Chemistry 3A – Spring 2011
First Midterm – March 1, 2011

Professor Carolyn Bertozzi **Page 1 of 15**

Your full signature______________________________

Print your full name______________________________
(Last Name, First Name, Middle)

Your SID______________________________

GSI's name or section number______________________________

This exam has **15** pages; **make sure that you have them all**. We will only grade answers that are in the designated spaces; please do your scratch work on the last page or the backs of pages. Write only **one** answer to each problem; multiple answers will receive **no** credit, even if one of them is correct.

Note: This examination runs for a total of 120 minutes. Please write legibly; ambiguous or illegible answers will receive **no credit**.

Partial Periodic Table

I	II	III	IV	V	VI	VII	VIII
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr
Rb	Sr	In	Sn	Sb	Te	I	Xe

Do Not Write in this Box:

1.________(8)

2.________(9)

3.________(20)

4.________(15)

5.________(9)

6.________(9)

7.________(12)

8.________(8)

9.________(10)

Total______(100)

1. [8 points]

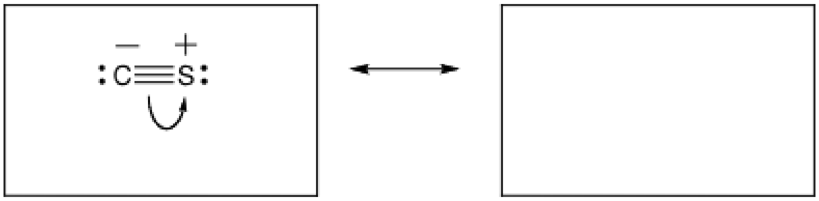
(a) Draw the Kekulé structure of the molecule BeH_2 and indicate the hybridization of Be as well as the molecule's bond angle:

(b) Draw a molecular orbital picture of BeH_2 labeling all of the pure and hybridized atomic orbitals as well as bond types (i.e., σ, π□.

(c) Based on your picture above, would you expect BeH_2 to be nucleophilic or electrophilic? Explain your answer below:

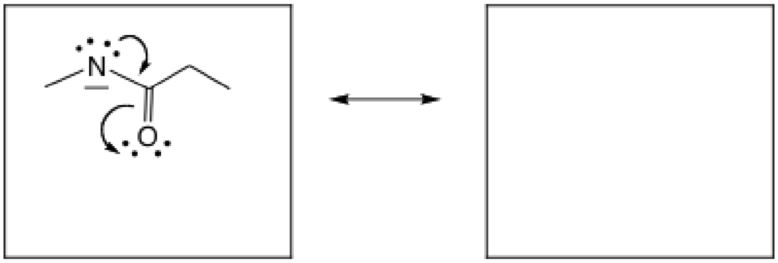
2. [9 points]
In the box on the right, show the resonance structure generated by the movement of electrons indicated with the curved arrows on the left-hand structure. Be sure to show all bonds, lone pairs of electrons, and formal charges. Indicate which is the major resonance structure by writing **"major"** in the box beneath that structure. Provide a brief explanation for your choice in the space below the structures:

(a)



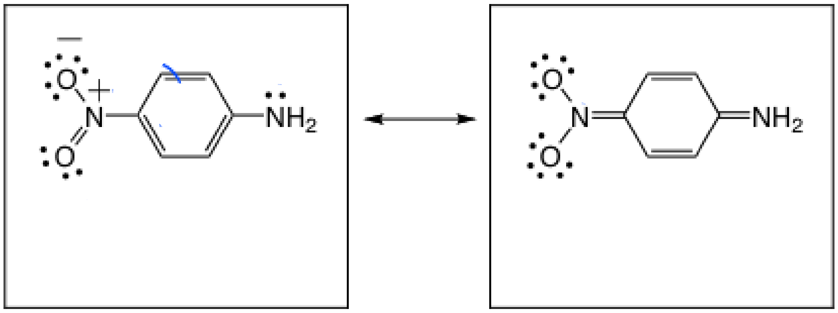
Explanation:

