CHEM 3311 **HARRINGTON**

Exam 4 **KEY**

10:30 AM – 1:00 PM December 13, 2016 in MATH 100

Instructions. No notes, books, laptops, phones, calculators, models, or stencils are allowed. Periodic Table, Electronegativity Chart, and Strain Energy Tables are provided.

NAME:

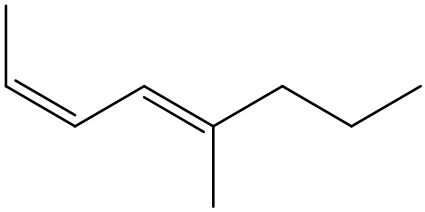
	Points Possible	Score
1	20	
2	20	
3	20	
4	20	
5	20	
6	20	
7	20	
8	20	
9	20	
10	20	
Exam 4 Total Raw Score	200	
Exam 4 Curve		
Exam 4 Curved Score		
Exam 4 Letter Grade		
Exam Score Replaced	#	
Quiz Points	50	
Total Points	550	
Final Letter Grade		

#

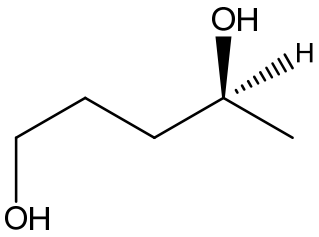
1(**20 points**) Draw a **structure** corresponding to each of the following IUPAC names.

5 points each correct structure **no partial credit**

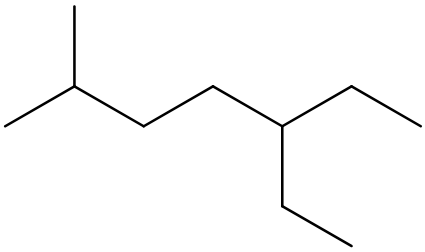
a. (2Z,4E)-5-methyl-2,4-octadiene



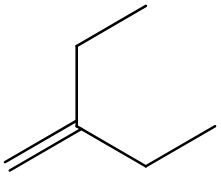
b. (S)-1,4-pentanediol



c. 5-ethyl-2-methylheptane

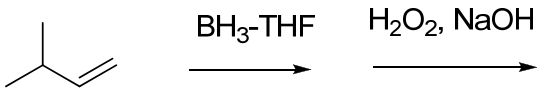


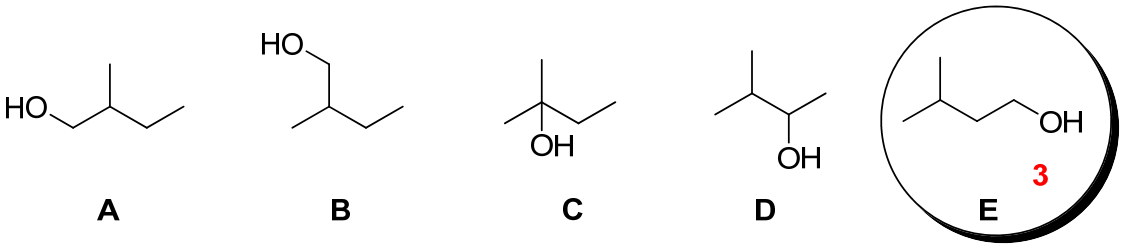
d. 2-ethyl-1-butene



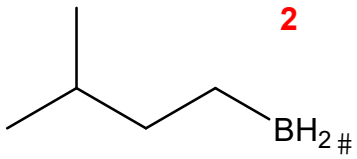
2. (**20 points**) **no partial credit** for intermediates

a. What is the major product of the following reaction? (**Circle the answer.**)

