Dr. Steven Pedersen October 6, 2014

Chemistry 3A
Midterm 1

Student name: ANSWER KEY

Student signature: _____

Problem 1 _____ (18 pts)

Problem 2 _____ (25 pts)

Problem 3 _____ (20 pts)

Problem 4 _____ (12 pts)

Problem 5 _____ (18 pts)

Problem 6 _____ (12 pts)

Problem 7 _____ (15 pts)

Problem 8 _____ (18 pts)

Problem 9 _____ (12 pts)

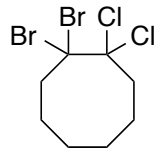
Total Points _____ (150 pts)

No Calculators Allowed
No Molecular Models Allowed
Be Sure Your Exam has 10 Pages

1 H							2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca					35 Br	36 Kr
						53 I	54 Xe

1. There will be NO partial credit for this problem. Avoid careless errors by checking over your answers. (18 pts)

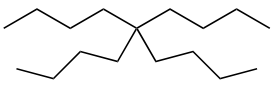
A. Provide a systematic name for the following compounds. Use common nomenclature for any branched substituents.



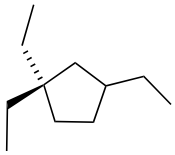
1,1-dibromo-2,2-dichlorocyclooctane OR

1,1-dichloro-2,2-dibromocyclooctane

(will also accept 1,1-dichloro (or dibromo)-8,8-dibromo (or dichloro)cyclooctane



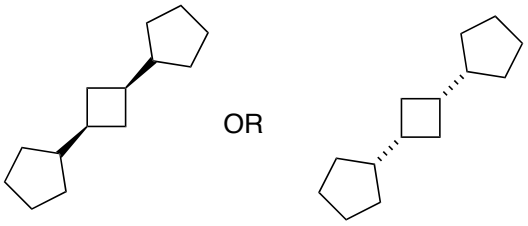
5,5-dibutylnonane



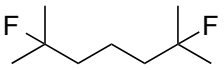
1,1,3-triethylcyclopentane OR
1,3,3-triethylcyclopentane OR
1,1,4-triethylcyclopentane OR
1,4,4-triethylcyclopentane

B. Draw a structure for each of the following names. For cycloalkanes use flat rings. For all others use bond-line notation.

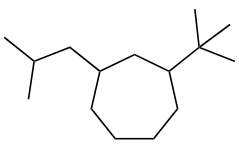
cis-1,3-dicyclopentylcyclobutane



2,6-difluoro-2,6-dimethylheptane



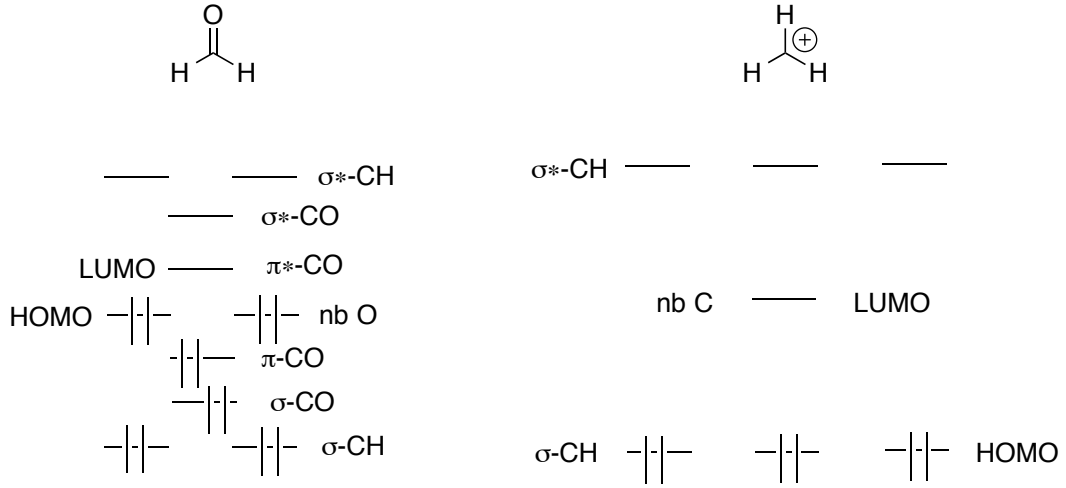
1-*tert*-butyl-3-isobutylcycloheptane



2. (25 pts)

