

CH 231 Elementary Organic Chemistry I

Chapters 4-6 Topics Review

*You are responsible for all concepts covered in Chapters 1-3, including Pauling electronegativity values.

Chapter 4: Stereochemistry of Alkanes and Cycloalkanes

A. Naming Cycloalkanes

Be able to differentiate between the following:

- Constitutional isomers
- Configurational isomers/Stereoisomers
- Conformational isomers (conformers)
- Regioisomers (specific subtype of constitutional isomers)

-Use systematic nomenclature to name alkanes and cycloalkanes and be able to draw the appropriate structure given the IUPAC name.

-Differentiate between *cis*- and *trans*-isomers. Use these stereochemical descriptors in naming polysubstituted cycloalkanes.

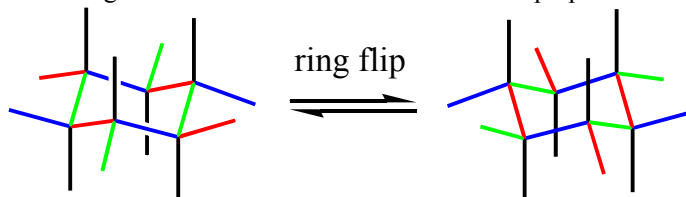
B. Conformations of Cycloalkanes

- You must be able to draw any of the low energy conformers of 3- to 6-membered rings.

- Explain how “puckered” conformations lead to a decrease in ring strain compared to planar conformers. What type(s) of strain is/are reduced with puckering?

- You must be able to draw *both* chair conformers with axial and equatorial substituents pointing in the proper directions and at the proper angles.

- Note that the bonds sharing colors within each conformer must be perpendicular!



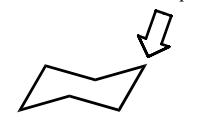

- Each ring carbon has:
 - 1 axial and 1 equatorial position
 - 1 “up”ward- and 1 “down”ward-pointing position
- Each axial position becomes an equatorial position after a ring flip, and each equatorial position becomes an axial position after a ring flip. (“axial flips to equatorial and equatorial flips to axial, but up stays up and down stays down”)

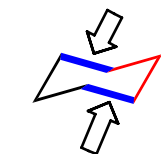
-You should know definitions for, and be able to apply, the following terms:

- Angle Strain (Baeyer Strain)
- Heat of Combustion
- Medium-sized Ring (8-11 membered)
- Bent Bonds (as in cyclopropane)
- Butterfly Conformation (cyclobutane)
- Envelope Conformation (cyclopentane)
- Half-Chair Conformation (cyclopentane)
- Chair Conformation (cyclohexane)
- Boat Conformation (cyclohexane)
- Axial Position
- Equatorial Position
- 1,3-Diaxial Interactions
- Conformational Analysis
- Transannular Strain (specific steric interactions across medium-sized rings)

You might find this approach helpful if you have trouble placing equatorial substituents at the proper angle:

How should I draw the equatorial bond from this ring carbon?

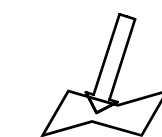
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- 1) Place the ring carbon in question at the point of a "V" (or inverted "V").
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- 2) Use the angle of the *ring bonds* extending from the ends of the "V" to draw your parallel equatorial bond.



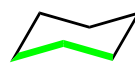
ANSWER:



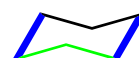
Okay, but what about the equatorial bond at this carbon?



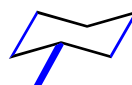
Step 1:



Step 2:



ANSWER:



-You should be able to predict and accurately draw the lowest energy conformer for monosubstituted (substituent should be in an equatorial position) and disubstituted cyclohexanes.

- With disubstituted cyclohexanes, the lowest energy conformer depends upon relative configuration, i.e. *cis*- or *trans*-, and relative sizes of substituents (see Text Table 4.2 or class notes). It's often helpful to draw both chair conformers (regular and ring-flipped) with the substituents present and then assess which conformer experiences the least 1,3-diaxial strain (so called 'A strain').

Chapter 5: Overview of Organic Reactions

A. Polar Reactions

- Be able to define *electrophile* and *nucleophile*. Give several examples of each and be able to predict the most electrophilic or nucleophilic atom or molecule within a molecule or list of molecules, respectively.
- Be able to use curved arrow (electron pushing) notation to show the flow of electrons in a reaction mechanism.

-You should know definitions for, and be able to apply, the following terms:

- Electrophile
- Nucleophile
- Radical
- Equilibrium constant
- Reaction Coordinate Diagram
- Gibbs Free Energy Change (ΔG°)
- Endergonic
- Exergonic
- Reaction Rate
- Transition State
- Reaction Intermediate
- Activation Energy (ΔG^\ddagger)
- Catalyst, Catalyzed, Catalysis
- Rate Limiting Step

B. Thermodynamics, Kinetics, and Reaction Coordinate Diagrams

-Given K_{eq} , information relating to the relative stability of reactants and products, or a reaction mechanism, you should be able to:

- draw a reasonable reaction coordinate diagram with the proper position of the transition state along the reaction coordinate (see Hammond Postulate in Chapter 6),
- state whether reactants or products are favored
- state whether the reaction is endergonic or exergonic

-Given a reaction coordinate diagram you should be able to:

- identify the number of reaction steps involved
- identify the number of intermediates involved
- state whether the reaction is endergonic, exergonic, or thermoneutral
- state whether $K_{eq} <$, $=$, or > 1
- identify the rate limiting step
- identify ΔG° and ΔG^\ddagger for a given reaction step or the overall reaction

Chapter 6: Alkenes: Structure and Reactivity

A. Degree of Unsaturation

- Be able to calculate the degrees of unsaturation (total # of rings and/or π -bonds) given a molecular formula or a skeletal structure. Be able to draw a possible structure from a molecular formula (using the degrees of unsaturation technique to assist you).

B. Alkene Nomenclature and Stability

- Be able to name mono- and polysubstituted alkenes using systematic (IUPAC) nomenclature. Be able to draw the structure corresponding to a given systematic name.

- Use the Cahn-Ingold-Prelog sequence rules to differentiate between *E*- (“Epposite) and *Z*- (“Zame Zide”) olefins.
- Differentiate between *cis*- and *trans*-disubstituted alkenes.

- Explain both alkene and carbocation stability as it relates to *hyperconjugation*.

- Explain how hybridization relates to alkene stability.

- Know the following common names of alkene substituents or molecules and be able to identify these groups:

- vinyl, allyl, ethylene, isoprene

C. Introduction to Reactions of Alkenes

- Know the reagents for and predict the products of the following reactions:

- Catalytic Hydrogenation
- Electrophilic Addition of HX to Alkenes
- Hydride or Alkyl Shifts in Carbocation Rearrangements

- Show electron pushing diagrams for the last two reactions listed above.

- You should know definitions for, and be able to apply, the following terms:

- Bonding molecular orbitals (BMOs) (be able to draw the π -BMO of ethylene)
- Antibonding molecular orbitals (ABMOs) (be able to draw the π -ABMO of ethylene)
- Node
- Hyperconjugation
- Markovnikov’s Rule
- Regioselectivity
- Carbocation Rearrangement
- Hydride Shift
- Alkyl Shift
- Hammond Postulate

The test will consist of 7-9 short answer questions (no matching, true/false, etc.) including up to ~~three~~ ⁴ questions directly from the assigned homework problems. Concepts related to the highlighted information above are most likely to be on the test. Several non-highlighted topics will also be represented.