The name of such branched chain alkyl group is placed in parenthesis while naming the compound. While writing the trivial names of substituents' in alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not considered to be the part of the fundamental name. The use of iso and related common prefixes for naming alkyl groups is also allowed by the IUPAC nomenclature as long as these are not further substituted. In multisubstituted compounds, the following rules may aso be remembered:

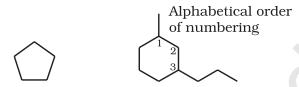
- If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.
- After selection of the chain, numbering is to be done from the end closer to the substituent.

5-(2-Ethylbutyl)-3,3-dimethyldecane [and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]

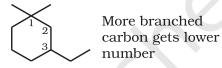
5-sec-Butyl-4-isopropyldecane

5-(2,2-Dimethylpropyl)nonane

Cyclic Compounds: A saturated monocyclic compound is named by prefixing 'cyclo' to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below.



Cyclopentane 1-Methyl-3-propylcyclohexane



3-Ethyl-1,1-dimethylcyclohexane (not 1-ethyl-3,3-dimethylcyclohexane)

Problem 8.7

Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect.

[and not 3,4,7-Trimethyloctane]

3-Ethyl-5-methylheptane [and not 5-Ethyl-3-methylheptane]

Solution

(a) Lowest locant number, 2,5,6 is lower than 3,5,7, (b) substituents are in equivalent position; lower number is given to the one that comes first in the name according to alphabetical order.

8.5.3 Nomenclature of Organic Compounds having Functional Group(s)

A functional group, as defined earlier, is an atom or a group of atoms bonded together in a unique manner which is usually the site of

chemical reactivity in an organic molecule. Compounds having the same functional group undergo similar reactions. For example, $\mathrm{CH_3OH}$, $\mathrm{CH_3CH_2OH}$, and $(\mathrm{CH_3)_2CHOH}$ —all having -OH functional group liberate hydrogen on reaction with sodium metal. The presence of functional groups enables systematisation of organic compounds into different classes. Examples of some functional groups with their prefixes and suffixes along with some examples of organic compounds possessing these are given in Table 8.4.

First of all, the functional group present in the molecule is identified which determines the choice of appropriate suffix. The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain. By using the suffix as given in Table 8.4, the name of the compound is arrived at.

In the case of polyfunctional compounds, one of the functional groups is chosen as the *principal functional group* and the compound is then named on that basis. The remaining functional groups, which are subordinate functional groups, are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of order of preference. **The order of decreasing priority for some functional groups is:**

-COOH, $-SO_3H$, -COOR (R=alkyl group), COCl, -CONH $_2$, -CN,-HC=O, >C=O, -OH, -NH $_2$, > C=C<, -C=C-.

The –R, $\rm C_6H_5$ -, halogens (F, Cl, Br, I), –NO $_2$, alkoxy (–OR) etc. are always prefix substituents. Thus, a compound containing both an alcohol and a keto group is named as hydroxyalkanone since the keto group is preferred to the hydroxyl group.

For example, $\mathrm{HOCH_2(CH_2)_3CH_2COCH_3}$ will be named as 7-hydroxyheptan-2-one and not as 2-oxoheptan -7-ol. Similarly, $\mathrm{BrCH_2CH=CH_2}$ is named as 3-bromoprop-1-ene and not 1-bromoprop-2-ene.

If more than one functional group of the same type are present, their number is indicated by adding di, tri, etc. before the class suffix. In such cases the full name of the parent alkane is written before the class suffix. For example $\mathrm{CH_2}(\mathrm{OH})\mathrm{CH_2}(\mathrm{OH})$ is named as ethane–1,2–diol. However, the ending – ne of the parent alkane is dropped in the case of compounds having more than one double or triple bond; for example, $\mathrm{CH_2}$ =CH-CH=CH₂ is named as buta–1,3–diene.

Problem 8.8

Write the IUPAC names of the compounds i-iv from their given structures.

Solution

- The functional group present is an alcohol (OH). Hence the suffix is '-ol'.
- The longest chain containing -OH has eight carbon atoms. Hence the corresponding saturated hydrocarbon is octane.
- The -OH is on carbon atom 3. In addition, a methyl group is attached at 6th carbon.

Hence, the systematic name of this compound is 6-Methyloctan-3-ol.

