Unit: 12 Basic Concepts of Organic reactions

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

(a) 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 structures (canonical structures) and this phenomenon is called resonance.

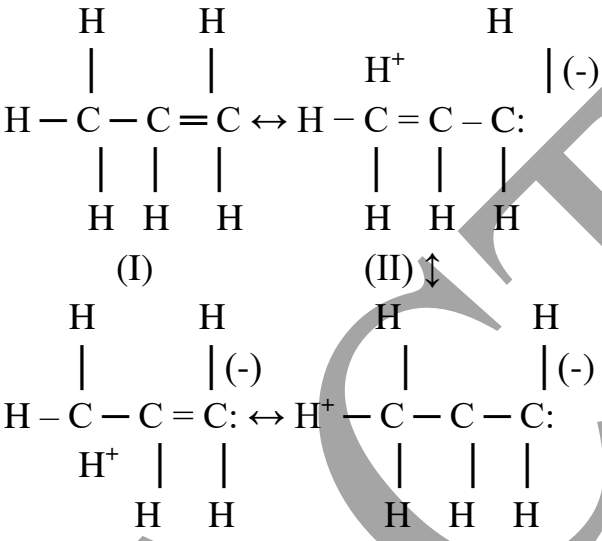
$H_2C = CH - CH = CH_2 \leftrightarrow H_2C_+ - CH = CH - {}_-CH_2 \leftrightarrow H_2C_- - CH = CH - {}_+CH_2$

1,3-BUTADIENE

b) Hyper conjugation :

- The delocalisation of electrons of **σ** bond is called as hyper conjugation.

It is a special stabilising effect that results due to the interaction of electrons of a **σ**-bond (usually **C-H** or **C-C**) with the adjacent, empty non-bonding p-orbital or an antibonding **σ*** or **π*-**orbitals resulting in an extended molecular orbital. Unlike electromeric effect, hyper conjugation is a permanent effect. In propene, the σ-electrons of C-H bond of methyl group can be delocalized into the π-orbital of doubly bonded carbon as represented below.



(I) (II) ↕

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

Nucleophiles:

Phile means affinity: Nucleophile means nucleus loving species ie species which that are attracted towards positive charge. Nucleophiles are electron rich species. They may be neutral, or negatively charged. Neutral nucleophiles possess one or more lone pair of electrons. All lewis bases are nucleophiles.

Neutral Nucleophiles: NH_3, RNH_2, R_2NH and R_3N

Negatively Charged Nucleophiles: Cl^-, Br^-, CN^-

Electrophiles: Electron

Electrophiles means : electron loving species ie species which that are attracted towards negative charge. Electrophiles are electron deficient species. They may be neutral, or positively charged. Neutral electrophiles possess electron deficient centre. All Lewis acids are Electrophiles.

Neutral Electrophiles : $AlCl_3$, BF_3 and $FeCl_3$

Positively charged electrophiles: R^+, H^+, RX, H_3O^+, NO^+, etc.,

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

(i) CH_3 - Br + KOH →

(ii) CH_3 - OCH_3 + HI →

(i) CH_3 - Br + KOH → CH_3 – OH + KBr

Methyl bromide Methanol

OH^- from KOH is the nuclephile.

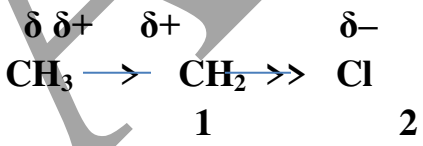
(ii) CH_3 – O - CH_3 + HI → CH_3I + CH_3OH

Dimethyl ether Methyl iodide Methanol

I from HI acts as a nucleophile

19. Explain inductive effect with suitable example.

- Inductive effect is defined as the change in the polarisation of a covalent bond due to the presence of adjacent bonds, atoms or groups in the molecule. This is a permanent phenomenon.
- Let us explain the inductive effect by considering ethane and ethyl chloride as examples. 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 electron between C-Cl in ethyl chloride towards itself. This develops a slight negative charge on chlorine and a 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.
- This effect is greatest for the adjacent bonds, but they also be felt farther away. However, the magnitude of the charge separation decreases rapidly, as we move away from C1 and is observed maximum for 2 carbons and almost insignificant after 4 bonds from the active group.

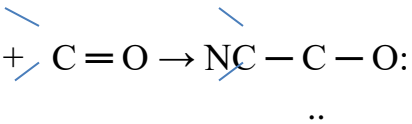


- It is important to note that the inductive effect does not transfer electrons from one atom to another but the displacement effect is permanent. The inductive effect represents the ability of a particular atom or a group to either withdraw or donate electron density to the attached carbon. Based on this ability the substituents are classified as +I groups and –I groups. Their ability to release or withdraw the electron through sigma covalent bond is called +I effect and -I effect respectively.

20. Explain electromeric effect.

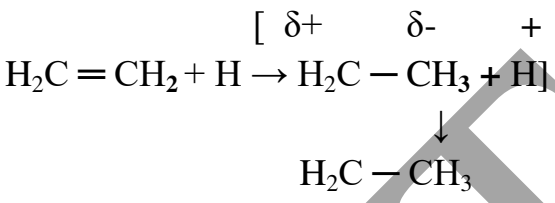
Electromeric effect (E) : Electromeric is a temporary effect which operates in unsaturated compounds (containing >C=C<, >C=O, etc...) in the presence of an attacking reagent. Let us consider two different compounds

(i) compounds containing carbonyl group (>C=O) : 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.

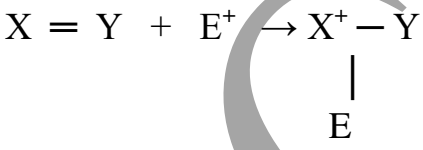


(ii) unsaturated compounds such as alkenes (>C=C<) :

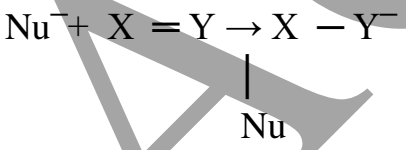
when an electrophile such as H+ approaches an alkene molecule, the **π electrons** are instantaneously shifted to the electrophile and a new bond is formed between carbon and hydrogen. This makes the other carbon electron deficient and hence it acquires a positive charge.



When the **π** electron is transferred towards the attacking reagent, it is called + E (positive electromeric) effect.



When the **π** electron is transferred away from the attacking reagent, it is called, -E (negative electromeric) effect



21. Give examples for the following types of organic reactions

(i) β – elimination (ii) electrophilic

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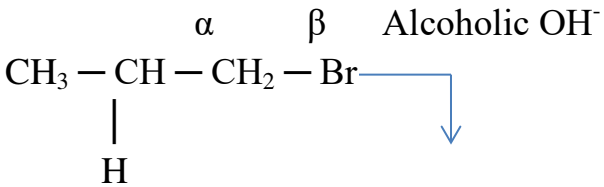

$$CH_3 - CH = CH_2 + H_2O + Br^-$$

(ii) electrophilic:

NO_2

$+ H_2O$