CHEM 3311 **HARRINGTON**

Exam 3 7:00 – 8:30 PM November 15, 2016 in MATH 100

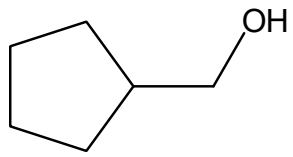
Instructions. No notes, books, laptops, phones, or calculators. Periodic Table, Electronegativity Chart, and 1,3-Diaxial Strain Table are provided.

NAME: KEY

	Points Possible	Score
1	13	
2	10	
3	21	
4	15	
5	14	
6	17	
7	10	
Exam 2 Total Raw Score	100	
Curve		
Exam 1 Curved Score		
Exam 1 Letter Grade		

NAME of Recitation TA:

1 (**13 points**) Name each of the following compounds using IUPAC substitutive nomenclature.



cyclopentylmethanol

1

$CH_3OCH_2CH_2OCH_3$

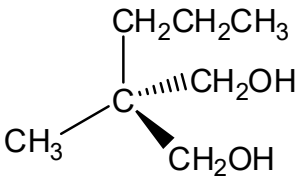
1,2-dimethoxyethane

1 1 1

$HSCH_2CH_2OH$

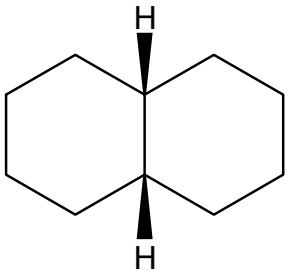
2-mercaptoethanol

1 1 1



2-methyl-2-propylpropane-1,3-diol

1 2



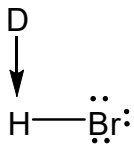
cis-bicyclo[4.4.0]decane

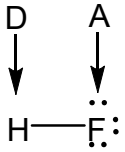
1 1 1

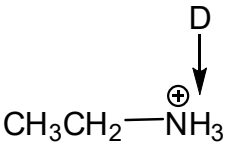
#

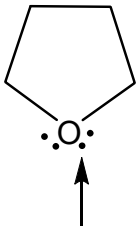
#

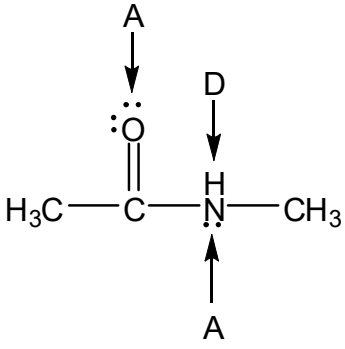
2. (**10 points**) Label each of the following molecules as a hydrogen bond acceptor, donor, or both. Label a hydrogen atom that is donated with a **D**. Label an atom that serves as the hydrogen-bond acceptor with an **A**. (Suggested Practice Problem 8.15) each correct D or A 1 (up to 10 points) each incorrect D or A -1

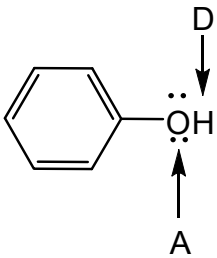


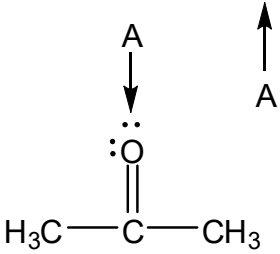












3. (**21 points**)

a. Identify each flat-ring structure as chiral or achiral. Explain in ten words or less.

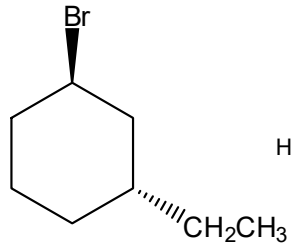
b. Draw a chair conformation corresponding to the flat-ring structure.

c. “Flip” the chair and draw a structure for the alternative chair conformation.

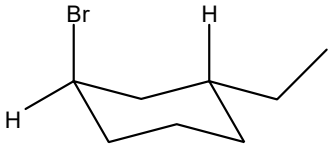
d. Determine the 1,3-diaxial strain (kcal/mol) for each chair using the data (**Table)**.

Chairs must clearly show groups are ax or eq. Chairs must be the correct enantiomer.

If all diaxial strain numbers are ½ of correct values, diaxial strain graded = 3/6.