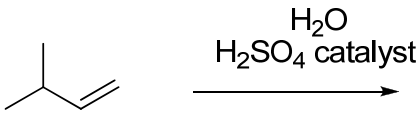


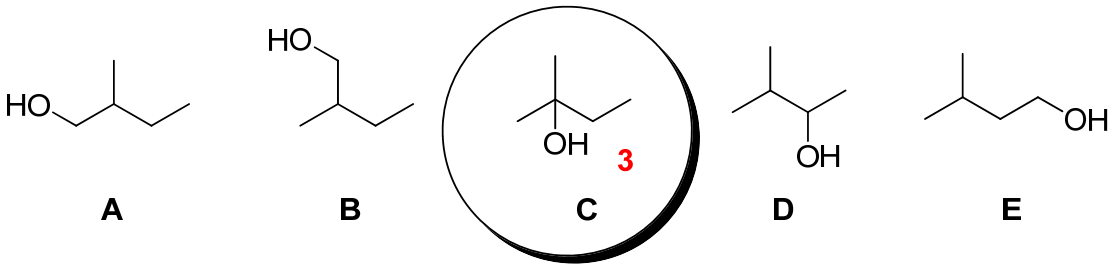


Draw the structure of the **first intermediate** in the proposed mechanism for the reaction.

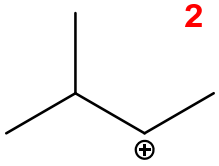


b. What is the major product of the following reaction? (**Circle the answer.**)

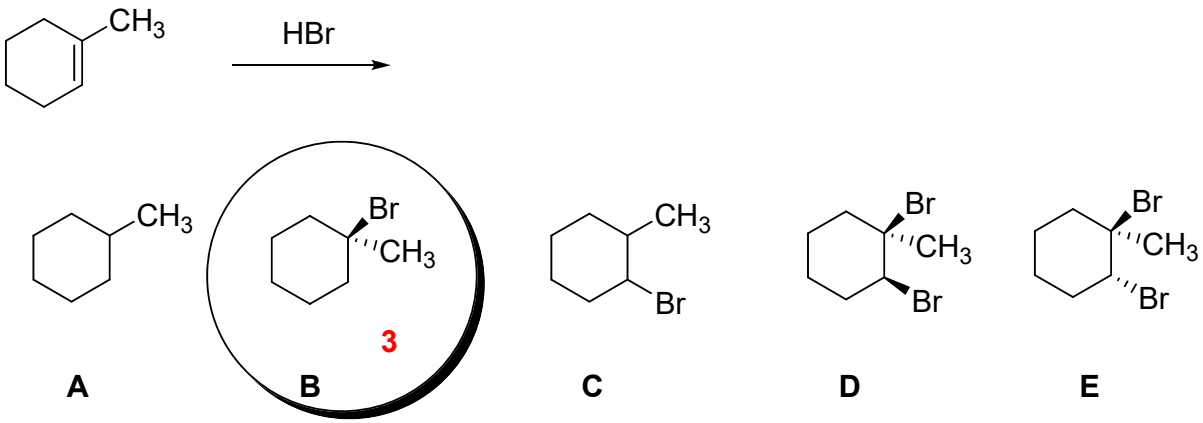




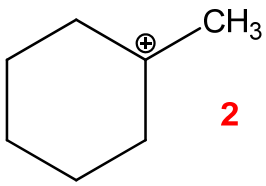
Draw the structure of the **first intermediate** in the proposed mechanism for the reaction.



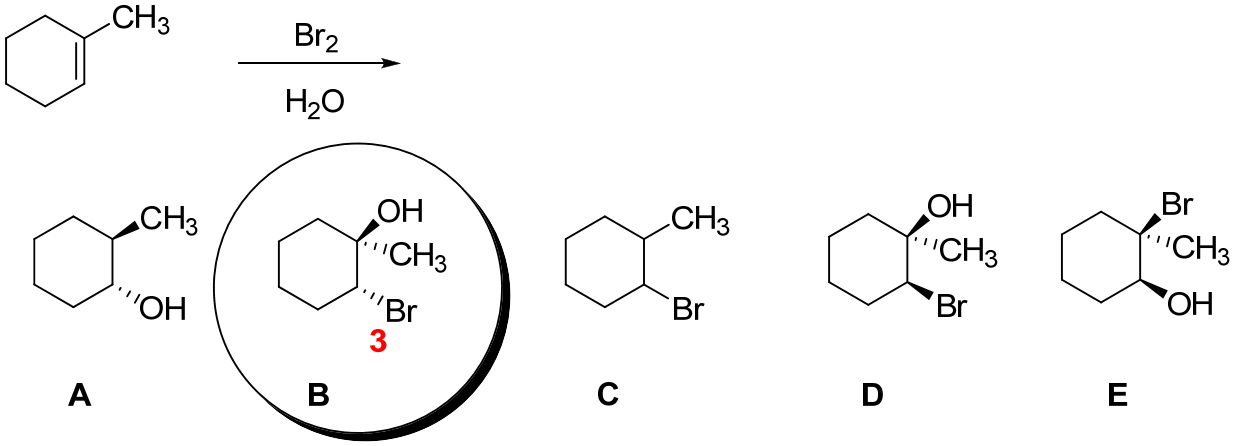
c. What is the major product of the following reaction? (**Circle the answer.**)