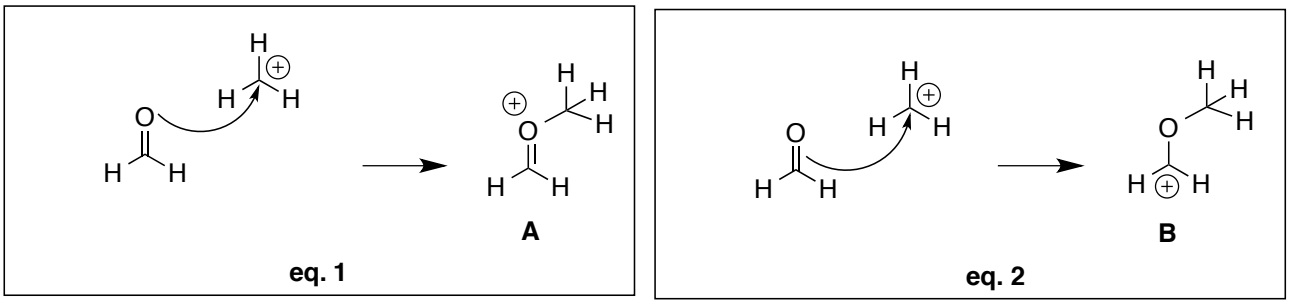
A. Shown below are molecular orbital diagrams for formaldehyde and methyl cation. On each diagram:

- Label each level as σ, π, non-bonding (nb), etc. and include the atom(s) involved with each designation, e.g. σ-CH, etc.
- Fill in the electrons.
- Label the HOMO and LUMO.



B. How are products A and B in equations 1 and 2 below related?

Write Answer Here: *RESONANCE STRUCTURES*



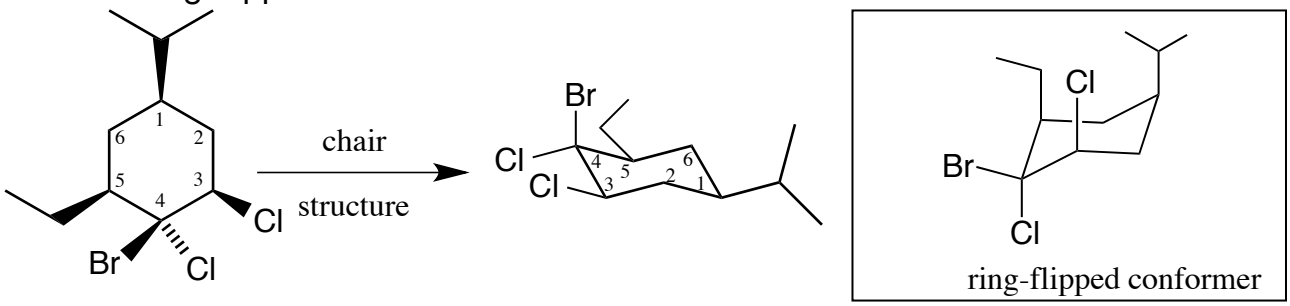
C. Based on what you know about Frontier Molecular Orbital theory which of the two equations above is a more reasonable depiction of how the reaction between formaldehyde and methyl cation occurs? **Circle one: eq.1 OR eq.2**

Provide a very short explanation regarding your choice (no points for a correct choice and wrong or no explanation). Keep your answer in the box.