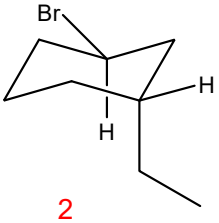


chiral 1
no plane/center of symmetry



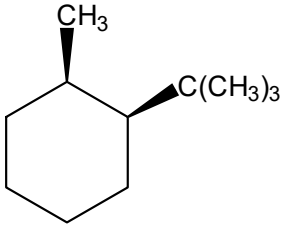
2

0.50
1

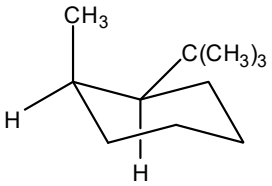


2

1.90
1

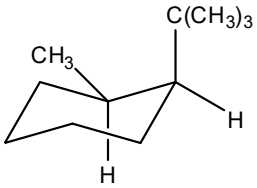


chiral 1
no plane/center of symmetry



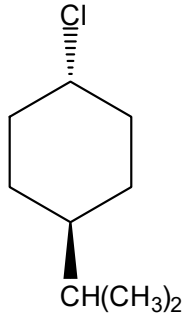
2

1.8
1

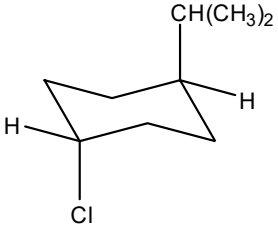


2

5.4
1

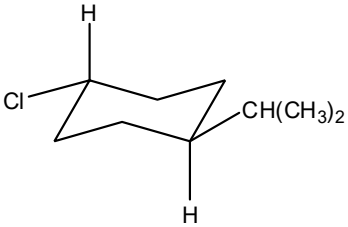


achiral 1
plane of symmetry
through C1 and C4



2

2.70
1



2

0
1

4. (**15 points**) For each of the following reactions, predict which one is faster and explain your prediction.

a. $(CH_3)_2CHCH_2Cl + N_3^- \xrightarrow[CH_3CH_2OH]{} (CH_3)_2CHCH_2N_3 + Cl^-$

$(CH_3)_2CHCH_2I + N_3^- \xrightarrow[CH_3CH_2OH]{\text{FASTER 1}} (CH_3)_2CHCH_2N_3 + I^-$

Explanation:
I- is a weaker base, a better leaving group, than Cl-
or
C-I bond is weaker than C-Cl bond 2

b. $CH_3CH_2CH_2CH_2Br + HS^- \xrightarrow{\text{FASTER 1}} CH_3CH_2CH_2CH_2SH + Br^-$

$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Br + HS^- \longrightarrow CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2SH + Br^-$

Explanation:
β-C branching raises the energy of transition state
slows the rate of the S_N2 reaction 2
just "β-branching" 1

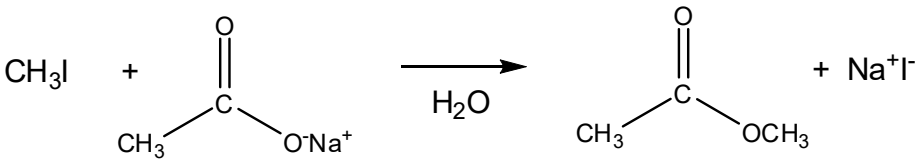
c. $(CH_3)_2CHCl + NH_3 \longrightarrow (CH_3)_2CHNH_3^+ \ Cl^-$

$CH_3CH_2CH_2Cl + NH_3 \xrightarrow{\text{FASTER 1}} CH_3CH_2CH_2NH_3^+ \ Cl^-$

Explanation:
α-C branching raises the energy of transition state
slows the rate of the S_N2 reaction
or 1^o alkyl chloride reacts faster than 2^o alkyl chloride 2

4. (continued)

d. $CH_3I + Na^+OH^- \xrightarrow[H_2O]{\text{FASTER 1}} CH_3OH + Na^+I^-$

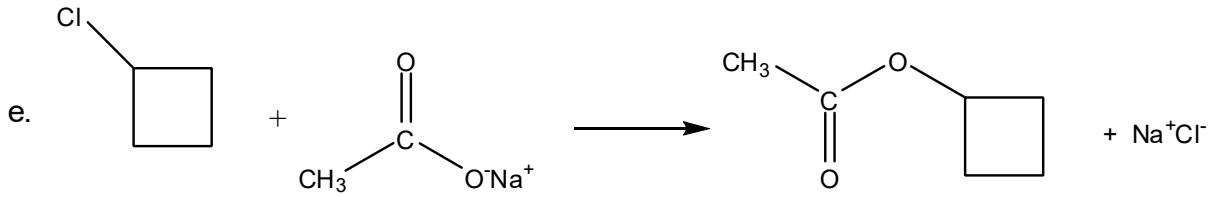


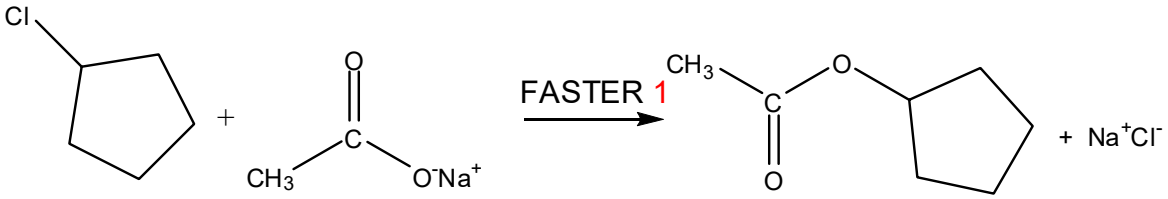
Explanation:

HO^- is a stronger base than AcO^- (AcO^- is stabilized by resonance)
HO^- is the more reactive nucleophile 2

just HO- is more reactive nucleophile 1

e.





