Answer Key

CHEMISTRY 12A FALL 2018

EXAM 1

SEPTEMBER 25, 2018

NAME- WRITE BIG _____

STUDENT ID: _____

SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: _____

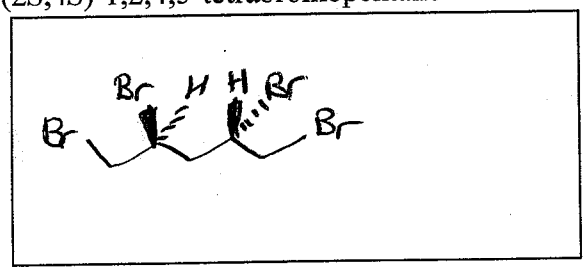
- **You will have 75 minutes in which to work.**
- **BE NEAT! Non-legible structure drawings will not be graded.**
- **Only answers in the answer boxes will be graded – you can write in other places, but we only grade the answers in the boxes.**
- **All pages of the exam must be turned in.**
- **No calculators**
- **No stencils**
- **Molecular models may be used**

Problem	Points (Maximum)
1	8
2	14
3	18
4	20
5	9
6	6
7	15
8	14
9	16
Total	*120*

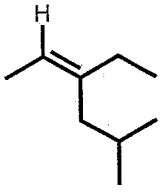
1. (8 points) Nomenclature questions:

a. Draw the molecule that the name represents.

(2*S*,4*S*)-1,2,4,5-tetrabromopentane

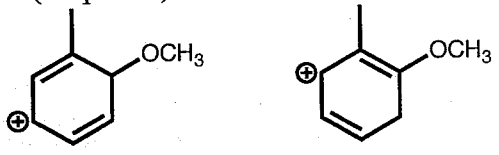


b. Name the following molecule, including stereochemistry.

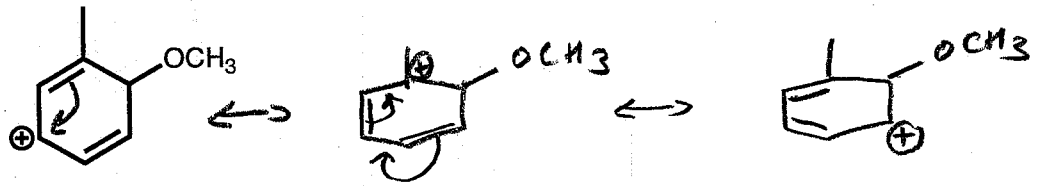


(Z)-3-ethyl-5-methyl-2-hexene

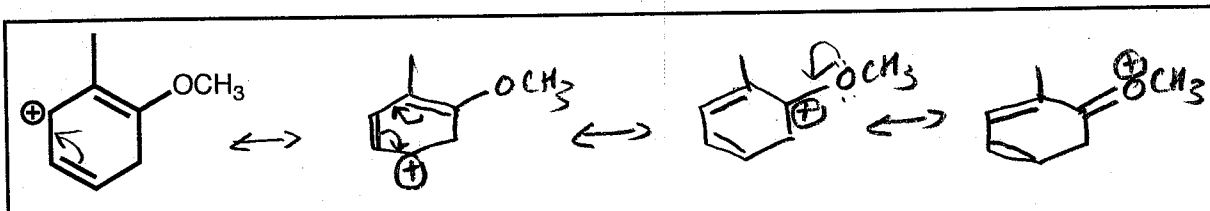
2. (14 points) Consider the two carbocations shown below



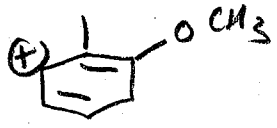
a. Draw the resonance structures of the molecule on the left. Use arrows to show the flow of electrons.



b. Draw the resonance structures of the molecule on the right. Use arrows to show the flow of electrons.

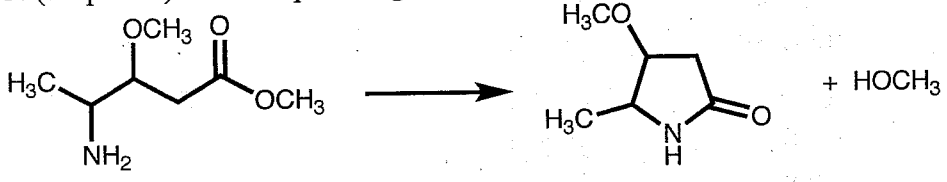


c. Which molecule is more stable? Explain your answer.