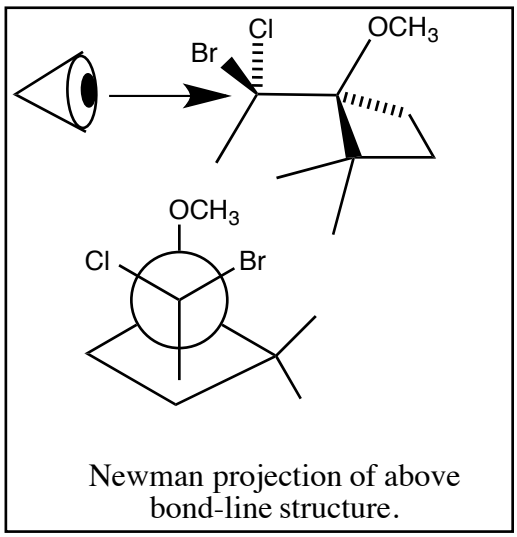
Frontier Molecular Orbital theory states that the HOMO of the nucleophile will interact with the LUMO of the electrophile. Based on the diagrams in Part A, the HOMO of nucleophile is the lone pair of electrons on oxygen. The LUMO of the electrophile is an empty p-orbital. Equation 1 is most consistent with this as it clearly shows the arrow beginning at oxygen and going to carbon. In the second equation, the arrow begins with the π-bonding electrons which are NOT the HOMO of this molecule.

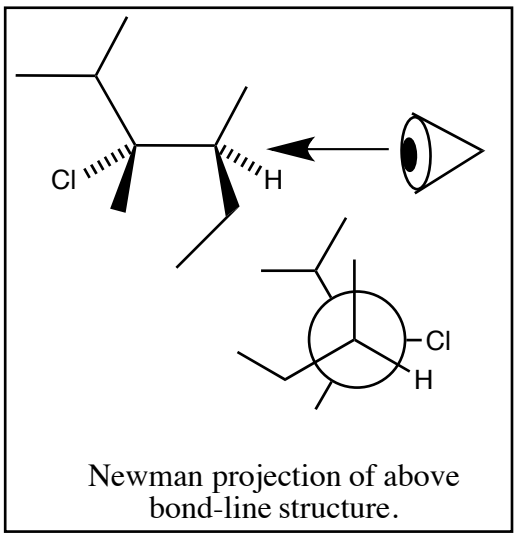
3. (20 pts)

A. Using the template given, draw the chair structure of the compound shown. Then draw the ring-flipped conformer of this chair structure.

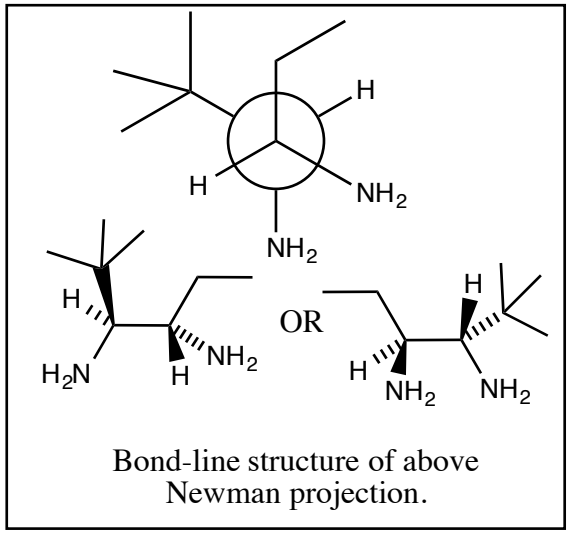


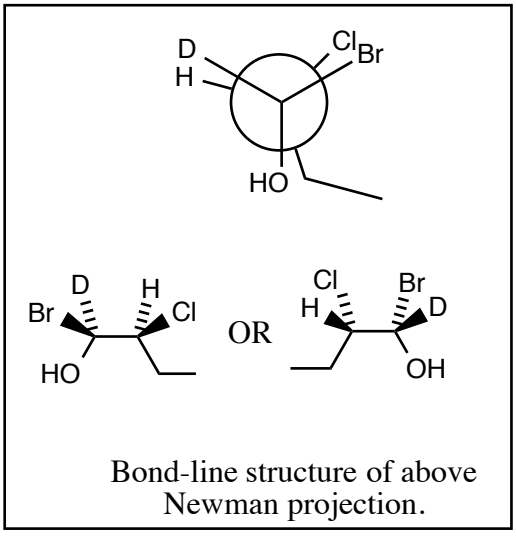
B. Draw a Newman projection representing the conformation of each molecule looking down the indicated bond.