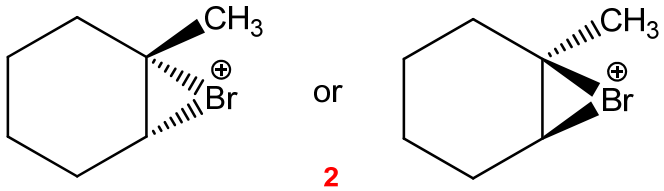
Draw the structure of the **first intermediate** in the proposed mechanism for the reaction.



d. What is the major product of the following reaction? (**Circle the answer.**)



Draw the structure of the **first intermediate** in the proposed mechanism for the reaction.



3. (**20 points**) Rank each of the three anions in order of nucleophilicity (1 = most nucleophilic, 3 = least nucleophilic). **Explain each ranking in 10 words or less.**

a. Br^- Cl^- F^-

1 **1** 3 **1**

All three anions have charge on atom from same column (7A). Nucleophilicity depends on **size**. Largest anion is most nucleophilic. **3**

b. CH_3O^- CH_3NH^- $CH_3CH_2^-$

3 **1** 1 **1**

All three anions have charge on atoms from same row (2nd). Nucleophilicity depends on **electronegativity**. Anion with charge on least electronegative atom is most nucleophilic. **3**

c. Cl^- HO^- HS^-

3 1 **2**

Cl and S are from same row (3nd). Nucleophilicity depends on **electronegativity**. S is less electronegative so S anion is more nucleophilic. 1

O and S are from same column (6A). Nucleophilicity depends on **size**. S is larger so S anion is more nucleophilic. **2**

d. $CF_3CH_2CH_2O^-$ $CF_3CH_2CH_2CH_2O^-$ $CF_3CH_2COO^-$

1 **1** 3 **1**

All three anions have charge on O. The first and third anions both have CF_3 group at same distance from O anion. The third anion has charge **delocalized by resonance** and is more stable. The first has charge **localized**. **2**

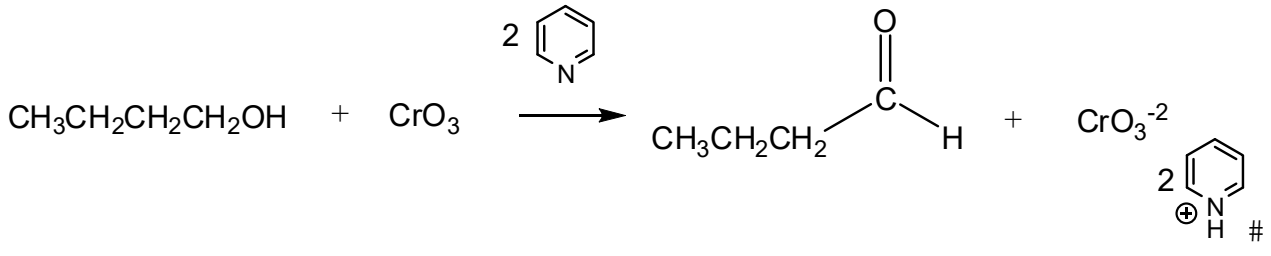
The first and second anions both have charge localized. The first anion has **CF_3 group (with δ+) closer to O anion** and is more stable. **1**

4. (**20 points**) A reaction and a proposed mechanism for the reaction are shown below.

a. Calculate the oxidation numbers for all carbons in the alcohol starting material and in the aldehyde product. Calculate the oxidation number for chromium in the starting material and in the chromium byproduct.

c. Draw the 2-electron curved arrows on each step of the mechanism.

