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Organic Chemistry Reactions (Quick Study Academic)

Quick Study ACADEMIC

ORGANIC CHEMISTRY REACTIONS

Features of an Organic Reaction

- Mechanism:** Describes the overall reaction using a series of single steps.
- Stoichiometry:** Calculate reactant and product masses using the balanced equation and molar masses.
- Kinetics:** Study of the reaction rate and mechanism.
- Theoretical Yield:** Mass of product given by a complete reaction, % yield = $\frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$.
- 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
- Coordination
- Substitution (S_N1, S_N2)
- Radical reaction
- Isomerization
- Elimination ($E1, E2$)
- Cyclization
- Hydrolysis
- Addition
- Radical reaction

Important Named Reactions

- Diels-Alder:** Forms cyclic alkenes.
- Friedel-Crafts:** Add aryl or alkyl group.
- Grignard:** Add alkyl or aryl group.
- Wittig:** Convert aldehydes/ketones to alkenes.

Kinetics & 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 ≈ 0 for exothermic reactions and $\approx +$ for endothermic reactions.

Hammett-Laurer Postulate: The TS is more like the reactant or product that is closer in energy. The endothermic TS is like the product and the 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." A large E_a 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-reaction thermodynamics.

Solvent Effects: A solvent may stabilize an intermediate, decreasing the E_a and increasing the rate of the reaction. Charged complexes are stabilized by polar solvents.

Organic Acid & Base

Acid

- Electron-pair acceptor (Lewis acid)
- Proton donor (Brønsted-Lowry acid)
- EX: Carboxylic acid

Base

- Electron-pair donor (Lewis base)
- Proton acceptor (Brønsted-Lowry base)
- EX: Amine

Factors Enhancing Acid Strength (H_A)

- Weaker H-A bond
- Greater electronegativity of "A"
- Inductive effect of substituent on "A" (electron-withdrawing 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, electron-rich species which shift electron density to the atom with the lone pair increases base strength

Alkane

Properties

- Hydrocarbon
- Weak intermolecular forces
- New Cyclic: General Formula C_nH_{2n}
- Tetrahedral: $C-C-C$ (109°)

Isomerism

- Add "one" to prefix
- Locate substituent by position #
- Halohalane: Substituted halide for H

Cycloalkane (C_nH_{2n})

- Bicyclic: Two fused or bridged rings
- Cyclopropane: $n = 3$ (highly strained)
- Cyclobutane: $n = 4$ (some flexibility)
- Cyclopentane: $n = 5$ (slight puckering)
- Cyclohexane: $n = 6$ (no strain)

Chair Conformation: Stable conformation

- Best Conformation:** Less stable
- Axial Position:** Perpendicular to ring
- Equatorial Position:** In ring plane
- See H_a and H_e in chair diagram below

Cis: Two substituents in the up position

Trans: One substituent up and one down

Synthesis

- Hydrogenate alkene or alkyne (H_2 , Pt catalyst)
- Free-radical reaction of alkane
- Radical halohalane (Zn, H^+)
- Friedel-Crafts alkylation

Reactions

- Combustion:** Alkane + $O_2 \rightarrow CO_2 + H_2O$
- Halogenation to halohalane (Cl_2, Br_2 , light or heat)

Alkene $>C=C<$

Properties

- Similar to alkane, non-polar, flammable

Nomenclature

- Add "ene" to prefix, use 1 to denote C=C position
- Isotactic: $C=C-C-C$
- Cumulative: $C=C=C$
- Polymersaturated Fatty Acid: 2 or more C=C
- Alkene: Adjacent 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: Alternate C=C and C-C (monomers)
- Alkadiene: 2 conjugated C=C (e.g., butadiene), cis and trans isomers about C=C bond
- Alkatriene: 3 conjugated C=C
- Aromatic: Conjugated monocyclic compound
- EX: (H) aniline = benzene
- Aromatic Cyclic base: 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

Nomenclature: Cis is less stable (steric hindrance)

- Cyclic: Cis is more stable
- Markovnikov Rule:** Form the most substituted alkene
- Markovnikov Addition:** H adds to C with more H's
- Zaitsev Elimination:** Favors alkene with most substitution

Synthesis

- Dehydrate alcohol (H^+ , heat) (elimination)
- Dehydrohalogenate halohalane (base, heat)
- Dehalogenate vic dihalide (Zn , acetic acid)
- Hydrogenate alkene
 - Reagents: H_2 , Pt catalyst
 - Reagents: H_2 , Pd/C catalyst
 - Reagents: H_2 , Ni catalyst
- Wittig: Aldehyde/ketone + phosphorus ylide

Reaction

- Combustion (O_2)
- Hydrate to 2°/3° alcohol (H^+ , H_2O , P from alkene, can rearrange (Markovnikov))
- Hydrate to alcohol: Hydroboration-oxidation (THF, $BH_3 \cdot THF$, $NaOH$, H_2O_2 , anti-Markovnikov)
- Oxymercuration-demercuration to alcohol
- Hydrohalogenation (HX) (Markovnikov)
- Halogenation (Cl_2, Br_2 , vic dihalohalide (X_2, CCl_4 , anti-addition)
- Hydrolysis (X_2, H_2O , anti-addition)
- Hydrolysis or base a 1,2-diol (OsO_4 , cold OH^- , syn-addition)
- Oxidize to carboxylic acid ($KMnO_4$, hot OH^-)
- Oxidation to ketone (O_3 , Zn, H_2O)
- Hydrogenate to alkane (H_2, Pt , syn-addition)
- Free radical polymerization
- Alkene reaction
 - Allylic halogenation (Cl_2 , heat)
 - Diels-Alder: Cyclohexene from diene + alkene/alkyne



Synopsis

Quick Reference for the core essentials of a subject and class that is challenging at best and that many students struggle with. In 6 laminated pages our experienced chemistry author and professor gathered key elements organized and designed to use along with your text and lectures, as a review before testing, or as a memory companion that keeps key answers always at your fingertips. As many students have said "a must have" • study tool. Suggested uses:

- Quick Reference " instead of digging into the textbook to find a core answer you need while studying, use the guide to reinforce quickly and repeatedly
- Memory " refreshing your memory repeatedly is a foundation of studying, have the core answers handy so you can focus on understanding the concepts
- Test Prep " no student should be cramming, but if you are, there is no better tool for that final review

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