

SCHOOL OF SCIENCE AND HUMNITIES DEPARTMENT OF CHEMISTRY

SCYA 5301 ORGANIC REACTION MECHANISM



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UNIT – 1 BONDING IN ORGANIC MOLECULES – SCYA 5301

UNIT 1: BONDING IN ORGANIC MOLECULES

Nature of the bonding in Organic Molecules

Organic compounds are covalent compounds According to the modern VBT, concept, a covalent bond is formed between two atoms if there is an overlapping of an atomic orbital of one atom with an atomic orbital of another atom. Sigma bond is stronger than π -bond. The electrons in the π -bond are loosely held. The pi-bond electrons will be polarizing and contributing to the stability of system. This is known as resonance. Some times sigma bond will involve in bond polarization. This concept can be explained with hyper conjugation.

Hyperconjugation

The Hyperconjugation is the interaction of the electrons in a sigma bond (usually C–H or C–C) with an adjacent empty (or partially filled) non-bonding p-orbital, antibonding σ or π orbital, or filled π orbital, to give an extended molecular orbital that increases the stability of the system. Only electrons in bonds that are β to the positively charged carbon can stabilize a carbocation by hyperconjugation

Applications of Hyperconjugation:

- 1. Stability of carbocations
- 2. Stability of free radicals
- 3. Stability of alkenes (More substituted alkene)

Example: The more substituted alkene is more stable due to hyper conjugation



Types of conjugation



Aromaticity

It is a property of organic molecule being cyclic planar conjugative system with unhybridized porbital and having $(4n+2)\pi$ electrons or it is a nature of organic compound being an aromatic.

Aromatic Compound Characteristics:

- 1. Cyclic planar molecule
- 2. Continuous Conjugation in Planar system
- 3. Every atom of ring should be with unhybridized p-orbital
- 4. Continuous overlapping of p-orbitals decreases the energy of molecule
- 5. System should follow Huckel's rule $(4n+2)\pi$ electrons
- 6. Molecule may with hetero atom also

Aromaticity of Benzene:



Anti Aromatic Compounds

- 1. Cyclic planar molecule with continuous conjugation
- 2. Every atom in the ring must be with unhybridized p-orbital
- 3. Cyclic overlapping of atomic p-orbitals increases energy of molecules
- 4. System should follow $(4n)\pi$ electrons

Non Aromatic compound

- 1. Cyclic molecule without planarity
- 2. Ring molecule will not have unhybridized Continuous p-orbitals
- 3. Huckel's rule is not applicable

APPLICATION OF HUCKEL'S RULE

Aromaticity of cyclopropyl cation and Cyclo butadiene:



Aromaticity of cyclopentadiene:



Aromaticity of Annulene



[10]annulene



[12]annulene



[14]annulene



[16]annulene





[18]annulene



[18]annulene

[20]annulene

Cycloheptatrienyl cation



Aromatic

Anti Aromatic

Trans annular Interaction and Homoaromaticity:



Trans annular Interaction



No Trans annular Interaction



No Trans annular Interaction



No Trans annular Interaction

Juxt opposition:

If Antiaromatic compound is fused to two aromatic molecules, Antiaromatic compound character enhances it's aromatic character this is known as Juxt opposition.

Example:



Biphenylene



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UNIT – 2 REACTION MECHANISM – REACTIVE INTERMEDIATES – SCYA 5301

UNIT 2: REACTION MECHANISM – REACTIVE INTERMEDIATES

FIELD EFFECTS

- a) Electronic Effects in organic Molecules and factors affecting the availability of electrons
- b) Electronegativity, hybridization and polarization effects
- c) Inductive, field and resonance effects
- d) Delocalization of electron involving π - π and π -p and hyperconjugation
- e) Acidic and basic character of organic compounds

Applications of Field effects:

Acidity of phenols:

Phenols are weak acids. They react with strong bases like NaOH to form salts. So phenols act as proton donors. Inductive effect is a short range effect. Mesomeric effect is a long range effect.