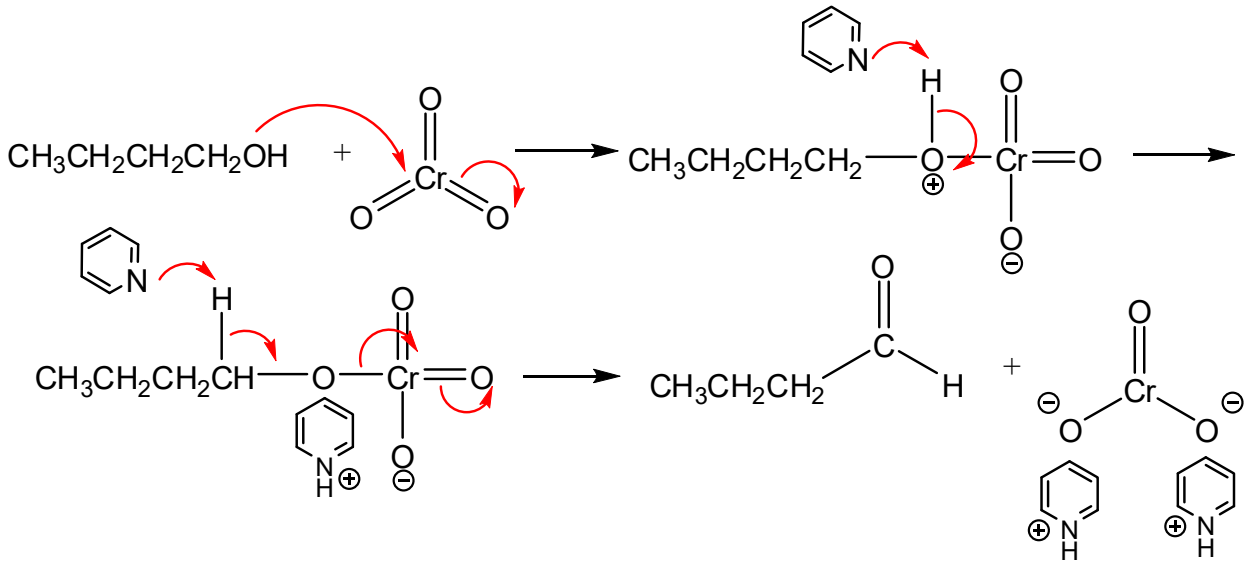
Reaction:



-3 -2 -2 -1 +6 -3 -2 -2 +1 +4

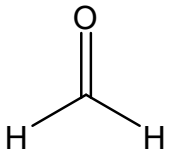
1 1 1 1

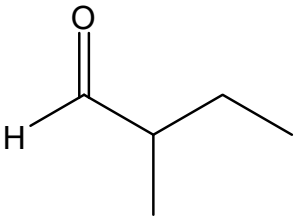
Mechanism: 8 arrows **2** points each



5. (**20 points**) Draw structures for the products expected from the treatment of each of the following compounds with ozone followed by dimethyl sulfide. Indicate **NR** if there is no reaction.

