



**Otto diels and Kurt Alder** describe an important reaction mechanism for the reaction between a conjugated diene and a substituted alkene. For this work they were awarded nobel prize in chemistry in 1950 Diels - Alder reaction is a powerful tool in synthetic organic chemistry.

### Learning Objectives

After learning this unit, students will be able to

- understand the concept of organic reaction mechanism
- describe homolytic and heterolytic fission of bonds
- identify free radicals, nucleophiles and electrophiles,
- classify organic reactions into substitution, elimination, addition, oxidation and reduction
- describe electron movement in organic reactions
- explain the electronic effects in co-valent bonds

### 12.1 Introduction

A chemical reaction can be treated as a process by which some existing bonds in the reacting molecules are broken and new bonds are formed. i.e., in a chemical reaction, a reactant is converted into a product. This conversion involves one or more steps. A In general an organic reaction can be represented as



Here the substrate is an organic molecule which undergoes chemical change. The reagent which may be an organic, inorganic or any agent like heat, photons etc., that brings about the chemical change

Many chemical reactions are depicted in one or more simple steps. Each step passes through an energy barrier, leading to the formation of short lived intermediates or transition states. The series of simple steps which collectively represent the chemical change, from substrate to product is called as the mechanism of the reaction. The slowest step in the

mechanism determines the overall rate of the reaction.

### 12.1.1 Fundamental concepts in organic reaction mechanism

The mechanism is the theoretical pathway which describes the changes occurring in each step during the course of the chemical change. An organic reaction can be understood by following the direction of flow of electrons and the type of intermediate formed during the course of the reaction. The direction of flow of electron is represented by curved arrow. The movement of a pair of electron is represented by a double headed arrow which starts from the negative and ends with the atom to which the electrons needs to be transferred.

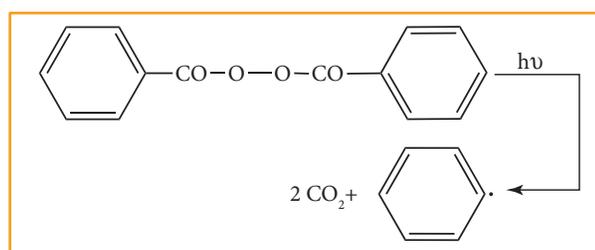
### 12.1.2 Fission of a covalent bond

All organic molecules contain covalent bonds which are formed by the mutual sharing of electrons between atoms. These covalent bonds break in two different ways, namely homolytic cleavage (symmetrical splitting) and heterolytic cleavage (unsymmetrical splitting). The cleavage of a bond in the substrate is influenced by the nature of the reagent (attacking agent).

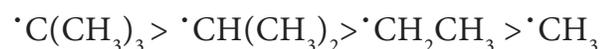
#### Homolytic Cleavage

Homolytic cleavage is the process in which a covalent bond breaks symmetrically in such way that each of the bonded atoms retains one electron. It is denoted by a half headed arrow (fish hook arrow). This type of cleavage occurs under high temperature or in the presence

of UV light in a compound containing non polar covalent bond formed between atoms of similar electronegativity. In such molecules, the cleavage of bonds results into free radicals. They are short lived and are highly reactive. The type of reagents that promote homolytic cleavage in substrate are called as free radical initiators. For example Azobisisobutyronitrile (AIBN) and peroxides such as benzoyl peroxide are used as free radical initiators in polymerisation reactions.



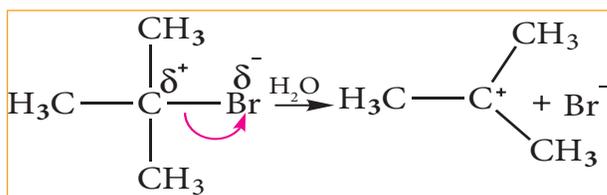
As a free radical with an unpaired electron is neutral and unstable, it has a tendency to gain an electron to attain stability. Organic reactions involve homolytic fission of C-C bonds to form alkyl free radicals. The stability of alkyl free radicals is in the following order



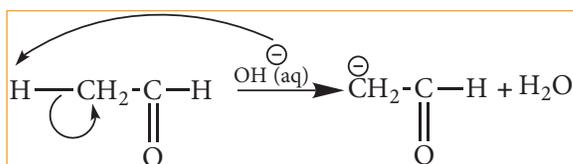
#### Heterolytic Cleavage

Heterolytic cleavage is the process in which a covalent bond breaks unsymmetrically such that one of the bonded atoms retains the bond pair of electrons. It results in the formation of a cation and an anion. Of the two bonded atoms, the most electronegative atom becomes the anion and the other atom becomes the cation. The cleavage is denoted by a curved arrow pointing towards the more electronegative atom.

For example, in tert-butyl bromide, the C-Br bond is polar as bromine is more electronegative than carbon. The bonding electrons of the C-Br bond are attracted more by bromine than carbon. Hence, the C-Br undergoes heterolytic cleavage to form a tert-butyl cation during hydrolysis.



Let us consider the cleavage in a carbon-hydrogen (C-H) bond of aldehydes or ketones. We know that the carbon is more electronegative than hydrogen and hence the heterolytic cleavage of C-H bonds results in the formation of carbanion (carbon bears a negative charge). For example in aldol condensation the  $\text{OH}^-$  ion abstracts a  $\alpha$ -hydrogen from the aldehyde, which leads to the formation of the below mentioned carbanion.