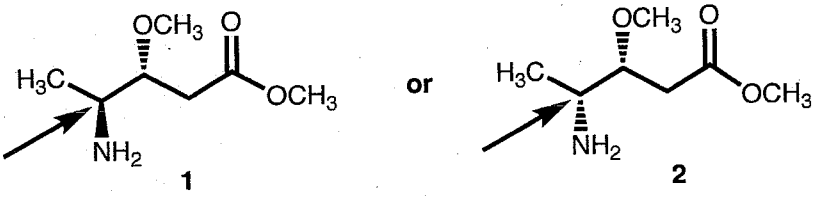


is more stable because one of the resonance structures has all octets which is more stable. In addition this structure has more resonance structures so charge is spread out over more atoms which is more stable

3. (18 points) You are planning to run the reaction below to synthesize this cyclic amide.



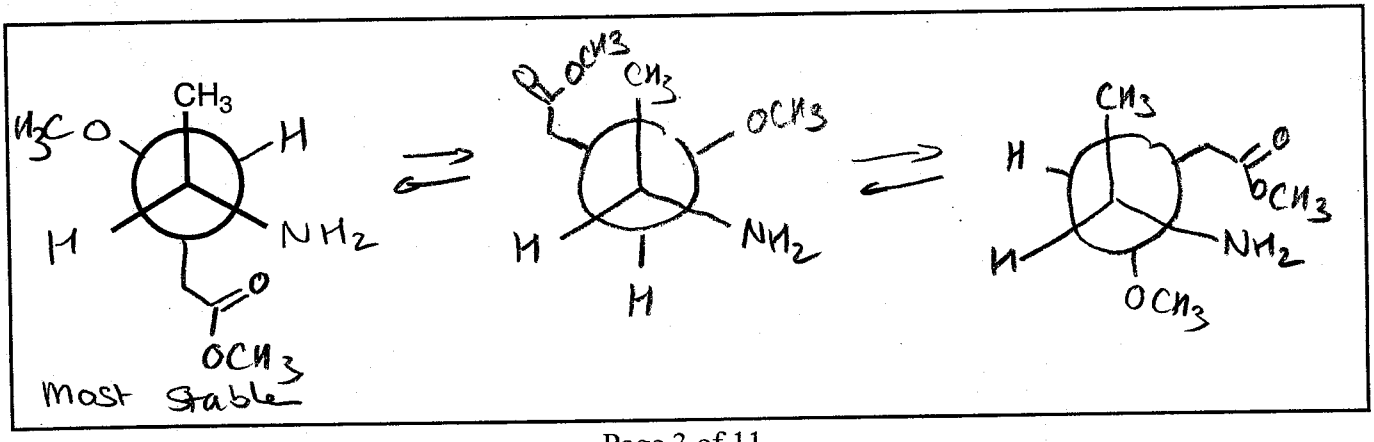
In order for this reaction to proceed rapidly, the NH_2 and the C=O need to be close to each other (gauche). You are trying to decide between the following two stereoisomers to use as a starting material.



