

## 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.

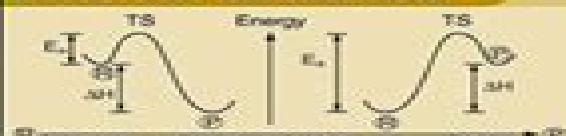
### Major reaction types

- 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 ( $\Delta H$ ) 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<sub>2</sub>)
- Hydrate to 2°/3° alcohol (H<sup>+</sup>, H<sub>2</sub>O, 1° from ethene, 2°/3° rearrange (Markovnikov))
- Hydrate to alcohol: by deboronate-iodination (TIBP, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>) (syn, anti-Markovnikov)
- Oxymercuration-demercuration to alcohol
- Hydroboration (BH<sub>3</sub>) (Markovnikov)
- Halogenate (Br<sub>2</sub>, Cl<sub>2</sub>, I<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>) via dithiobane (N<sub>2</sub>CCl<sub>4</sub>, anti)
- Halohydrin (Cl<sub>2</sub>, H<sub>2</sub>O, anti-addition)
- Hydroxylation to form a 1,2-diol (KMnO<sub>4</sub>, cold OH<sup>-</sup>, syn addition)
- Oxidize to carboxylic acid (KMnO<sub>4</sub>, hot OH<sup>-</sup>)
- Ozonolysis to ketone (O<sub>3</sub>, Zn, H<sub>2</sub>O)
- Hydrogenate to alkane (P<sub>2</sub>, H<sub>2</sub>, syn-addition)
- Free-radical polymerization
- Alkene Reactions
  - allylic Substitution (Cl<sub>2</sub>, 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: H<sub>2</sub>C=CH-
- Methylene group: H<sub>2</sub>C=
- Allyl group: H<sub>2</sub>C=CH-CH<sub>3</sub>
- 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: penultimate groups for atomic weight (Z = higher priority groups on the same side)
- For monocyclic: syn is less stable (trans: hindrance)
- For cyclic, cis 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

**Robert J. Ouellette, J. David Rawn**

## Organic Reactions Study Guide:

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**Manual** T. W. Graham Solomons,Craig B. Fryhle,Scott A. Snyder,2016-04-11 This is the Student Study Guide Solutions Manual to accompany Organic Chemistry 12th Edition The 12th edition of Organic Chemistry continues Solomons Fryhle Snyder's tradition of excellence in teaching and preparing students for success in the organic classroom and beyond A central theme of the authors approach to organic chemistry is to emphasize the relationship between structure and reactivity To accomplish this the content is organized in a way that combines the most useful features of a functional group approach with one largely based on reaction mechanisms The authors philosophy is to emphasize mechanisms and their common aspects as often as possible and at the same time use the unifying features of functional groups as the basis for most chapters The structural aspects of the authors approach show students what organic chemistry is Mechanistic aspects of their approach show students how it works And wherever an opportunity arises the authors show students what it does in living systems and the physical world around us

### **Organic Chemistry Reactions: A Study Guide** Cybellium,2024-10-26

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