### Hybridisation of carbon in carbocation:

In a carbocation, the carbon bearing positive charge is  $\text{sp}^2$  hybridised and hence it has a planar structure. In the reaction involving such a carbocation, the attack of a negatively charged species (nucleophiles) take place on either side of the carbocation as shown below.

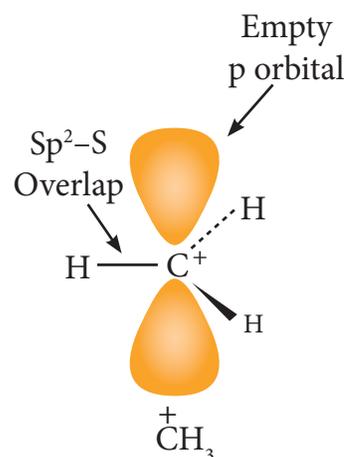


Fig 12.1(a) Shape of Carbocation

The carbanions are generally pyramidal in shape and the lone pair occupies one of the  $\text{sp}^3$  hybridised orbitals. An alkyl free radical may be either pyramidal or planar.

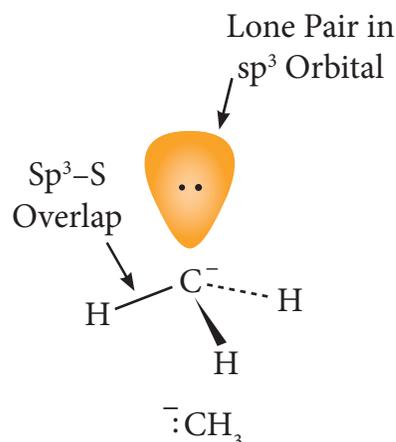


Fig 12.1(b) Shape of Carbanion

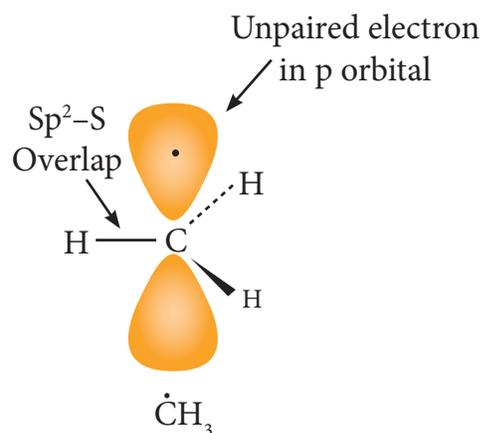
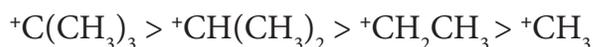


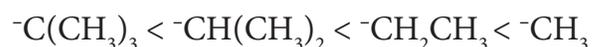
Fig 12.1(c) Shape of Carbon radical

The relative stability of the alkyl carbocations and carbanions are given below.

Relative stability carbocations.



relative stability of carbanions



The energy required to bring about homolytic splitting is greater than that of heterolytic splitting.

### 12.1.3 Nucleophiles and electrophiles

Nucleophiles are reagents that has high affinity for electro 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.

Types	Examples	Electron rich site
Neutral molecules having unshared pair of electron	Ammonia ( $\text{NH}_3$ ) and amines ( $\text{RNH}_2$ )	N:
	Water ( $\text{H}_2\text{O}$ ), alcohols ( $\text{ROH}$ ) and ethers ( $\text{R-O-R}$ )	:O:
	Hydrogen sulphide ( $\text{H}_2\text{S}$ ) and thiols ( $\text{RSH}$ )	:S:
Negatively charged nucleophiles	Chlorides ( $\text{Cl}^-$ ), bromides ( $\text{Br}^-$ ) and iodides ( $\text{I}^-$ )	$\text{X}^-$
	Hydroxide ( $\text{HO}^-$ ), alkoxide ( $\text{RO}^-$ ) and Carboxlate ions ( $\text{RCOO}^-$ )	$\text{O}^-$
	Cyanide ( $\text{CN}^-$ )	$\text{N}^-$

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 act as electrophiles. Neutral molecules like  $\text{SnCl}_4$  can also act as an electrophile, as it has vacant d-orbitals which can accommodate the electrons from others.

Types	Examples	Electron deficient entity
Neutral electrophiles	Carbon dioxide ( $\text{CO}_2$ ), dichlorocarbene ( $:\text{CCl}_2$ )	C
	Aluminium chloride ( $\text{AlCl}_3$ ), boron trifluoride ( $\text{BF}_3$ ) and ferric chloride ( $\text{FeCl}_3$ )	Metal (M)
Positively charged electrophiles	Carbocations ( $\text{R}^+$ )	$\text{C}^+$
	Proton ( $\text{H}^+$ )	$\text{H}^+$
	Alkyl halides ( $\text{RX}$ )	$\text{X}^+$
	Nitrosonium ion ( $\text{NO}^+$ )	$\text{O}^+$
	Nitronium ion ( ${}^+\text{NO}_2$ )	$\text{N}^+$

**DO YOU KNOW?**

Human body produces free radicals when it is exposed to x-rays, cigarette smoke, industrial chemicals and air pollutants. Free radicals can disrupt cell membranes, increase the risk of many forms of cancer, damage the interior lining of blood vessels and lead to a high risk of heart disease and stroke. Body uses vitamins and minerals to counter the effects of free radicals. Fruits contains antioxidants which decrease the effects of free radicals.

