4.7
$NH_4^{\oplus}$	9.3
H_2O	15.7
CH_4	60

e) Arrange the constitutional isomers of C_5H_{12} in order of increasing boiling points.

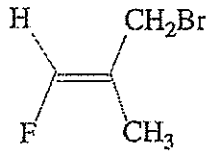
A) $CH_3(CH_2)_3CH_3 < (CH_3)_2CHCH_2CH_3 < (CH_3)_4C$

B) $(CH_3)_2CHCH_2CH_3 < CH_3(CH_2)_3CH_3 < (CH_3)_4C$

C) $(CH_3)_4C < CH_3(CH_2)_3CH_3 < (CH_3)_2CHCH_2CH_3$

D) $(CH_3)_4C < (CH_3)_2CHCH_2CH_3 < CH_3(CH_2)_3CH_3$

f) Select the IUPAC name of the compound shown below.



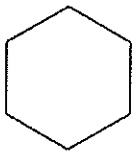
(A) (E)-3-bromo-1-fluoro-2-methylpropene

(B) (Z)-3-bromo-1-fluoro-2-methylpropene

(C) (E)-1-bromo-3-fluoro-2-methylpropene

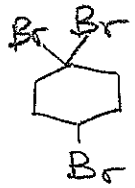
(D) (Z)-1-bromo-3-fluoro-2-methylpropene

2. (8 pts) Write line structures for each of the following compounds. I have done cyclohexane as an example.

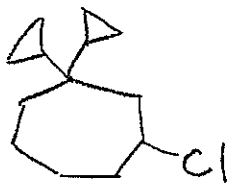


a) 1-ethyl-2-propylcyclopentane

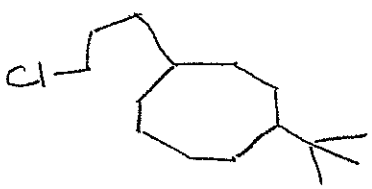
b) 1, 1, 4-tribromocyclohexane



c) 3-chloro-1,1-dicyclopropylcycloheptane

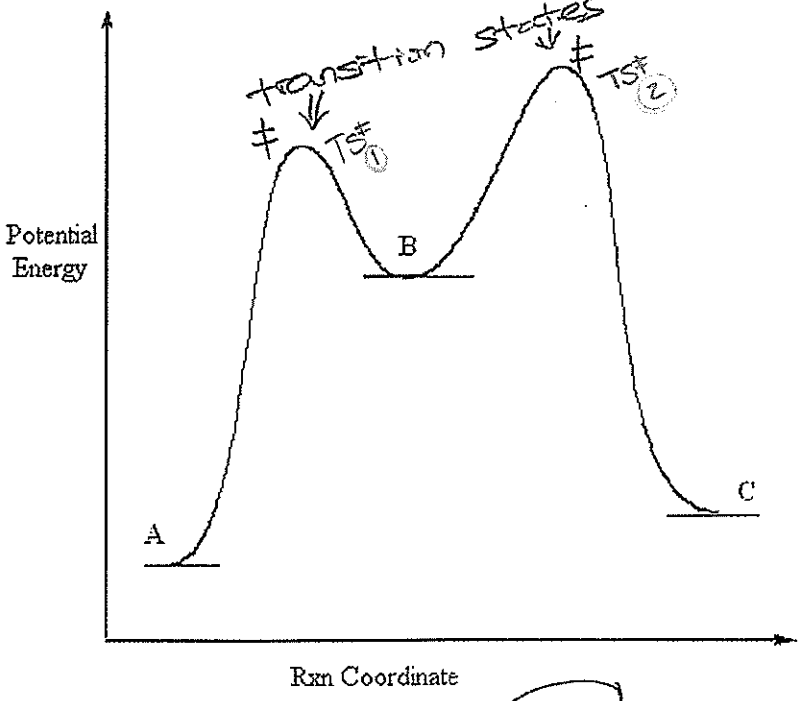


d) 1-(3-chloropropyl)-4-*tert*-butylcyclooctane



4. (10 pts) Consider the hypothetical two-step reaction.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C$$



a) Is the overall reaction (A → C) exothermic or endothermic?

b) Label the transition states. Which transition state is rate limiting? $TS^{\ddagger}_{(2)}$ is rate limiting

c) What is the correct order of magnitude of the rate constants.