(b)



Explanation:

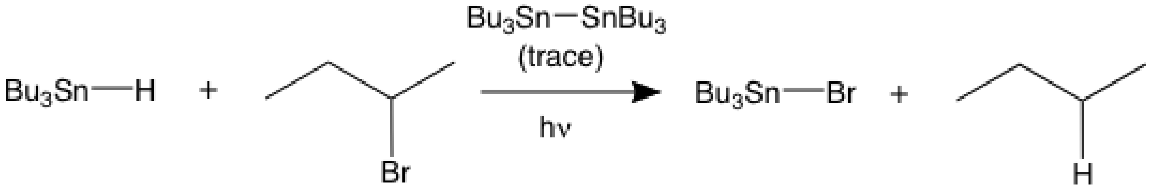
(c) In the following case, add curved arrows to the structure on the left to generate the resonance structure on the right. Note that the right-hand structure lacks formal charges – add them yourself. Indicate the major structure.



Explanation:

3. [20 points]

Free radical dehalogenation using tri-*n*-butyltin hydride (Bu_3SnH, an example of a "stannane") is often used to convert haloalkanes to alkanes (you will find tin (Sn) in the partial periodic table on the front page). Analogous to the free radical halogenations discussed in class, this dehalogenation reaction involves three stages: initiation, propagation and termination.



In the transformation above, $Bu_3Sn—SnBu_3$ is used to initiate the reaction; its weak Sn—Sn bond is cleaved by irradiation with light (hν), generating a small amount of $Bu_3Sn•$ radical. The mechanism of the initiation step is shown below:

Initiation:

(a) Using the same curved arrow formalism, show the mechanisms of the two propagation steps of the reaction:

Step 1:

Step 2:

(b) Show the mechanism of <u>one</u> termination step (your choice which one):

(c) Using the bond dissociation energies in the table on the next page, <u>calculate the change in enthalpy (ΔH°) corresponding to each propagation step, as well as the overall ΔH°</u> for the dehalogenation reaction. <u>Place your answers in the spaces below</u>:

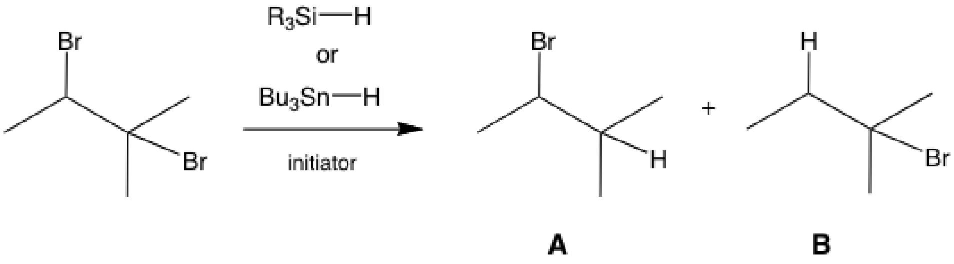
ΔH° for propagation Step 1:

ΔH° for propagation Step 2:

ΔH° for the overall reaction:

(d) Depict the propagation steps on the reaction coordinate diagram below, clearly showing the relative energies of reactants, transition states, intermediates and products. Label the transition states in your diagram:

(e) Free radical dehalogenation can also be accomplished using tri-substituted silanes ($R_3Si–H$), a process that proceeds similarly to the previous $Bu_3Sn–H$ reaction. When 2,3-dibromo-2-methylbutane is reacted with either reagent, two products are formed, **A** and **B**:



Using $Bu_3Sn–H$, the product ratio **A:B** = 2:1.

Would you expect the **A:B** ratio obtained using $R_3Si–H$ to be greater than, less than, or equal to the above ratio? Explain your reasoning.