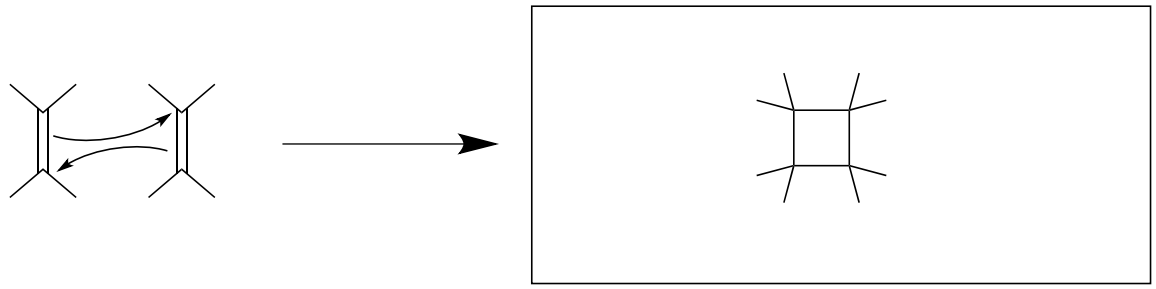


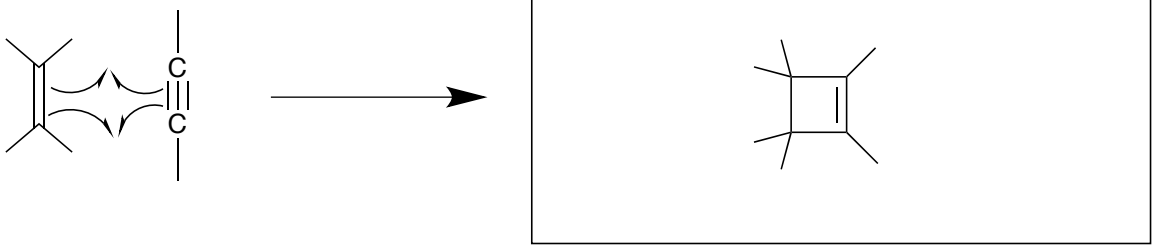
C. For each Newman projection, draw a bond-line structure that exactly depicts the conformation shown.

