

ORGANIC CHEMISTRY

REACTIONS

FEATURES OF AN ORGANIC REACTION

Mechanism: Describes the overall reaction using a series of simple steps.

Stoichiometry: Calculate reactant and product masses using the balanced equation and molar masses.

Kinetics: The study of the reaction rate and mechanism.

Theoretical yield: Mass of product given by a complete reaction.

$\% \text{ yield} = 100 \times (\text{product mass}) / (\text{theoretical yield})$

Equilibrium: Reaction does not proceed to completion, instead, it reaches a balanced state of forward and reverse reactions.

Major reaction types:

- Acid
- Base
- Oxidation/Reduction
- Condensation
- Substitution (S_N1, S_N2)
- Ionic Reaction
- Elimination (E1, E2)
- Cyclization
- Hydrolysis
- Addition
- Radical reaction

Important named reactions:

- **Diels-Alder:** form cyclic alkene
- **Friedel-Crafts:** add acyl or alkyl group
- **Grignard:** add alkyl or aryl group
- **Wittig:** convert aldehyde/ketone to alkene
- **Wittig:** convert aldehyde/ketone to alkene

KINETICS AND REACTION MECHANISM



Transition state (TS): Maximum on the reaction-coordinate curve; the least stable intermediate.

Activation Energy (E_a): Energy of the TS relative to the reactant. The change in enthalpy (ΔH) is < 0 for exothermic; > 0 for endothermic.

Hammond-Leffler postulate: The TS is more like the reactant or product that is closer in energy; exothermic TS is like the product, endothermic TS is like the reactant.

Kinetic vs. thermodynamic control: ΔG and ΔH describe Thermodynamic Stability.

- If ΔG is large and negative (energetic), the product formation is likely controlled by "thermodynamics."
- Large K_{eq} corresponds to a large amount of product, relative to reactant.

• A large E_a may give rise to "kinetic" control; the energy of the TS controls the reaction, instead of the product-reactant thermodynamics.

Solvent effects: A solvent may stabilize an intermediate, decreasing E_a and increasing the rate of the reaction. Charged-complexes are stabilized by polar solvents.

ORGANIC ACID AND BASE

Acid:

- Electron-pair acceptor (Lewis acid)
- Proton donor (Bronsted-Lowry acid); example: carboxylic acid

Base:

- Electron-pair donor (Lewis base)
- Proton acceptor (Bronsted-Lowry base); example: amine

Factors enhancing acid strength (H_A):

- Weaker H-A bond
- Greater electronegativity of "A"
- Inductive effect of substituent on "A" (electron withdrawal enhances transfer)
- More "s" character in hybrid orbital (s-orbital is lower in energy than p-orbital)
- Resonance stabilized conjugate base (A⁻)

Factors enhancing base strength:

- Reverse of acid-strength guidelines
- A base is a nucleophile; Electronic effects which shift electron density to the atom with the lone-pair increase base-strength.

ALKANE



Properties:

- Hydrocarbon
- Weak intermolecular forces
- Non-cyclic: general formula C_nH_{2n+2}
- Tetrahedral C-C-C (109°)

Nomenclature:

- Add "-ane" to prefix.
- Locate substituent by position #
- Haloalkane: substitute halide for -H

Cycloalkanes (C_nH_{2n}):

- Bicyclic - two fused or bridged rings
- n = 3: **cyclopropane** (highly strained)
- n = 4: **cyclobutane** (some flexibility)
- n = 5: **cyclopentane** (slight puckering)
- n = 6: **cyclohexane**: chair - stable conformer; boat - less stable; Axial position: "perpendicular" to ring; Equatorial position: in ring "plane" (see H_a and H_e in chair diagram below)
- Cis - two substituents in up position
- Trans - one up and one down



Synthesis:

- Hydrogenate alkene or alkyne (H₂, Pt catalyst)
- Free-radical reaction of alkane
- Reduce haloalkane (Zn, H⁺)
- Friedel-Crafts alkylation

Reaction:

- Combustion: alkane + O₂ → CO₂ + H₂O
- Halogenation to haloalkane (Cl₂/Br₂, light or heat)

ALKENE >C=C<

Properties: Similar to alkane, non-polar, flammable

Nomenclature:

- Add "-ene" to prefix. Use # to denote C=C position
- **Isolated** C-C=C-C-C=C, **conjugative** -C=C-C-
- Polyunsaturated fatty acid: 2 or more C=C
- **Alkene**: adjacent C=C-C
- **Vinyl** group: H₂C=CH-
- **Methylene** group: H₂C=
- **Allyl** group: H₂C=CH-CH₂-
- **Vinyl** halide: halide replaces -H on >C=C<
- **Conjugated**: alternate C=C and C-C (resonance)
- **Alkadiene**: 2 conjugated C=C; example: butadiene; s-cis and s-trans (rotate about C-C bond)
- **Alkatene**: 3 conjugated C=C
- **Annulene**: conjugated monocyclic compound; example: [6] annulene = benzene
- **Aromatic** cyclic ions: cyclopentadiene anion, cycloheptatriene cation (6 electrons)

