Exam 1 Summer 2017

Name Key Seat Number_____

Student ID_____

The exam consists of 10 questions worth 102 points on a total of 6 pages. It will be scored out of 100 points.

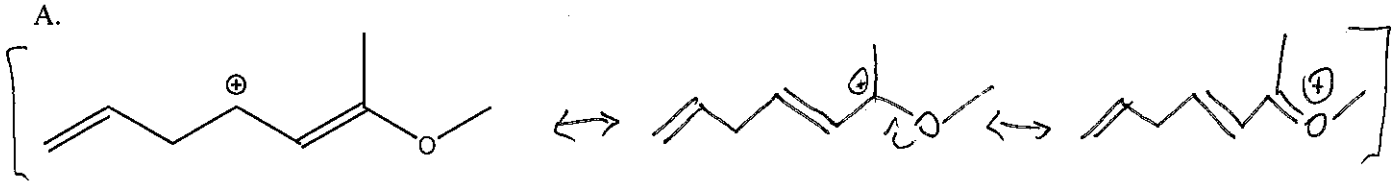
1. _____/12
2. _____/10
3. _____/8
4. _____/10
5. _____/12
6. _____/16
7. _____/8
8. _____/8
9. _____/10
10. _____/6

Total:

Regrading: All requests for regrades must be submitted in writing within 48 hours of the return of the exam. You must explicitly state what has been misgraded and why it is an error. The entire exam will be regraded, which could result in points being added or deducted overall.

1. (12pts) Draw all significant resonance structures for the following compounds, and then draw a resonance hybrid, indicating all atoms bearing partial positive or negative charges.

A.



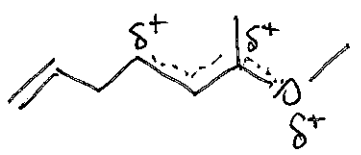
Additional, incorrect structures are point deductions.

-0.5, additional

-1, incorrect

+4

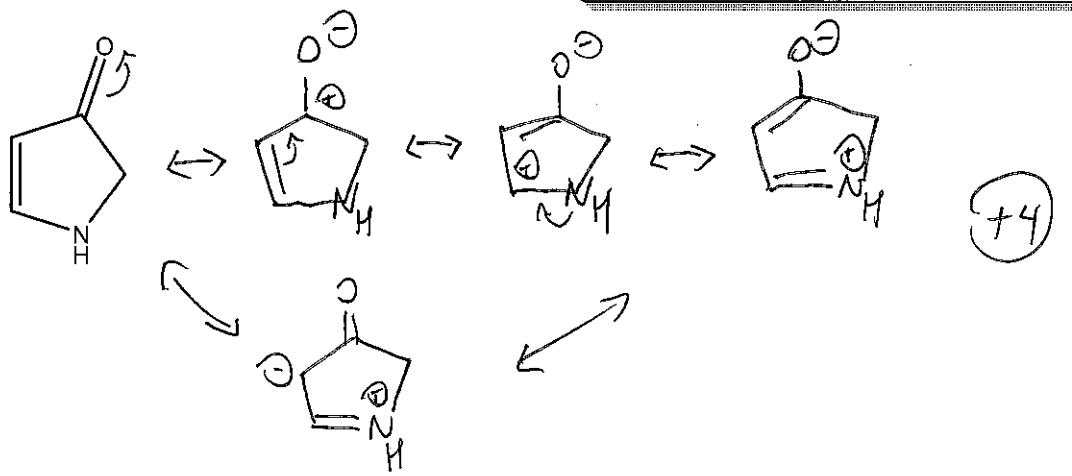
hybrid:



-0.5 each error

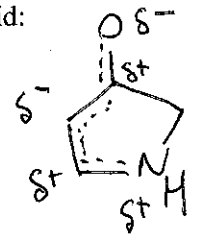
+2

B



+4

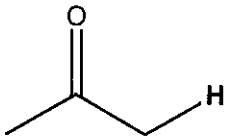
hybrid:

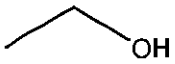


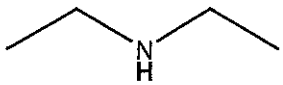
+2

2. (10pts) Give the name of the functional group in each molecule. Indicate the pKa of each proton in bold, and indicate which of the four acids is the strongest and which is the weakest.

