Chapter – 12

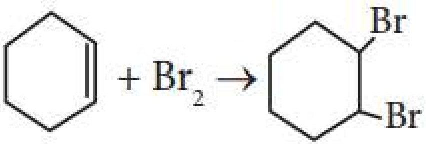
Basic Concepts of Organic Reactions

Textbook Evaluation:

I. Choose the best answer:

Question 1.
For the following reactions
(A) $CH_3CH_2CH_2Br + KOH \rightarrow CH_3 - CH = CH_2 + KBr + H_2O$

(B) $(CH_3)_3CBr + KOH \rightarrow (CH_3)_3COH + KBr$

(C)


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

Answer:
d) (A) is elimination, (B) is substitution and (C) is addition reaction

Question 2.
What is the hybridisation state of benzyl carbonium ion?
a) sp^2
b) spd^2
c) sp^3
d) sp^2d

Answer:
a) sp^2

Question 3.
Decreasing order of nucleophilicity is
a) $OH^- > NH_2^- > -OCH_3 > RNH_2$
b) $NH_2^- > OH^- > -OCH3 > RNH_2$
c) $NH_2^- > CH_3O^- > OH^- > RNH_2$
d) $CH_3O^- > NH_2^- > OH^- > RNH_2$

Answer:
b) $NH_2^- > OH^- > -OCH3 > RNH_2$

Question 4.
Which of the following species is not electrophilic in nature?
a) Cl^+
b) BH_3
c) H_3O^+
d) $^+NO_2$

Answer:
c) H_3O^+

Question 5.
Homolytic fission of covalent bond leads to the formation of
a) electrophile
b) nucleophile
c) carbocation
d) free radical

Answer:
d) free radical

Question 6.
Hyper conjucation is also known as
a) no bond resonance
b) Baker – nathan effect
c) both (a) and (b)
d) none of these

Answer:
c) both (a) and (b)

Question 7.

Which of the group has highest + I effect?

a) CH_3-

b) $CH_3 - CH_2 -$

c) $(CH_3)_2 - CH-$

d) $(CH_3)_3 - C -$

Answer:

d) $(CH_3)_3 - C -$

Question 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) $C_6H_5NH_3$

Answer:

d) $C_6H_5NH_3$

Question 9.

– I effect is shown by

a) – Cl

b) – Br

c) both (a) and (b)

d) $- CH_3$

Answer:

c) both (a) and (b)

Question 10.

Which of the following carbocation will be most stable?

a) $Ph_3{}^+C -$

b) $CH_3 - {}^+CH_2 -$

c) $(CH_3)_2 - {}^+CH$

d) $CH_2 = CH - {}^+CH_2$

Answer:

d) $CH_2 = CH - {}^+CH_2$

Question 11.

Assertion:

Tertiary Carbocations are generally formed more easily than primary Carbocations ions.

Reason:

Hyper conjucation as well as inductive effect due to additional alkyl group stabilize tertiary carbonium ions.

a) both assertion and reason are 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.

Answer:

a) both assertion and reason are true and reason is the correct explanation of assertion.

Question 12.

Heterolytic fission of C – Br bond results in the formation of

a) free radical

b) Carbanion

c) Carbocation

d) Carbanion and Carbocation

Answer:

d) Carbanion and Carbocation

Question 13.

Which of the following represent a set of nucleophiles?

a) BF_3, H_2O, NH^{2-}

b) $AlCl_3$, BF_3, NH_3

c) CN, RCH_2^-, ROH

d) H^+, RNH_3^+, $:CCl_2$

Answer:

c) CN, RCH_2^-, ROH

Question 14.
Which of the following species does not acts as a nucleophile?
a) ROH
b) ROR
c) PCl_3
d) BF_3

Answer:
d) BF_3

Question 15.
The geometrical shape of carbocation is
a) Linear
b) tetrahedral
c) Planar
d) Pyramidal

Answer:
c) Planar

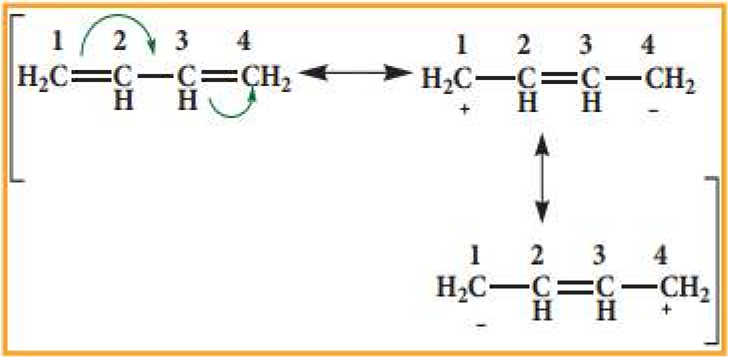
II. Write brief answer to the following questions:

Question 16.
Write short notes on
a) Resonance
b) Hyper Conjucation

Answer:
a) Resonance (or) Mesomeric effect:
The resonance is a chemical phenomenon which is observed in certain organic compounds possessing double bonds at a suitable position. 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. This phenomenon is also called mesomerism or mesomeric effect.