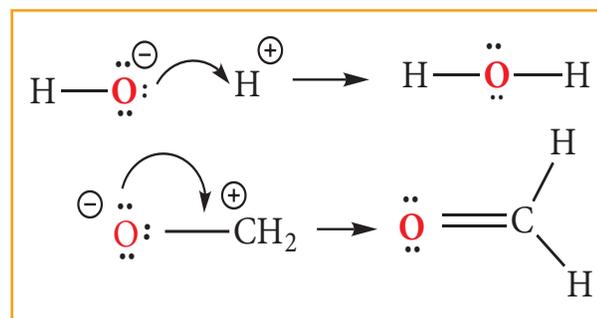
#### 12.1.4 Electron movement in organic reactions

All organic reactions can be understood by following the electron movements, i.e. the electron redistribution during the reaction. The electron movement depends on the nature of the substrate, reagent and the prevailing conditions. The flow of electrons is represented by curved arrows which show how electrons move as shown in the figure. These electron movements result in breaking or formation of a bond (sigma or pi bond). The movement of single electron is indicated by a half-headed curved arrows.

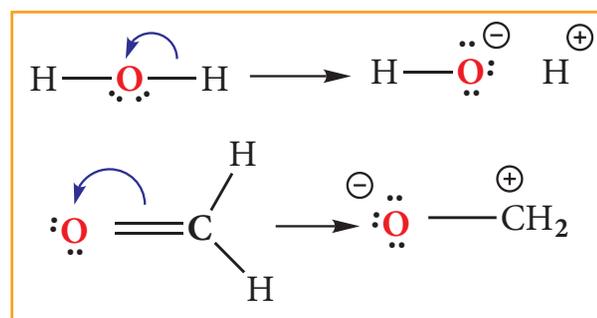
There are three types of electron movement viz.,

- lone pair becomes a bonding pair.
- bonding pair becomes a lone pair
- a bond breaks and becomes another bond.

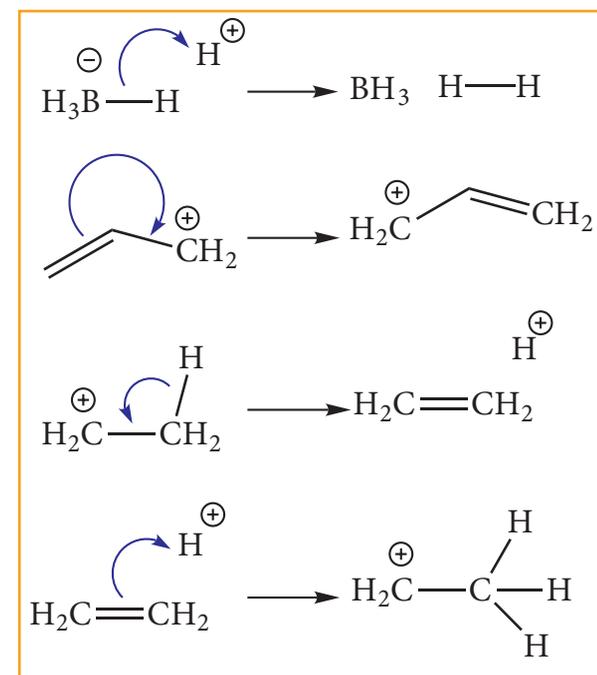
#### Type 1: A lone pair to a bonding pair



#### Type 2: A bonding pair to a lone pair



#### Type 3: A bonding pair to an another bonding pair



#### 12.1.5 Electron displacement effects in co-valent bonds

Some of the properties of organic molecules such as stability, reactivity,



such as methyl, ethyl, negatively charged groups such as  $\text{CH}_3\text{O}^-$ ,  $\text{C}_2\text{H}_5\text{O}^-$ ,  $\text{COO}^-$  etc

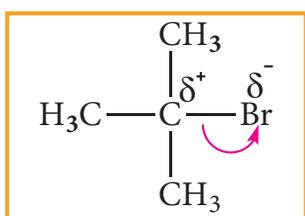
Lesser the electronegativity of the elements, greater is the +I effect. The relative order of +I effect of some alkyl groups is given below



Let us understand the influence of inductive effect on some properties of organic compounds.

### Reactivity:

When a highly electronegative atom such as halogen is attached to a carbon then it makes the C-X bond polar. In such cases the -I effect of halogen facilitates the attack of an incoming nucleophile at the polarised carbon, and hence increases the reactivity.



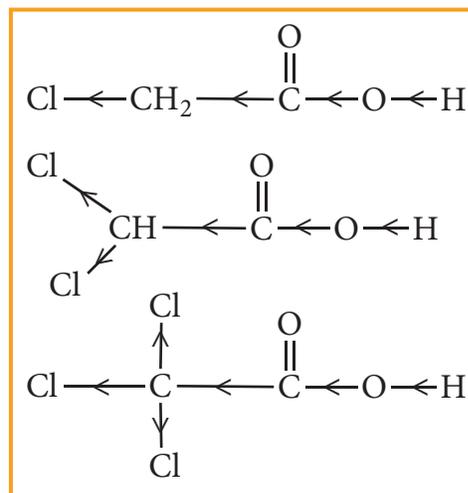
If a -I group is attached nearer to a carbonyl carbon, it decreases the availability of electron density on the carbonyl carbon, and hence increases the rate of the nucleophilic addition reaction.