i) $k_1 > k_2 > k_3 > k_4$

ii) $k_2 > k_3 > k_1 > k_4$

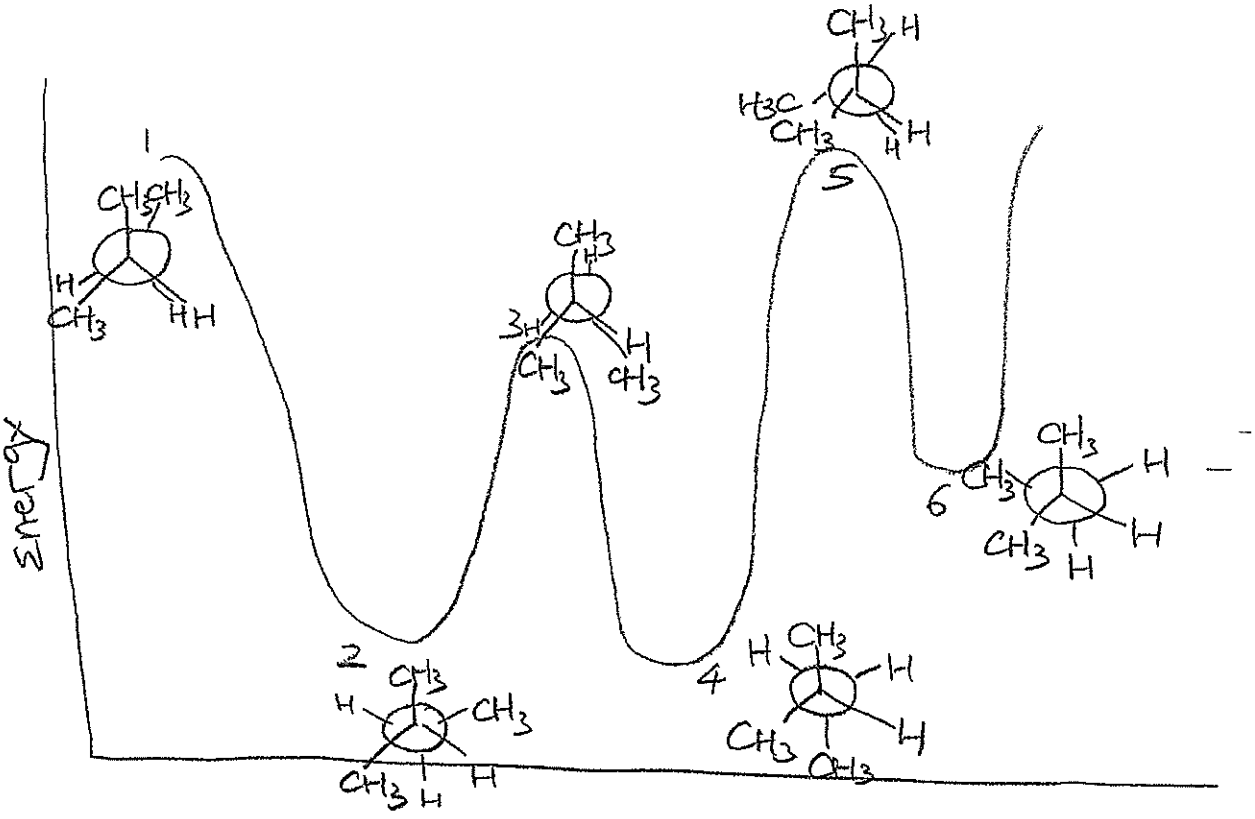
iii) $k_4 > k_1 > k_3 > k_2$

iv) $k_3 > k_2 > k_4 > k_1$

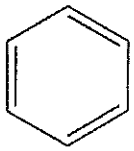
d) Which is the thermodynamically most stable compound? A

e) Which is the thermodynamically least stable compound? B

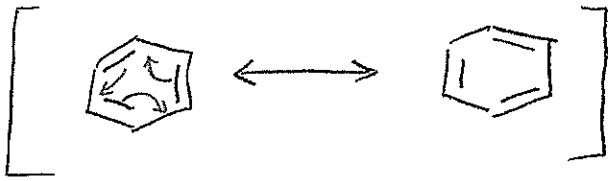
5. (10 pts) Using Newman projections, draw a potential energy diagram for rotation about the C_2—C_3 bond of 2-methylbutane.



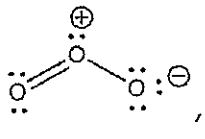
6. (4 pts) The compound benzene has only one type of carbon-carbon bond, and this bond has a length intermediate between that of a single bond and a double bond. Draw a resonance structure of benzene, that with the following structures, account for the carbon-carbon bond length.

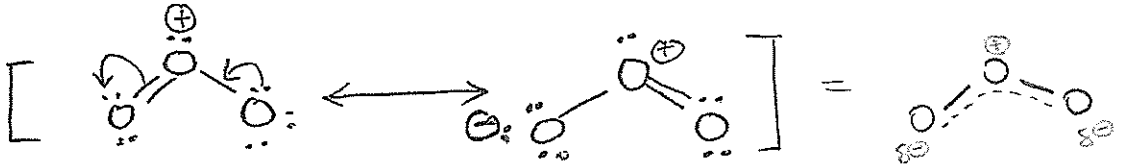


benzene

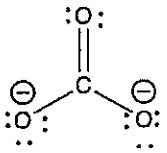


7. (9 pts) Use the curved-arrow notation to derive resonance structures that convey the following ideas. In each case, also draw a single hybrid structure using dashed lines and partial charges that conveys the same meaning as the resonance structures.