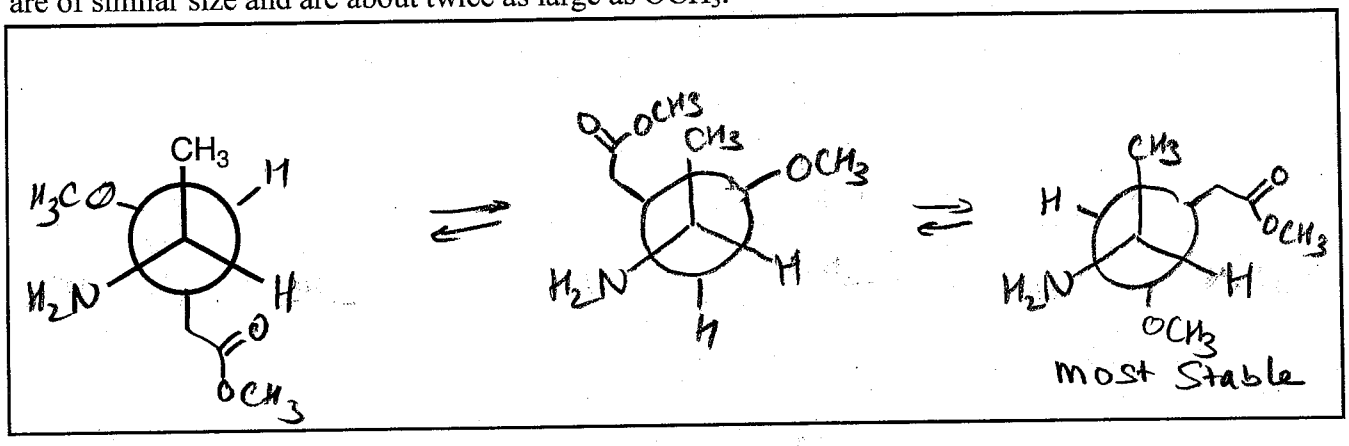
a. What is the relationship between stereoisomers **1** and **2**?

diastereomers

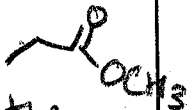
b. Draw Newman projections of **1** looking down the bond indicated with the arrow. Draw the three staggered conformations and identify the most stable conformer. *Note:* CH_3, NH_2, and $CH_2C(O)OCH_3$ are of similar size and are about twice as large as OCH3.



c. Draw Newman projections of **2** looking down the bond indicated with the arrow. Draw the three staggered conformations and identify the most stable conformer. *Note:* CH_3, NH_2, and $CH_2C(O)OCH_3$ are of similar size and are about twice as large as OCH_3.



d. Considering the stability of the staggered conformations you determined in part b and c, which stereoisomer is the best choice for this reaction? Remember that the NH_2 and the C=O need to be close to each other (gauche) for this reaction to proceed. Explain your answer briefly.

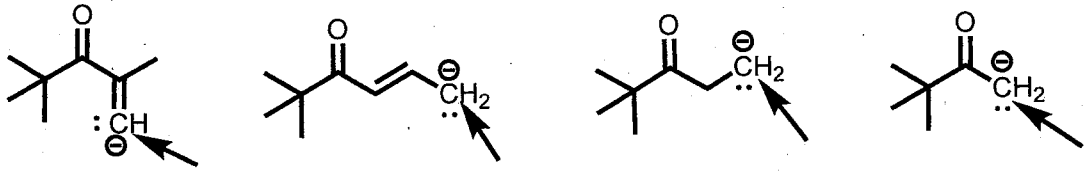
Compound 2 is the best choice. The most stable staggered conformation has the NH_2 gauche to  It is the most stable conformer because it has the lowest number of gauche interactions. It has the highest reactive concentration

In compound 2, the most stable conformer has $-NH_2$ and  anti to each other

4. (20 points) Consider the series of molecules below.

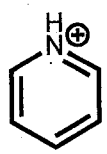
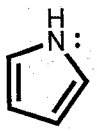
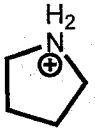
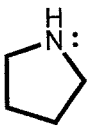
a. Identify the hybridization and lone pair orbital for the indicated atoms. If there are no lone pairs, write N/A.

i.



Hybridization of indicated carbon	sp^2	sp^2	sp^3	sp^2
Type of orbital for lone pair on indicated carbon	sp^2	p	sp^3	p

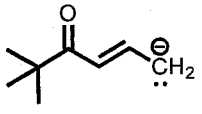
ii.

