

Chem 164/261
Assignment & Lecture Outline 4:

**Stereochemistry, Nucleophilic Substitution and Elimination
Reactions (SN1, SN2, E1, and E2)**

Read

From TWG Solomons and CB Fryhle "Organic Chemistry" 10e Edition (2011) (8th or 9th editions OK)

- Functional Group List on pp 73-74 (pp 68-69 -9th Edition; pp 70-71 - 8th Edition) and (Periodic Table) one page back from Inside Back Cover:
- Chapter 5 – Stereochemistry: Chiral Molecules
- Chapter 6 - Ionic Reactions – Nucleophilic Substitution and Elimination Reactions
- Chapter 7 – Alkenes and Alkynes I: Properties and Synthesis – re-read

Problems

Do **Not** turn in, answers available in "Study Guide and Solutions Manual for Organic Chemistry" for Solomons.

- **Chapter 5:** 5.1 to 5.5; 5.7 to 5.19; 5.23; 5.24; 5.30; 5.33; 5.35
- **Chapter 6:** 6.1 to 6.5; 6.7 to 6.9; 6.12 to 6.14; 6.30
- **Chapter 7:** 7.1; 7.3; 7.5 to 7.9; 7.13; 7.14; 7.26; 7.29; 7.34

Lecture Outline 4

I. Comparison of 2 Structures:

Same Molecular Formula ? -> If Yes, Possibly Isomers or Identical

Same Arrangement (Sequence) of Groups ?

If No -> Structural Isomers

If Yes -> Superposable?

If Yes -> Identical Structures

If No -> Stereoisomers

Non-Superposable Mirror Images ?

If NO -> Diastereomers

If Yes -> Enantiomers

II. Chirality and Stereoisomers

A. The Concept of Chirality

1. Identification of chiral objects and molecules - definitions

achiral = not chiral

planes of symmetry within a molecule

2. Types of stereoisomers - enantiomers and diastereomers

B. Location of Stereogenic (Chiral) centers - 4 different groups on tetrahedral atom

1. Enantiomers and Diastereomers

2. Meso compounds - chiral centers with plane of symmetry within molecule

3. Molecules with more than one chiral center -

4. Recognition of chiral centers in complex molecules - cholesterol - 8 chiral centers

drawing the enantiomer of cholesterol

relationship of cholesterol and its potential 255 stereoisomers

5. Fisher Projections

C. R and S Nomenclature

1. Rules for assignment of R and S configurations
2. Treatment of multiple bonds - example - 3-bromo-1-pentene

III. Optical Rotation, Optical Purity, and Resolution of Enantiomers

A. Optical Rotation

1. Measurement, factors, and absolute rotation
2. Optical purity and enantiomeric excess
3. Physical Properties of Enantiomers and Diastereomers
4. Racemic mixtures - 50-50 mixtures of enantiomers
5. Optical Purity = enantiomeric excess

B. Separation (Resolution) of Enantiomers (e.g. Racemic mixtures)

1. Creation of diastereomers
2. Biological recognition

IV. Nucleophilic Substitution Reactions (S_N1 and S_N2)

A. General Features of Nucleophilic Substitution vs. Elimination Reactions

1. Definitions: S_N1 and S_N2
2. Mechanisms

B. S_N2 Reactions

1. Stereochemistry - Walden Inversion (inversion of configuration)
2. Substitution of Primary and Secondary Alkyl Halides
3. Synthesis of alcohols, ethers, other halides, etc.
4. Replacement of Acetylenic Hydrogen
 - a. Acidity of Alkynes
 - b. Alkylation - Substitution Reactions

C. S_N1 Reactions

1. Stereochemical Aspects (loss of stereochemistry via carbocations)
2. Substitution of Tertiary Alkyl Halides and Other Tertiary Carbons
3. Synthesis of alcohols, ethers, halides

V. Elimination Reactions - E1 & E2 Competition with Substitution Reactions (S_N1 and S_N2)

A. E1 Mechanism - Saytzeff (Zaitsev) Rule, Leaving Groups

B. E2 Mechanism - Stereochemistry

C. Competition of Elimination Reactions (E_2 and E_1 versus S_N1 and S_N2)