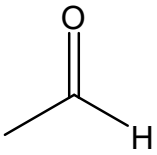
3-methyl-1-pentene

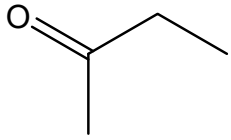




2 **2**

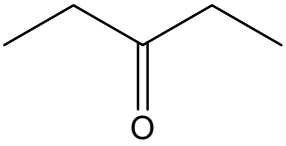
3-methyl-2-pentene

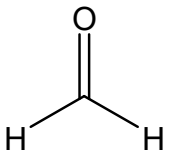




2 **2**

2-ethyl-1-butene





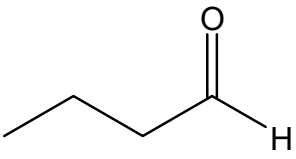
2 **2**

2-methylpentane

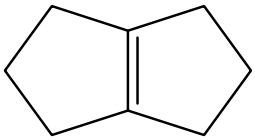
NR

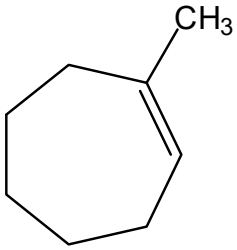
2

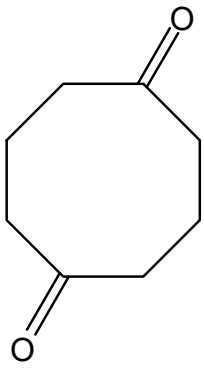
(E)-4-octene



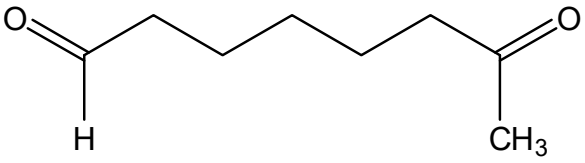
2







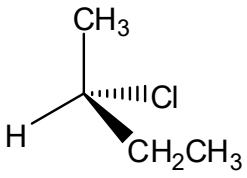
2

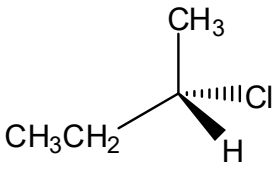


2

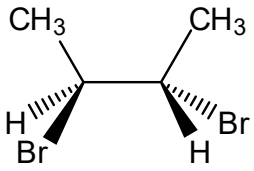
#

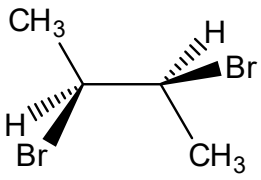
6. (**20 points**) Identify the relationship between each of the following pairs of molecules. The options are: not isomers, constitutional isomers, enantiomers, diastereomers, or same molecule. **No explanation is required.**



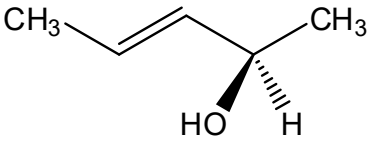


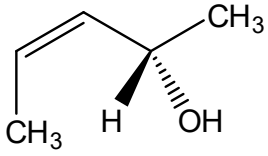
2 groups switched at C*
enantiomers **4**



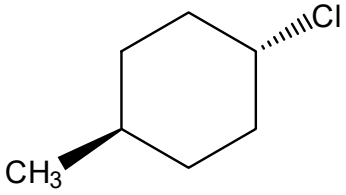


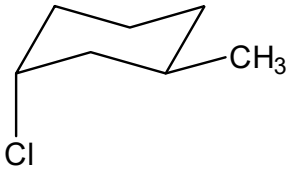
rotate R C* of R structure
to bring CH_3 up
same molecule **4**



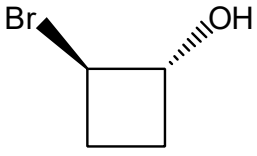


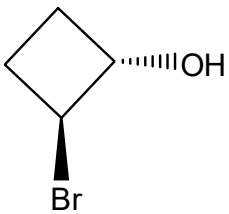
stereoisomers that are not
mirror images
diastereomers **4**





same formula but
1,4-substituted and 1,3-substituted
constitutional isomers **4**

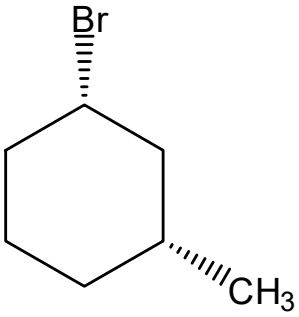




rotate right molecule to bring
two substituents to top to see
these are mirror images
enantiomers **4**

7. (**20 points**)
a. Draw planar-ring (flat-ring) structures corresponding to the IUPAC names
b. Draw the two chair conformations corresponding to each of the flat-ring structures.
c. Use the **Data Table** to calculate the 1,3-diaxial strain for each chair conformation and then indicate which chair conformation is more stable.

