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

Professor Carolyn Bertozzi

Your full signature_ Key____

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**.

Do Not Write in this Box:

1.________(8)

2.________(9)

3.________(20)

4.________(15)

5.________(9)

6.________(9)

7.________(12)

8.________(8)

9.________(10)

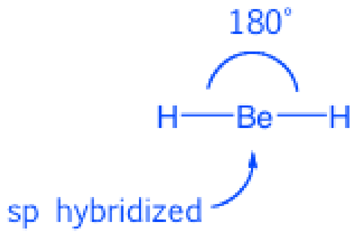
Total______(100)

Partial Periodic Table

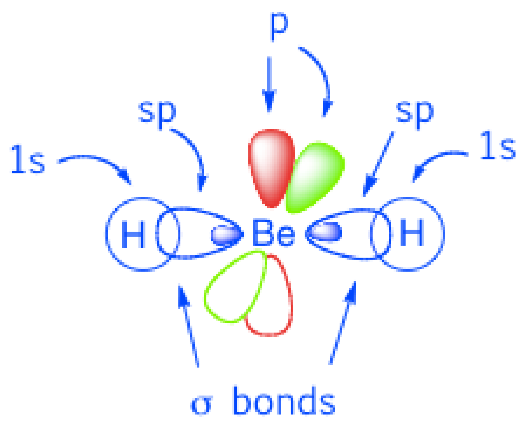
I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr
Rb	Sr	In	Sn	Sb	Te	I	Xe

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□.

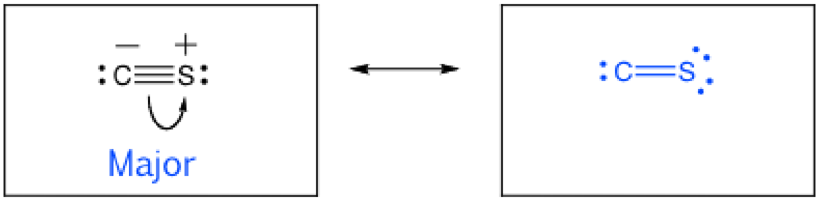


(c) Based on your picture above, would you expect BeH_2 to be nucleophilic or electrophilic? Explain your answer below:

BeH_2 is electrophilic because the Be atom has two empty P orbitals that are eager to react with electron pairs.

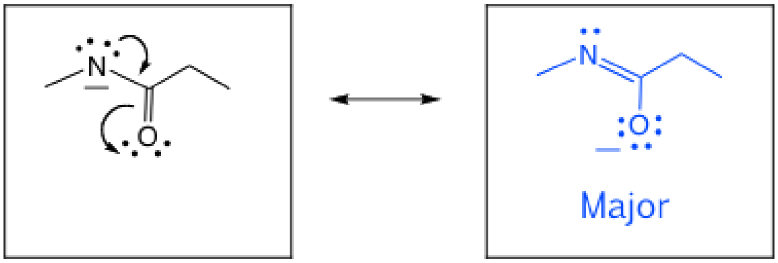
2. [9 points]
In the box on the right, show the resonance structure generated by the movement of electrons indicated with the curved arrows on the left-hand structure. Be sure to show all bonds, lone pairs of electrons, and formal charges. Indicate which is the major resonance structure by writing **"major"**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

(a)



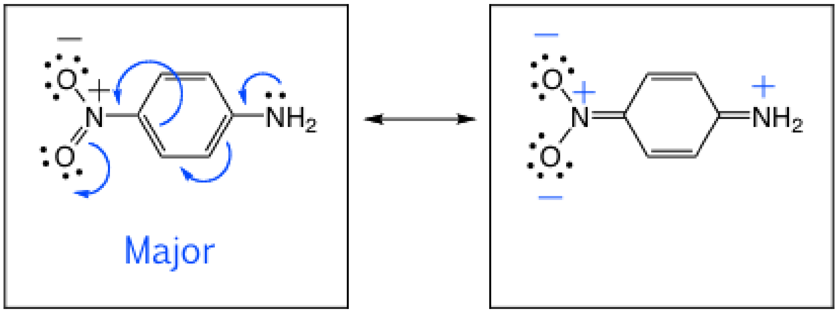
Explanation:
The major structure has octets on both atoms whereas the other structure lacks an octet on carbon. (Note that the major structure has more charge separation but this is superceded by the "maximize octets" rule.)

(b)



Explanation:
The major structure has the negative charge on the more electronegative atom.