O O
$$\parallel$$
 \parallel \parallel (ii) $CH_3-CH_2-C-CH_2-C-CH_3$ 6 5 4 3 2 1

Solution

The functional group present is ketone (>C=O), hence suffix '-one'. Presence of two keto groups is indicated by 'di', hence suffix becomes 'dione'. The two keto groups are at carbons 2 and 4. The longest chain contains 6 carbon atoms, hence, parent hydrocarbon is hexane. Thus, the systematic name is Hexane-2,4-dione.

Table 8.4 Some Functional Groups and Classes of Organic Compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alkanes	-	-	-ane	Butane, CH ₃ (CH ₂) ₂ CH ₃
Alkenes	>C=C<	-	-ene	But-1-ene, CH ₂ =CHCH ₂ CH ₃
Alkynes	-C≡C-	-	-yne	But-1-yne, CH≡CCH ₂ CH ₃
Arenes	-	-	-	Benzene,
Halides	-X (X=F,Cl,Br,I)	halo-	-	1-Bromobutane, CH ₃ (CH ₂) ₂ CH ₂ Br
Alcohols	-ОН	hydroxy-	-ol	Butan-2-ol, CH ₃ CH ₂ CHOHCH ₃
Aldehydes	-СНО	formyl, or oxo	-al	Butanal, CH ₃ (CH ₂) ₂ CHO
Ketones	>C=O	oxo-	-one	Butan-2-one, CH ₃ CH ₂ COCH ₃
Nitriles	-C≡N	cyano	nitrile	$\begin{array}{c} {\sf Pentanenitrile,} \\ {\sf CH_3CH_2CH_2CH_2CN} \end{array}$
Ethers	-R-O-R-	alkoxy-		Ethoxyethane, CH ₃ CH ₂ OCH ₂ CH ₃
Carboxylic acids	-соон	carboxy	-oic acid	Butanoic acid, CH ₃ (CH ₂) ₂ CO ₂ H
Carboxylate ions	-COO ⁻	0,	-oate	Sodium butanoate, CH ₃ (CH ₂) ₂ CO ₂ Na ⁺
Esters	-COOR	alkoxycarbonyl	-oate	Methyl propanoate, CH ₃ CH ₂ COOCH ₃
Acyl halides	-COX (X=F,Cl,Br,I)	halocarbonyl	-oyl halide	Butanoyl chloride, CH ₃ (CH ₂) ₂ COCl
Amines	-NH ₂ , >NH,>N-	amino-	-amine	Butan -2-amine , CH ₃ CHNH ₂ CH ₂ CH ₃
Amides	-CONH ₂ , -CONHR, -CONR ₂	-carbamoyl	-amide	Butanamide, CH ₃ (CH ₂) ₂ CONH ₂
Nitro compounds	-NO ₂	nitro	-	1-Nitrobutane, CH ₃ (CH ₂) ₃ NO ₂
Sulphonic acids	−SO ₃ H	sulpho	sulphonic acid	Methylsulphonic acid CH ₃ SO ₃ H

Solution

Here, two functional groups namely ketone and carboxylic acid are present. The principal functional group is the carboxylic acid group; hence the parent chain will be suffixed with 'oic' acid. Numbering of the chain starts from carbon of – COOH functional group. The keto group in the chain at carbon 5 is indicated by 'oxo'. The longest chain including the principal functional group has 6 carbon atoms; hence the parent hydrocarbon is hexane. The compound is, therefore, named as 5-Oxohexanoic acid.

(iv)
$$CH \equiv C - CH = CH - CH = CH_2$$

6 5 4 3 2 1

Solution

The two C=C functional groups are present at carbon atoms 1 and 3, while the C=C functional group is present at carbon 5. These groups are indicated by suffixes 'diene' and 'yne' respectively. The longest chain containing the functional groups has 6 carbon atoms; hence the parent hydrocarbon is hexane. The name of compound, therefore, is Hexa-1,3-dien-5-yne.

Problem 8.9

Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3-Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxyheptanal.