*(*1S,3R*)*-1-bromo-3-methylcyclohexane



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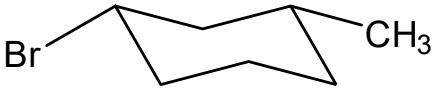
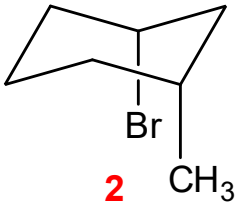


2

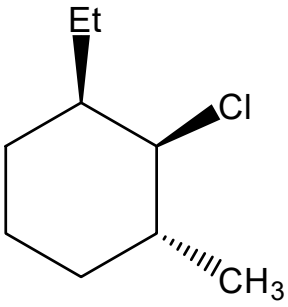


2

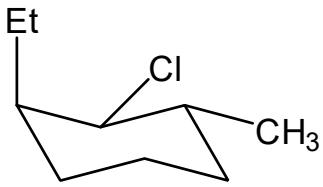
0 kcal/mol **1**
more stable **1**

4.8 kcal/mol **1**

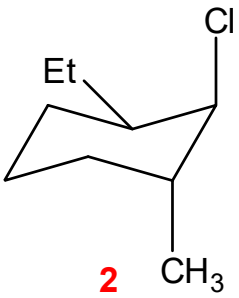
(1R,2S,3R)-2-chloro-1-ethyl-3-methylcyclohexane



3



2



2

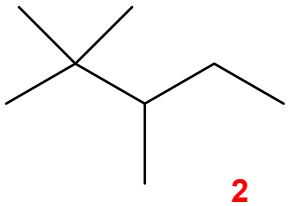
1.90 kcal/mol **1**
more stable **1**

2.3 kcal/mol **1**

Planar-ring structure **no partial credit**
If planar ring structure is not correct but chairs are created correctly from that structure **2** each
If chairs are not correct **no credit** for the calculations or stability conclusion

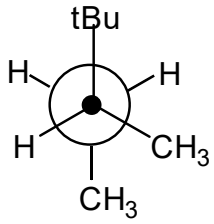
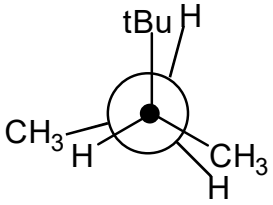
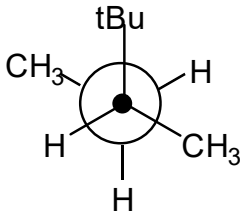
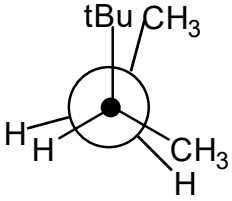
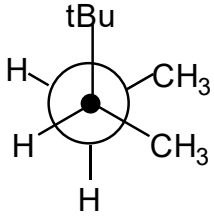
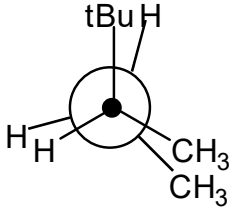
8. (**20 points**) The ***barrier to rotation*** is the difference in energy between the lowest energy conformation and the highest energy conformation. Using data in the **Tables** provided, calculate the barrier to rotation about the C3-C4 bond of 2,2,3-trimethylpentane.

Structure of 2,2,3-trimethylpentane:



2

Draw all Newman projections for the clockwise rotation about C3-C4 bond in 60° increments:

#1 **2**  2	#2 **2**  	#3 **2** 
#4 **2**  	#5 **2**  	#6 **2** 

Strain energy calculations for each Newman projection:

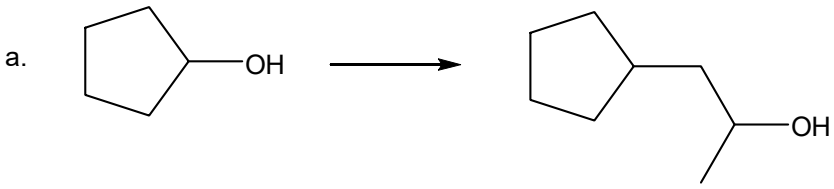
#1	#2	#3	#4	#5	#6
0.5 0.5 0.8	3.0 1.4 1.4	2.7 0.5	8.5 1.4 1.0	2.7 0.5 0.8	3.0 2.5 1.0
1.8 **2**	5.8	3.2	10.9 **2**	4.0	6.5

The barrier to rotation is:

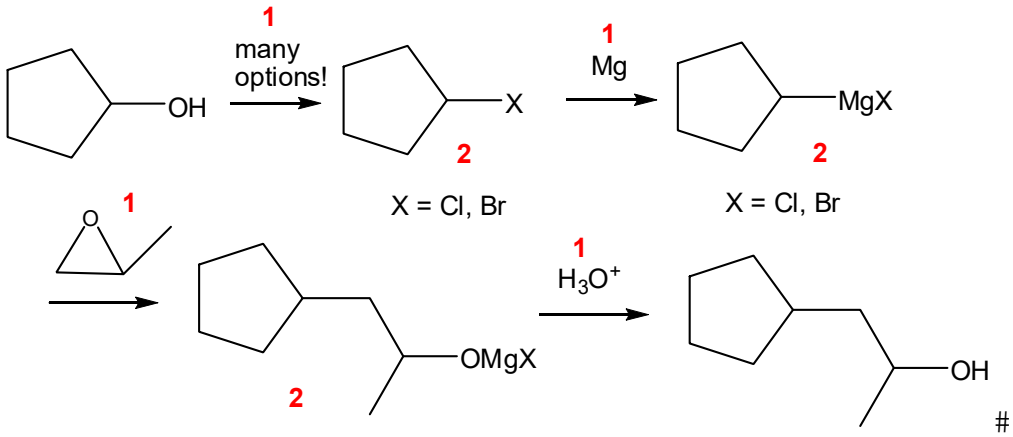
#	#	#
#	9.1	kcal/mol **2**

9. (**20 points**) Design a synthesis of each **Target Molecule** from the starting material provided. List the reagent(s) you will need for each step and draw a structure for the product of each step.

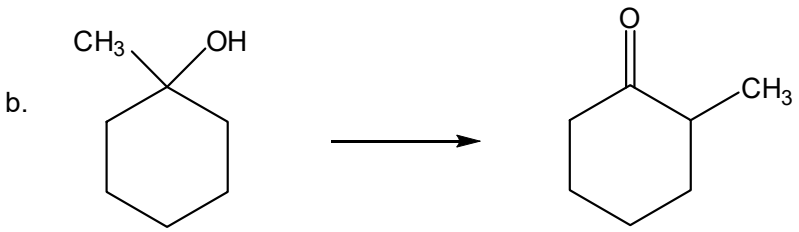
a.



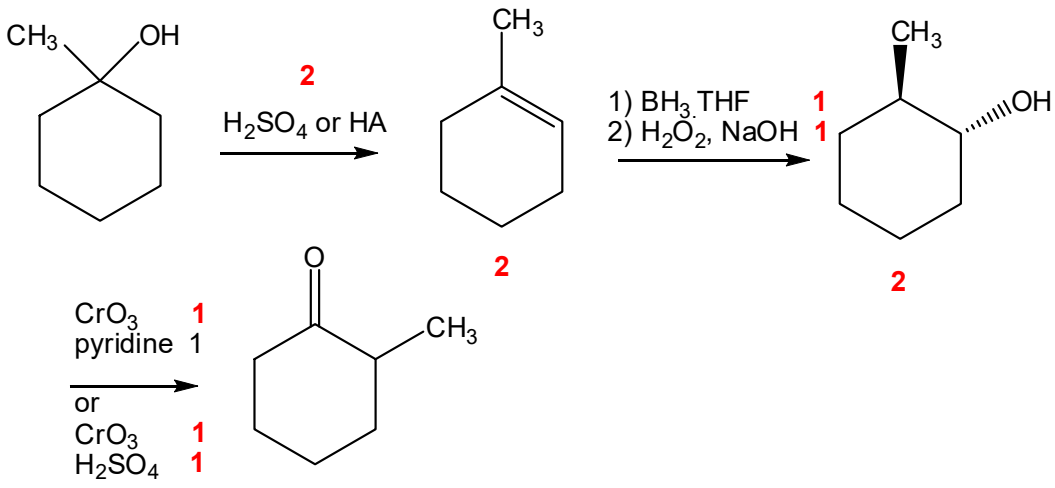
Target Molecule



b.