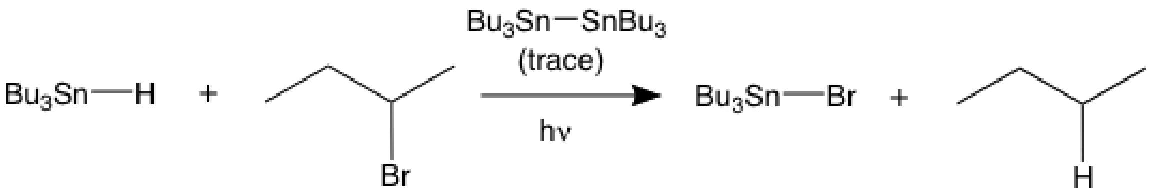
(c) In the following case, add curved arrows to the structure on the left to generate the resonance structure on the right. Note that the right-hand structure lacks formal charges – add them yourself. Indicate the major structure.



Explanation:
The major structure has less charge separation.

3. [20 points]

Free radical dehalogenation using tri-*n*-butyltin hydride (Bu$_3$SnH, 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.

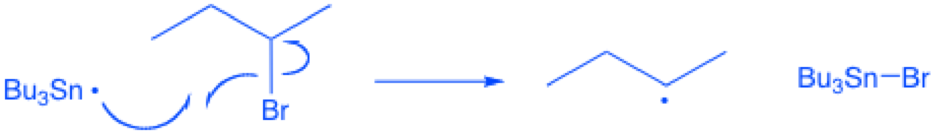


In the transformation above, Bu$_3$Sn—SnBu$_3$ is used to initiate the reaction; its weak Sn—Sn bond is cleaved by irradiation with light (hν), generating a small amount of Bu$_3$Sn• radical. The mechanism of the initiation step is shown below:

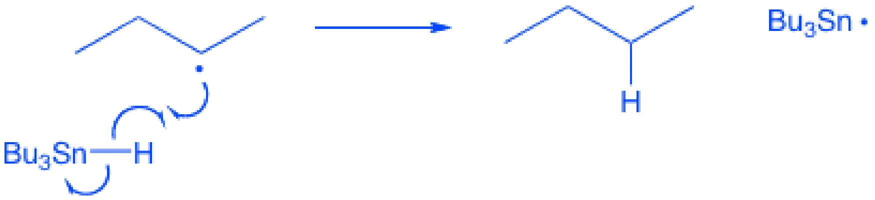
Initiation:

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

Step 1:

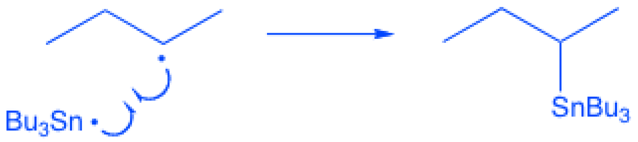


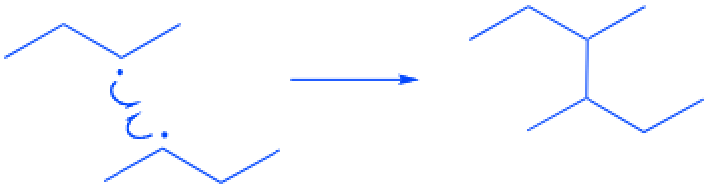
Step 2:



(b) Show the mechanism of one termination step (your choice which one):

Any one of the following is correct:





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

ΔH° for propagation Step 1: - 19 kcal/mol

ΔH° for propagation Step 2: - 24 kcal/mol

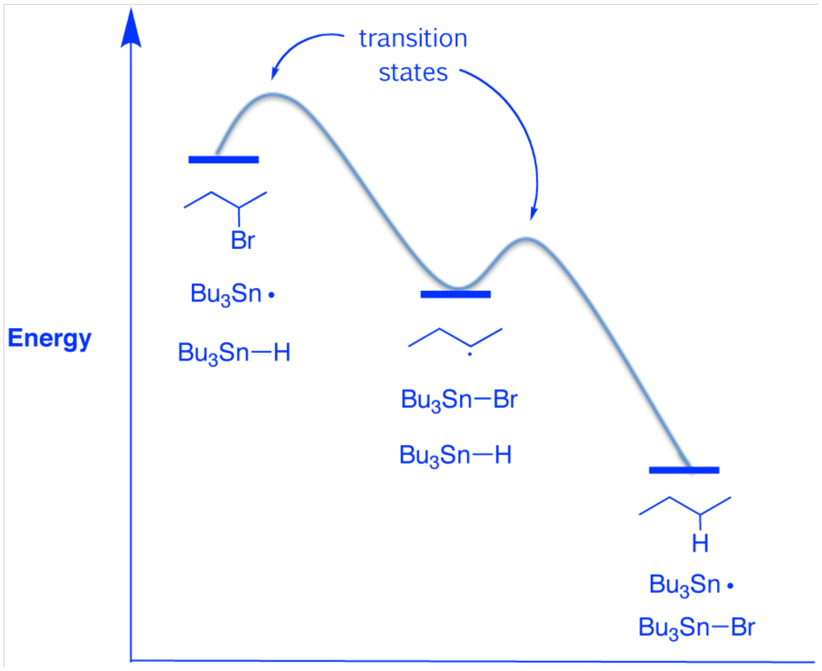
ΔH° for the overall reaction: - 43 kcal/mol

