

# 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<sub>N</sub>1, S<sub>N</sub>2)
- 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
- **Wolff-Kishner, Clemmensen:** reduce ketone to alkane

### KINETICS AND REACTION MECHANISM



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

**Activation Energy (E<sub>a</sub>):** 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<sub>eq</sub> corresponds to a large amount of product, relative to reactant.

• A large E<sub>a</sub> 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<sub>a</sub> 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<sub>A</sub>):**

- 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<sup>-</sup>)

**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<sub>n</sub>H<sub>2n+2</sub>
- Tetrahedral C-C-C (109°)

**Nomenclature:**

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

**Cycloalkanes (C<sub>n</sub>H<sub>2n</sub>):**

- 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<sub>a</sub> and H<sub>e</sub> in chair diagram below)
- Cis - two substituents in up position
- Trans - one up and one down



**Synthesis:**

- Hydrogenate alkene or alkyne (H<sub>2</sub>, Pt catalyst)
- Free-radical reaction of alkane
- Reduce haloalkane (Zn, H<sup>+</sup>)
- Friedel-Crafts alkylation

**Reaction:**

- Combustion: alkane + O<sub>2</sub> → CO<sub>2</sub> + H<sub>2</sub>O
- Halogenation to haloalkane (Cl<sub>2</sub>/Br<sub>2</sub>, 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**: H<sub>2</sub>C=CH-
- **Methylene group**: H<sub>2</sub>C=
- **Allyl group**: H<sub>2</sub>C=CH-CH<sub>2</sub>-
- **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<sup>+</sup>, heat) (elimination)
- Dehydrohalogenate haloalkane (base, heat)
- Dehalogenate vic dihalide (Zn, acetic acid)
- Hydrogenate alkyne:
  - syn, Z/cis-isomer (H<sub>2</sub>, Pt catalyst)
  - anti, E/trans-isomer (Li, NH<sub>3</sub>, -78°C)
- Wittig: aldehyde/ketone + phosphorous ylide

**Reaction:**

- Combustion (O<sub>2</sub>)
- Hydrate to 2°/3° alcohol (H<sup>+</sup>, H<sub>2</sub>O), 1° from ethene, can rearrange (Markovnikov)
- Hydrate to alcohol; hydroboration/oxidation (THF/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O/OH<sup>-</sup>) (syn, anti-Markovnikov)
- Oxymercuration-demercuration to alcohol
- Hydrohalogenate (HX) (Markovnikov)
- Halogenate (Br<sub>2</sub>/Cl<sub>2</sub>), vic dihaloalkane (N<sub>2</sub>/CCl<sub>4</sub>, anti)
- Halohydrin (N<sub>2</sub>, H<sub>2</sub>O; anti-addition)
- Hydroxylate to form a 1,2-diol (KMnO<sub>4</sub>, cold OH<sup>-</sup>; syn addition)
- Oxidize to carboxylic acid (KMnO<sub>4</sub>, hot OH<sup>-</sup>)
- Ozonolyse to ketone (O<sub>3</sub>; Zn, H<sub>2</sub>O)
- Hydrogenate to alkane (Pt, H<sub>2</sub>; syn-addition)
- Free radical polymerization
- Alkadiene Reaction:
  - allylic halogenation (Cl<sub>2</sub>, heat)
- Diels-Alder: cycloalkene from diene + alkene/alkyne

# Organic Reactions Study Guide

**William Henry Brown**



## Organic Reactions Study Guide:

*Organic Chemistry, 13e Student Study Guide and Solutions Manual* T. W. Graham Solomons, Craig B. Fryhle, Scott A. Snyder, 2022-05-03 Organic Chemistry Student Study Guide and Solutions Manual 13th Edition offers the full solutions for select exercises from the text [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, 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 **Organic Chemistry Reactions: A Study Guide** Cybellium, 2024-10-26 Designed for professionals students and enthusiasts alike our comprehensive books empower you to stay ahead in a rapidly evolving digital world Expert Insights Our books provide deep actionable insights that bridge the gap between theory and practical application Up to Date Content Stay current with the latest advancements trends and best practices in IT AI Cybersecurity Business Economics and Science Each guide is regularly updated to reflect the newest developments and challenges Comprehensive Coverage Whether you re a beginner or an advanced learner Cybellium books cover a wide range of topics from foundational principles to specialized knowledge tailored to your level of expertise Become part of a global network of learners and professionals who trust Cybellium to guide their educational journey [www cybellium com](http://www.cybellium.com) *Organic Chemistry Reactions* Speedy Publishing, 2014-09-03 Students of

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