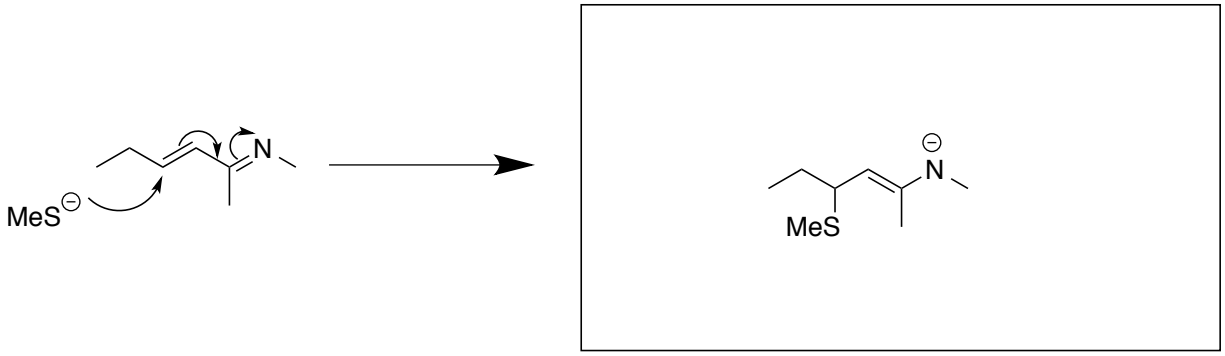


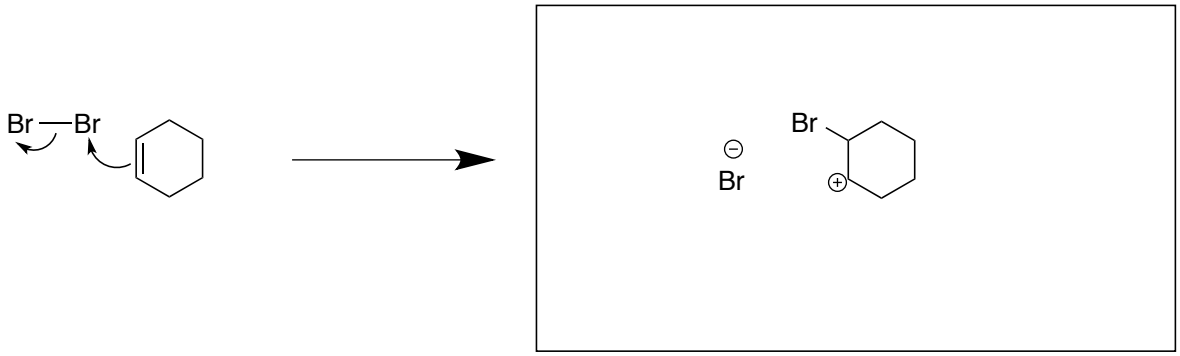


4. (12 pts)
Draw ALL of the product(s) you would expect to get based on each arrow-pushing diagram. Be sure to include any relevant charges.



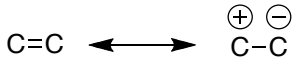




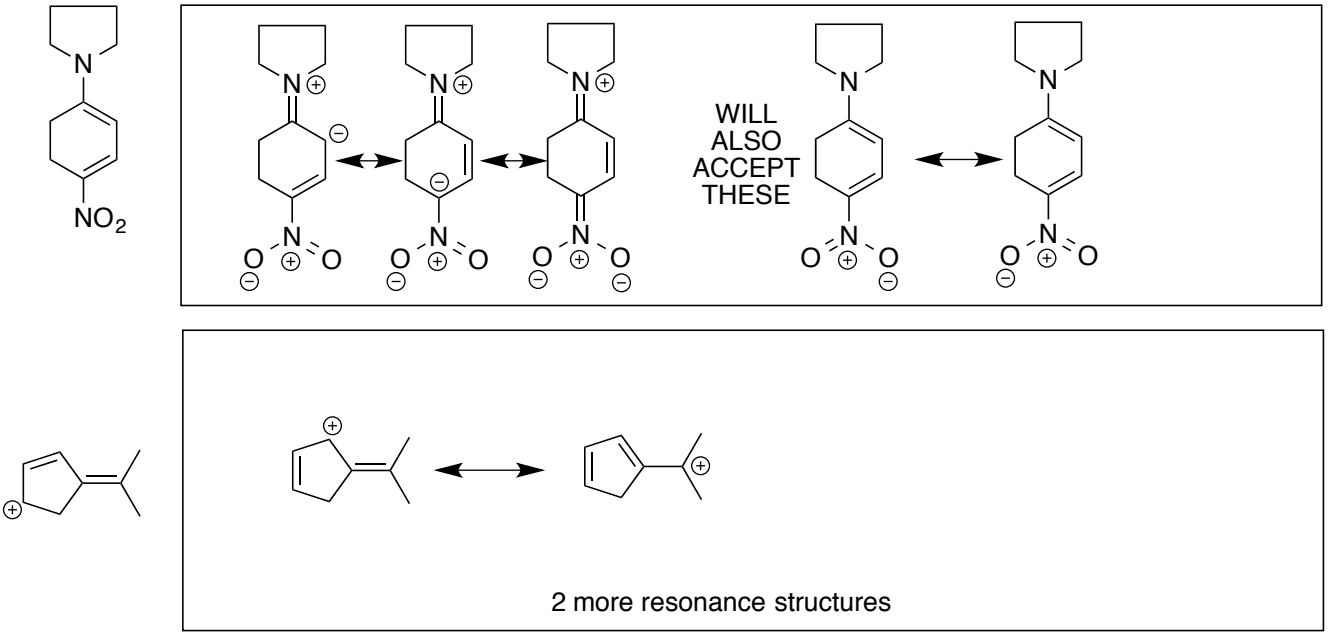


5. (18 pts)

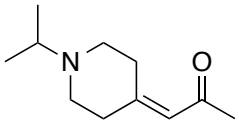
A. Write as many valid and reasonable resonance structures as asked for in each box. No points will be given for any resonance structure that simply separates a carbon-carbon double bond into a plus charge on one carbon and a minus on the other carbon.