Solution

- (i) 'hexane' indicates the presence of 6 carbon atoms in the chain. The functional group chloro is present at carbon 2. Hence, the structure of the compound is CH₃CH₂CH₂CH₂CH(Cl)CH₃.
- (ii) 'pent' indicates that parent hydrocarbon contains 5 carbon atoms in the chain. 'en' and 'ol' correspond to the functional groups C=C and -OH at carbon atoms 4 and 2 respectively. Thus, the structure is

CH₂=CHCH₂CH (OH)CH₂.

(iii) Six membered ring containing a carbon-carbon double bond is implied by cyclohexene, which is numbered as shown in (I). The prefix 3-nitro means that a nitro group is present on C-3. Thus, complete structural formula of the compound is (II). Double bond is suffixed functional group whereas NO₂ is prefixed functional group therefore double bond gets preference over -NO₂ group:

(iv) '1-ol' means that a -OH group is present at C-1. OH is suffixed functional group and gets preference over C=C bond. Thus the structure is as shown in (II):

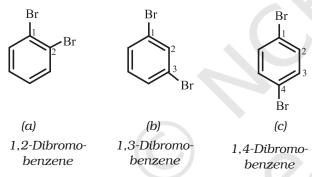
$$\begin{array}{c}
\text{OH} \\
\text{II}
\end{array}$$

(v) 'heptanal' indicates the compound to be an aldehyde containing 7 carbon atoms in the parent chain. The '6-hydroxy' indicates that -OH group is present at carbon 6. Thus, the structural formula of the compound is: CH₃CH(OH) CH₂CH₂CH₂CH₂CHO. Carbon atom of -CHO group is included while numbering the carbon chain.

8.5.4 Nomenclature of Substituted Benzene Compounds

For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word *benzene* as shown in the following examples. However, common names (written in bracket below) of many substituted benzene compounds are also universally used.

If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible. For example, the compound(b) is named as 1,3-dibromobenzene and not as 1.5-dibromobenzene.



In the trivial system of nomenclature the terms *ortho* (*o*), *meta* (*m*) and *para* (*p*) are used as prefixes to indicate the relative positions 1,2;1,3 and 1,4 respectively. Thus, 1,3-dibromobenzene (b) is named as *m*-dibromobenzene (*meta* is abbreviated as *m*-) and the other isomers of dibromobenzene 1,2-(a) and 1,4-(c), are named as *ortho* (or just *o*-) and *para* (or just *p*-)-dibromobenzene, respectively.

For tri - or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound.

Substituent of the base compound is assigned number1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in alphabetical order. Some examples are given below.

$$O_2N$$
 NO_2

1-Chloro-2,4-dinitrobenzene (not 4-chloro,1,3-dinitrobenzene)

2-Chloro-1-methyl-4-nitrobenzene (not 4-methyl-5-chloro-nitrobenzene)

OMe
$$\frac{1}{2}$$
 Cl $\frac{1}{2}$ CH₃ $\frac{2}{2}$ CH₃ $\frac{2}{2}$ CH₃

2-Chloro-4-methylanisole 4-Ethyl-2-methylaniline

3,4-Dimethylphenol

When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is *phenyl* ($\rm C_6H_5$ -, also abbreviated as Ph).

Problem 8.10

Write the structural formula of:

- (a) *o*-Ethylanisole, (b) *p*-Nitroaniline,
- (c) 2,3-Dibromo-1-phenylpentane,
- (d) 4-Ethyl-1-fluoro-2-nitrobenzene.

Solution
$$\begin{array}{c} NH_2 \\ NO_2 \\ NO_3 \\ NO_4 \\ NO_2 \\ NO_2 \\ NO_2 \\ NO_2 \\ NO_3 \\ NO_4 \\ NO_4 \\ NO_5 \\$$

8.6 ISOMERISM

The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. The following flow chart shows different types of isomerism.

8.6.1 Structural Isomerism

Compounds having the same molecular formula but different structures (manners in which atoms are linked) are classified as structural isomers. Some typical examples of different types of structural isomerism are given below:

(i) Chain isomerism: When two or more compounds have similar molecular formula but