 $NO_2CH_2COOH > CICH_2COOH > HCOOH > CH_3COOH$

Acidity of carboxilic acids



TYPES OF REACTION MECHANISM

1. Concerted reaction mechanism

The mechanism which involves the breaking and making of bond that takes place simultaneously on approach of reacting molecules without formation of intermediate is called concerted reaction mechanism.

2. Nonconcerted reaction mechanism

The mechanism of reactions which proceed through the formation of intermediate species before the product species are finally formed are called the activation Nonconcerted reaction mechanism.

Reactive Intermediates

- 1. Carbocations
- 2. Carbanions
- 3. Freeradicals
- 4. Carbenes
- 5. Nitrenes
- 6. Arynes

CARBOCATIONS

Definition: A carbon with positive charge containing 6 electrons in valency shell is known as carbocation.

Characteristics: Planar structure (which destabilizes), Bond angle: 120°

Classification:

1. Classical Carbocation - Examples: Primary, Secondary, tertiary



tertiary

Secondary

Primary

2. Nonclassical carbocation - Bridged carbocation



Reactivity:

Carbocations react with anions, molecules containing loan pair of electrons. (i.e. Water, hydroxide anions)

Generation and formation:

- a) Ionization of alkyl halides
- b) Addition of H^+ to un saturation
- c) Addition of H^+ to alcohols, acids, esters, acid anhydrides

- d) Friedal craft reaction
- e) Unstable cation gives carbocation (like diazonium salts)

Carbocation Stability: 3°> 2°> 1°

Explained by

- a. Inductive effect
- b. Hyper conjugation effect
- c. Conjugation with double bond
- i. Allylic, benzylic, triphenyl carbocation, tropielium cation
- d. Solvent
- i. Polar solvents stabilizes the carbocation
- e. Substituent
- i. Electron donating, electron withdrawing and loan pair of electron containing atom attached carbocation

Classification of Carbocations:

1] Transient Carbocation

- a) Short lived
- b) Stabilized by +I effect and hyper conjugation
- c) These are transitory intermediates
- d) These are highly reactive with molecule containing loan pair of electrons
- e) Tertiary, secondary and primary

2] Stable carbocation

These can be isolated and studied Ex: Adamentyl carbocation, bornyl cation, triphenyl

carbocation



Reactions of Carbocations:

- a) Reaction with nucleophiles or anions
- b) Reaction with molecule containing loan pair of electrons
- c) Elemination reactions Ex: Zaitsevs rule, Dehydration, Dehalogination,
- d) Dehydrohaloginations, NGP reactions
- e) Rearrangement reactions Ex: pinacolpinacalone rearrangement,

Wagner meerwin rearrangement

f) Electrophilic substitution

Ex: Friedal crafts alkylation, Friedal crafts acylation

g) Electrophilic addition reaction Ex: Marconikoffs addition

Carbanions:

Definition: Trivalent carbon containing negative charge is known as a carbanion.

Characteristics:

It acts like a Lewis base

It is anion and structure is like ammonia

Generation:

- i] Heterolytic fission
- ii] From hydrocarbons
- iii]Organo metallic compounds
- iv] Addition anion to double bond
- v] Decarbonylation

Stability of Carbanion

- 1. Conjugate acid theory
- 2. Inductive effect
- 3. S-Character
- 4. Resonance
- 5. Aromatization

Reactions of Carbanion:

- 1] Addition reactions: Perkins, knovelgel, Reformatsky, claissen, aldol condensation reactions.
- 2] Substitutions: Haloform reaction, Reimer timer, Wurtz reactions
- 3] Rearrangement reactions:Wittig reaction.Witting rearrangement,Favour sky reaction, Stevense rearrangement, Fries and Claissen rearrangement

Free Radicals

Free Radicals - Two possible structures have been postulated.