For step 1: Broke a 2° C-Br bond (72 kcal/mol) and formed a Sn-Br bond (91 kcal/mol). ΔH° = 72-91 = - 19 kcal/mol.

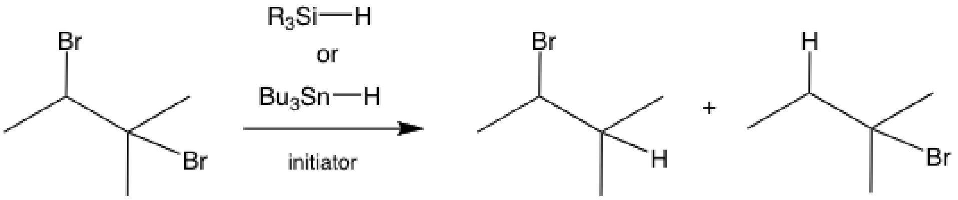
For step 2: Broke a Sn-H bond (74 kcal/mol) and formed a 2° C-H bond (98 kcal/mol). ΔH° = 74-98 = - 24 kcal/mol

The overall ΔH° of the reaction is the sum of the ΔH°s for the two propagation steps.

(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**:



A **B**

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

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

Analogous to the situation in free radical halogenation reactions, selectivity for dehalogenation of 2° vs 3° C-Br bonds should be governed by ΔH° of the first step in the propagation phase of the reaction.

Using Bu_3Sn-H as a reagent, we expect ΔH° for the first step of the reaction to be – 19 kcal/mol for a 2° C-Br bond, and – 21 kcal/mol for a 3° C-Br bond. For either C-Br bond type, this step is <u>highly exothermic</u>.

Using R_3Si-H as a reagent, ΔH° for the first step is + 3 kcal/mol for a 2° C-Br bond and + 1 kcal/mol for a 3° C-Br bond. For either C-Br bond type, this step is <u>slightly endothermic</u>.

According to Hammond's postulate, abstraction of the Br atom by a Sn radical will have an <u>earlier transition state</u> than abstraction of the Br atom with a Si radical. Thus, we expect Sn to be less selective for 3° vs 2° C-Br bonds than Si. Consequently, the A:B ratio observed with the <u>more selective Si reagent</u> should be <u>greater than 2:1</u>. [No partial credit was awarded for this problem]

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

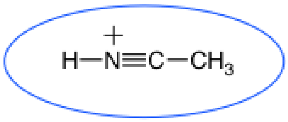
4. [15 points]

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

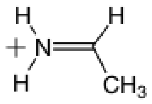
[✓ H_2S] vs PH_3

Across a row of the periodic table, the more electronegative atoms make stronger acids.

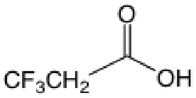


$H-\overset{+}{N}\equiv C-CH_3$

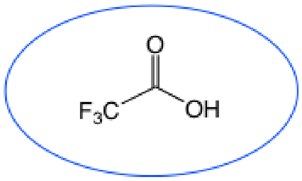
vs



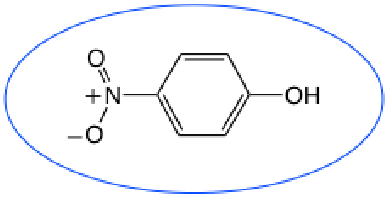
The conjugate base carries the lone pair in an sp rather than sp^2 hybridized orbital, which holds the electrons more tightly.



vs



The CF_3 group imparts inductive stabilization on the conjugate bases, and this effect is distance dependent.



