

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:** 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; 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

Essential Organic Chemistry 1st Study Guide

Singh



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Study guide and solutions manual to Essential organic chemistry (2nd edition). Paula Yurkanis Bruice, 2010

Conceptual Problems In Organic Chemistry (Volume I) Singh, 2009-09 *Organic Chemistry, 5e Student Study Guide and Solutions Manual* David R. Klein, Laurie S. Starkey, 2025-03-18 Success in organic chemistry requires mastery in two core aspects fundamental concepts and the skills needed to apply those concepts and solve problems With Organic Chemistry Student Study Guide and Solutions Manual 5th Edition students can learn to become proficient at approaching new situations methodically based on a repertoire of skills These skills are vital for successful problem solving in organic chemistry

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Organic Chemistry Reactions: A Study

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Organic Chemistry as a Second Language David R. Klein, 2012 From the publisher Readers continue to turn to Klein because it enables them to better understand fundamental principles solve problems and focus on what they need to know to succeed This edition explores the major principles in the field and explains why they are relevant It is written in a way that clearly shows the patterns in organic chemistry so that readers can gain a deeper conceptual understanding of the material Topics are

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Laboratory Manual of Organic Chemistry Harry Linn Fisher,1920 *Organic Chemistry, Part 1 of 3* Richard Daley,2005-07-26 This textbook is where you the student have an introduction to organic chemistry Regular time spent in learning these concepts will make your work here both easier and more fun

Invitation to Organic Chemistry Alyn William Johnson,1999 Colorful graphics and 19 chapters featuring such learning aids as chemistry at work and conceptual problems characterize this large text on a large subject Cited by the American Association for the Advancement of Science for his pioneering work in the chemistry of ylides Johnson who spent most of his career at the U of North Dakota explores the smorgasbord of subject matter that is organic chemistry and new developments in the field Appends a summary of nomenclature spectra group assignments and values of selected important compounds The index is combined with a glossary Annotation copyrighted by Book News Inc Portland OR

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