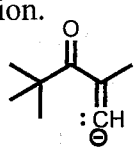





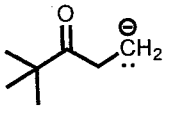
Hybridization of nitrogen	sp^2	sp^2	sp^3	sp^3
Type of orbital for lone pair on nitrogen	N/A	p	N/A	sp^3

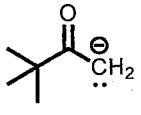
c. Rank the following sets of molecules by the property indicated. Explain your ranking and include relevant structures in your explanation.

i. Basicity


1


2


3

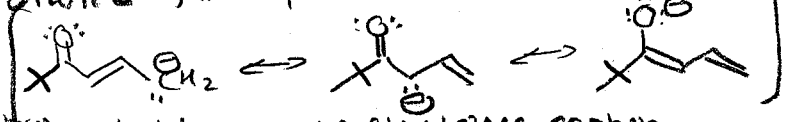
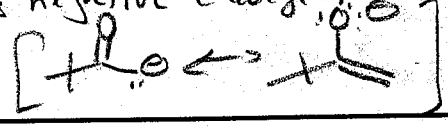

4

Rank Basicity by putting compound numbers in the boxes

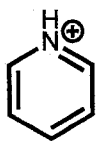
3	2	4	1

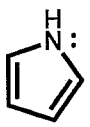
More Basic → Less Basic

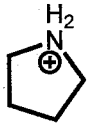
Give an explanation for each compound's position in the ranking. Include relevant structures in your explanation.

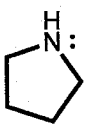
Compound	Explanation
1	most stable Extended resonance that spreads ⊖ over a 2nd carbon & an oxygen stabilizes base  Negative charge is more stable on more electroneg. carbon
2	Negative charge is not resonance stabilized. Negative charge is on an sp^2 hybridized carbon this is more stable than sp^3 carbon of 3 because electrons are closer to the nucleus in an orbital that is a higher percentage s
3	Least stable. Negative charge localized on carbon. There is no resonance to distribute charge. Carbon is sp^3 hybridized. This is a very strong base
4	Negative charge is stabilized by resonance. Resonance structure puts negative charge on more electroneg. oxygen 

ii. Acidity


1


2


3

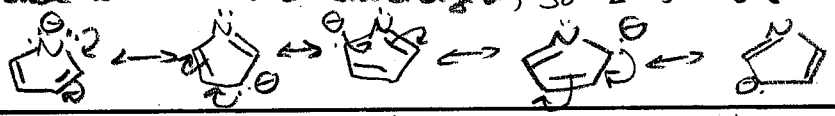

4

Rank Acidity by putting compound numbers in the boxes

1	3	2	4

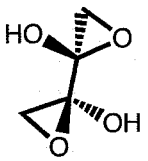
More Acidic → Less Acidic

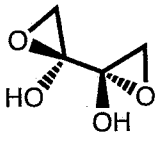
Give an explanation for each compound's position in the ranking. Include relevant structures in your explanation.

Compound	Explanation
1	Most acidic. Molecule is positively charged and N is sp^2 hybridized. Lone pair is more stable in sp^2 hybridized orbital than sp^3 because closer to nucleus. This conjugate base is more stable than that of 2 & 4 so 1 is most acidic
2	Neutral - less acidic than positively charged. Conjugate base is resonance stabilized, so 2 is more acidic than 4 
3	Positively charged N-H will be more acidic than neutral N-H. This is the conjugate acid of a normal amine sp^3 hybridized & no resonance
4	Least acidic. Neutral, no resonance, sp^3 hybridized N

5. (9 points) Consider the pairs of molecules below and identify them as chiral, achiral and/or meso. Indicate whether the molecules are constitutional isomers, enantiomers, diastereomers, identical or different molecules that are not isomers.

a.





Circle one: constitutional isomers enantiomers diateromers (identical) different molecules

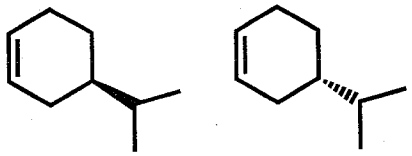
Circle: (chiral) achiral meso (chiral) achiral meso

b.

Circle one: constitutional isomers enantiomers diateromers
identical different molecules

Circle: chiral achiral chiral achiral
meso meso

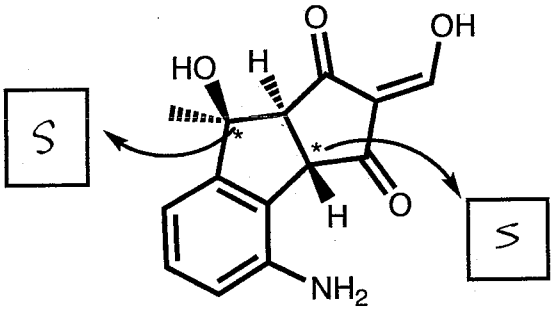
c.