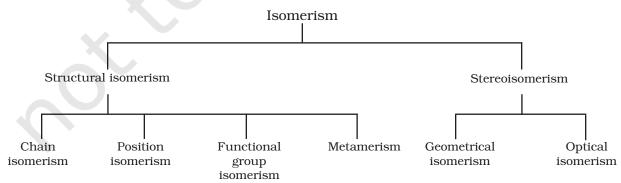
different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C_5H_{12} represents three compounds:

$$\begin{array}{c|c} & CH_3\\ & |\\ CH_3CH_2CH_2CH_2CH_3 & CH_3-CHCH_2CH_3\\ Pentane & Isopentane\\ & (2-Methylbutane)\\ \hline & CH_3\\ & |\\ CH_3-C-CH_3\\ & |\\ & CH_3\\ \hline & CH_3\\ & Neopentane\\ & (2,2-Dimethylpropane)\\ \end{array}$$

(ii) Position isomerism: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula C_3H_8O represents two alcohols:

$$\begin{array}{c} & \text{OH} \\ | \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} & \text{CH}_3\text{-CH-CH}_3 \\ \\ \text{Propan-1-ol} & \text{Propan-2-ol} \end{array}$$

(iii) Functional group isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism. For example, the molecular formula C_3H_6O represents an aldehyde and a ketone:



$$\begin{array}{ccc} & & & & H \\ \parallel & & & \mid \\ CH_3-C-CH_3 & & CH_3-CH_2-C=O \\ & & Propanone & Propanal \end{array}$$

(iv) Metamerism: It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane $(CH_3OC_3H_7)$ and ethoxyethane $(C_9H_5OC_9H_5)$.

8.6.2 Stereoisomerism

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This special type of isomerism is called as stereoisomerism and can be classified as *geometrical* and optical *isomerism*.

8.7 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s)

The general reaction is depicted as follows:

$$\begin{array}{c} \text{Attacking} \\ \text{Organic} \xrightarrow{\text{Reagent}} [\text{Intermediate}] \longrightarrow \text{Product(s)} \\ \text{molecule} \\ \text{(Substrate)} \end{array}$$

Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called *substrate*.

In such a reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism. The knowledge of reaction mechanism helps

in understanding the reactivity of organic compounds and in planning strategy for their synthesis.

In the following sections, we shall learn some of the principles that explain how these reactions take place.

8.7.1 Fission of a Covalent Bond

A covalent bond can get cleaved either by : (i) **heterolytic cleavage**, or by (ii) **homolytic cleavage**.

In *heterolytic cleavage*, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

After heterolysis, one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give $\dot{C}H_3$ and Br^- as shown below.

$$H_3C \stackrel{\frown}{-} Br \longrightarrow H_3^{\dagger}C + Br^{\dagger}$$

A species having a carbon atom possessing sextext of electrons and a positive charge is called a carbocation (earlier called carbonium ion). The CH₃ ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Some other examples of carbocations are: CH₃CH₂ (ethyl cation, a primary carbocation), (CH₃)₂CH (isopropyl cation, a secondary carbocation), and (CH₂)₂Č (tert-butyl cation, a tertiary carbocation). Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects, which you will be studying in the sections 8.7.5 and 8.7.9. The observed order of carbocation stability is: $CH_3 < CH_3CH_2 < (CH_3)_2CH < (CH_3)_3C$. These carbocations have trigonal planar shape with positively charged carbon being sp^2 hybridised. Thus, the shape of CH₃ may be considered as being derived from the overlap of three equivalent $C(sp^2)$ hybridised orbitals with 1s orbital of each of the three hydrogen

atoms. Each bond may be represented as $C(sp^2)$ -H(1s) sigma bond. The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons. [Fig. 8.3(a)].

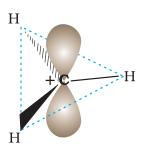


Fig. 8.3(a) Shape of methyl carbocation

The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons. For example, when group Z attached to the carbon leaves without

$$CH_3 \longrightarrow H_3C\overline{:} + Z^+$$

electron pair, the methyl anion (H_3C^-) is

formed. Such a carbon species carrying a negative charge on carbon atom is called *carbanion*. Carbon in carbanion is generally sp³ hybridised and its structure is distorted tetrahedron as shown in Fig. 8.3(b).



Fig. 8.3(b) Shape of methyl carbanion

Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called **ionic** or **heteropolar** or just polar reactions.