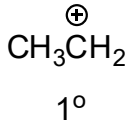
Target Molecule

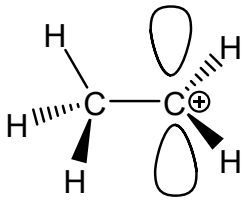


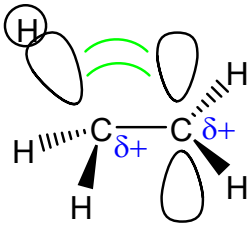
10. (**20 points**) For each orbital interaction or bond type given below, draw an orbital picture and then describe (20 words or less for each picture/use only the space provided) what the picture tells us (such as stability, bond strengths, bond lengths, bond angles, other ideas).

a. hyperconjugation **3** for drawing **2** for what it tells us

+C is sp^2 hybridized
+C and atoms directly attached to it are in the x-z plane (trigonal planar with < 120°)
+C has an empty p-orbital aligned with the y-axis (perpendicular to the x-z plane)





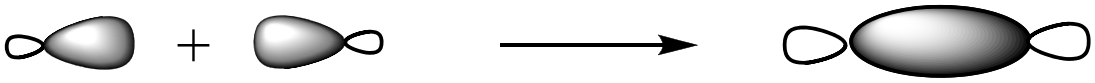


The C – C bond is rotated to align one C – H bond with the empty p-orbital.
The bond can share some electron density by side-on overlap with the empty p-orbital.
This hyperconjugation reduces the amount of + charge on the +C and gives some of the charge to the sp^3 C. We can show this using δ+ on 2 C's.

b. σ–bond (sigma bond) **3** for drawing **2** for what it tells us

The C – H σ–bonds in an alkane result from overlap of an sp^3 orbital on C with an s orbital on H. The resulting σ–bond is cylindrically symmetrical around the C – H internuclear axis.

The C – C bonds in an alkane result from overlap of two sp^3-orbitals. The angle between these two orbitals is 0° to achieve maximum overlap and the strongest possible bond. The resulting σ–bond is cylindrically symmetrical around the C – C internuclear axis.

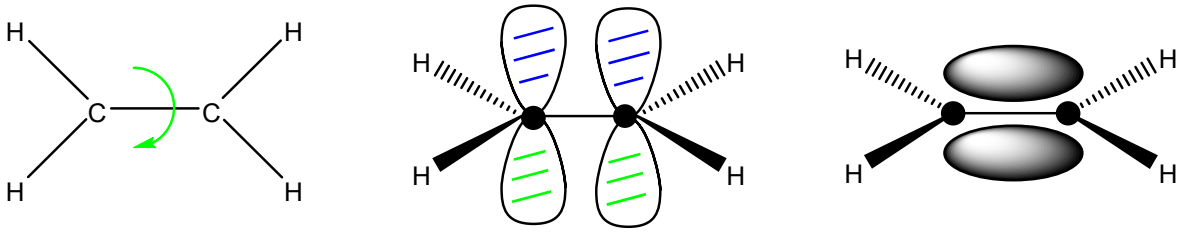


c. π-bond (pi-bond) **3** for drawing **2** for what it tells us
Recall each C has a $2p_z$ orbital containing 1 electron. These are coming out of the page at you. Rotate the molecule on the x-axis so we can see these $2p_z$ orbitals.

Side-on overlap of the 2p orbitals gives the second bond of the C – C double bond.

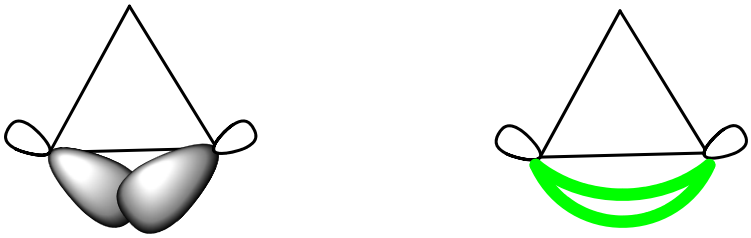
This bond has a nodal plane, a region of zero electron density. All atoms are in the nodal plane. Since there is no electron density along the C – C axis this is not a σ – bond.

KEY! Bonds formed by side-on overlap of p-orbitals are π – bonds (pi – bonds).



d. “banana bond” **3** for drawing **2** for what it tells us

In the C – C σ-bonds of cyclopropane, the overlap of the sp^3 orbitals is off-line. The sp^3-sp^3 orbital angle is estimated to be 105°, not 0°. The decreased overlap results in a weaker bond.



off-line overlap or banana bond

Interesting Fact: While the C-C bond in cyclopropane is weaker than in propane, the C-C bond length in cyclopropane (151 pm) is shorter than in propane (154 pm)!

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