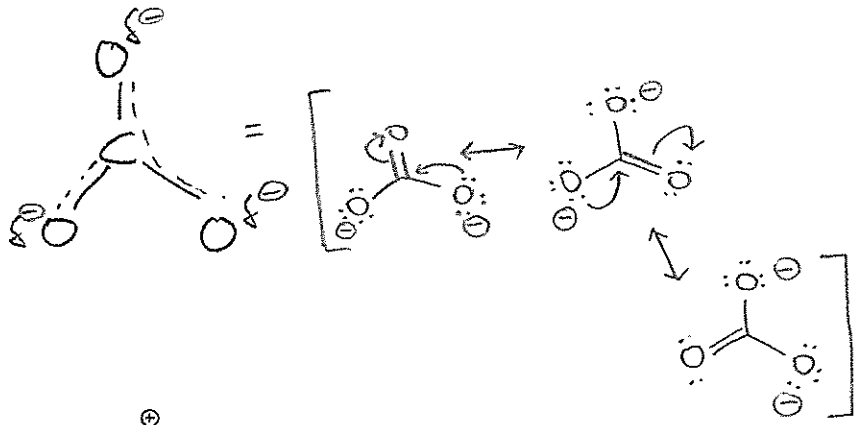
a) The outer oxygen of ozone,  , have an equal amount of negative charge.



b) All C-O bonds in the carbonate ion are of equal length.

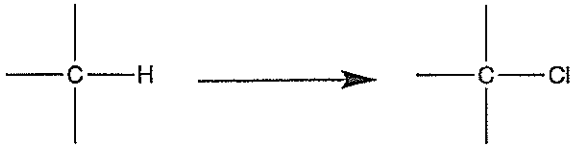


carbonate ion

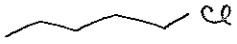


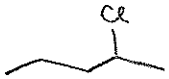
c) The conjugate acid of formaldehyde, , has substantial positive charge on carbon.

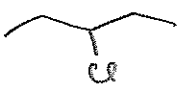
8. (10 pts) Imagine a reaction that can replace one hydrogen atom of an alkane at random with a chlorine atom.



a) If *n*-pentane were subjected to such a reaction, how many different compounds with the formula $C_5H_{11}Cl$ would be obtained? Give their line structures.

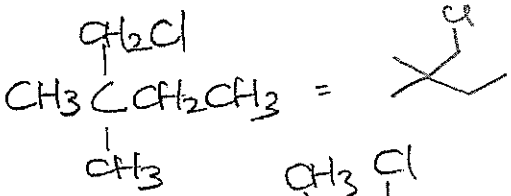
A $CH_3CH_2CH_2CH_2CH_2-Cl$ = 

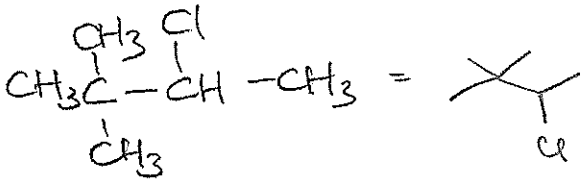
B $CH_3CH_2CH_2CH(Cl)CH_3$ = 

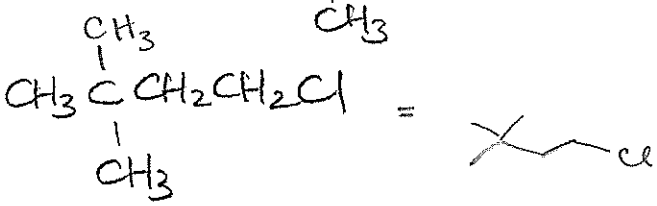
C $CH_3CH_2CH(Cl)CH_2CH_3$ = 

pls give students who answer that (B) has two isomers 2 extra points!!

b) Provide the same analysis as in part (a) for the same reaction carried out on 2,2-dimethylbutane.

A 

B 

C 

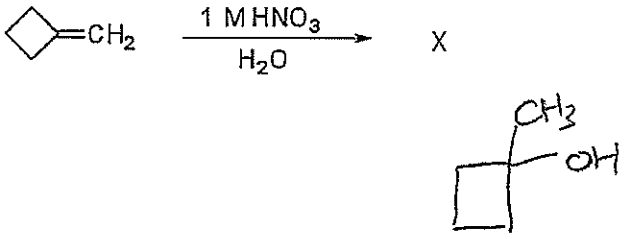
Also, 2 extra points for answering that B has two nonsuperimposable structures.