- i] Planar SP² hybridized radical similar to carbocation
- ii] Pyramidal SP³ hybridized radical similar to carbanion

But there is no chemical evidence for both. But physical methods like ESR, UV and IR is believed that free radicals have the planar structures.

Generation of Free radical

- Thermolysis or Thermal cleavage of C-C covalent bond: Ex:Inpresence of heat peroxides, Azocompounds, diazonium salts
- Photolysis or photo chemical cleavage of C-C covalent bond Ex: In presence of light peroxides, Azocompounds, diazonium salts
- Redox reaction or electron transfer method: Sandamayers reaction, Fentons reaction, Cyclic azo compounds, Colbe electrolysis reaction

Classification of free radicals:

- a) Short lived free radicals: Can't isolated, high reactive
- b) Long lived free radicals: Cant isolated, less reactive

Reactions of free radicals:

- i] Polymerization reactions
- ii] Halogination reactions
- iii] addition reactions
- iv] auto oxidation reactions
- v] Aromatic substitutions

Carbenes

These are highly reactive with very short life time. They are neutral bivalent carbon intermediates and have been isolated only entrapment in matrices at very low temperatures.

Carbenes are electron deficient in nature.

Classification of Carbenes

a. i] Singlet carbene:

 SP^2 hybridization. Two SP2 hybridised orbitals are utilized and one is having unshared pair of electrons and vacant P orbital. It resembles the carbocations structure. It acts like a lewis base and acid. With ESR we cant identify.

b. ii] Triplet carbene:

SP hybridization. Two SP hybridised orbitals are utilized and two unhybridised porbitals are having one electron each. Triplet carbene is paramagnetic. With ESR we can identify.

Generation of Carbenes:

- a) Decomposition reactions
 - i. Aliphatic diazo compounds
 - ii. Ketenes, Epoxides, Diazirines, tetrazole, Chloroform, Bromoform, Ylides.
- b) By Elimination methods: From alkyl halides

Stability of Carbene:

- 1. In nonaqueous media carbenes can be trapped as cyclopropanes
- Carbene in the carbene carbon attached to two atoms which are bearing a loan pair of electrons are more stable due to resonance.

Nitrenes:

Electron deficient monovalent nitrogen species. The nitrogen atom in nitrene has a sextet of electrons. Nitrenes cant isolated. But trapped by CO and can get in the form of isocyanate.

Types: Singlet nitrene & triplet nitrene



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UNIT – 3 ELECTROPHILIC AND NUCLEOPHILIC ALIPHATIC SUBSTITUTION REACTIONS SCYA 5301

UNIT 3: ELECTROPHILIC AND NUCLEOPHILIC ALIPHATIC SUBSTITUTION REACTIONS

Aliphatic Nucleophilic substitution

Nucleophiles are chemical species that react with centers of positive ionic character. When the center is an aliphatic carbon, the process is called aliphatic nucleophilic substitution. Chemical reactions of this type are extremely important for the synthesis of new compounds and for understanding the mechanisms in organic chemistry. All nucleophilic substitution reactions may take several reaction courses, but all have similar appearances at the outset. All reactions have an attacking species, a nucleophile (Nu) that bears a pair of electrons either as an anion or as a neutral compound. The organic compound known as the substrate has a structure that greatly influences the outcome of the reaction and it contains the leaving group (L) that is lost in the reaction. The conditions of the reaction, especially solvent and temperature, are also important contributors to the process. In order to understand the products of the reaction and how they are formed, the reaction is studied from a mechanistic point of view. The Nucleophilic Substitution Second-Order reaction (SN2).





