

# 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.

**%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 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<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; 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<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 (Brønsted-Lowry acid; example: carboxylic acid)

**Base:**

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

**Reactions:**

- 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/B<sub>2</sub>H<sub>6</sub>/H<sub>2</sub>O<sub>2</sub>/OH<sup>-</sup>) (syn, anti-Markovnikov)
- Oxymorcurate-demercurate 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>)
- Ozonolysis 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

# Essential Organic Chemistry 1st Study Guide

**Michael Rajnik**



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