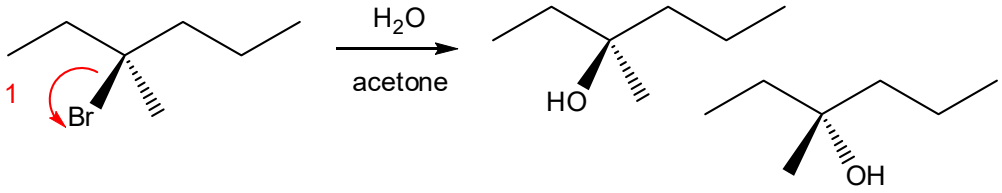
Explanation:

The α-C becomes sp^2 hybridized in the S_N2 transition state.
The transition state is higher in energy/reaction is slower
when C-αC-C angle is in a 4-membered ring (angle strain). 2

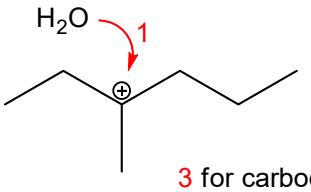
5. (**14 points**) Explain each of the following observations. Your explanation should include 1) the structures corresponding to the names in the reaction description, 2) the complete mechanism (with curved arrows to track the electron pairs) for each reaction, and 3) an explanation (in twenty words or less) for the observed results based on the mechanism.

Drawing shows carbocation intermediate not flat/planar grade for structure = 2/3

a. (S)-3-Bromo-3-methylhexane reacts with H_2O in acetone solvent to give a 1:1 mixture of the enantiomers of 3-methyl-3-hexanol.



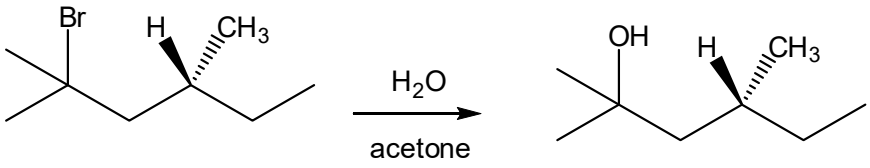
Mechanism via:



3 for carbocation structure

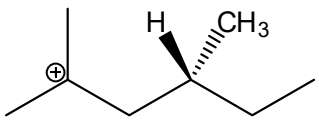
Explanation: The carbocation intermediate is flat/planar. Attack of H_2O on the carbocation is equally likely from the top or bottom to give 1:1 mixture of alcohol products. 2

b. (R)-2-Bromo-2,4-dimethylhexane reacts with H_2O in acetone solvent to give (R)-2,4-dimethyl-2-hexanol.



correct structure 1 correct structure 1

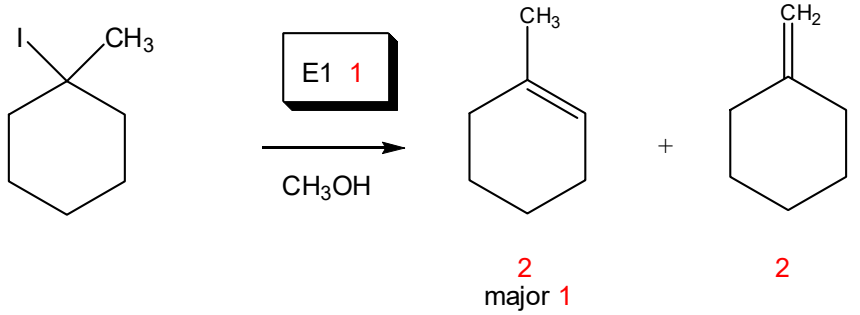
Mechanism via:

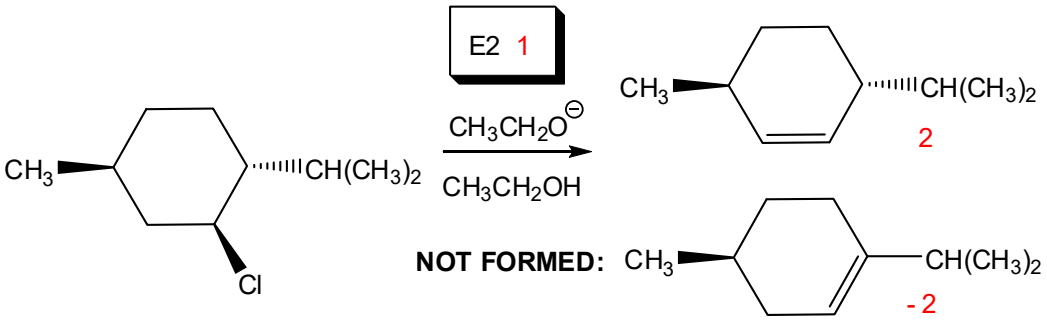


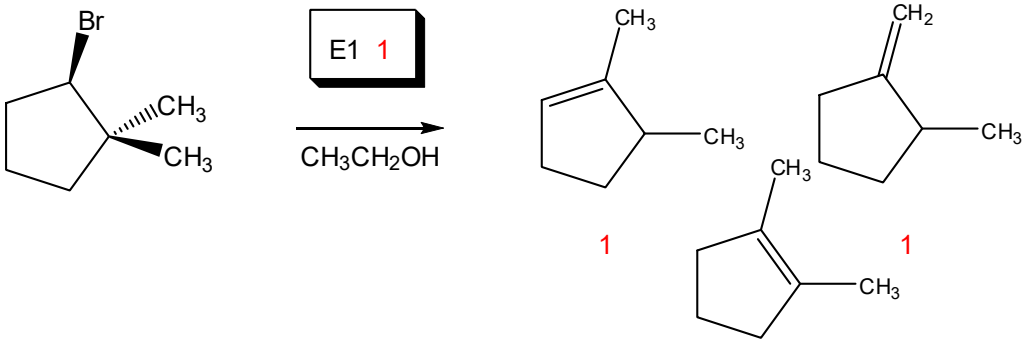
3 for carbocation structure

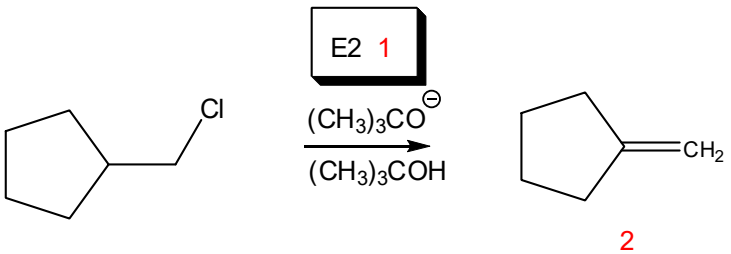
Explanation: The carbocation intermediate is flat/planar. Attack of H_2O on the carbocation is equally likely from the top or bottom to give 1:1 mixture of alcohol products. **Chirality is maintained since no bonds to C* are broken/formed in this reaction.** 2

6. (**16 points**) Assign a mechanism (E1 or E2) for each of the elimination reactions below. Draw structures for the alkenes formed in each reaction. If more than one alkene is formed in the reaction, predict which alkene will be the major component of the mixture.



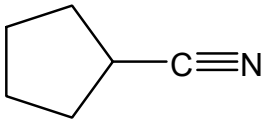




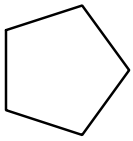


7. (**10 points**) Using reactions discussed in Chapters 7-9, design a two-step synthesis of each **Target Molecule** from the starting material provided. List the reagent(s) you will use and draw a structure for the product of each step.

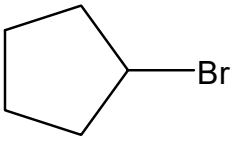
(*Hint:* Work backwards from the **Target Molecule**.)

a. cyclopentane → 

Target Molecule



hv 1
Br_2 1

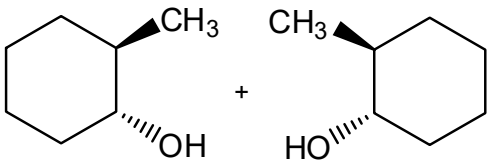


NaCN 1
or $CN^{\ominus}$

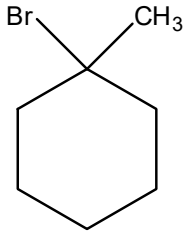
Target

2

b. 1-bromo-1-methylcyclohexane →

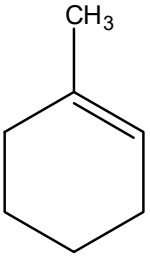


Target Molecule
1:1 mixture



E1
CH_3OH or H_2O
or
E2
CH_3ONa or $CH_3O^{\ominus}$

1



1) BH_3 THF 1
2) H_2O_2, NaOH 1

Target

2