9. (10 pts) Calculate the standard free energy change for the dissociation of acetic acid (pKa = 4.76).

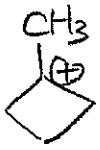
$\Delta G^\circ = 2.3RT(pKa) = (5.71)(4.76) = 27.2\ kJ/mol$

10. (10 pts)

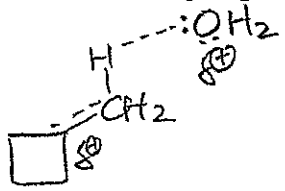
a) Give the product X expected when methylenecyclobutane undergoes acid-catalyzed hydration.



b) The rate-limiting step is protonation of the double bond; use $H_3O^{\oplus}$ as the acid catalyst. Draw the structure of the reactive intermediate formed in the rate-limiting step.



c) Draw the transition state for the rate-limiting step.

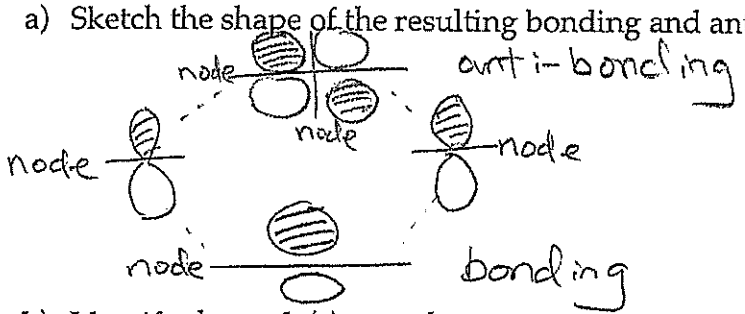


d) What is the rate-limiting step for dehydration of X (the reverse of the reaction shown above)?

If the rate limiting step is protonation of the double bond in the hydration direction, then the rate-limiting step in the reverse direction is the reverse of the same step.

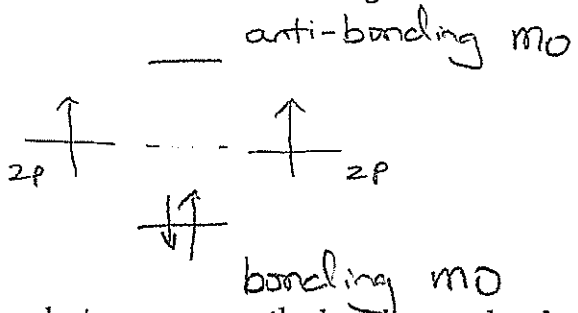
11. (10 pts) Consider two 2*p* orbitals, one on each of two different atoms, oriented side to side , as shown below. Imaging bringing these nuclei together so that overlap occurs as shown in the figure. This overlap results in a system of molecular orbitals.

a) Sketch the shape of the resulting bonding and anti-bonding molecular orbitals.



b) Identify the node(s) in each.

c) Construct an orbital interaction diagram for molecular orbital formation.

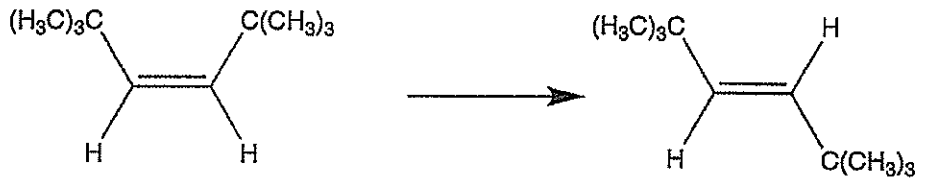


d) When two electrons occupy the bonding molecular orbitals, is the resulting bond a σ bond? Explain.

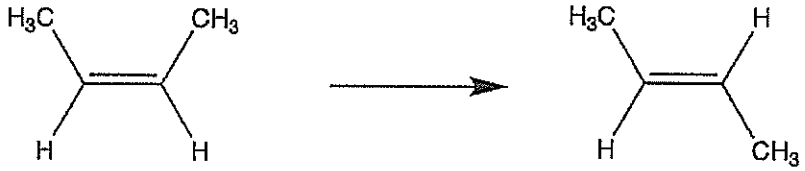
the resulting bond is not a σ bond because it is not cylindrically symmetrical about the internuclear axis.

12. (10 pts) Which of the following reactions should have the greatest ΔH° change? Why?

(1)



(2)



In each trans-isomer, the large groups have little van der Waals repulsions. However, the tert-butyl groups in the cis-isomer of (1) suffer more severe van der Waals repulsions because tert-butyl groups are much larger than methyl groups. Therefore, more energy is released in the conversion shown in (1) than in the conversion shown in (2).