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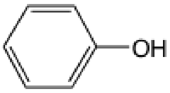
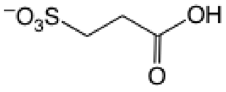
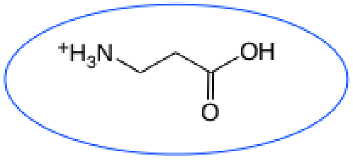


The stronger acid's conjugate base can distribute the electrons and negative charge among more resonance structures.



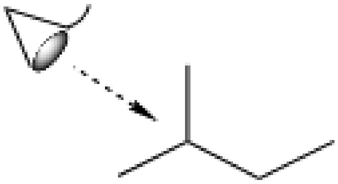
vs



The positive charge stabilizes the conjugate base's negative charge. Conversely, the negative charge of the acid on the left destabilizes additional negative charge that would be generated by deprotonation.

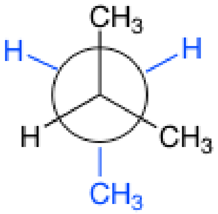
5. [9 points]

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

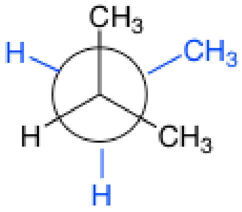


2-Methylbutane

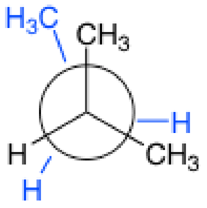
<u>Depict the indicated conformers</u> by completing the following templates:



Lowest energy conformer



Highest energy staggered conformer



Highest energy eclipsed conformer

Minimum number of gauche interactions

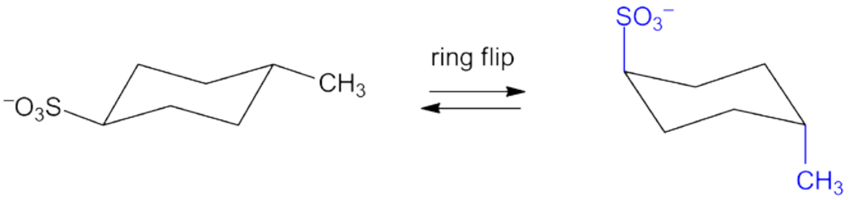
Maximum number of gauche interactions

Methyl groups eclipsed with each other

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):

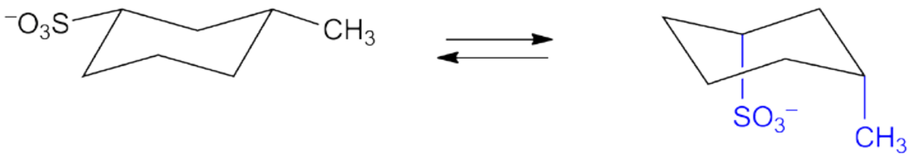
(a)



ΔG° = +3.6 kcal/mol

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:

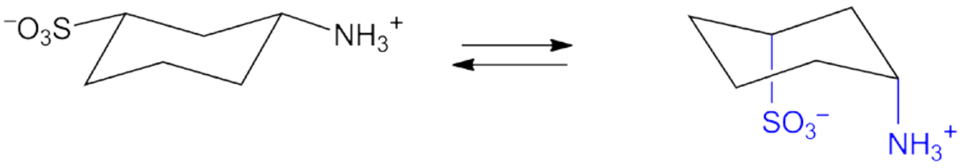


Circle one: ΔG° = **(a)** ΔG° < **(a)** [✓ ΔG° > **(a)**]

Explanation:

The ΔG° for a ring flip in which one substituent is converted from the equatorial position to the axial position is defined as the A-value for that subsitutent. This value is the consequence of the steric interactions between the axial substituent and the two axial hydrogens that reside in the 1,3 relationship to the substituent. The ΔG° is greater than part (a) because in this example two substituents are in a 1,3-diaxial relationship to one another, exacerbating the unfavorable steric interactions.

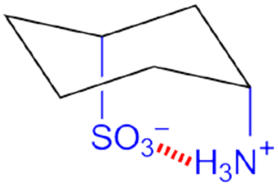
(c) How would ΔG° for the following process compare to that in **(b)** (circle one)? Explain your reasoning in the space provided:



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

Explanation:

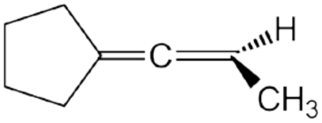
The ΔG° is less than part (b) due to the fact that in this case the diaxial conformation possesses a favorable coulombic/electrostatic attraction, while keeping the steric interaction constant. Similarly, the more favorable ΔG° can be rationalized by an intramolecular hydrogen bond in the diaxial conformation.



