UNIT-12 BASIC CONCEPTS OF ORGANIC REACTIONS

MY REVISION TIMELINE:-

SUMMARY:-

- Chemical reaction is a process in which existing bonds are broken and new bonds are formed.
- A reagent is an organic or inorganic substance or agents like heat, photons (light), etc... which brings about a chemical change.
- Substrate is a substance which undergoes chemical change.
- Fission of a covalent bond
 - Homolytic cleavage (bond breaks symmetrically)
 - Heterolytic cleavage (bond breaks unsymmetrically)
- Hybridisation of carbon in
 - Carbocation sp² (planar)
 - Carbanion sp³ (pyramidal)
 - Carbon free radical sp^2 (planar)
- \blacktriangleright Relative stability of carbocations: $^{+}C(CH)_{3} > ^{+}CH(CH_{3})_{2} > ^{+}CH_{2}CH_{3} > ^{+}CH_{3}$
- Relative stability of carbanions: $^{-}C(CH)_{3} < ^{-}CH(CH_{3})_{2} < ^{-}CH_{2}CH_{3} < ^{-}CH_{3}$
- Nucleophiles are reagents which have high affinity for electro positive centers. Usually negative charged ions or e⁻ rich neutral molecules contains one or more lone pairs. Eg: Cl⁻, NH₃, H₂S, R-O-R etc...
- Electrophiles are reagents that are attracted towards negative charge or e⁻ rich center. Usually positive charged ions or electron deficient neutral molecules. Eg: CO₂, :CCl₂, AlCl₃, FeCl₃, R⁺, RX etc...
- > Types of electron movement:
 - Lone pair becomes a bonding pair
 - Bonding pair becomes a lone pair
 - A bond breaks and becomes another bond
- Electron displacement effects in covalent bonds
 - Inductive effect (I)
 - Resonance effect (R)
 - Electromeric effect (E)
 - Hyper conjugation
- Different types of organic reactions:
 - Substitution reactions
 - Addition reactions
 - Elimination reactions
- +1 Chemistry

- Oxidation and reduction reactions
- Rearrangement reactions
- Combination of the above

> Functional group inter conversion \rightarrow particular functional group can be converted into other functional group by reacting it with suitable reagents.

TEXTBOOK EVALUATION

Multiple choice questions:-

1.	For the Following reactions	4				
	(a) $CH_3 CH_2 CH_2 Br + KOH \rightarrow CH_3 - CH + KBr + H_2O$					
	(b) $(CH_3)_3 CBr + KOH \rightarrow (CH_3)_3 COH + KBr$					
	(c) + Br Br					
	Br	\mathcal{O}^{γ}				
	Which of the following statement is correct?					
	(a) (A) is elimination, (B) and (C) are substitution					
	(b) (A) is substitution, (B) and (C) are elimination					
	(c) (A) and (B) are elimination and (C) is addition reaction					
	(d) (A) is elimination, B is substitution and (C) is addition reaction.					
2.	What is the hybridisation state of benzyl carbonium ion?					
	(a) sp^2	(b) spd^2				
	(c) sp^3	(d) sp^2d				
3.	Decreasing order of nucleophilicity is					
	(a) $OH^{-} > RNH_2^{-} > OCH_3 > RNH_2$	(b) $NH_2 > OH > OCH_3 > RNH_2$				
	(c) NH,> CH ₃ O >OH ⁻ > RNH ₂	(d) $CH_3O > NH_2 > OH > RNH_2$				
4.	'hich of the tollowing species is not eLectrophilic in nature?					
	(a) Cl^+	(b) BH ₃				
	(c) H_3O^+	(d) $^{+}NO_{2}$				
5.	Homolytic fission of covalent bond leads to the formation of –					
	(a) electrophile	(b) nucicophile				
_	(c) Carbocation	(d) free radical				
6.	Hyper Conjugation is also known as –					
	(a) no bond resonance	(b) Baker – nathan effect				
	(c) both (a) and (b)	(d) none of these				
7.	Which of the group has highest +I effect?					
	(a) CH_3^-	(b) $CH_3CH_2^-$				
	(c) $(CH_3)_2$ -CH-	$(d) (CH_3)_3$ -C-				
8.	Which of the following species does not exert a resonance effect?					
	(a) C_6H_5OH	(b) C_6H_5Cl				
	(c) $C_6H_5NH_2$	$(d) C_6H_5NH_3$				