### Acidity of carboxylic acids:

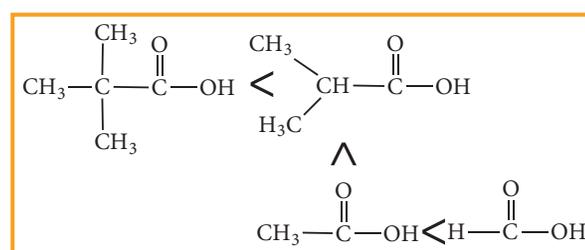
When a halogen atom is attached to the carbon which is nearer to the carboxylic acid group, its -I effect withdraws the bonded electrons towards itself and makes the ionisation of  $\text{H}^+$  easy. The acidity of various chloro acetic acid is in the following order. The strength of the acid increases with increase in the -I effect of the group attached

to the carboxyl group.

Trichloro acetic acid > Dichloro acetic acid > Chloro acetic acid > acetic acid



Similarly, the following order of acidity in the carboxylic acids is due to the +I effect of alkyl group.



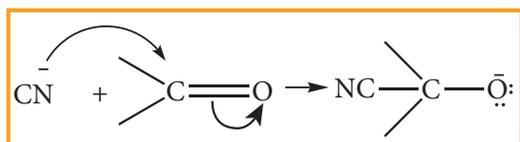
### Electromeric effect (E)

Electromeric is a temporary effect which operates in unsaturated compounds (containing  $>\text{C}=\text{C}<$ ,  $>\text{C}=\text{O}$ , etc...) in the presence of an attacking reagent.

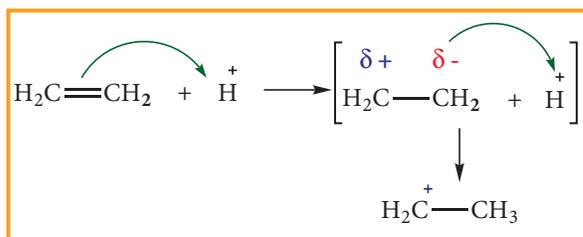
Let us consider two different compounds (i) compounds containing carbonyl group ( $>\text{C}=\text{O}$ ) and (ii) unsaturated compounds such as alkenes ( $>\text{C}=\text{C}<$ ).

When a nucleophile approaches the carbonyl compound, the  $\pi$  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.

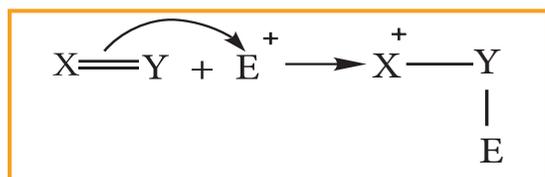


On the other hand when an electrophile such as  $H^+$  approaches an alkene molecule, the  $\pi$  electrons are instantaneously shifted to the electrophile and a new bond is formed between carbon and hydrogen. This makes the other carbon electron deficient and hence it acquires a positive charge.



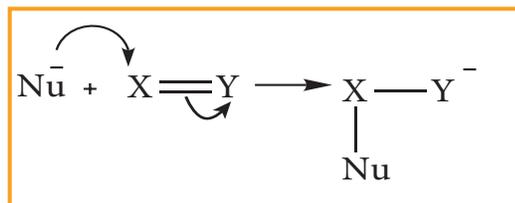
The electromeric effect, is denoted as E effect. Like the inductive effect, the electromeric effect is also classified as +E and -E based on the direction in which the pair of electron is transferred to form a new bond with the attacking agent.

When the  $\pi$  electron is transferred towards the attacking reagent, it is called +E (positive electromeric) effect.



The addition of  $H^+$  to alkene as shown above is an example of +E effect.

When the  $\pi$  electron is transferred away from the attacking reagent, it is called, -E (negative electromeric) effect



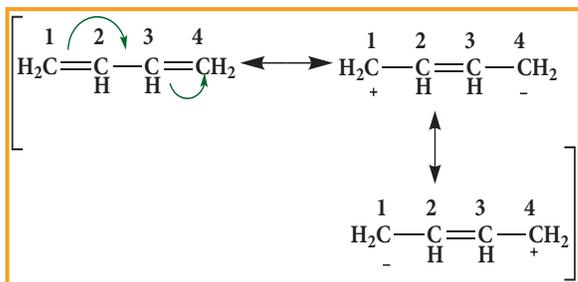
The attack of  $CN^-$  on a carbonyl carbon, as shown above, is an example of -E effect.

### 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 buta diene, 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  $\pi$  bonds localised between  $C^1-C^2$  and  $C^3-C^4$ . Actually the  $\pi$  electrons are delocalised as shown below.



These 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.



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.