For example, the structure of aromatic compounds such as benzene and conjugated systems like 1,3 – butadiene cannot be represented by a single structure, and their, observed properties can be explained on the basis of a resonance hybrid.

In 1,3 butadiene, it is expected that the bond between $C^1 – C^2$ and $C^3 – C^4$ should be shorter than that of $C^2 – C^3$, but the observed bond lengths are of same. This property cannot be explained by a simple structure in which two n bonds localised between $C^1 – C^2$ and $C^3 – C^4$. Actually, the n electrons are delocalised as shown below.



The resonating structures are called canonical forms and the actual structure lies between these three resonating structures, and is called a resonance hybrid. The resonance hybrid is represented as below.


$H_2C{\cdots}\underset{H}{C}{\cdots}\underset{H}{C}{\cdots}CH_2$

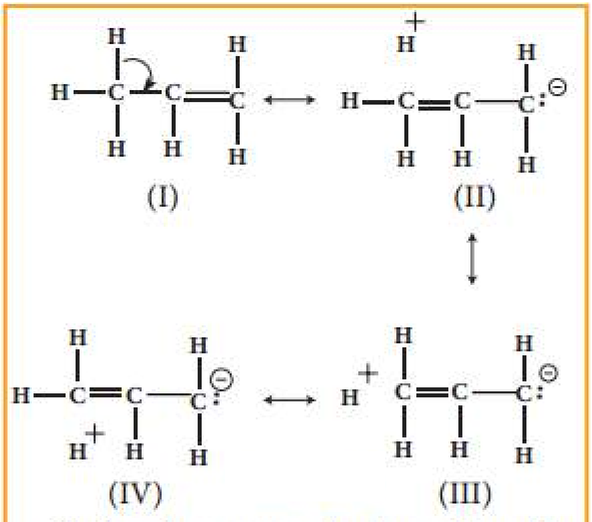
Similar to the other electron displacement effect, mesomeric effect is also classified into positive mesomeric effect (+M or +R) and negative mesomeric effect (-M or -R) based on the nature of the functional group present adjacent to the multiple bond.

b) Hyper Conjucation:

The delocalisation of electrons of a 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 anti¬bonding σ* or π*-orbitals resulting in an extended molecular orbital. Unlike electromeric effect, hyper conjugation is a permanent effect.

It requires an α-CH group or a lone pair on atom like N, O adjacent to a π bond (sp^2 hybrid carbon). It occurs by the overlapping of the σ-bonding orbitai or the orbital containing a lone pair with the adjacent π-orbital or p-orbital.

Example:
In propene, the σ -electrons of C-H bond of methyl group can be delocalised into the π -orbital of doubly bonded carbonas represented below.



No bond resonance structures shown by propene are due to hyperconjugation

In the above structure the sigma bond is involved in resonance and breaks in order to supply electrons for delocalization giving rise to 3 new canonical forms. In the contributing canonical structures: (Il), (III) & (IV) of propene, there is no bond between an α-carbon and one of the hydrogen atoms. Hence the hyper conjugation is also known as “no bond resonance” or “Baker Nathan effect”. The structures (II), (III) & (IV) are polar in nature.

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

Answer:
Nucleophiles are reagents that has high affinity for electron positive centers. They possess an atom has an unshared pair of electrons, and hence it is in search for an electro positive centre where it can have an opportunity to share its electrons to form a covalent bond, and gets stabilised. They are usually negatively charged ions or electron rich neutral molecules (contains one or more lone pair of electrons). All Lewis bases act as nucleophiles.

Example :
Ammonia(NH_3) and amines (RNH_2), water (H_2O), alcohols (ROH) and ethers ((R-O-R)

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. All Lewis acids acts as electrophiles. Neutral molecules like SnCl4 can also act as an electrophile, as it has vacant d – orbitals which can accommodate the electrons from others.

Example:
Carbon dioxide (CO_2), dichlorocarbene (: CCl_2), Aluminium chloride ($AlCl_3$), boron trifluoride (BF_3) and Ferric Chloride ($FeCl_3$)

Question 18.
Show the heterolysis of covalent bond by using curved arrow notation and complete the following equations. Identify the nucelophile in each case.
i) $CH_3 – Br + KOH \rightarrow$
ii) $CH_3 – O – CH_3 + HI \rightarrow$

Answer:
(i) $CH_3 – Br + KOH \rightarrow$
$CH_3 – Br + KQH \rightarrow CH_3OH + KBr$
Nucleophile is : OH^-

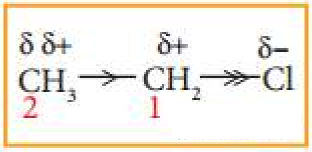
ii) $CH_3 – O – CH_3 + HI \rightarrow$
H I
$CH_3 – O – CH_3 + HI \rightarrow CH_3OH + CH_3 I$
Nucleophile is : I^-

Question 19.
Explain inductive effect with suitable example.