Inversion of configuration

reaction = k [Nu][Substrate} rate

The SN2 reaction occurs when a Nucleophile attack a primary substrate and sometimes a secondary substrate. The reaction of a secondary substrate depends on the nucleophile and the leaving group. Tertiary substrates do not undergo reactions by the SN2 mechanism. The overall rate of the reaction depends of the concentration of the nucleophile and the concentration of the substrate, thus it is called second-order. The mechanism requires that the nucleophile attack the substrate from the backside of the leaving group to give a pentavalent transition state (*). The organic substituents reverse their configuration (an S enantiomer would change into an R enantiomer) The process is sometimes called Walden inversion. Sometimes when the nucleophile has strongly basic characteristics, such as alkoxides, and alkene is formed also. This product is formed in a reaction known as the E2 reaction (Elimination Second-order).

SN1 reaction mechanism



Stereochemistry of SN1 reaction



SN2 REACTION

SN2 reactions are bimolecular in rate of reaction and have a concerted mechanism. The process involves simultaneous bond formation by the nucleophile and bond cleavage by the leaving group. The transition state looks like this. Because the reaction is concerted, Sn2 mechanisms will always lead to an inversion of stereochemistry! For reactivity using an Sn2 mechanism, primary >> secondary >> tertiary carbon centers.



Substitution vs Elimination

1. Determine if the base/Nu is strong or weak

If strong $-S_N 2$ or E2

If weak $-S_N 1$ or E1

2. If it is a strong, bulky base – E2 only. If it is a non-bulky base, look further into the substrate – primary substrates do S_N2 , secondary and tertiary do E2 as the major mechanism.

The S_N2 and E2 are bimolecular reactions, meaning that the substrate (alkyl halide) and the base/nucleophile both participate in the rate-determining step. This only happens when the base (if the mechanism is E2) or the nucleophile (if S_N2) is strong – very reactive.

Strong Base/Nu - Bimolecular (E2 or S_N2)



If the base/nucleophile is weak, then the mechanism is unimolecular -E1 or S_N1 . The weak reactants are is mainly going to be the water and alcohols. And choosing between E1 and S_N1 is easy – the main factor is the heat. If heat is mentioned, then it is a hint that E1 elimination is the main mechanism in that reaction.



Nighbouring Group Participation – Mechanism:



Nighbouring Group Participation – Example – 1:



Nighbouring Group Participation – Example – 2:





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UNIT – 4 ELECTROPHILIC AND NUCLEOPHILIC AROMATIC SUBSTITUTION REACTIONS SCYA 5301

UNIT 4 : ELECTROPHILIC AND NUCLEOPHILIC AROMATIC SUBSTITUTION REACTIONS

AROMATIC ELECTROPHILIC SUBSTITUTION REACTION

- a) Sulphonation
- b) Halogenation
- c) Friedel-Craft's reaction
- d) Coupling reactions
- e) Kolbe's reaction

Aromatic Electrophilic substitution - General mechanism



Step wise Sulphonation Reaction mechansim



Friedel-Craft's Alkylation reaction



Friedel-Craft's Acylation reaction



Coupling Reaction

(i) Diazotisation

NaNO₂ + HCl $\longrightarrow 0 - 5^{\circ} C$ > HNO₂ + NaCl



(ii) Diazo coupling (electrophlic substitution)





4-HYDROXY PHENYL AZO BENZENE

Kolbe's Reaction



Kolbe's Reaction Mechanism





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UNIT – 5 ADDITION AND ELIMINATION REACTIONS - SCYA 5301

UNIT 5: ADDITION AND ELIMINATION REACTIONS

Addition to C-C Multiple Bond

- 1) Electrophilic Addition
- 2) Nucleophilic Addition
- 3) Freeradical Addition

Addition of symmetrical reagents



Addition of symmetrical reagents



Factors affecting the addition of halogen to olefin: Effect of added nucleophiles



Proof for cyclic bromonium ion at low temperature NMR



Unsymmetrical Olefines - Markovnikov Rule



Mechanism of Markonikov Rule





Antimarkovnikov Rule or Karasch effect



Addition of hydrogen to cycloalkenes



Cis addition of hydrogen to cyclic olefin