Bond	BDE	Bond	BDE (kcal/mol)
1° C–H	101	Sn–H	74
2° C–H	98	Sn–Br	91
3° C–H	96	Sn–Sn	45
2° C–Br	72	Si–Br	69
3° C–Br	70	Si–H	79

4. [15 points]

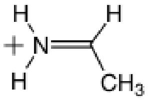
For each pair below, circle the acid with the lowest pKa and provide a brief explanation for your choice on the right side of the page.

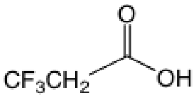
Explanation

H_2S vs PH_3

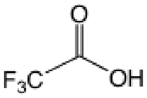
$H-\overset{+}{N}\equiv C-CH_3$

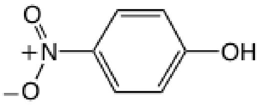
vs



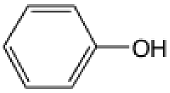


vs

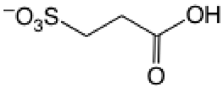


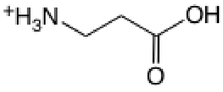


vs



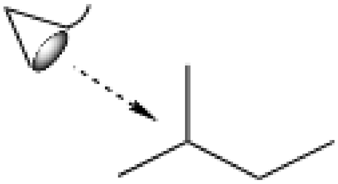
vs





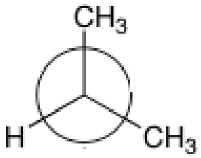
5. [9 points]

Rotation around the central C–C bond in 2-methylbutane can be depicted using Newman projections derived from the view shown below:

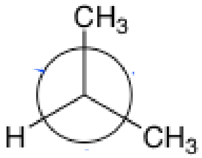


2-Methylbutane

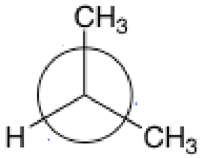
<u>Depict the indicated conformers</u> by completing the following templates:



Lowest energy conformer



Highest energy staggered conformer

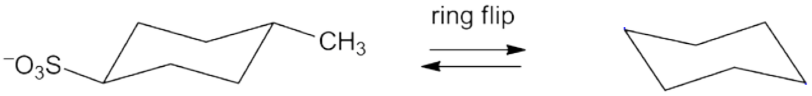


Highest energy eclipsed conformer

6. [9 points]

Show the structure obtained by a "ring flip" of the cyclohexane derivative on the left by completing the template on the right. Using the table of A-values on the next page, estimate the change in free energy (ΔG°) for the process (assume that all molecules in this problem are dissolved in CCl_4):

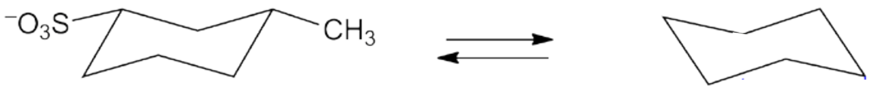
(a)



ΔG° = [illegible]

In parts **(b)** and **(c)**, complete the templates on the right to show the ring flipped conformer.

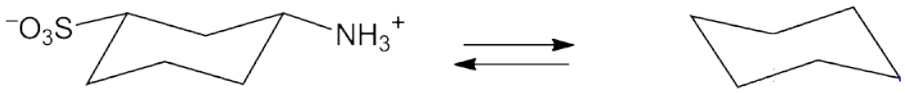
(b) Would you expect ΔG° for the following process to be equal to, less than, or greater than the ΔG° calculated in **(a)** (circle one)? Briefly explain your reasoning in the space provided:



Circle one: ΔG° = **(a)** ΔG° < **(a)** ΔG° > **(a)**

Explanation:

(c) How would ΔG° for the following process compare to that in **(b)** (circle one)? Explain your reasoning in the space provided:



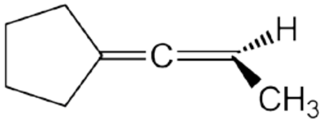
Circle one: ΔG° = **(b)** ΔG° < **(b)** ΔG° > **(b)**