Isomers: no free rotation of C=C



- E/Z: prioritize groups by atomic weight (Z - higher priority groups on the same side)
- For monocyclic: cis is less stable (steric hindrance). For cyclic, cis more stable.
- **Hofmann Rule:** Form the least-substituted alkene
- **Markovnikov Addition:** H adds to C with most -H's
- **Zaitsev Elimination:** Form alkene with more substitution

Synthesis:

- Dehydrate alcohol (H⁺, heat) (elimination)
- Dehydrohalogenate haloalkane (base, heat)
- Dehalogenate vic dihalide (Zn, acetic acid)
- Hydrogenate alkyne:
 - syn, Z/cis-isomer (H₂, Pt catalyst)
 - anti, E/trans-isomer (Li, NH₃, -78°C)
- Wittig: aldehyde/ketone + phosphorous ylide

Reaction:

- Combustion (O₂)
- Hydrate to 2°/3° alcohol (H⁺, H₂O), 1° from ethene, can rearrange (Markovnikov)
- Hydrate to alcohol; hydroboration/oxidation (THF/H₂O₂/H₂O/OH⁻) (syn, anti-Markovnikov)
- Oxymercuration-demercuration to alcohol
- Hydrohalogenation (HX) (Markovnikov)
- Halogenation (Br₂/Cl₂), vic dihaloalkane (N₂/CCl₄, anti)
- Halohydrin (N₂, H₂O; anti-addition)
- Hydroxylate to form a 1,2-diol (KMnO₄, cold OH⁻; syn addition)
- Oxidize to carboxylic acid (KMnO₄, hot OH⁻)
- Ozonolysis to ketone (O₃; Zn, H₂O)
- Hydrogenate to alkane (Pt, H₂; syn-addition)
- Free radical polymerization
- Alkadiene Reaction:
 - allylic halogenation (Cl₂, heat)
 - Diels-Alder: cycloalkene from diene + alkene/alkyne

Organic Reactions Study Guide

Susan McMurry



Organic Reactions Study Guide:

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Solutions Manual and Study Guide to Accompany Introduction to Organic Chemistry, 4th Ed Paul A. Bartlett, Judith G. Koch, 1992 Study Guide and Solutions Manual to Accompany Fundamentals of Organic Chemistry McMurry, Susan McMurry, 1990 *Study Guide, Answer Book to Accompany Organic Chemistry* Alan S. Wingrove, Robert L. Caret, 1981 Fundamentals of Organic Chemistry, Textbook, Study Guide and Solutions Manual T. W. Graham Solomons, 1996-08-15 A realistic approach to the study of mechanisms The book addresses real functional group chemistry with an emphasis on the biological environmental and medical applications of organic chemistry **Study Guide and Solutions Manual for Fundamentals of Organic Chemistry** Susan McMurry, 1994 Following a brief review of structure and bonding organic molecules and functional groups are presented as early as possible The text is organized primarily by functional group beginning with simple alkanes and moving toward more complex compounds Emphasis is placed on the fundamental mechanistic similarities of organic reactions McMurry's thorough revision continues to present the solid content necessary for this course without sacrifice of important subjects and pedagogical tools Text and reaction summaries full problem sets and outstanding artwork are just some of the features in the Third Edition usually found in a full year book McMurry's clear well written explanations remain a highlight of the book

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Table of Contents **Organic Reactions Study Guide**

1. Understanding the eBook Organic Reactions Study Guide
 - The Rise of Digital Reading Organic Reactions Study Guide
 - Advantages of eBooks Over Traditional Books
2. Identifying Organic Reactions Study Guide
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Organic Reactions Study Guide
 - User-Friendly Interface
4. Exploring eBook Recommendations from Organic Reactions Study Guide
 - Personalized Recommendations
 - Organic Reactions Study Guide User Reviews and Ratings
 - Organic Reactions Study Guide and Bestseller Lists

5. Accessing Organic Reactions Study Guide Free and Paid eBooks
 - Organic Reactions Study Guide Public Domain eBooks
 - Organic Reactions Study Guide eBook Subscription Services
 - Organic Reactions Study Guide Budget-Friendly Options
6. Navigating Organic Reactions Study Guide eBook Formats
 - ePub, PDF, MOBI, and More
 - Organic Reactions Study Guide Compatibility with Devices
 - Organic Reactions Study Guide Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Organic Reactions Study Guide
 - Highlighting and Note-Taking Organic Reactions Study Guide
 - Interactive Elements Organic Reactions Study Guide
8. Staying Engaged with Organic Reactions Study Guide
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Organic Reactions Study Guide
9. Balancing eBooks and Physical Books Organic Reactions Study Guide
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Organic Reactions Study Guide
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
11. Cultivating a Reading Routine Organic Reactions Study Guide
 - Setting Reading Goals Organic Reactions Study Guide
 - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Organic Reactions Study Guide
 - Fact-Checking eBook Content of Organic Reactions Study Guide
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning

- Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
- Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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