9. -I effect is shown by – (a) - Cl(b) -Br (c) both (a) and (b) (d) -CH₃ **10.** Which of the following carbocation will be most stable? (a) PH_3C^+ (b) $CH_3 - C^+H_2$ -(c) $(CH_3)_2 - C^+H$ (d) $CH_2 = CH - C^+ H_2$ **11.** Assertion : Tertiary Carbocations are generally formed more easily than primary Carbocations. Reason : Hyper conjugation as well as inductive effect due to additional alkyl group stabilize tertiary carbonium ions. (a) both assertion and reason arc true and reason is the correct explanation of assertion. (b) both assertion and reason are true but reason is not the correct explanation of assertion. (c) Assertion is true but reason is false (d) Both assertion and reason are false 12. Heterolytic fission of C-C bond results in the formation of – (b) Carbanion (a) free radical (c) Carbocation (d) Carbanion and Carbocation **13.** Which of the following represent a set of nucleophiles? (a) BF₃, H₂O, NH²⁻ (b) AlCl₃, BF₃, NH₃ (c) CN⁻, RCH⁻₂, ROH (d) H^+ , RNH⁺₂, CCl₂ 14. Which of the following species does not acts as a nucleophile? (b) ROR (a) ROH (c) PCl_3 (d) **BF**₃ 15. The geometrical shape of carbocation is (a) Linear (b) tetrahedral (c) Planar (d) Pyramidal

Write brief answers to the following questions:-

16. Write short notes on (a) Resonance (b) Hyperconjucation

> Resonance:

Certain **organic compounds** can be represented by more than one structure and they differ only in the **position of bonding** and **lone pair of electrons**. Such structures are called **resonance structure** and this phenomenon is called as **resonance**. This phenomenon is also called as mesomerism or mesomeric effect.

For example, the structure of **aromatic compounds** such as **benzene** and conjugated system like **1**, **3 butadiene** cannot be represent by a single structure and their observed properties can be explained on the base of a resonance hybrid.

Resonance or mesomeric effect is classified into **positive** and **negative mesomeric** or **resonance effect**. (+R or +M and –R or -M)



> Hyperconjucation:

The **denationalization** of electrons of σ **bond** is called as hyper conjugation. It is a special stabilizing effect that results due to the **interaction of electrons** of a σ **bond** with the **adjacent empty non-bonding p-orbitais** resulting in an extended molecular orbital.

Hyper conjugation is a **permanent effect**.

For example, in **propane**, the σ - electrons of C-H bond of methyl group can be delocalised into the π - orbital of doubly bonded carbon as represented below.



17. What are electrophiles and nucleophiles? Give suitable examples for each.

> Electrophiles:

Electrophiles are reagents that are **attracted towards negative charge** or **electron rich center**. They are either **positively charged ions** or **electron deficient neutral molecules**.

Example: CO₂, AlCl₃, BF₃, FeCl₃, NO⁺, NO⁺₂,, etc.

> Nucleophiles:

Nucleophiles are reagents that has **high affinity** for **electropositive centers**. They possess an atom has an unshared pair of electrons. They are usually **negatively charged ions** or **electron rich neutral molecules**.

Example: NH₃, R-NH₂, R-SH, H₂O, R-OH, CN⁻. OH⁻ etc.

18. Show the heterolysis of covalent bond by using curved arrow notation and complete the following equations. Identify the nucleophile in each case.

i)
$$CH_3 - Br + KOH \rightarrow$$

ii) $CH_3 - OCH_3 + HI \rightarrow$
 \rightarrow
 $+1 Che_1 CH_3 - Br \xrightarrow{Slow} H H H$
(Methyl bromide) H (Carbocation)

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Br⁻ (leaving) and **OH**⁻ (incoming) are the nucleophiles.



