

## 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

### Important named reactions:

- Diels-Alder: form cyclic alkene
- Friedel-Crafts: add acyl or alkyl 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 ( $\Delta H$ ) 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:**  $\Delta G$  and  $\Delta H$  describe Thermodynamic Stability.

• If  $\Delta G$  is large and negative (exergonic), the product formation is likely controlled by "thermodynamics." Larger  $\Delta G$  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<sup>-</sup>)

### 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 H<sub>1</sub> and H<sub>2</sub> in chair diagram below)
- Cis - two substituents in up position
- Trans - over up and over down



### Synthesis:

- Hydrogenate alkene (H<sub>2</sub>, heat) (elimination)
- Dehydrohalogenate haloalkane (base, heat)
- Dehalogenate via dithiobane (Zn, acetic acid)
- Hydrogenate alkyne

  - syn, Zn-catalyst (H<sub>2</sub>, P-2 catalyst)
  - anti, Et<sub>3</sub>N-catalyst (Li, NH<sub>3</sub>, -78°C)

- Witting: alkylidenebenzene = phosphorus ylide

### Reactions:

- Combustion ( $O_2$ )
- Hydrate to 2°/3° alcohol (H<sub>2</sub>, H<sub>2</sub>O, 1° from ethene, gas exchange (Markovnikov))
- Hydrate to alcohol: by deborane-addition (LiBH<sub>4</sub>,  $CH_3COCl$ ) (anti-Markovnikov)
- Oxymercuration-demercuration to alcohol
- Hydroboration (BH<sub>3</sub>) via dithiobane ( $N_2CCl_4$ , anti)
- Halogenation ( $Cl_2$ ,  $H_2O$ , anti-addition)
- Hydroboration to form a 1,2-diol (KMnO<sub>4</sub>, cold  $CH_3OH$ , syn addition)
- Oxidize to carboxylic acid (KMnO<sub>4</sub>, hot  $CH_3OH$ )
- Oxidize to ketone ( $O_2$ , Zn,  $H_2O$ )
- Hydrogenate to alkane (Pd, H<sub>2</sub>, 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:  $\pi$ -ex and  $\pi$ -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



- EOC: prioritizes groups by atomic weight (C = 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

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# Organic Reactions Study Guide

**Susan McMurry**

## **Organic Reactions Study Guide:**

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