### Positive Mesomeric Effect:

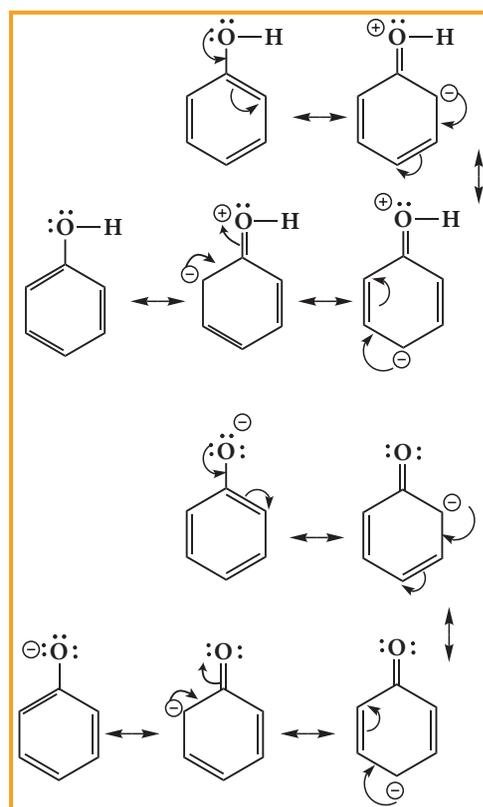
Positive resonance effect occurs, when the electrons move away from substituent attached to the conjugated system. It occurs, if the electron releasing substituents are attached to the conjugated system. In such cases, the attached group has a tendency to release electrons through resonance. These electron releasing groups are usually denoted as +R or +M groups. **Examples :** -OH, -SH, -OR, -SR, -NH<sub>2</sub>, -O- etc.

### Negative Mesomeric Effect

Negative resonance effect occurs, when the electrons move towards the substituent attached to the conjugated system. It occurs if the electron withdrawing

substituents are attached to the conjugated system. In such cases, the attached group has a tendency to withdraw electrons through resonance. These electron withdrawing groups are usually denoted as -R or -M groups. **Examples :** NO<sub>2</sub>, >C=O, -COOH, -C≡N etc

Resonance is useful in explaining certain properties such as acidity of phenol. The phenoxide ion is more stabilised than phenol by resonance effect (+M effect) and hence resonance favours ionisation of phenol to form H<sup>+</sup> and shows acidity.



The above structures shows that there is a charge separation in the resonance structure of phenol which needs energy, whereas there is no such hybrid structures in the case of phenoxide ion. This increased stability accounts for the acidic character of phenol.

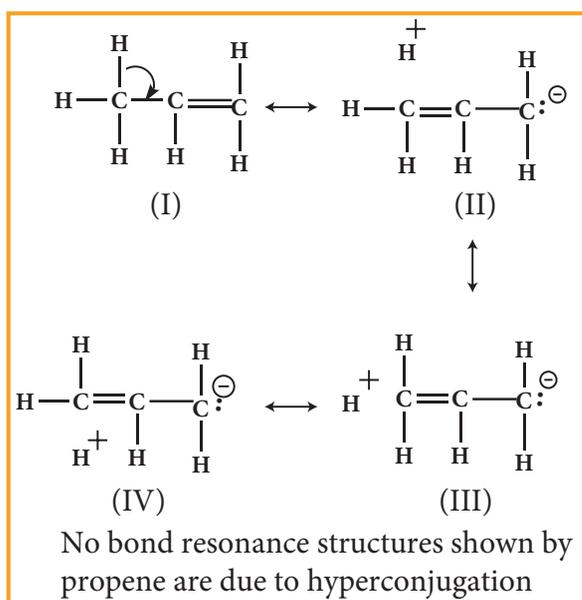
## Hyper conjugation

The delocalisation of electrons of  $\sigma$  bond is called as hyper conjugation. It is a special stabilising effect that results due to the interaction of electrons of a  $\sigma$ -bond (usually C-H or C-C) with the adjacent, empty non-bonding p-orbital or an anti-bonding  $\sigma^*$  or  $\pi^*$ -orbitals resulting in an extended molecular orbital. Unlike electromeric effect, hyper conjugation is a permanent effect.

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

### Example 1:

In propene, the  $\sigma$ -electrons of C-H bond of methyl group can be delocalised into the  $\pi$ -orbital of doubly bonded carbon as represented below.

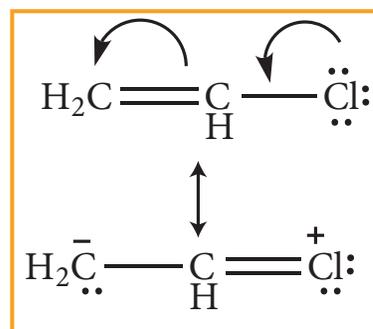


In the above structure the sigma bond is involved in resonance and breaks in

order to supply electrons for delocalisation giving rise to 3 new canonical forms. In the contributing canonical structures: (II), (III) & (IV) of propene, there is no bond between an  $\alpha$ -carbon and one of the hydrogen atoms. Hence the hyperconjugation is also known as “no bond resonance” or “Baker-Nathan effect”. The structures (II), (III) & (IV) are polar in nature.

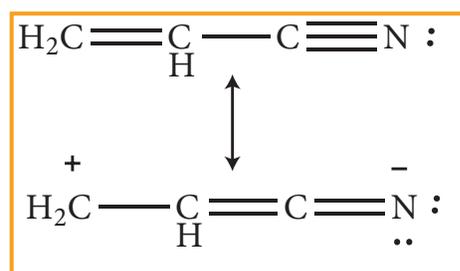
### Example 2:

Hyper conjugation effect is also observed when atoms / groups having lone pair of electrons are attached by a single bond, and in conjugation with a  $\pi$  bond. The lone pair of electrons enters into resonance and displaces  $\pi$  electrons resulting in more than one structure



### Example 3:

When electronegative atoms or group of atoms are in conjugation with a  $\pi$ -bond, they pull  $\pi$ -electrons from the multiple bond.