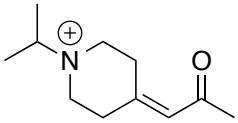
no credit



B. Underneath each structure shown below are the terms: valid and reasonable; valid and unreasonable; not a resonance structure. Compare each structure with the structure shown directly below this problem and circle the correct term. Wrong answers cancel correct circled answers so don't guess.



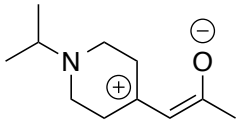
Compare the structures to this one.



valid and reasonable

valid and unreasonable

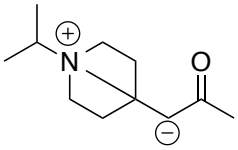
not a resonance structure



valid and reasonable

valid and unreasonable

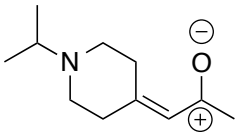
not a resonance structure



valid and reasonable

valid and unreasonable

not a resonance structure

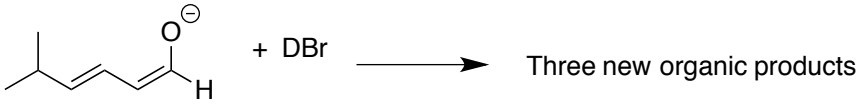


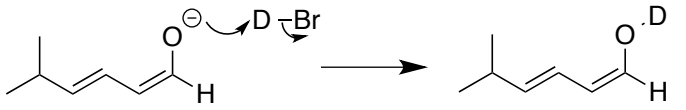
valid and reasonable

valid and unreasonable

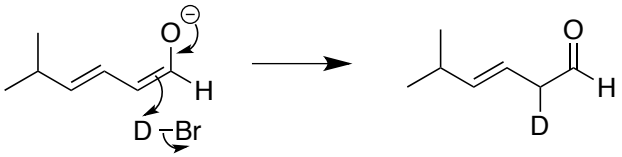
not a resonance structure

6. (12 pts)
The compound shown below reacts with deuterium bromide (DBr) to yield a mixture of three new organic compounds. Show the arrow-pushing scheme leading to the formation of each compound in the boxes provided.

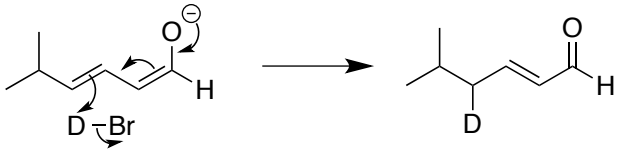




Arrow-pushing mechanism for one of the three products



Arrow-pushing mechanism for one of the three products



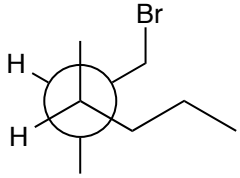
Arrow-pushing mechanism for one of the three products

ALTERNATIVELY, YOU CAN SHOW THE APPROPRIATE RESONANCE STRUCTURES FIRST AND THEN HAVE THOSE REACT WITH THE DBr. YOU WILL STILL NEED TO HAVE USED ARROW-PUSHING TO GET TO THE RESONANCE STRUCTURES.

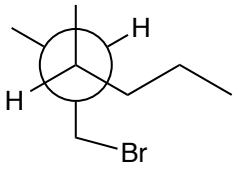
In both cases the products must be shown.

7. (15 points)

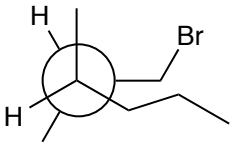
A. Six Newman projections of a compound are shown below. Note that these projections are in no particular order. Match each projection with its relative location on the potential energy diagram (place the letter of a projection on the small horizontal lines located at each rotation).



