

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 alkenes
- **Friedel-Crafts:** add acyl or alkyl group
- **Grignard:** add alkyl or aryl group
- **Wittig-Kricheldorf, Clemmensen:** reduce ketone to alkane
- **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; endothermic TS is like the product, exothermic TS is like the reactant.

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

- If ΔG is large and negative (exergonic), 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 (Brønsted-Lowry acid; example: carboxylic acid)

Base:

- Electron-pair donor (Lewis base)
- Proton acceptor (Brønsted-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 on 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

Reactions:

- 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/B₂H₆/H₂O₂/OH⁻) (syn, anti-Markovnikov)
- Oxymorcurate-demercurate to alcohol
- Hydrohalogenate (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

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Terry C. Jones



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Table of Contents Essential Organic Chemistry 1st Study Guide

1. Understanding the eBook Essential Organic Chemistry 1st Study Guide
 - The Rise of Digital Reading Essential Organic Chemistry 1st Study Guide
 - Advantages of eBooks Over Traditional Books
2. Identifying Essential Organic Chemistry 1st 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 Essential Organic Chemistry 1st Study Guide
 - User-Friendly Interface
4. Exploring eBook Recommendations from Essential Organic Chemistry 1st Study Guide
 - Personalized Recommendations
 - Essential Organic Chemistry 1st Study Guide User Reviews and Ratings
 - Essential Organic Chemistry 1st Study Guide and Bestseller Lists
5. Accessing Essential Organic Chemistry 1st Study Guide Free and Paid eBooks
 - Essential Organic Chemistry 1st Study Guide Public Domain eBooks
 - Essential Organic Chemistry 1st Study Guide eBook Subscription Services
 - Essential Organic Chemistry 1st Study Guide Budget-Friendly Options
6. Navigating Essential Organic Chemistry 1st Study Guide eBook Formats

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 - Essential Organic Chemistry 1st Study Guide Compatibility with Devices
 - Essential Organic Chemistry 1st Study Guide Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Essential Organic Chemistry 1st Study Guide
 - Highlighting and Note-Taking Essential Organic Chemistry 1st Study Guide
 - Interactive Elements Essential Organic Chemistry 1st Study Guide
 8. Staying Engaged with Essential Organic Chemistry 1st Study Guide
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Essential Organic Chemistry 1st Study Guide
 9. Balancing eBooks and Physical Books Essential Organic Chemistry 1st Study Guide
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Essential Organic Chemistry 1st Study Guide
 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
 11. Cultivating a Reading Routine Essential Organic Chemistry 1st Study Guide
 - Setting Reading Goals Essential Organic Chemistry 1st Study Guide
 - Carving Out Dedicated Reading Time
 12. Sourcing Reliable Information of Essential Organic Chemistry 1st Study Guide
 - Fact-Checking eBook Content of Essential Organic Chemistry 1st 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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