

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
- Elimination (E1, E2)
- Cyclization
- Hydrolysis
- Addition

Important named reactions:

- Diels-Alder: form cyclic alkene
- Friedel-Crafts: add acyl or aryl group
- Grignard: add alkyl or aryl group
- Wittig-Kirchhoff: 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, 2°/3° rearrange (Markovnikov))
- Hydrate to alcohol: by deboronate-iodination (TIBP, BF_3 , H_2O , CH_2Cl_2) (syn, anti-Markovnikov)
- Oxymercuration-demercuration to alcohol
- Hydrohalogenate (HX) (Markovnikov)
- Halogenate (Cl_2 , Br_2 , CH_2Cl_2 , via dithiobane (N_2CCl_4 , anti))
- Halohydrin (Cl_2 , H_2O , anti-addition)
- Hydroxylate to form a 1,2-diol (KMnO₄, cold OH^- , syn addition)
- Oxidize to carboxylic acid (KMnO₄, hot OH^-)
- Oxidize to ketone (O_2 , Zn , H_2O)
- Hydrogenate to alkane (P, 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



- EGC: prioritized groups for atomic weight (Z = higher priority groups on the same side)
- For monocyclic: cis is less stable (trans: more stable)
- 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:

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Organic Reactions Study Guide

Seyhan N. Eğe

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