Circle one: constitutional isomers enantiomers diateromers
identical different molecules

Circle: chiral achiral chiral achiral
meso meso

6. (6 points) Consider the molecule below.



a. Fill in R or S for the indicated chiral centers in the structure above.

b. You recently completed a synthesis of this molecule. You are concerned that you may have a mixture of enantiomers. The specific rotation of the pure compound is 60°. If your isolated compound has a specific rotation of 54°, what is the ratio of the desired molecule to its enantiomer? Show your work.

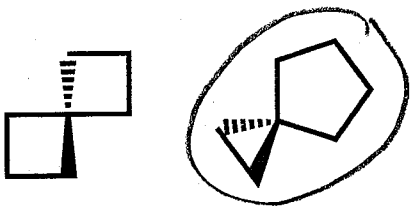
$\%ee = \frac{54}{60} \times 100 = \frac{9}{10} \times 100 = 90\%$

90% (+) 10% 1:1 (+):(-) racemate

95% (+) 5% (-)

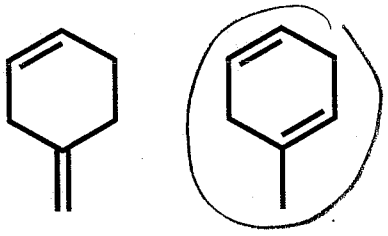
7. (15 points) Consider the pairs of molecules shown below. Circle the molecule that is the most stable in each pair. Describe the factors that destabilize one compared to the other in the box provided.

a.



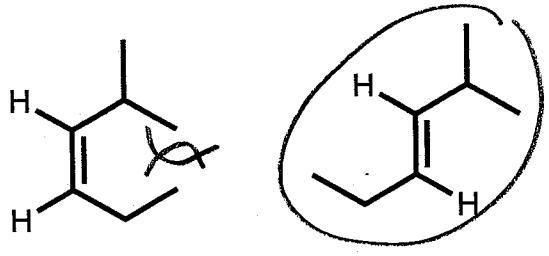
Circled ring has one strained ring
Four 3 membered rings have about the same amount of ring strain so the molecule w/ two 4-membered rings is less stable
Both angle & torsional strain
↳ 60° or 90° angles instead of 109.5
torsional → eclipsing interactions

b.



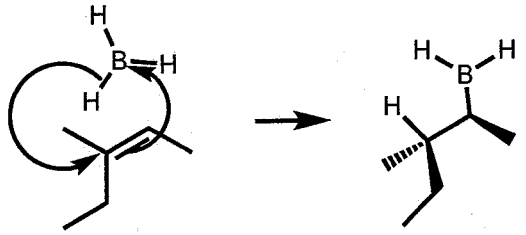
Circled more stable because it has more substituted alkenes which are more stable

c.

