CONCEPT MAP

GENERAL ORGANIC CHEMISTRY (Part-2)

Organic Compounds

I : Nature of Attacking Reagents

Types

Nucleophiles (nucleus loving)	Electrophiles (electron loving)
Expressed by a symbol : Nu^-	Expressed by a symbol E^+
Electron rich	Electron deficient
Donate an electron pair	Accept an electron pair
Attack on electron deficient atoms (*i.e.*, low e^- density)	Attack on electron rich atoms (*i.e.*, high e^- density)
Lewis bases (e^- pair donor)	Lewis acids (e^- pair acceptors)
Carry neutral or –ve charge	Carry neutral or +ve charge
Possess an unshared pair of electrons which are not too strongly held to the atomic nucleus.	Possess an empty orbital to receive the electron pair from the nucleophile.
Able to increase their covalency by one unit.	Able to form an extra or alternative bond with the nucleophile.
e.g., $\ddot{N}H_3$, $R-\ddot{N}H_2$, CN^-, OH^-	*e.g.*, BF_3, $AlCl_3$, Cl^+, NO^+

II : Electronic Displacements in Organic Molecules

Organic compounds undergo electronic displacements on their own or under the influence of an attacking agent.

Inductive effect :

- Permanent effect
- Observed in saturated compounds
- Operate through σ-bonds
- Represented by ➤ arrow
- **+*I* effect :** $\overset{\delta\delta\delta^-}{C} \leftarrow \overset{\delta\delta^-}{C} \leftarrow \overset{\delta^-}{C} \leftarrow \overset{\delta^+}{C}H_3$

  [Substituent attached to the end of the carbon chain is electron donating.]
- **–*I* effect :** $\overset{\delta\delta\delta^+}{C} \rightarrow \overset{\delta\delta^+}{C} \rightarrow \overset{\delta^+}{C} \rightarrow \overset{\delta^-}{X}$

  [Substituent attached to the end of the carbon chain is electron withdrawing. (X = F, Cl, CN etc.)]

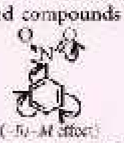
> - Stability of carbocation/free radical $\propto +I \propto \frac{1}{I} \propto$ Strength of base cation (conjugate acid)
>
>   Thus, order is 1° < 2° < 3°.
> - Stability of carbanion ∼ $-I \sim \frac{1}{+I} \sim$ Strength of acid anion (conjugate base)
>
>   Thus, order is 1° > 2° > 3°.

Mesomeric/Resonance effect :

- Permanent effect
- Represented by a curved (↷) arrow
- Operate through two π-bonds or a π-bond with the lone pair
- Observed in unsaturated and conjugated compounds

(+R/+M effect)

[Electrons move away from the atom.]



(–R/–M effect)

[Electrons are transferred towards the atom.]

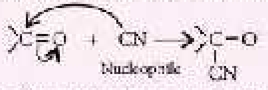
Electromeric effect :

- Temporary effect
- Represented by a curved (↷) arrow
- Operates in multiple covalent bonds or an atom with a lone pair of electrons
- **+*E* effect :**

$>C=C< + H^+ \longrightarrow >\overset{+}{C}-C<$ (with H on second C)

(Transfer of electrons of the π-bond towards the attacking reagent.)

- **–*E* effect :**

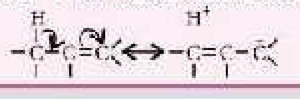


$>C=O + CN \longrightarrow >C(CN)-O$

(Transfer of π-electrons takes place to more electronegative atom (i.e. O, N, S) joined by multiple bonds.)

Hyperconjugation/No bond resonance/σ-π conjugation :

- Permanent effect
- Delocalization of σ and π-bond orbitals



III : Types of Organic Reactions

Substitution Reactions

(*Replacement of an atom by a different atom.*)

Reaction is done by –

- **Free radical:** (*e.g.*, Wurtz reaction)
- **Ionic**
  - Electrophilic (by electrophiles), S_E
  - Nucleophilic (by nucleophiles), S_N

S_N1	S_N2
Unimolecular	Bimolecular
First order	Second order
Two steps reaction	One step reaction
(i) $R:X \underset{\text{Carbocation}}{\overset{\text{Slow}}{\rightleftharpoons}} R^+ + X^-$ (ii) $R^+ + :Nu^- \xrightarrow{\text{Fast}} R:Nu$	$R:X + :Nu^- \longrightarrow R:Nu + :X^-$ (through transition state)
Low and mild concentration of nucleophile.	High and strong concentration of nucleophile.
Solvents of high polarity	Solvents of low polarity.
Catalysed by Lewis and Brönsted acids	Catalyst not involved.
e.g., Hydrolysis of *tert*.butyl halide.	*e.g.*, Hydrolysis of methyl halide.

Addition Reactions

(*Compounds containing = or ≡ bonds.*)

$$>C\overset{\sigma}{\underset{\pi}{=}}C< + X_2 \longrightarrow >\underset{X}{C}\overset{\sigma}{-}\underset{X}{C}<$$

Reaction is done by –

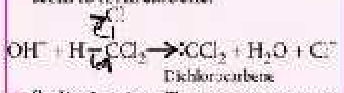
- **Free radical** – (*e.g.*, Peroxide effect)
- **Ionic**
  - Nucleophilic, A_N
  - Electrophilic, A_E

  (*e.g.*, Markownikoff's rule)

Elimination Reactions

(*Reverse of addition reaction.*)

- **α-elimination :** Two atoms or groups are lost from the same carbon atom to form carbene.



$$OH^- + H-CCl_2 \longrightarrow :CCl_2 + H_2O + Cl^-$$

Dichlorocarbene

- **β-elimination :** Two atoms or groups are lost from adjacent carbon atoms to form an unsaturated compound.

$$>\underset{H}{C}-\underset{X}{C}< \longrightarrow >C=C< - HX$$

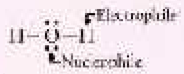
Rearrangement Reactions

(*Migration of an atom/group within the molecule.*)

$$NH_4CNO \xrightarrow{\Delta} NH_2CONH_2$$

Have A Look!

- Lewis acid and base are terms that are used generally, but when one or the other reacts to form a bond to a carbon atom, we usually call it an *electrophile* or a *nucleophile*.
- Ambiphile (ambident) reagents, behave both like electrophiles and nucleophiles.



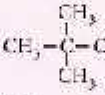
$H-\ddot{O}-H$

- 4-Characteristic patterns of electron flow are:
  - Nucleophilic attack ➡

  - Loss of leaving group ➡

  - Proton transfer ➡

  - Rearrangement ➡

- When inductive and electromeric effects both are operative in the same molecule but in the opposite directions, the *electromeric effect* predominates.
- 

  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Br$ shows
  - S_N1 reaction with C_2H_5OH
  - S_N2 reaction with $C_2H_5O^-$
- If the reactant is a 1° alkyl halide → Undergoes only S_N2/E2 reactions.
- If the reactant is a 2°/3° alkyl halide,
  - Undergoes S_N2/E2 reactions favoured by a high concentration of a good nucleophile/strong base.
  - Undergoes S_N1/E1 reactions favoured by a poor nucleophile/weak base.