+1 each





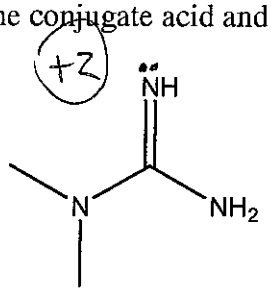


pKa: 25 | 20 | 16-18 | 38-40

functional group: alkyne | ketone | alcohol | amine

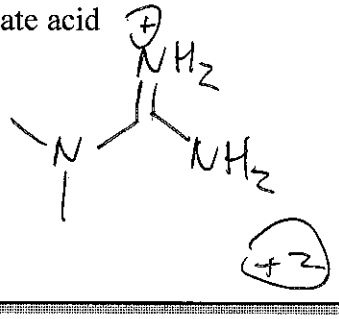
strongest weakest

3. (8pts) In the molecule below, mark the least stable lone pair, and explain how you came to this conclusion. Then draw the conjugate acid and conjugate base of the compound.

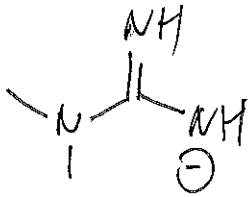


+2 explain - draw resonance or
- localized vs delocalized

conjugate acid

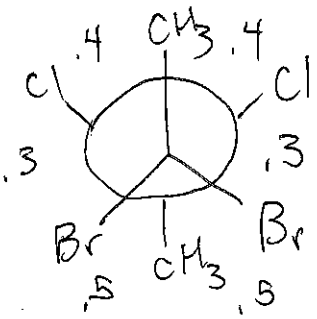


conjugate base

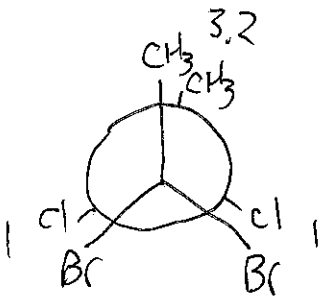


4. (10pts) Draw a Newman projection for the most and least stable conformations of 2,2-dibromo-3,3-dichlorobutane around the C2-C3 bond. Calculate the difference in energy between these conformations using these data: Cl/Cl eclipse strain: 0.9 kcal/mol; Br/Br eclipse strain: 1.1 kcal/mol; Cl/Br eclipse strain: 1.0 kcal/mol; methyl/methyl eclipse strain: 3.2 kcal/mol; methyl/Cl eclipse strain: 1.4 kcal/mol; methyl/Br eclipse strain: 1.5 kcal/mol; methyl/ethyl gauche strain: 1.0 kcal/mol; CH_3/Br gauche strain: 0.5 kcal/mol; CH_3/Cl gauche strain: 0.4 kcal/mol; Cl/Br gauche strain: 0.3 kcal/mol; Cl/Cl gauche strain: 0.2 kcal/mol.

most stable



2.4 Kcal/mol



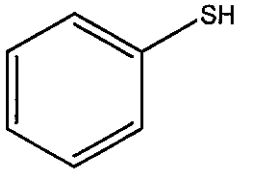
5.2 Kcal/mol

+3/ drawing
+2/ calculation

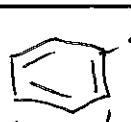
= 2.8 Kcal/mol

5. (12pts) Indicate whether or not each of the following compounds would be completely deprotonated by NaOH, and explain how you came to your answer using pKa values or base stability principles.

+4 A.

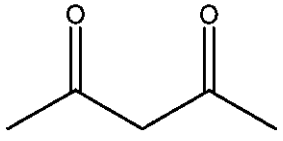


Yes.



This charge is more stable than HO^- because it is on a larger atom (and delocalized.)

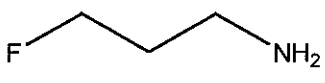
+4 B.



pKa = 9

Yes. The pK_a of this molecule makes it a stronger acid than H_2O (15.7.)

+4 C.



No. pK_a of this compound is ~38.
or
⊖ on nitrogen less stable.

