

ORGANIC CHEMISTRY

REACTIONS

FEATURES OF AN ORGANIC REACTION

Mechanism: Describes the overall reaction using a series of simple steps.

Stoichiometry: Calculate reactants 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: $\frac{\text{actual}}{\text{theoretical}}$ mass (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)
- Ionic Reaction
- Elimination (E1, E2)
- Cationic
- Hydrolysis
- Addition
- Radical reaction

Important named reactions:

- **Halo-Alkane:** from alkyl halide
- **Free-radical:** alkyl or aryl group
- **Grignard:** alkyl or aryl group
- **Witt:** ketone/aldehyde + phosphorus ylide 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 reactants. The change in enthalpy (ΔH) is $-E_a$ for exothermic, $+E_a$ for endothermic.

Hammett-Laurer 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: (a) and (b) describe Thermodynamic stability.

• If (a) is large and negative (exergonic), the product formation is likely controlled by "thermodynamic". 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. Charge-complexes are stabilized by polar solvents.

ORGANIC ACID AND BASE

Acid:

- Electrophile: accepts δ^- ions acids
- Proton donor (Brønsted-Lowry acid)
- example: carboxylic acid

Base:

- Electrophile: donates (Lewis base)
- Proton acceptor (Brønsted-Lowry base)
- example: amine

Factors enhancing acid strength (HA):

- Medium H-A bond
- Greater electronegativity of "A"
- Inductive effect of substituents on "A" (electron withdrawal enhances transfer)
- More "s" character in hybrid orbital involved in bond to group that is pulled
- Resonance stabilization conjugate base (A⁻)

Factors enhancing base strength:

- Resonance of conjugate acid/bases
- A base is a nucleophile. Electrons effects which shift electron density to the atom with the lone-pair increases base strength.

ALKANE

Properties:

- Hydrocarbon
- Weak intermolecular forces
- Non-polar, general formula C_nH_{2n+2}
- Saturated C-C & C-H

Nomenclature:

- Add "-ane" to prefix
- Lowest substituents by priority
- Halobutane: substituent halide for alk

Cycloalkane (C_nH_{2n}):

- Bicyclic: two fused or bridged rings
- $n = 2$: cyclopropane (highly strained)
- $n = 3$: cyclobutane (some flexibility)
- $n = 4$: cyclopentane (slight puckering)
- $n = 5$: cyclohexane: chair = stable conformation
- Axial: less stable, axial position, "perpendicular" to ring. Equatorial position, in ring "plane"
- Cis: two substituents on up position
- Trans: one up and one down



Synthesis:

- Hydrogenate alkene or alkyne (H_2 , Pt catalyst)
- Free-radical reaction of alkene
- Radical halobutane (Zn, HX)
- Free-radical alkylation

Reaction:

- Combustion: alkane + $O_2 \rightarrow CO_2 + H_2O$
- Halogenation to halobutane (Cl_2/H_2 , light or heat)

ALKENE $>C=C<$

Properties: Similar to alkane, non-polar, flammable

Nomenclature:

- Add "-ene" to prefix, Use E to denote C=C position
- Saturated C-C & C-H & C=C, unsaturated C=C & C-H
- Polyunsaturated fatty acid: 2 or more C=C
- Alkene: adjacent C-C & C=C
- Vinyl group: $H_2C=CH-$
- Methylene group: H_2C-
- Allyl group: $H_2C=CH-CH_2-$
- Vinyl halide: halide replaces H on C=C
- Conjugated alkenes: C=C and C=C (consecutive)
- Alkadiene, 2 conjugated C=C, example: butadiene, cis and trans isomers about C=C bonds
- Alkatriene, 3 conjugated C=C
- Aromatic: conjugated monocyclic compound, example: (H) benzene = benzene
- Aromatic: cyclic, non-cyclopentadiene anion, cyclopentadienyl anion (5 electrons)

Synthesis via free reaction of C=C



- E/Z: priority groups by atomic weight of - higher priority groups on the same side
- For monosubstituted, cis is less stable (more branching), the opposite, cis more stable
- **Hydrogen:** H₂ from the least substituted alkene
- **Hydrohalic acid:** HX with a C with more H's
- **Alkyl:** Alkylhalide from alkene with more substitution

Synthesis:

- Dehydration: alcohol (H^+ , heat) (elimination)
- Dehydrohalogenation: halobutane (heat, base)
- Dehalogenation: vic. dihalide (Zn, acidic work)
- Hydrogenation: alkene
- α -alkene: Diels-Alder (H_2 , Pt catalyst)
- α -alkene: Diels-Alder (H_2 , Pt catalyst)
- Wittig: aldehyde/ketone + phosphorus ylide

Reaction:

- Combustion: alkene
- Hydrogen to H^+ alcohol (H_2 , Pt catalyst) from alkene, see mechanism (Markovnikov)
- Hydrogen to alcohol: hydroboration/oxidation ($2H_2O/H_2O_2/H_2O$ (aq), anti-Markovnikov)
- Hydroboration-oxidation to alcohol
- Hydrohalogenation (HX) (Markovnikov)
- Halogenation (Br_2/H_2O or Br_2/CH_2Cl_2 , anti addition)
- Halohydrin (Br_2 , H_2O , anti addition)
- Hydrohalogen to form a 1,2-diol (alkene, acid (H⁺), anti addition)
- Oxidation to carboxylic acid (KMnO₄, hot (H⁺))
- Oxidation to ketone (H₂, Zn, H_2O)
- Hydrogenation to alkane (Pt, H_2 , anti addition)
- Free-radical polymerization
- Alkylation: Reaction
- α -alkene: hydrogenation (H₂, heat)
- Diels-Alder: cyclopentadiene from diene + alkene/diophile

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**Barron's Educational Series, Mark
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Organic Chemistry Reactions Mark Jackson, 2001-09-19 This guide is packed with useful and up to date information regarding Organic Chemistry Reactions The laminated 4 page guide contains information on features of an organic reaction kinetics reaction mechanism organic acid base benzene arene alkyne alcohol and much more *ADVANCED ORGANIC CHEMISTRY: REACTIONS, MECHANISMS AND STRUCTURE, 4TH ED* March, 2006 Market_Desc Professors in Organic Chemistry Students in Organic Chemistry Organic Chemists Special Features The book Describes the structure of organic compounds including chemical bonding and stereochemistry Reviews general reaction mechanisms including ordinary reactions and photochemical reactions Includes a survey of reactions arranged by reaction type and by which bonds are broken and formed Includes IUPAC s newest system for designating reaction mechanisms Features an index to the methods used for preparing given types of compounds Contains more than 15 000 references 5 000 new to this edition to original papers About The Book The book covers the three fundamental aspects of the study of organic chemistry reactions mechanisms and structure Part One explores the structure of organic compounds providing the necessary background for understanding mechanisms Part Two discusses reactions and mechanisms Organized by reaction type each of these chapters discusses the basic mechanisms along with reactivity and orientation as well as the scope and mechanisms of each reaction Organic Chemistry Fundamentals BarCharts, Inc, 2015 **Understanding Organic**

Reaction Mechanisms Adam Jacobs, 1997-07-17 This book describes the principles that govern chemical reactivity and shows how these principles can be used to make predictions about the mechanisms and outcomes of chemical reactions Molecular orbital theory is used to provide up to date explanations of chemical reactivity in an entirely nonmathematical approach suited to organic chemists A valuable section explains the use of curly arrows vital for describing reaction mechanisms An entire chapter is devoted to exploring the thought processes involved in predicting the mechanisms of unfamiliar reactions Each chapter is followed by a summary of the important points and a selection of problems to help the reader make sure that the material in that chapter has been assimilated The book concludes with a comprehensive glossary of technical terms This text will be of interest to first and second year chemistry undergraduates studying organic chemistry

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Thomas Laue, Andreas Plagens, 2005-08-19 This Second edition contains concise information on 134 carefully chosen named organic reactions the standard set of undergraduate and graduate synthetic organic chemistry courses Each reaction is detailed with clearly drawn mechanisms references from the primary literature and well written accounts covering the mechanistic aspects of the reactions and the details of side reactions and substrate limitations For the 2nd edition the complete text has been revised and updated and four new reactions have been added Baylis Hillmann Reaction Sonogashira Reaction Pummerer Reaction and the Swern Oxidation and Cyclopropanation An essential text for students preparing for exams in organic chemistry

Summary of International Energy Research and Development Activities Smithsonian Science Information Exchange, 1974

Advanced Organic Chemistry: Reactions and Mechanisms Singh, Maya Shankar, 2004 Advanced Organic Chemistry Reactions and Mechanisms covers the four types of reactions substitution addition elimination and rearrangement the three types of reagents nucleophiles electrophiles and radicals and the two effects electronic

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