

ORGANIC CHEMISTRY

REACTIONS

FEATURES OF AN ORGANIC REACTION

Mechanism: Describes the overall reaction using a series of step-by-step steps.
Reactants: Contains reactants and product species using the following equations and reaction schemes.

Reaction: The study of the reaction rate and mechanisms.

Theoretical yield: Mass of product given by a chemical reaction.

Actual yield: Theoretical mass of 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, S_NAr)
- Rearrangement

Important named reactions:

- Fittig: Alkene from alkyl ethers
- Friedel-Crafts: Alkene or alkyl group
- Kolbe-Kemps: Alkene and carbon dioxide
- Wittig: Alkene from alkyl halides or alkynes

ENZYME AND CATALYST MECHANISMS



Transition state (TS): Minimum 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°rxn) is +10 for exotherms, -10 for endotherms.

Transition State potential: The TS is more like the reactant or product that is absent in energy. Therefore, TS is like the product, intermediate, TS is like the reactant.

Kinetic vs. thermodynamically control: E_a and ΔH_{rxn} describe thermodynamic stability.

- If E_a is large and negative (exothermic), the product becomes less favored by thermodynamics.
- Large ΔH_{rxn} corresponds to a large amount of product relative to reactants.
- A large E_a that gives rise to "transition" control, the energy of the TS controls the reaction, instead of the product controls thermodynamics.

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

ORGANIC ADD AND BASE

Acid:

- Electronegative acceptor of proton acids
- Proton donor (donates & reacts with, accepts electron pair)

Base:

- Electronegative donor (Lewis bases)
- Proton acceptor (donates & reacts with, accepts electron pair)

Reactions involving acid strengths (pK_a):

- Brønsted-Lowry acid
- Lewis acid: acceptor of "N"
- Brønsted-Lowry acid of inclusions in "A"
- Inclusion: addition of solvents to "A"
- Inclusion "A" solvation in hydroxyl alcohol

Reactions involving base strengths:

- Brønsted-Lowry bases
- Lewis bases: electron-rich species which don't share bonds, or the same with the Brønsted-Lowry base concept

ALKANE

Properties:

- Nonpolar
- Weak intermolecular forces
- Nonpolar general formula C_nH_{2n+2}
- Branched C-C (isomers)

Reactions:

- Acid "base" in profile
- Lewis solvation by position #
- Halohydrin: halogen halide for #

Cycloalkane (C_nH_{2n})

- Cyclohexane: two fused or bridged rings
- 1-methylcyclohexane: slightly smooth
- 1,2-dimethylcyclohexane: smooth
- 1,3-dimethylcyclohexane: slightly protruding
- 1,4-dimethylcyclohexane: smooth
- 1,5-dimethylcyclohexane: smooth
- 1,2,3-trimethylcyclohexane: "perpendicular" to ring, 1,2,3-trimethylcyclohexane: "parallel" to ring
- 1,2,4-trimethylcyclohexane: smooth
- 1,2,5-trimethylcyclohexane: smooth
- 1,2,3,4-tetramethylcyclohexane: smooth



Reactions:

- Hydrogenation (H₂)
- Reaction in 2°/3° alkyl (CH₃, CH₂, CH) these ethers are intermediate (alkyl ethers)
- Reaction in alkene: addition-elimination (CH₃Br, CH₃Cl, CH₃I, CH₃Br, CH₃Cl, CH₃I)
- Electrophilic aromatic substitution (EAS)
- Electrophilic addition (EAS) with more H's
- Radical: substitution: forms alkene with more electrons

Reactions:

- Combustion (O₂)
- Combustion: alkene + O₂ → CO₂ + H₂O
- Halogenation: alkene (P_{Cl}, Br₂, I₂)

ALKENE xC=Cx

Properties: Similar to alkenes, more polar. Branched hydrocarbons.

- Acid: very no profile, like hydrocarbons C=C=C
- Branched C=C: C=C=C, C=C=C, branched C=C=C
- Branched: addition (alkene + H or more C=C)
- Branched: addition C=C=C
- Weak group: H₂C=C
- Hydrogen group: H₂C=C
- Radical group: H₂C=C

Reactions involving addition:

- Weak addition: H₂ and C=C=C
- Branched addition: C=C and C=C (isomers)
- Addition: 2 branched C=C, example: branched acids and esters (isomers: CH₃CH₂COOH)
- Alkylations: C=C=C
- Addition: conjugated: conjugative: conjugated: conjugate (H₂) (isomers) → isomers
- Addition: radical: non-conjugative: non-conjugate: radical: radical (isomers) → isomers

Reactions involving addition of C=C:



- ESR: pentavalent groups: 5 electrons weight off - higher priority groups on the same side
- Branched: one is less stable: more branched than another, less stable
- Branched: More: Branched is more substituted alkene
- Markovnikov: addition (H adds to C with more H's)
- Zaitsev: Elimination: forms alkene with more carbons

Reactions:

- Electrophilic addition (H₂)
- Reaction in 2°/3° alkyl (CH₃, CH₂, CH) these ethers are intermediate (alkyl ethers)
- Reaction in alkene: addition-elimination (CH₃Br, CH₃Cl, CH₃I, CH₃Br, CH₃Cl, CH₃I)
- Electrophilic aromatic substitution (EAS)
- Radical: substitution: forms alkene with more electrons
- Hydrogen, alkene, H₂ (H₂) (isomers) → isomers

Reactions:

- Combustion (O₂)
- Combustion: alkene + O₂ → CO₂ + H₂O
- Electrophilic addition (P_{Cl}, Br₂, I₂)
- Electrophilic addition: alkene (P_{Cl}, Br₂, I₂)
- Electrophilic addition: alkene (P_{Cl}, Br₂, I₂)
- Radical addition
- Oxidation: alkene to acid (CH₃COOH, but-COOH)
- Oxidation: alkene (O₂, H₂O₂)
- Electrophilic addition: alkene (P_{Cl}, Br₂, I₂)
- Radical addition
- Electrophilic: Markovnikov
- Electrophilic: Zaitsev
- Electrophilic: Markovnikov
- Electrophilic: Zaitsev

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Maya Shankar Singh,Singh

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Reaction Mechanisms Adam Jacobs,1997-07-17 This book describes the principles that govern chemical reactivity and shows how these principles can be used to make predictions about the mechanisms and outcomes of chemical reactions Molecular orbital theory is used to provide up to date explanations of chemical reactivity in an entirely nonmathematical approach suited to organic chemists A valuable section explains the use of curly arrows vital for describing reaction mechanisms An entire chapter is devoted to exploring the thought processes involved in predicting the mechanisms of unfamiliar reactions Each chapter is followed by a summary of the important points and a selection of problems to help the reader make sure that the material in that chapter has been assimilated The book concludes with a comprehensive glossary of technical terms This text will be of interest to first and second year chemistry undergraduates studying organic chemistry

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