⁻OCH₃ (leaving) and I⁻ (incoming) are the nucleophiles.

19. Explain inductive effect with suitable example.

- Inductive effect is defined as the change in the **polarization** of a **covalent bond** due to the presence of **adjacent bonded atoms** or **groups** in the molecule. This is a **permanent phenomenon.**
- ➢ It is denoted as I-effect.
- The ability to release or withdraw the electron through sigma covalent bond is called +I and –I effect.
- Highly electropositive atoms and atoms or groups which lose electron towards a carbon atom are said to have a +I effect. Example: CH₃-,(CH₃)₂ CH-,(CH₃)₂ C- etc.
- Highly electronegative atoms and atoms or groups which draw electrons away from a carbon atom are said to have a -I effect. Example: -NO₂. -I, -Br, -OH, C₆H₅ etc.
- For example, consider ethane and ethyl chloride. The C-C bond in ethane is non polar while the C-C bond in ethyl chloride is polar. We know that chlorine is more electronegative than carbon and hence it attracts the shared pair of electrons between C-Cl in ethyl chloride towards itself.

$$\delta \delta + \delta + \delta + \delta - CH_2 \longrightarrow Cl$$

This develops a slight negative charge on chlorine and slight positive charge on carbon to which chlorine is attached. To compensate it, the C₁ draws the shared pair of electron between itself and C₂. This polarisation effect is called inductive effect.

20. Explain electromeric effect.

- Electromeric is a temporary effect which operates in unsaturated compounds (containing >C=C<, >C=O, etc...) in the presence of an attacking reagent.
- Let us consider two different compounds (i) compounds containing carbonyl group (>C=O) and (ii) unsaturated compounds such as alkenes (>C=C<).</p>

> When a **nucleophile** approaches the carbonyl compound, the π electrons between C and O is instantaneously shifted to the more electronegative oxygen. This makes the **carbon electron deficient** and thus facilitating the formation of a new bond between the **incoming nucleophile** and the **carbonyl carbon atom**.



> On the other hand when an electrophile such as H+ approaches an alkene molecule, the π electrons are instantaneously shifted to the electrophile and a new bond is formed between **carbon** and **hydrogen**. This makes the other carbon electron deficient and hence it acquires a positive charge.

$$H_{2}C = CH_{2} + H + H = \begin{bmatrix} \delta + \delta - \\ H_{2}C - CH_{2} + H \end{bmatrix}$$

$$H_{2}C - CH_{3} + H = \begin{bmatrix} \delta + \delta - \\ H_{2}C - CH_{3} + H \end{bmatrix}$$

- > The electromeric effect, is denoted as **E effect**.
- ➤ The electromeric effect is classified as +E and -E based on the direction in which the pair of electron is transferred to form a new bond with the attacking agent.
- > When the π electron is transferred towards the attacking reagent, it is called +E (positive electromeric) effect. The addition of H+ to alkene as shown below is an example of +E effect.

$$X \xrightarrow{Y} + E^+ \xrightarrow{Y} X \xrightarrow{Y}$$

When the π electron is transferred away from the attacking reagent, it is called, -E (negative electromeric) effect The attack of CN- on a carbonyl carbon, as shown below, is an example of -E effect.

$$N\overline{u} + X = Y \longrightarrow X - Y$$

- 21. Give examples for the following types of organic reactions (i) β elimination
 - (ii) electrophilic substitution.
 - n-Propyl bromide on reaction with alcoholic KOH gives propene. In this reaction hydrogen and Br are eliminated.

$$CH_{3} \longrightarrow \begin{array}{c} & \beta \\ & CH_{2} \longrightarrow \begin{array}{c} & CH_{2} & CH_{2} \end{array} \xrightarrow{Alcoholic OH^{-1}} \\ & H & \\ & CH_{3} \longrightarrow \begin{array}{c} & CH = CH_{2} + H_{2}O + Br^{-1} \end{array}$$

> Nitration of benzene:



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