In **homolytic cleavage**, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by 'half-headed' (fish hook:)

curved arrow. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called *free radicals*. Like carbocations and carbanions, free radicals are also very reactive. A homolytic cleavage can be shown as:

Alkyl radicals are classified as *primary*, *secondary*, or *tertiary*. Alkyl radical stability increases as we proceed from primary to tertiary:

$$\dot{C} H_3 < \dot{C} H_2 CH_3 < \dot{C} H (CH_3)_2 < \dot{C} (CH_3)_3$$
Methyl Ethyl Isopropyl Tert-butyl free free free free radical radical radical

Organic reactions, which proceed by homolytic fission are called *free radical* or *homopolar* or *nonpolar* reactions.

8.7.2 Substrate and Reagent

Ions are generally not formed in the reactions of organic compounds. Molecules as such participate in the reaction. It is convenient to name one reagent as substrate and other as reagent. In general, a molecule whose carbon is involved in new bond formation is called substrate and the other one is called reagent. When carbon-carbon bond is formed, the choice of naming the reactants as substrate and reagent is arbitrary and depends on molecule under observation. Example:

(i)
$$CH_2 = CH_2 + Br_2 \rightarrow CH_2 Br - CH_2 Br$$

Substrate Reagent Product

(ii)
$$CH_3$$

$$+ CH_3Cl \longrightarrow + HCl$$
Reagent Product

Nucleophiles and Electrophiles

Reagents attack the reactive site of the substrate. The reactive site may be electron

deficient portion of the molecule (a positive reactive site) e.g., an atom with incomplete electron shell or the positive end of the dipole in the molecule. If the attacking species is electron rich, it attacks these sites. If attacking species is electron deficient, the reactive site for it is that part of the substrate molecule which can supply electrons, e.g., π electrons in a double bond.

A reagent that brings an electron pair to the reactive site is called a **nucleophile** (Nu:) i.e., nucleus seeking and the reaction is then called **nucleophilic**. A reagent that takes away an electron pair from reactive site is called **electrophile** (E⁺) i.e., electron seeking and the reaction is called **electrophilic**.

During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that specific atom or part of the substrate which is electron deficient. Similarly, the electrophiles attack at nucleophilic centre, which is the electron rich centre of the substrate. Thus, the electrophiles receive electron pair from the substrate when the two undergo bonding interaction. A curved-arrow notation is used to show the movement of an electron pair from the nucleophile to the electrophile. Some examples of nucleophiles are the negatively charged ions with lone pair of electrons such as hydroxide (HO-), cyanide (NC-) ions and carbanions (R₂C:-). Neutral molecules such as H₂O:, R₃N:, R₂NH etc., can also act as nucleophiles due to the presence of lone pair of electrons. Examples of electrophiles include carbocations ($\dot{C}H_3$) and neutral molecules having functional groups like carbonyl group (>C=O) or alkyl halides (R₂C-X, where X is a halogen atom). The carbon atom in carbocations has sextet configuration; hence, it is electron deficient and can receive a pair of electrons from the nucleophiles. In neutral molecules such as alkyl halides, due to the polarity of the C-X bond a partial positive charge is generated on the carbon atom and hence the carbon atom becomes an electrophilic centre at which a nucleophile can attack.

Problem 8.11

Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.

(a) CH₃-SCH₃, (b) CH₃-CN, (c) CH₃-Cu

Solution

(a)
$$CH_3 \longrightarrow SCH_3 \longrightarrow CH_3 + SCH_3$$

(b)
$$CH_3 \stackrel{\longleftarrow}{\frown} CN \longrightarrow \overset{+}{C}H_3 + \overset{-}{C}N$$

(c) $CH_3 \stackrel{-}{\frown} Cu \longrightarrow \overset{-}{C}H_3 + \overset{+}{C}u$

(c)
$$CH_3 - Cu \longrightarrow CH_3 + Cu$$

Problem 8.12

Giving justification, categorise the following molecules/ions as nucleophile or electrophile:

$$HS^{-}, BF_{3}, C_{2}H_{5}O^{-}, (CH_{3})_{3} N:,$$

$$C_{1}^{\dagger}, C_{1}^{\dagger}, C_{2}^{\dagger} = O, H_{2}N_{1}^{\dagger}, N_{2}^{\dagger}$$

Solution

Nucleophiles: HS-,C₂H₅O-,(CH₃)₃N:H₂N: These species have unshared pair of electrons, which can be donated and shared with an electrophile.