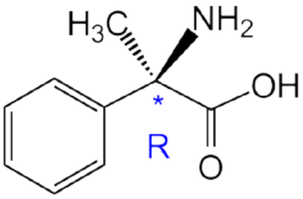
Substituent	A-value in CCl_4
$-CH_3$	1.6
$-NH_3^+$	1.6
$-SO_3^-$	2.0

7. [12 points]

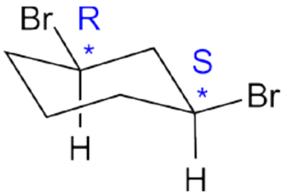
(a) Label each molecule below as either chiral or achiral. Identify all stereocenters with an asterisk (*) and assign them the R or S configuration:



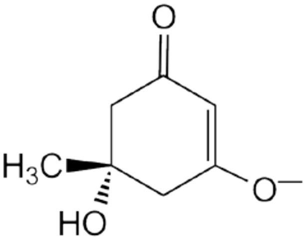
Achiral



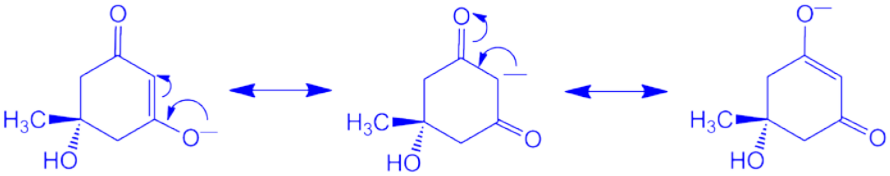
Chiral

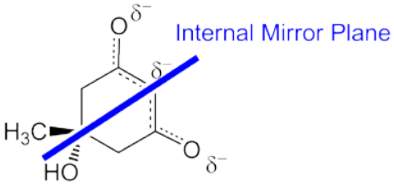


Achiral



Achiral

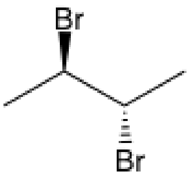




8. [8 points]

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

<u>Relationship of pair:</u>



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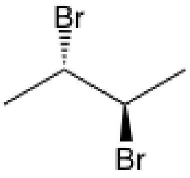
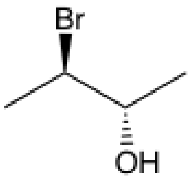


Identical



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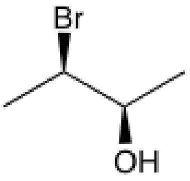
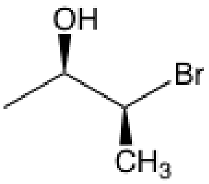


Diastereomers



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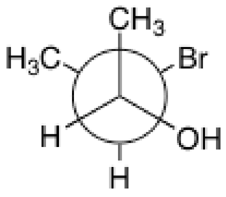
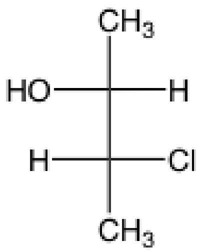


Enantiomers



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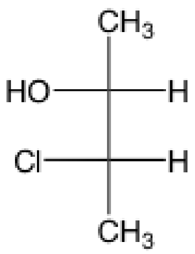
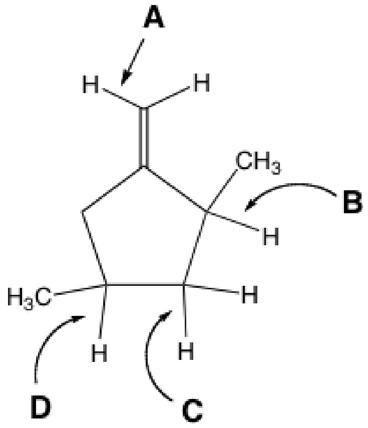


Diastereomers

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?



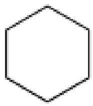
A ______

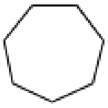
B __X__

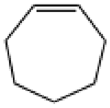
C ______

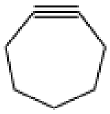
D ______

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


A


B


C


D

A ______

B ______

C ______

D __X__

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

______ low activation energies

__X___ late transition states

______ favorable thermodynamics

______ weak bonds

(d) The molecule NH_3 is a:

______ Lewis acid

__X___ Lewis base

______ electrophile

______ enantiomer

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

______ teratogen

______ pure enantiomer

______ mixture of diastereomers

__X___ racemic mixture

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