In case of carbocations, greater the number of alkyl groups attached to the

carbon bearing positive charge, greater is number of the hyper conjugate structure. thus the stability of various carbocations decreases in the order

$3^\circ$  Carbocation >  $2^\circ$  Carbocation >  $1^\circ$  Carbocation

## 12.2 Different types of organic reactions

Organic compounds undergo many number of reactions, however in actual sense we can fit all those reactions into the below mentioned six categories.

- Substitution reactions
- Addition reactions
- Elimination reactions
- Oxidation and reduction reactions
- Rearrangement reactions
- Combination of the above

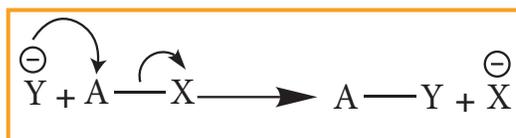
### 12.2.1 Substitution reaction (Displacement reaction)

In this reaction an atom or a group of atoms attached to a carbon atom is replaced by a new atom or a group of atoms. Based on the nature of the attacking reagent, this reactions can be classified as

- Nucleophilic substitution
- Electrophilic substitution
- Free radical substitution

#### Nucleophilic substitution:

This reaction can be represented as



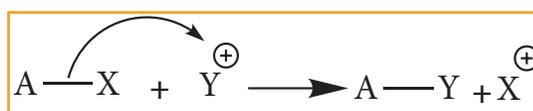
Here  $Y^-$  is the incoming nucleophile or attacking species and  $X^-$  is the leaving group.

Example: Hydrolysis of alkyl halides



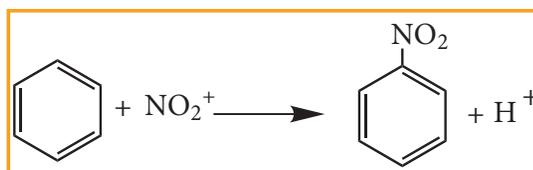
Aliphatic nucleophilic substitution reactions take place either by  $S_N1$  or  $S_N2$  mechanism. Detailed study of the mechanisms is given in unit 14.

#### Electrophilic Substitution



Here  $Y^+$  is an electrophile

#### Example: Nitration of Benzene



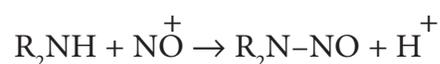
Mechanism of aromatic electrophilic substitution reactions (EAS) is discussed in detail in unit 13.

#### Free radical substitution



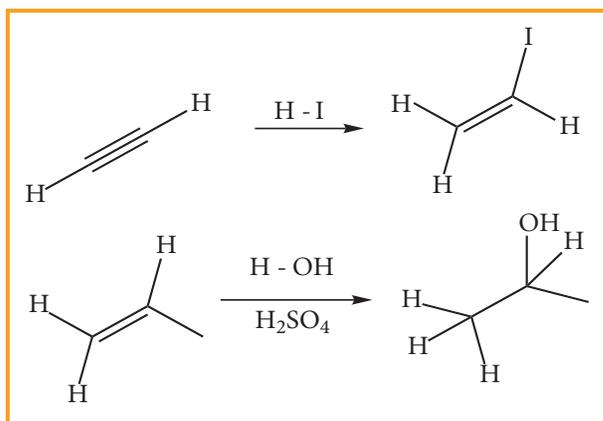
#### Aliphatic electrophilic substitution

A general aliphatic electrophilic substitution is represented as



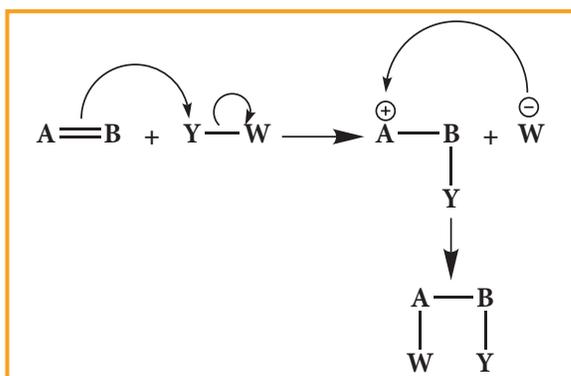
## 12.2.2 Addition reactions

It is a characteristic reaction of an unsaturated compound (compounds containing C-C localised double or triple bond). In this reaction two molecules combine to give a single product. Like substitution this reaction also can be classified as nucleophilic, electrophilic and freeradical addition reactions depending the type of reagent which initiates the reaction. During the addition reaction the hybridisation of the substrate changes (from  $sp^2 \rightarrow sp^3$  in the addition reaction of alkenes or  $sp \rightarrow sp^2$  in the addition reaction of alkynes) as only one bond breaks and two new bonds are formed.