~~+4 — 28~~

6. (16 pts) A. Provide a mechanism for this reaction, including initiation and propagation steps.

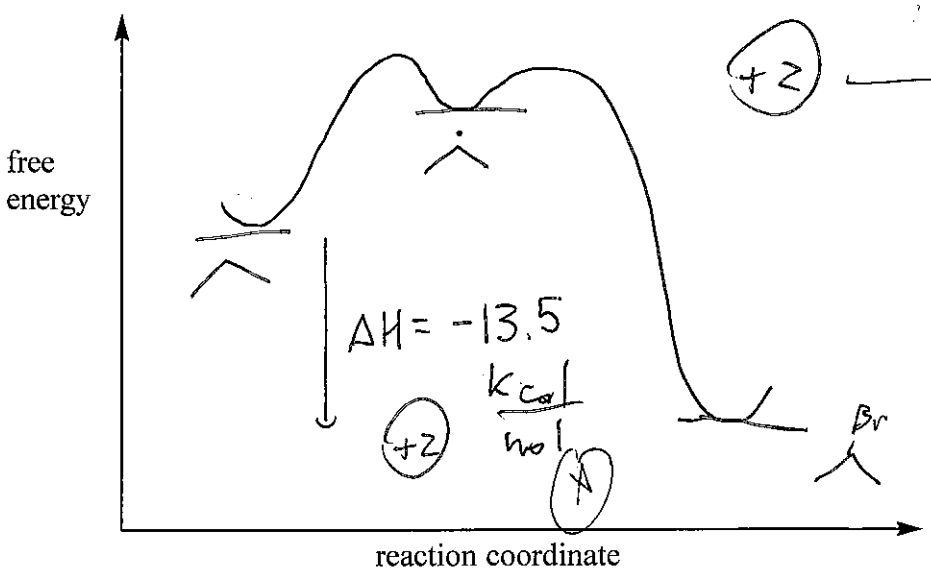
propane $\xrightarrow{Br_2,\ UV\ light}$ 2-bromopropane

+2 $Br-Br \rightarrow Br\cdot \quad Br\cdot$ x4 ← +4

+6 $\Delta H^\circ = 98.5 - 87 = 11.5$ kcal/mol

$\Delta H^\circ = 46 - 71 = -25$ kcal/mol

B. Calculate the change in enthalpy for both propagation steps. (Show all calculations.) Draw an energy diagram, to scale, for the propagation steps of this reaction. What is the overall change in enthalpy for this reaction?

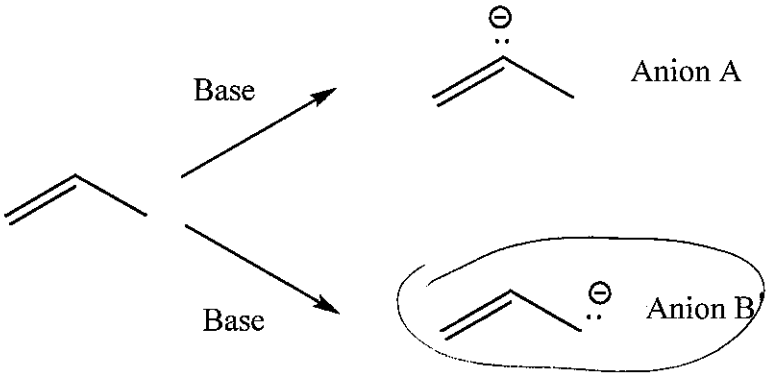


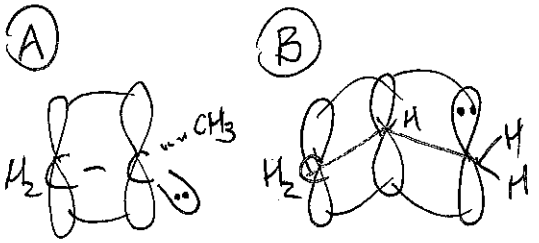
+2 → +4

+2 2 steps

+2 - Endo/Exo

7. (8pts) Which of the following anions would you expect to form preferentially from this starting material? Draw a simplified orbital overlap picture of each anion as part of your explanation.





