

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)
- **Alkatriene**: 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)
- Halogenate (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⁻)
- Ozonolyse 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

Seyhan N. Ege



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A Self-study Guide to the Principles of Organic Chemistry Jiben Roy, 2013 A Self Study Guide to the Principles of Organic Chemistry Key Concepts Reaction Mechanisms and Practice Questions for the Beginner will help students new to organic chemistry grasp the key concepts of the subject quickly and easily as well as build a strong foundation for future study Starting with the definition of atom the author explains molecules electronic configuration bonding hydrocarbons polar reaction mechanisms stereochemistry reaction varieties organic spectroscopy aromaticity and aromatic reactions biomolecules organic polymers and a synthetic approach to organic compounds The over one hundred diagrams and charts contained in this volume will help students visualize the structures and bonds as they read the text and make the logic of organic chemistry clear and easily understood Each chapter ends with a list of frequently asked questions and answers followed by additional practice problems Answers are included in the Appendix

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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

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- 7. Enhancing Your Reading Experience
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 - 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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