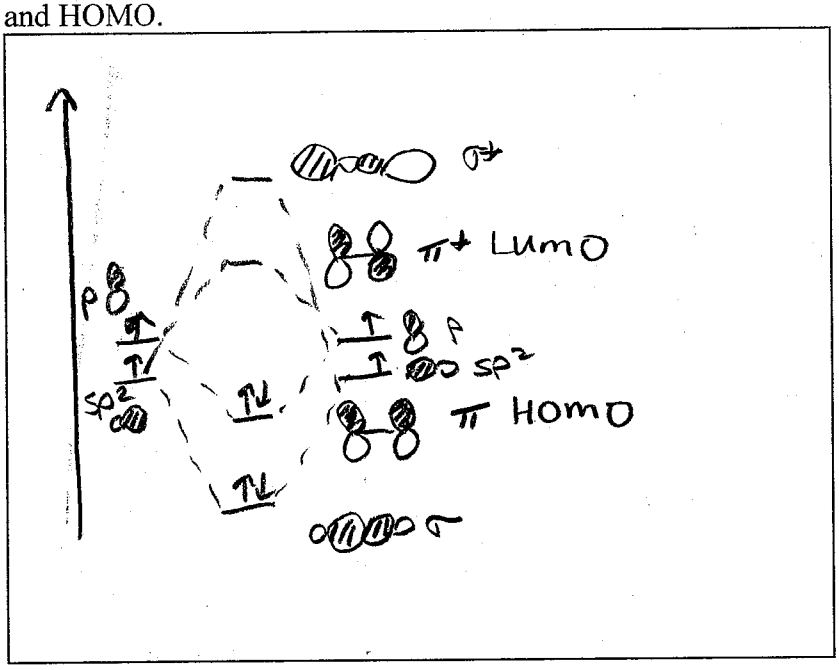


Trans is more stable than cis because cis is destabilized by steric interactions between the two groups that are cis.

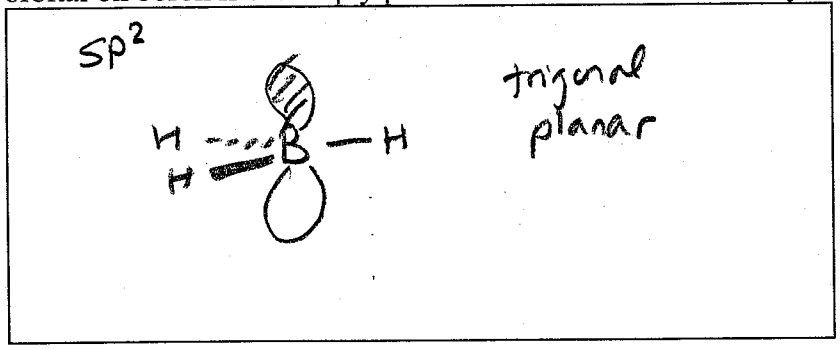
8. (14 points) Alkenes can undergo addition of boranes as part of the hydroboration reaction, as shown below. The B-H bond is broken and the double bond system forms a bond with the boron all in one step as shown with the arrows.



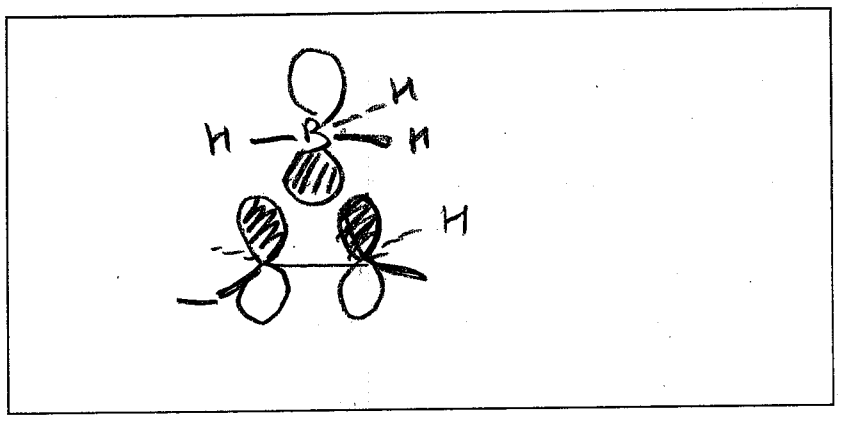
a. Draw a molecular orbital diagram of the C=C bond. Sketch and label all orbitals and label the LUMO and HOMO.



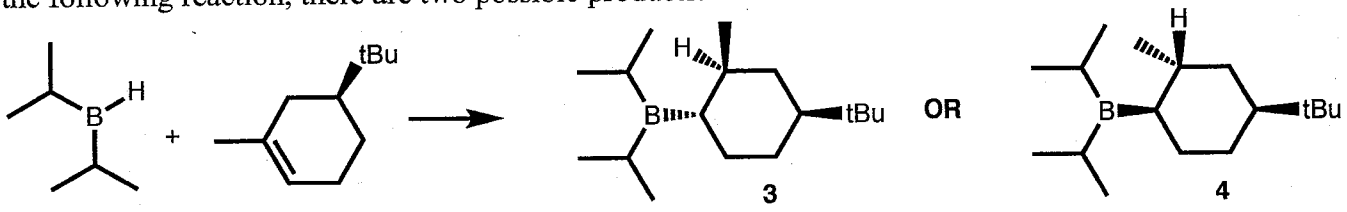
b. What is the hybridization of boron in BH_3? Sketch the geometry of BH_3. The lowest unoccupied orbital on boron is the empty p orbital. Sketch this orbital on your drawing of BH_3 below.