Electrophiles: BF_3 , $C\dot{1}H_3-\dot{C}=0$, $\dot{N}O_3$. Reactive sites have only six valence electrons; can accept electron pair from a nucleophile.

Problem 8.13

Identify electrophilic centre in the following: CH₃CH=O, CH₃CN, CH₃I.

Solution

Among $CH_3HC^*=O$, $H_3CC^*\equiv N$, and H₃C -I, the starred carbon atoms are electrophilic centers as they will have partial positive charge due to polarity of the bond.

8.7.3 Electron Movement in Organic **Reactions**

The movement of electrons in organic reactions can be shown by curved-arrow

notation. It shows how changes in bonding occur due to electronic redistribution during the reaction. To show the change in position of a pair of electrons, curved arrow starts from the point from where an electron pair is shifted and it ends at a location to which the pair of electron may move.

Presentation of shifting of electron pair is given below :

(i)
$$= \dot{\gamma} \xrightarrow{\bullet} \leftarrow \rightarrow -\dot{\gamma} = \text{from } \pi \text{ bond to}$$
adjacent bond position

(ii) $= \dot{\dot{\gamma}} \xrightarrow{\bullet} \leftarrow \rightarrow -\ddot{\dot{\gamma}} = \text{from } \pi \text{ bond to}$
adjacent atom

(iii) $= \ddot{\dot{\gamma}} \xrightarrow{\bullet} \leftarrow \rightarrow -\dot{\gamma} = \text{from atom to adjacent bond position}$

Movement of single electron is indicated by a single barbed 'fish hooks' (i.e. half headed curved arrow). For example, in transfer of hydroxide ion giving ethanol and in the dissociation of chloromethane, the movement of electron using curved arrows can be depicted as follows:

$$H \overset{\frown}{\text{CH}_3} - \overset{\frown}{\text{CH}_3} - \overset{\frown}{\text{Br}} : \longrightarrow \text{CH}_3 \text{OH} + : \overset{\frown}{\text{Br}} :$$
 $C \overset{\frown}{\text{H}_3} - \overset{\frown}{\text{Cl}} \longrightarrow \overset{\frown}{\text{CH}_3} + \overset{\frown}{\text{Cl}}$

8.7.4 Electron Displacement Effects in Covalent Bonds

The electron displacement in an organic molecule may take place either in the ground state under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent. The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarlisation of the bond. Inductive effect and resonance effects are examples of this type of electron displacements. Temporary electron displacement effects are seen in a molecule when a reagent approaches to attack it. This type of electron displacement is called electromeric effect or polarisability effect. In the following sections we will learn about these types of electronic displacements.

8.7.5 Inductive Effect

When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond. Such a shift of electron density results in a polar covalent bond. Bond polarity leads to various electronic effects in organic compounds.

Let us consider cholorethane (CH $_3$ CH $_2$ Cl) in which the C–Cl bond is a polar covalent bond. It is polarised in such a way that the carbon-1 gains some positive charge (δ^+) and the chlorine some negative charge (δ^-). The fractional electronic charges on the two atoms in a polar covalent bond are denoted by symbol δ (delta) and the shift of electron density is shown by an arrow that points from δ^+ to δ^- end of the polar bond.

$$\delta\delta^{+}$$
 δ^{+} δ^{-} CH_{3} CH_{2} CI

2 1

carbon-1 which has

In turn carbon-1, which has developed partial positive charge (δ^+) draws some electron density towards it from the adjacent C-C bond. Consequently, some positive charge $(\delta\delta^+)$ develops on carbon-2 also, where $\delta\delta^+$ symbolises relatively smaller positive charge as compared to that on carbon – 1. In other words, the polar C – Cl bond induces polarity in the adjacent bonds. Such polarisation of σ-bond caused by the polarisation of adjacent σ -bond is referred to as the **inductive effect**. This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds. The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom. Based on this ability, the substitutents can be classified as electron-withdrawing or electron donating groups relative to hydrogen. Halogens and many other groups such as nitro (- NO_o), cyano (- CN), carboxy (- COOH), ester (COOR), aryloxy (-OAr, e.g. – OC₆H₅), etc. are electron-withdrawing groups. On the other hand, the alkyl groups like methyl (-CH3) and ethyl (-CH₂-CH₃) are usually considered as electron donating groups.