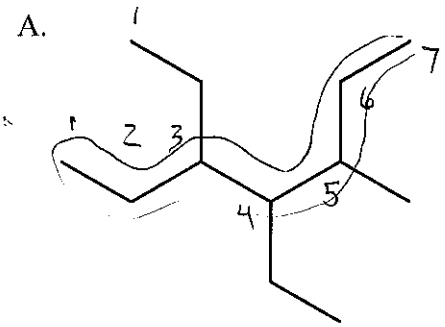
+3 +3

The lone pair on anion B is stabilized through conjugation with the double bond, but the lone pair on A is localized in an sp^2 orbital.

+2

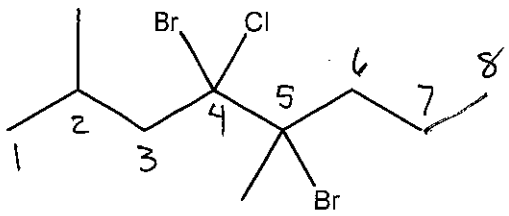
8. (8pts) Give a systematic names for both of these molecules:

A.



3,4-diethyl-5-methylheptane

B.

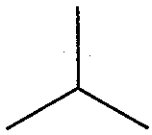
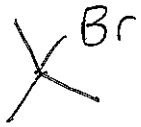
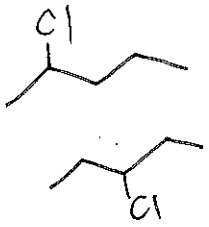
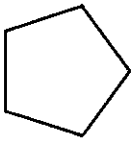
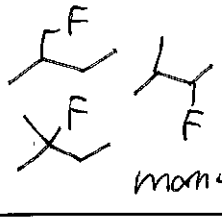


4,5-dibromo-4-chloro-2,5-dimethyloctane

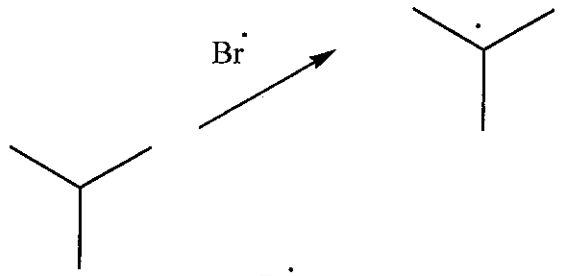
+4 each
-1 for each mistake

+1 each

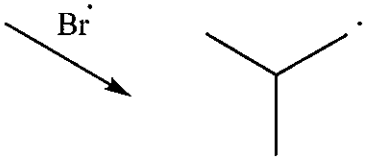
9. (10pts) Predict the major product(s) of each of these radical monohalogenations or write "no reaction." In each case, is the reaction synthetically useful or not?

	major pdt(s)	synthetically useful?
A.  Br_2, heat →		yes
B. pentane Cl_2, hν →		no
C.  Cl_2,hν →		yes
D. ethane I_2, heat →	no rxn	no
E. 2-methylbutane F_2, hν →	 many	no

10 (6pts) Draw transition states for both of these reactions, assuming both are endothermic. Describe each transition state as either "early" or "late."



Reaction A

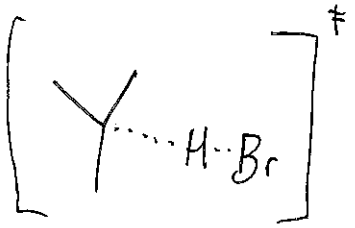


Reaction B

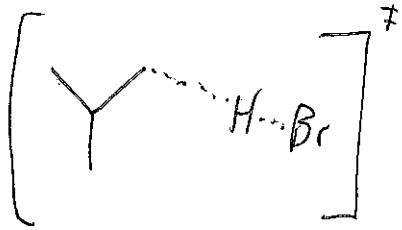
+1 late

+1 late

Transition State A:



Transition State B:



+1 +1

B. Use the transition state structures you drew to explain the high level of selectivity observed in radical bromination. DO NOT write outside the box with your answer!

+2 +2

According to the Hammond Postulate, these endothermic rxns have late TSs. TS A is significantly more stable than TS B because of its 3° radical character, meaning the 3° radical forms significantly faster, making the rxn selective.