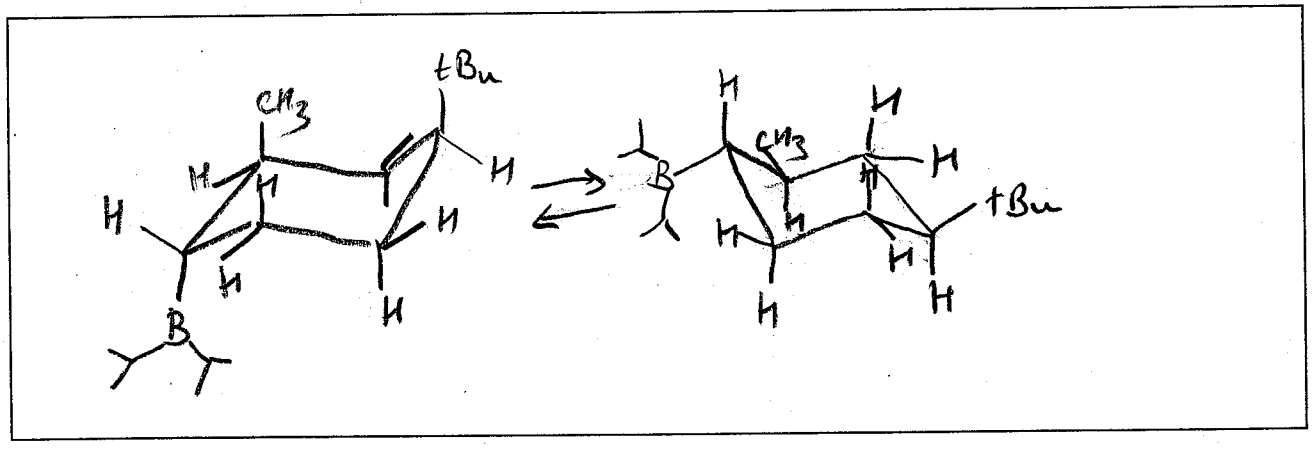
c. In this reaction, the LUMO of BH_3 interacts with the HOMO of the C=C bond. On a line drawing of the molecules, sketch the HOMO of the C=C bond interacting with the LUMO of BH_3.



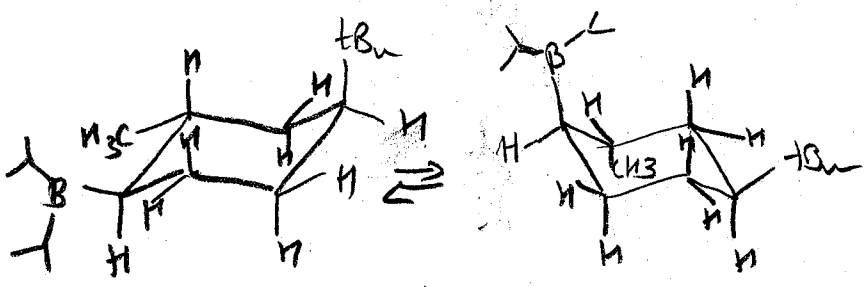
9. (16 points) The reaction of B-H bonds with alkenes from problem 8 occurs in one step, and therefore, both new bonds (C-H and C-B) will be formed on the same side of the molecule. When the boron is substituted with large alkyl groups it will bond to the less substituted carbon of the alkene. Therefore, in the following reaction, there are two possible products.



a. Draw both chair conformations compound **3**. Draw in all hydrogens on the cyclohexane ring.



b. Draw both chair conformations of compound **4**. Draw in all hydrogens on the cyclohexane ring.



c. Which product is more stable? Explain your answer.

Product 3; All groups are equatorial in one of its conformations. This reduces 1,3-diaxial (gauche, steric) interactions & stabilizes conformation.