5.12 Spring 2003
Review Session: Exam # 2

VI. Alkanes
- A. Molecular Formulas
  - 1. Degrees of Unsaturation
  - 2. Constitutional Isomers
- B. IUPAC Nomenclature
- C. Conformational Analysis
  - 1. Ethane
    - a) Newman Projections
  - 2. Propane
  - 3. Butane

VII. Cycloalkanes
- A. Ring Size and Strain
- B. Cyclopropane
- C. Cyclobutane
- D. Cyclopentane
- E. Cyclohexane
  - 1. Conformational Analysis
    - a) Drawing Chairs
    - b) Ring Flip
  - 2. Mono-Substituted Cyclohexane
    - a) Axial versus Equatorial: A-Values
  - 3. Di-Substituted Cyclohexane
    - a) Cis/Trans Isomerism
    - b) Preferred Conformers
  - 4. Bicyclic Ring Systems

VIII. Stereochemistry
- A. Stereoisomers
- B. Chirality and Stereocenters
- C. Enantiomers
  - 1. Cahn–Ingold–Prelog Convention (R/S)
  - 2. Optical Activity
  - 3. Description of Samples
- D. Diastereomers
  - 1. Cis/Trans Isomers (Geometric)
  - 2. Molecules with >1 Stereocenter

IX. Free Radical Reactions
- A. Chlorination of Methane
  - 1. Mechanism
- B. Review of Thermodynamics
- C. Review of Kinetics
- D. Reaction-Energy Diagrams
  - 1. Thermodynamic Control
  - 2. Kinetic Control
  - 3. Hammond Postulate
  - 4. Multi-Step Reactions
  - 5. Chlorination of Methane
- E. Chlorination of Propane
  - 1. Inequivalent Hydrogens (1°,2°,3°)
  - 2. Relative Reactivity
  - 3. Selectivity
- F. Bromination of Propane
  - 1. Selectivity (Hammond Postulate)
- G. Radical Stability
- H. General Selectivity of Radical Halogenations

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You need to be able to:

- Draw constitutional isomers for a given molecular formula.
- Calculate degrees of unsaturation.
- Draw structures corresponding to IUPAC names.
- Draw Newman projections.
- Determine relative energies of rotational conformers. **Know the rotational energy values on the handout!**
- Draw potential energy diagrams for bond rotations.

1. Draw all of the constitutional isomers of C_5H_{12} and name them using IUPAC nomenclature.

2. For each molecular formula, calculate the degrees of unsaturation and draw two possible constitutional isomers.

C_7H_{12} C_3H_6 C_5H_6

3. a) Approximate the barrier to rotation around the C2–C3 bond of 2,2-dimethylbutane. Draw Newman projections to illustrate your answer.

b) Draw a potential energy diagram for rotation around theC2–C3 bond of 2,2-dimethylbutane.

***The solutions for these problems can be found in the key for the first review session.**

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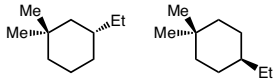
  4. Bicyclic Ring Systems

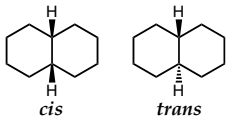
You need to be able to:
- Provide the approximate ring strains and preferred conformations of the rings discussed in class.
- Analyze ring strain in terms of torsional and angle strain.
- Draw Newman projections to compare conformations of cycloalkanes.
- Draw and flip cyclohexane chairs. **Be sure you carefully differentiate between axial and equatorial bonds.**
- Provide the details of a cyclohexane ring flip.
- Use A-values and diaxial interactions to predict the preferred conformers of substituted cyclohexanes. **Know your A-values!**
- Draw and differentiate between *cis*- and *trans*-isomers.

1. Draw the two possible chairs for each molecule, and indicate the preferred conformer.



Which molecule would you expect to have the largest conformational preference. Why?

2. Draw chair conformers for *cis*- and *trans*-decalin. Which would you expect to be more stable?



cis ***trans***

3. Using Newman projections, predict the energy difference between the two. **Hint:** Look for gauche-butane interactions in the higher energy structure.

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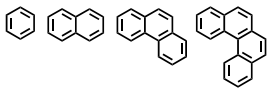
You need to be able to:
- Recognize stereoisomers: enantiomers & diastereomers.
- Draw all possible stereoisomers for a given molecule: **Remember the 2^n rule.**
- Determine whether molecules are chiral or achiral: **a) Count stereocenters; b) Look for mirror planes; c) Compare mirror images.**
- Recognize meso compounds.
- Assign R/S stereochemistry to stereocenters.
- Correlate chirality with optical activity.
- Describe ratios of enantiomers using optical activity (optically pure, racemic, etc.).

1. Draw all of the stereoisomers of 1,2- and 1,3-dimethylcyclohexane. Assign each stereocenter as R or S. How many are chiral? Achiral?

Try to draw a chiral stereoisomer of 1,4-dimethylcyclohexane. Can you do it? Why or why not?

2. Practice assigning R and S stereochemistry until you feel like your head will explode! There are ample examples in the book and lecture.



3. All of the above molecules are achiral; however, hexahelicene (below) is chiral. Why?

Hexahelicene

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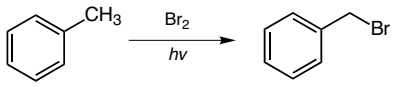
G. Radical Stability
H. General Selectivity of Radical Halogenations

You need to be able to:

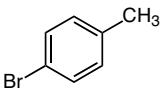
- Write a complete mechanism for a free radical chain reaction. **Use fishhook arrows!**
- Draw and completely label a reaction-energy diagram.
- Determine the rate-determining step of a multi-step reaction-energy diagram.
- Differentiate between transition states and intermediates.
- Differentiate between kinetic and thermodynamic control.
- Use the Hammond postulate to predict whether a kinetically controlled transformation will be selective.
- Use BDEs to estimate ΔH and ΔG.
- Rate the stability of radicals, and explain.
- Predict the products of radical bromination.
- Calculate the relative reactivity of inequivalent hydrogens from reaction selectivities.

1. Radical stability is strongly dependent on substitution (3° > 2° > 1° > methyl). Why? Draw pictures to illustrate.

2. Draw resonance structures to explain the selectivity of the following reaction.



Aside from resonance, why isn't the following product observed?



3. Provide a complete reaction mechanism for the bromination in number **2**. Draw a complete reaction energy diagram for the propagation steps. You can assume that a benzylic C–Br bond is approximately 68 kcal/mol.

4. Rank the stability of each of the following radicals (1 = most stable). Radicals with the same energy should be given the same number.