Answer:
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 C_1 draws the shared pair of electron between itself and C_2 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 C_2 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.

Highly electronegative atoms and atoms of groups which are cany a positive charge are electron withdrawing or-I group.
Example :
-F , -Cl, -COOH, $-NO_2$ NH_2

Higher the electronegativity of the substituent, greater is the -I effect. The order of the -I effect of some groups are given below.
$NH_3 > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$

Highly electropositive atoms and atoms are groups which carry a negative charge are electron donating or +1 groups.

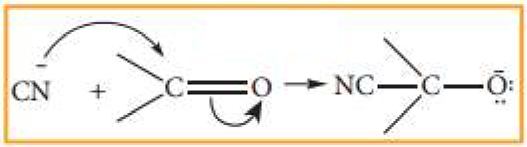
Example:
Alkali metals, alkyl groups such as methyl, ethyl, negatively charged groups such as CH_3O^-, $C_2H_5O^-$, COO^- etc.

Lesser the electronegativity of the elements, greater is the +1 effect. The relative order of +1 effect of some alkyl groups is given below.
$-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3$

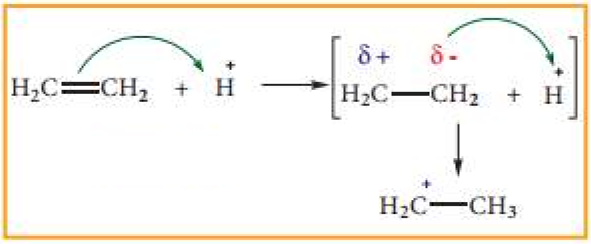
Question 20.
Explain electromeric effect with suitable example.

Answer:
Electromeric is a temporary effect which operates in unsaturated compounds (containing $> C = C <$, $> C = 0$, etc...) in the presence of an attacking reagent. Let us consider two different compounds.
(i) compounds containing carbonyl group ($> C = O$)
(ii) unsaturated compounds such as alkenes ($> C = C <$)

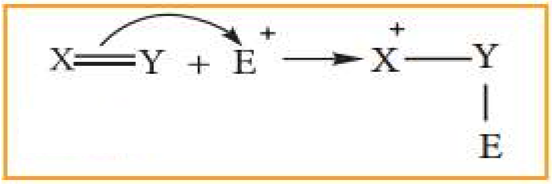
When a nucleophile approaches the carbonyl compound, the n electrons between C and O is instantaneously shifted to the more electronegative oxygen. This makes the carbon electron deficient and thus facilitating the formation of a new bond between the incoming nucleophile and the carbonyl carbon atom.



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.

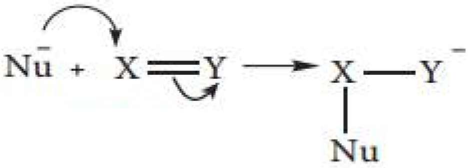


The electrometric effect, is denoted as E effect. Like the inductive effect, the electrometric effect is also classified as + E and – E based on the direction in which the pair of electron is transferred to form a new bond with the attacking agent.



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

The addition of H+ to alkene as shown above is an example of +E effect. When the n electron is transferred away from the attacking reagent, it is called, -E (negative electrometric) effect.



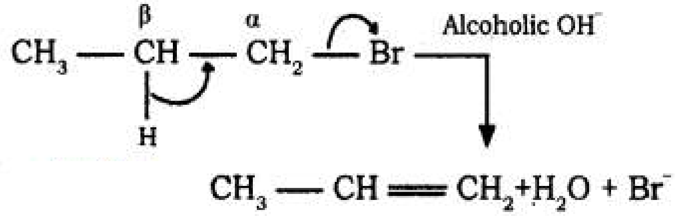
The attack of CN^- on a carbonyl carbon, as shown above, is an example of – E effect.

Question 21.
Give examples for the following types of organic reactions
(i) β – elimination
(ii) Electrophilic substitution

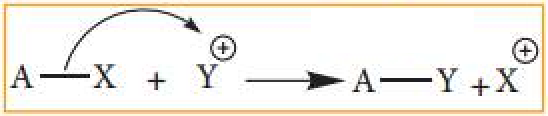
Answer:
(i) β – elimination:
In this reaction two substituents are eliminated from the molecule, and a new C – C double bond is formed between the carbon atoms to which the eliminated atoms/groups are previously attached. Elimination reaction is always accompanied with change in hybridisation.

Example:
n – Propyl bromide on reaction with alcoholic KOH gives propene. In this

reaction hydrogen and Br are eliminated.



(ii) Electrophilic substitution:



Here, Y^+ is an electrophile.

Example :
Nitration of Benzene