

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.

$(\text{Theoretical yield} \times \text{product mass}) / (\text{Theoretical yield})$

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 (SN1, SN2)
- Radical reaction
- Ionic Reaction

Important named reactions:

- Diels-Alder: form cyclic alkene
- Friedel-Crafts: add acyl or alkyl group
- Grignard: add alkyl or aryl group
- Wolff-Kishner: Chromatography: reduce 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-Lefèvre 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." Larger ΔG 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: water

Factors enhancing acid strength (HAc):

- Weaker H-A bond
- Greater electronegativity of "A"
- Reductive effect of substituents 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 increases bond-strength.

ALKANE

Properties:

- Hydrocarbons
- Weak intermolecular forces
- Non-cyclic: general formula C_nH_{2n+2}
- Tetrahedral C-C-C (109°)

Nomenclature:

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

Cycloalkanes (C_nH_{2n})

- bicyclic - two fused or bridged rings
- $n = 3$: cyclopropane (slightly strained)
- $n = 4$: cyclobutane (some flexibility)
- $n = 5$: cyclopentane (slight puckering)
- $n = 6$: cyclohexane: chair - stable conformation; boat - less stable; axial position: "perpendicular" to ring; equatorial position: in ring ("plane") (see H₁ and H₂ in chair diagram below)
- Cis - two substituents in up position
- Trans - over up and over down



Synthesis:

- Hydrogenate alkene (H₂, heat) (elimination)
- Dehydrohalogenate haloalkane (base, heat)
- Dehalogenate via dithiobane (Zn, acetic acid)
- Hydrogenate alkyne

 - syn, Zn-catalyst (H₂, P-2 catalyst)
 - anti, Et₃Si-catalyst (Li, NH₃, -78°C)

- Witting: alkylidenebenzene = phosphorus ylide

Reactions:

- Combustion (O_2)
- Hydrate to 2°/3° alcohol (H₂, H₂O, 1° from ethene, gas exchange (Markovnikov))
- Hydrate to alcohol: by deborane-addition (LiBH₄, CH_3COCl) (anti-Markovnikov)
- Oxymercuration-demercuration to alcohol
- Hydroboration (BH₃) via dithiobane (N_2CCl_4 , anti)
- Halogenation (Cl_2 , H_2O , anti-addition)
- Hydroboration to form a 1,2-diol (KMnO₄, cold CH_3OH , syn addition)
- Oxidize to carboxylic acid (KMnO₄, hot CH_3OH)
- Oxidize to ketone (O_2 , Zn, H_2O)
- Hydrogenate to alkane (Pd, H₂, syn-addition)
- Free-radical polymerization
- Alkene Reactions

 - allylic Substitution (Cl_2 , heat)
 - Dieckmann condensation: thione + alkene = alkene-alkyne

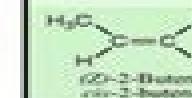
ALKENE $>C=C<$

Properties: Similar to alkane, non-polar, flammable

Nomenclature:

- Add "-ene" to prefix. Use # to denote C=C position
- Isolated C-C-C-C-C, cumulative -C=C-C-
- Polyunsaturated fatty acid: 2 or more C=C
- Alkene: adjacent C=C-C
- Vinyl group: $CH_2=CH-$
- Methylene group: CH_2-
- Vinyl halide: halide replaces -H on >C=C<
- Conjugated: alternate C=C and C=C (resonance)
- Alkadiene: 2 conjugated C=C, example butadiene: π -ex and π -trans (rotate about C=C bond)
- Alkatriene: 3 conjugated C=C
- Aromatic: conjugated monocyclic compound, example: [6] annulene = benzene
- Aromatic cyclic ions: cyclopentadiene anion, cycloheptatriene cation (6 electrons)

Isomers: no shear rotation of C=C



- EOC: penultimate groups for atomic weight (Z = higher priority groups on the same side)
- For monocyclic: cis is less stable (trans: hindrance)
- Hoffmann Rule: Form the least-substituted alkene
- Markovnikov: Addition: H adds to C with most-H's
- Zaitsev: Elimination: Form alkene with more substitution

Synthesis:

- Dehydro-alcohol (H₂, heat) (elimination)
- Dehydrohalogenate haloalkane (base, heat)
- Dehalogenate via dithiobane (Zn, acetic acid)
- Hydrogenate alkyne

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Organic Reactions Study Guide

William Henry Brown

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Solutions Manual and Study Guide to Accompany Introduction to Organic Chemistry, 4th Ed Paul A. Bartlett, Judith G. Koch, 1992 Study Guide and Solutions Manual to Accompany Fundamentals of Organic Chemistry McMurry, Susan McMurry, 1990 Study Guide, Answer Book to Accompany Organic Chemistry Alan S. Wingrove, Robert L. Caret, 1981 Fundamentals of Organic Chemistry, Textbook, Study Guide and Solutions Manual T. W. Graham Solomons, 1996-08-15 A realistic approach to the study of mechanisms The book addresses real functional group chemistry with an emphasis on the biological environmental and medical applications of organic chemistry **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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