

ORGANIC CHEMISTRY

At a glance... (12th)

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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;

$\% \text{yield} = 100\% \times (\text{product mass}) / (\text{theoretical yield})$.

Equilibrium: Reaction does not proceed to completion, instead, it reaches a balanced state of forward and reverse reactions.

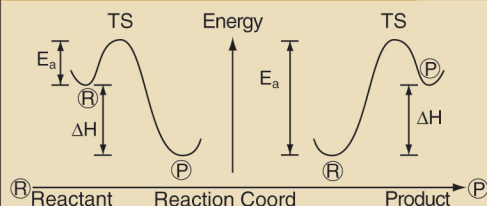
Major reaction types:

- Acid
- Base
- Oxidation Reduction
- Condensation
- Substitution (SN1, SN2)
- Ionic Reaction
- Elimination (E1, E2)
- Cyclization
- Hydrolysis
- Addition
- Radical reaction

Important named reactions:

- **Diels Alder:** form cyclic alkene
- **Friedel-Crafts:** add acyl or alkyl group
- **Grignard:** add alkyl or aryl group
- **Wolf-Kirschner, 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 reactant. The change in enthalpy (ΔH) is < 0 for **exothermic**; > 0 for **endothermic**.

Hammond-Leffler 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." 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. Charged-complexes are stabilized by polar solvents.

ORGANIC ACID AND BASE

Acid:

- Electron-pair acceptor (Lewis acid)
- Proton donor (Bronsted-Lowry acid); example: carboxylic acid

Base:

- Electron-pair donor (Lewis base)
- Proton acceptor (Bronsted-Lowry base); example: *amine*

Factors enhancing acid strength (HA):

- Weaker H-A bond
- Greater electronegativity of "A"
- Inductive effect of substituent 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 base-strength.

ALKANE



Properties:

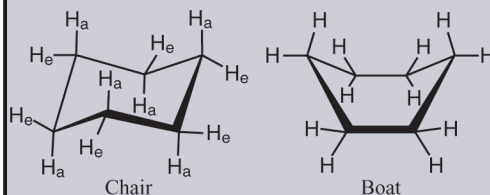
- Hydrocarbon
- Weak intermolecular forces
- Non-cyclic: general formula C_nH_{2n+2}
- Tetrahedral C-C-C (109°)

Nomenclature:

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

Cycloalkane: (C_nH_{2n})

- Bicyclic - two fused or bridged rings
- n = 3: **cyclopropane**: (highly strained)
- n = 4: **cyclobutane**: (some flexibility)
- n = 5: **cyclopentane**: (slight puckering)
- n = 6: **cyclohexane**: *chair* - stable conformer; *boat* - 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 *up* position
- Trans - *one* up and *one* down



Synthesis:

- Hydrogenate alkene or alkyne (H₂, Pt catalyst)
- Free-radical reaction of alkene
- Reduce haloalkane (Zn, H⁺)
- Friedel-Crafts alkylation

Reaction:

- Combustion: alkane + O₂ => CO₂ + H₂O
- Halogenation to haloalkane (Cl₂/Br₂, light or heat)

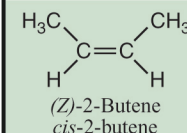
ALKENE >C=C<

Properties: Similar to alkane; non-polar, flammable

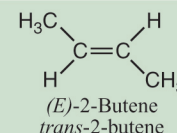
Nomenclature:

- Add -ene to prefix; Use # to denote C=C position
- **Isolated** C-C=C-C-C=C; **cumulative** -C=C=C-
- Polyunsaturated fatty acid: 2 or more C=C
- Allene: adjacent C=C=C
- Vinyl group: H₂C=CH-
- Methylene group: H₂C=
- Allyl group: H₂C=CH-CH₂-
- Vinyl halide: halide replaces -H on >C=C<
- Conjugated: alternate C-C and C=C (resonance)
- Alkadiene, 2 conjugated C=C; example: butadiene; s-cis and s-trans (rotate about C-C bond)
- Alkatriline, 3 conjugated C=C
- Annulene: conjugated monocyclic compound; example: [6] annulene = benzene
- Aromatic cyclic ions: cyclopentadiene anion, cycloheptatriene cation (6 electrons)

Isomers: no free rotation of C=C



(Z)-2-Butene
cis-2-butene



(E)-2-Butene
trans-2-butene

- E/Z; prioritize groups by atomic weight (Z - higher priority groups on the same side)
- For noncyclic: *cis* is less stable (steric hindrance). For cyclic, *cis* more stable.
- **Hofmann Rule:** Form the least-substituted alkene
- **Markovnikov Addition:** H adds to C with most -H's
- **Zaitsev Elimination:** Form alkene with more substitution

Synthesis:

- Dehydrate alcohol (H⁺, heat) (elimination)
- Dehydrohalogenate haloalkane (base, heat)
- Dehalogenate vic dihalide (Zn, acetic acid)
- Hydrogenate alkyne:
 - syn, Z/*cis*-isomer (H₂, P-2 catalyst)
 - anti, E/*trans*-isomer (Li, NH₃, -78°C)
- Wittig, aldehyde/ketone + phosphorous ylide

Reaction:

- Combustion (O₂)
- Hydrate to 2°/3° alcohol (H⁺, H₂O); 1° from ethene; can rearrange (Markovnikov)
- Hydrate to alcohol; hydroborate/oxidize (THF/B₂H₆, H₂O₂/OH⁻) (syn, anti-Markovnikov)
- Oxymercuration-demercuration to alcohol
- Hydrohalogenate (HX) (Markovnikov)
- Halogenate (Br₂/Cl₂), vic dihaloalkane (X₂, CCl₄; anti)
- Halohydrin (X₂, H₂O; anti-addition)
- Hydroxylate to form a 1,2-diol (KMnO₄, cold OH⁻; syn addition)
- Oxidize to carboxylic acid (KMnO₄, hot OH⁻)
- Ozonolyse to ketone (O₃; Zn, H₂O)
- Hydrogenate to alkane (Pt, H₂; syn-addition)
- Free radical polymerization
- Alkadiene Reaction
 - allylic halogenation (Cl₂, heat)
 - Diels-Alder: cycloalkene from diene + alkene/alkyne