

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⁻)
- 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

Seyhan N. Ege



Organic Reactions Study Guide:

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Organic Chemistry, 12e Binder Ready Version Study Guide & Student Solutions Manual T. W. Graham Solomons, Craig B. Fryhle, Scott A. Snyder, 2016-04-11 This is the Student Study Guide Solutions Manual to accompany Organic Chemistry 12th Edition The 12th edition of Organic Chemistry continues Solomons Fryhle Snyder's tradition of excellence in teaching and preparing students for success in the organic classroom and beyond A central theme of the authors approach to organic chemistry is to emphasize the relationship between structure and reactivity To accomplish this the content is organized in a way that combines the most useful features of a functional group approach with one largely based on reaction mechanisms The authors philosophy is to emphasize mechanisms and their common aspects as often as possible and at the same time use the unifying features of functional groups as the basis for most chapters The structural aspects of the authors approach show students what organic chemistry is Mechanistic aspects of their approach show students how it works And wherever an opportunity arises the authors show students what it does in living systems and the physical world around us

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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

Organic Chemistry Reactions Speedy

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Organic Chemistry Study Guide Robert J. Ouellette,J. David Rawn,2014-11-04 Organic Chemistry Study Guide Key Concepts Problems and Solutions features hundreds of problems from the companion book Organic Chemistry and includes solutions for every problem Key concept summaries reinforce critical material from the primary book and enhance mastery of this complex subject Organic chemistry is a constantly evolving field that has great relevance for all scientists not just chemists For chemical engineers understanding the properties of organic molecules and how reactions occur is critically important to understanding the processes in an industrial plant For biologists and health professionals it is essential because nearly all of biochemistry springs from organic chemistry Additionally all scientists can benefit from improved critical thinking and problem solving skills that are developed from the study of organic chemistry Organic chemistry like any skill is best learned by doing It is difficult to learn by rote memorization and true understanding comes only from concentrated reading and working as many problems as possible In fact problem sets are the best way to ensure that concepts are not only well understood but can also be applied to real world problems in the work place Helps readers learn to categorize analyze and solve organic chemistry problems at all levels of difficulty Hundreds of fully worked practice problems all with solutions Key concept summaries for every chapter reinforces core content from the companion book **Study Guide and Solutions Manual for McMurry's Organic Chemistry, Fifth Edition** Susan McMurry,2000 Provides answers and explanations to all in text and end of chapter exercises Also includes summaries of name reactions functional group synthesis and reactions lists of reagents and abbreviations and articles on topics ranging from infrared absorption frequencies to the Nobel Price winners in Chemistry This edition now includes all new artwork expanded in text problems summary quizzes approximately every three chapters more detailed explanations in solutions and chapter outlines Organic Chemistry, Study Guide T. W.

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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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