

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
- **Friedel-Crafts:** alkyl or acyl group
- **Grignard:** alkyl or acyl group
- **Witt-Renbaum, Clemmensen:** reduce ketone to alkane
- **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 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 donor (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 (109°)

Nomenclature:

- Add "-ane" to prefix
- Lowest substituents by priority
- Halobutane: substitute halide for H

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"
- Equ: two substituents in eq position
- Trans: one up and one down



Synthesis:

- Hydrogenate alkene or alkyne (H_2 , Pt catalyst)
- Free-radical reaction of alkane
- Radical halobutane (Br, $h\nu$)
- Friedel-Crafts alkylation

Reactions:

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

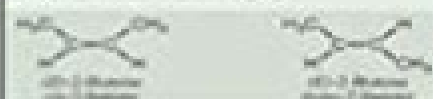
ALKENE $>C=C<$

Properties: Similar to alkane, non-polar, flammable

Nomenclature:

- Add "-ene" to prefix, Use E to denote C=C position
- Saturated C-C-C-C-C-C, unsaturated C=C-C-C
- Polyunsaturated fatty acid: 2 or more C=C
- Alkene: adjacent 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)

Isomers: no free rotation 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
- **Markovnikov Rule:** from the less substituted alkene
- **Anti-Markovnikov addition:** H adds to C with more H's
- **Zaitsev Elimination:** from alkene with more substitution

Synthesis:

- Dehydration: alcohol (H^+ , heat) (elimination)
- Dehydrohalogenation: halobutane (base, heat)
- Dehalogenation: vic. dihalide (Zn , acidic aq.)
- Hydrogenation: alkene
- sp^2 , Diels-Alder (H_2 , $h\nu$ control)
- sp^2 , Diels-Alder (OsO_4 , $h\nu$)
- Wittig: aldehyde/ketone + phosphorus ylide

Reactions:

- Combustion: alkene
- Hydrogen to $2H^+$ alcohol (H^+ , H_2 , $h\nu$) from alkene, see mechanism (Markovnikov)
- Hydrogen to alcohol: hydroboration-oxidation ($2H^+$, H_2 , $h\nu$, $NaOH$, Na_2O_2 , Na_2O , Na_2O_2)
- Hydroboration-oxidation to alcohol
- Hydrohalogenation (HCl/Markovnikov)
- Halogenation ($Br_2/h\nu$ or dihalide ($Na_2C_2O_4$, $h\nu$))
- Halohydrin (Br_2 , H_2O , $h\nu$ addition)
- Hydrohalogen to form a 1,2-diol (alkene, acid H^+ , $h\nu$ addition)
- Oxidation to carboxylic acid (KMnO₄, heat $h\nu$)
- Oxidation to ketone (OsO_4 , $h\nu$, H_2)
- Hydrogenation to alkane (H_2 , Pt, $h\nu$ addition)
- Free-radical polymerization
- Alkylation: Reaction
- alkyl halogenation (Cl_2 , heat)
- Diels-Alder: cycloaddition from diene + alkene/alkyne

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ADVANCED ORGANIC CHEMISTRY: REACTIONS, MECHANISMS AND STRUCTURE, 4TH ED March, 2006
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Advanced Organic Chemistry Jerry March,1985 This survey of advanced chemistry covers virtually all the useful reactions 600 all told with the scope limitations and mechanism of each described in detail Extensive general sections on the mechanisms of the important reaction types and five chapters on the structure and stereochemistry of organic compounds and reactive intermediates are included as well Of the more than 10 000 references included 5 000 are new in this edition

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Named Organic Reactions

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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