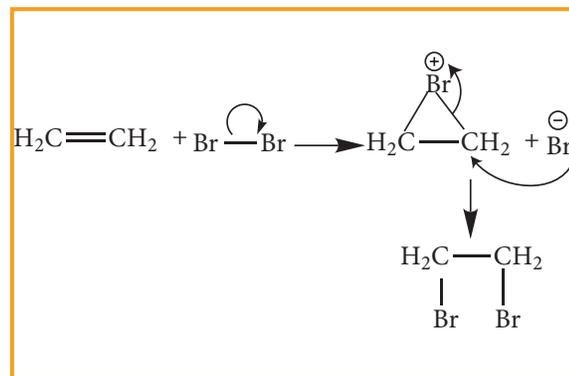


### Electrophilic Addition reaction

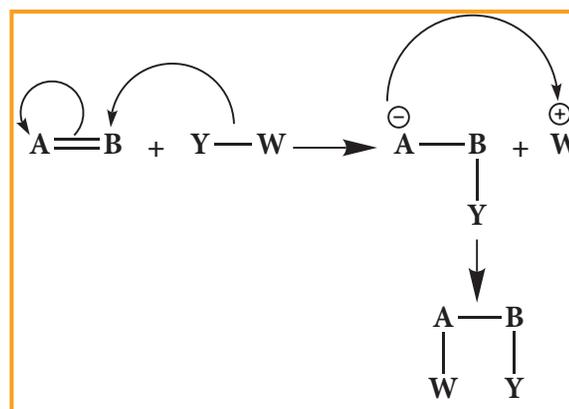
A general electrophilic addition reaction can be represented as below.



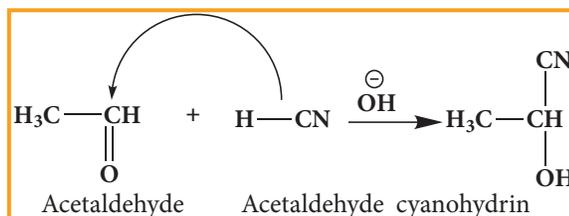
Bromination of alkene to give bromo alkane is an example for this reaction.



### Nucleophilic addition reaction

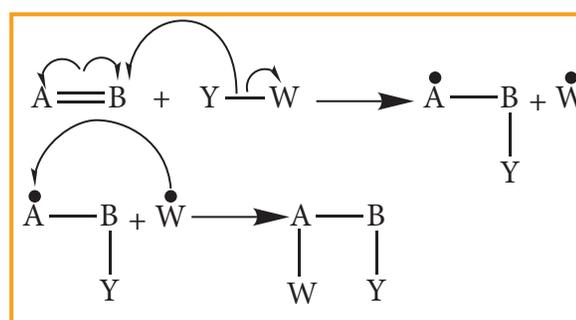


### Example: addition of HCN to acetaldehyde



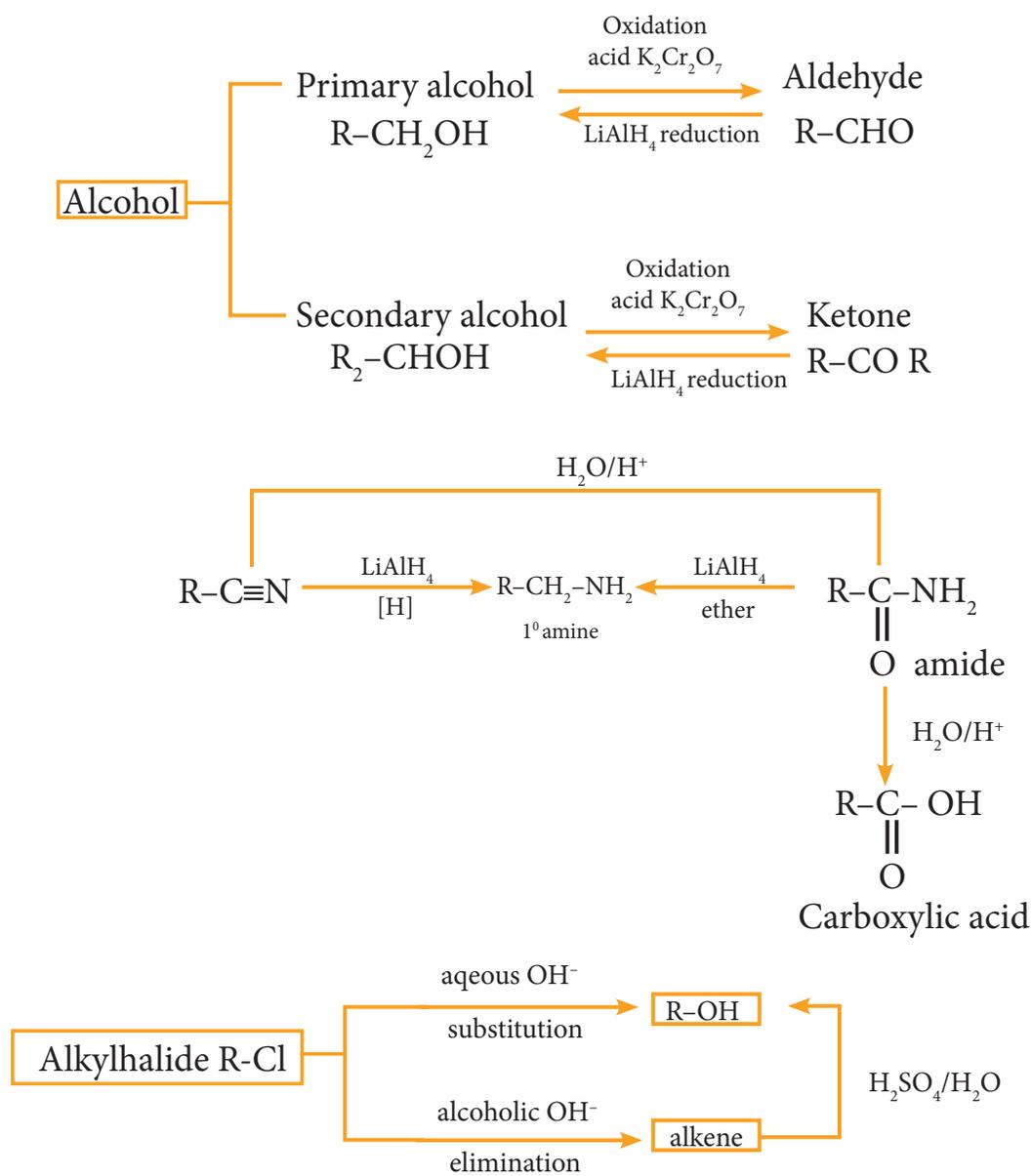
### Free radical addition Reaction:

A General freeradical addition reaction can be represented as below.





Some of the important functional group interconversions of Organic compounds are summarised in the below mentioned Flow chart.

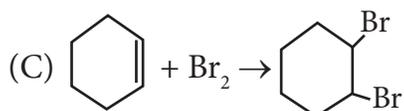
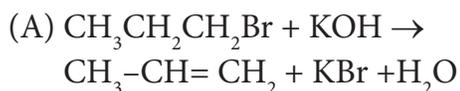


## Evaluation



### I. Choose the best answer.

1. For the following reactions



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)  $\text{sp}^2$  (b)  $\text{sp}^{\text{d}^2}$   
(c)  $\text{sp}^3$  (d)  $\text{sp}^{\text{d}}$
3. Decreasing order of nucleophilicity is
- (a)  $\text{OH}^- > \text{NH}_2^- > \text{OCH}_3^- > \text{RNH}_2$   
(b)  $\text{NH}_2^- > \text{OH}^- > \text{OCH}_3^- > \text{RNH}_2$   
(c)  $\text{NH}_2^- > \text{CH}_3\text{O}^- > \text{OH}^- > \text{RNH}_2$   
(d)  $\text{CH}_3\text{O}^- > \text{NH}_2^- > \text{OH}^- > \text{RNH}_2$
4. Which of the following species is not electrophilic in nature?
- (a)  $\text{Cl}^+$  (b)  $\text{BH}_3$  (c)  $\text{H}_3\text{O}^+$  (d)  $^+\text{NO}_2$

5. Homolytic fission of covalent bond leads to the formation of
- (a) electrophile (b) nucleophile  
(c) Carbo cation (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)  $\text{CH}_3\text{-}$  (b)  $\text{CH}_3\text{-CH}_2\text{-}$   
(c)  $(\text{CH}_3)_2\text{-CH-}$  (d)  $(\text{CH}_3)_3\text{-C-}$
8. Which of the following species does not exert a resonance effect?
- (a)  $\text{C}_6\text{H}_5\text{OH}$  (b)  $\text{C}_6\text{H}_5\text{Cl}$   
(c)  $\text{C}_6\text{H}_5\text{NH}_2$  (d)  $\text{C}_6\text{H}_5\text{NH}_3^+$
9. -I effect is shown by
- (a)  $\text{-Cl}$  (b)  $\text{-Br}$   
(c) both (a) and (b) (d)  $\text{-CH}_3$
10. Which of the following carbocation will be most stable?
- (a)  $\text{Ph}_3\text{C}^+$  (b)  $\text{CH}_3\text{-}\overset{+}{\text{C}}\text{H}_2\text{-}$   
(c)  $(\text{CH}_3)_2\text{-}\overset{+}{\text{C}}\text{H}$  (d)  $\text{CH}_2=\text{CH-}\overset{+}{\text{C}}\text{H}_2$
11. Assertion: Tertiary Carbocations are generally formed more easily than primary Carbocations ions.
- Reason: Hyper conjugation 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
12. Heterolytic fission of C–C bond results in the formation of
- (a) free radical (b) Carbanion
- (c) Carbocation (d) Carbanion and Carbocation
13. Which of the following represent a set of nucleophiles?
- (a)  $\text{BF}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_2^-$
- (b)  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{NH}_3$
- (c)  $\text{CN}^-$ ,  $\text{RCH}_2^-$ ,  $\text{ROH}$
- (d)  $\text{H}^+$ ,  $\text{RNH}_3^+$ ,  $:\text{CCl}_2$
14. Which of the following species does not act as a nucleophile?
- (a)  $\text{ROH}$  (b)  $\text{ROR}$
- (c)  $\text{PCl}_3$  (d)  $\text{BF}_3$
15. The geometrical shape of carbocation is
- (a) Linear (b) tetrahedral
- (c) Planar (d) Pyramidal
- II. Write brief answer to the following questions.**
16. Write short notes on
- (a) Resonance
- (b) Hyperconjugation
17. What are electrophiles and nucleophiles? Give suitable examples for each.
18. Show the heterolysis of covalent bond by using curved arrow notation and complete the following equations. Identify the nucleophile in each case.
- (i)  $\text{CH}_3 - \text{Br} + \text{KOH} \rightarrow$
- (ii)  $\text{CH}_3 - \text{OCH}_3 + \text{HI} \rightarrow$
19. Explain inductive effect with suitable example.
20. Explain electromeric effect.
21. Give examples for the following types of organic reactions
- (i)  $\beta$  - elimination
- (ii) electrophilic substitution.



## CONCEPT MAP