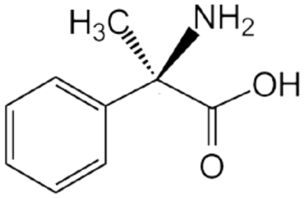
Explanation:

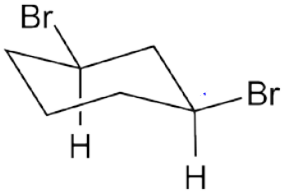
Substituent	**A-value in CCl_4**
$–CH_3$	1.6
$–NH_3^+$	1.6
$–SO_3^-$	2.0

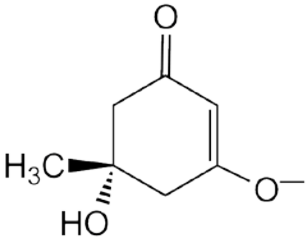
7. [12 points]

(a) Label each molecule below as either chiral or achiral. Identify all stereocenters with an asterisk (*) and assign them the R or S configuration:





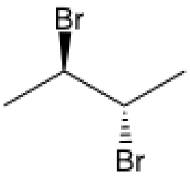




8. [8 points]

In the space on the right, label the following pairs of molecules as enantiomers, diastereomers or identical:

Relationship of pair:



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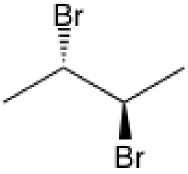

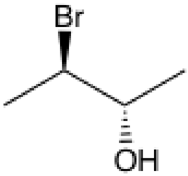

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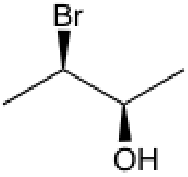

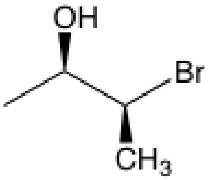

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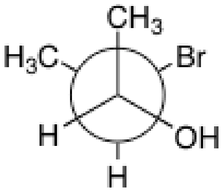

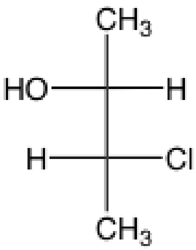

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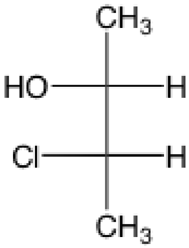
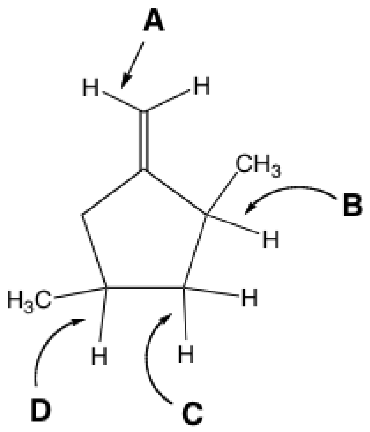


9. [10 points]

For each multiple choice question, mark with an “X” the single answer that you deem most correct.

(a) Which of the indicated C–H bonds is weakest?



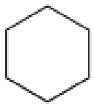
A ______

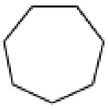
B ______

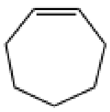
C ______

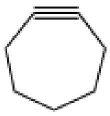
D ______

(b) Which compound below has the most bond angle strain?


A


B


C


D

A ______

B ______

C ______

D ______

(c) Hammond's postulate correlates endothermic reactions with:

______ low activation energies

______ late transition states

______ favorable thermodynamics

______ weak bonds

(d) The molecule NH_3 is a:

______ Lewis acid

______ Lewis base

______ electrophile

______ enantiomer

(e) Thalidomide was originally sold to customers as a:

______ teratogen

______ pure enantiomer

______ mixture of diastereomers

______ racemic mixture

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