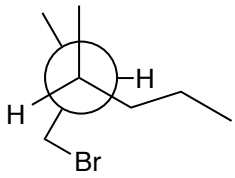
A



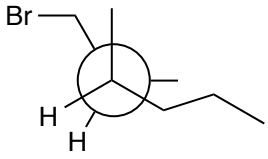
B



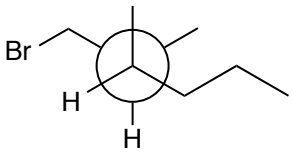
C



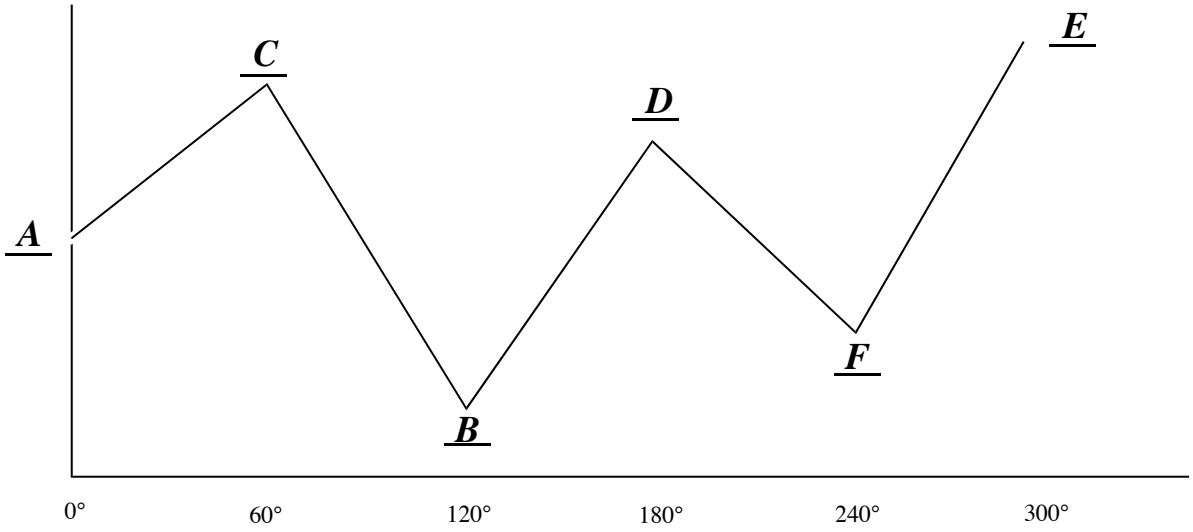
D



E



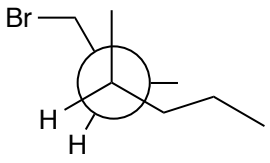
F



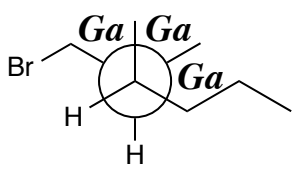
B. What is the IUPAC name for the molecule shown in question A?

1-bromo-2,3-dimethylhexane OR 6-bromo-4,5-dimethylhexane

C. Indicate all gauche interactions on projections E and F (shown here) with the label Ga. Wrong answers cancel right answers so do not guess.



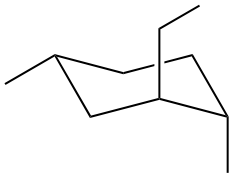
E

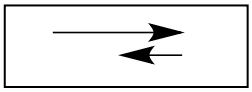


F

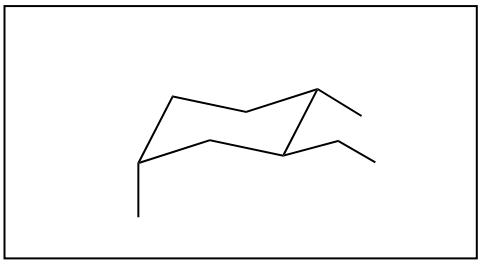
8. (18 pts)

A. Draw the ring-flipped conformer for the molecule shown.





$K_{equilibrium}$



ring-flipped conformer

B. If you were to calculate ΔG for the ring flip shown in question A, would the value be (circle one; note, you do not need a table of values to answer this question):

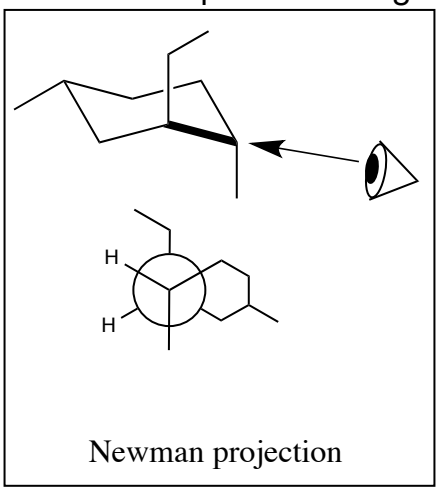
$\Delta G > 0$ $\Delta G = 0$ $\boxed{\Delta G < 0}$

C. In the box labeled $K_{equilibrium}$ in question A, indicate the direction of the equilibrium between the two conformers based on your answer in question B.

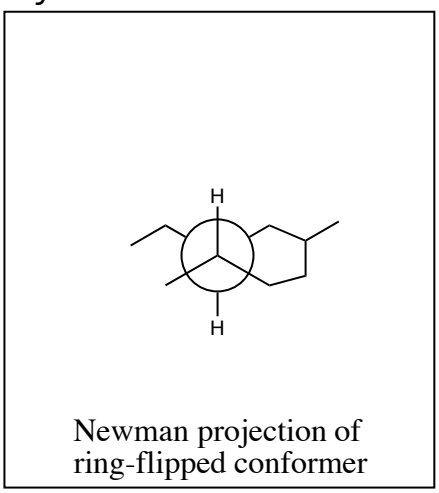
D. In question A, is there any additional interaction in either ring-flipped conformer that is not accounted for in the ΔG values associated with methylcyclohexane or ethylcyclohexane? If not, then state this. If so, describe this interaction using terms you have learned in class. Be sure to note which substituents are involved.

There is an additional gauche interaction between the methyl and ethyl groups on adjacent carbons that is not accounted for in the ΔG values associated with either methyl or ethylcyclohexane.

E. Draw a Newman projection of both conformers (from Part A) looking down the SAME bond and in the SAME direction as indicated on the first structure shown below. The bond in question is highlighted to avoid any confusion.

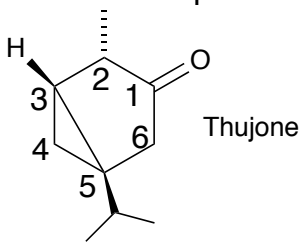


Newman projection



Newman projection of ring-flipped conformer

9. (12 pts)
Most countries banned the green liquor known as absinthe at the turn of the century due to the presence of thujone, a hallucinogen that, if abused, can lead to serious medical complications. Questions A-D are related to this molecule.



Thujone

A. The methyl and isopropyl groups in thujone are best described as being (circle one):

resonance structures conformers cis trans

B. The carbon labeled 3 is best described as (circle one):

Primary Secondary Tertiary Quaternary

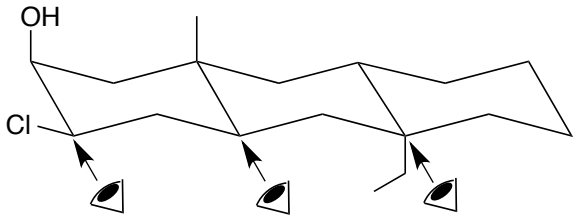
C. The oxygen atom in thujone is best described as (circle one):

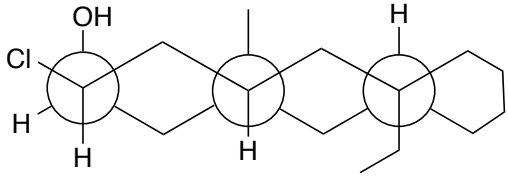
SP hybridized SP^2 hybridized SP^3 hybridized

D. Which two carbons in thujone are considered the bridgehead carbons? Place your answer in the box below.

3 and 5

E. In class we have used the term "double-barrel" Newman projection when looking down two parallel bonds in chair cyclohexane. Draw a "triple-barrel" Newman projection looking down the three bonds indicated on the structure below.





"triple-barrel" Newman projection