Chemistry

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(Chapter – 12) (Organic Chemistry – Some Basic Principles and Techniques)

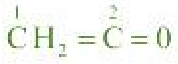
(Class – XI)

Exercises

Question 12.1:
What are hybridisation states of each carbon atom in the following compounds?

$CH_2=C=O$, $CH_3CH=CH_2$, $(CH_3)_2CO$, $CH_2=CHCN$, C_6H_6

Answer 12.1:

(i) 

$\overset{1}{C}H_2=\overset{2}{C}=O$

C–1 is sp^2 hybridised.

C–2 is sp hybridised.

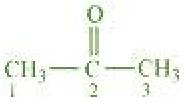
(ii) 

$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H_2$

C–1 is sp^3 hybridised.

C–2 is sp^2 hybridised.

C–3 is sp^2 hybridised.

(iii) 

$\underset{1}{CH_3}-\overset{O}{\overset{\|}{\underset{2}{C}}}-\underset{3}{CH_3}$

C–1 and C–3 are sp^3 hybridised.

C–2 is sp^2 hybridised.

(iv) 

$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}\equiv N$

C–1 is sp^2 hybridised.

C–2 is sp^2 hybridised.

C–3 is sp hybridised.

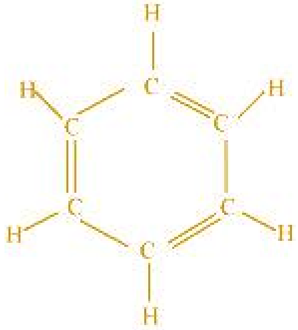
(v) C_6H_6
All the 6 carbon atoms in benzene are sp^2 hybridised.

Question 12.2:
Indicate the σ and π bonds in the following molecules:

C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2 = C = CH_2$, CH_3NO_2, $HCONHCH_3$

Answer 12.2:

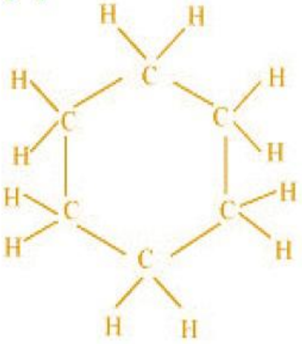
(i) C_6H_6



)

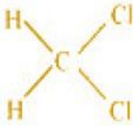
There are six C – C sigma (σ_{C-C}) bonds, six C–H sigma (σ_{C-H}) bonds, and three C=C pi (π_{C-C}) resonating bonds in the given compound.

(ii) C_6H_{12}



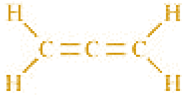
There are six C – C sigma (σ_{C-C}) bonds and twelve C–H sigma (σ_{C-H}) bonds in the given compound.

(iii) CH_2Cl_2



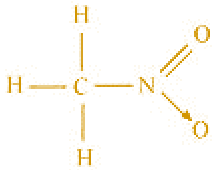
There two C–H sigma (σ_{C-H}) bonds and two C–Cl sigma (σ_{C-Cl}) bonds in the given compound.

(iv) $CH_2 = C = CH_2$



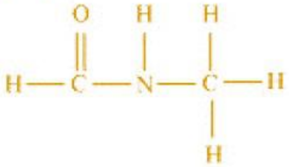
There are two C–C sigma (σ_{C-C}) bonds, four C–H sigma (σ_{C-H}) bonds, and two C=C pi (π_{C-C}) bonds in the given compound.

(v) CH_3NO_2



There are three C–H sigma (σ_{C-H}) bonds, one C–N sigma (σ_{C-N}) bond, one N–O sigma (σ_{N-O}) bond, and one N=O pi (π_{N-O}) bond in the given compound.

(vi) $HCONHCH_3$

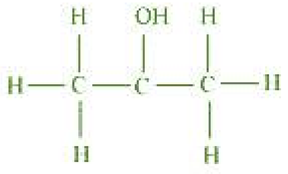


There are two C–N sigma (σ_{C-N}) bonds, four C–H sigma (σ_{C-H}) bonds, one N–H sigma (σ_{N-H}) bond, and one C=O pi (π_{C-O}) bond in the given compound.

Question 12.3:
Write bond line formulas for: Isopropyl alcohol, 2,3-Dimethyl butanal, Heptan-4-one.

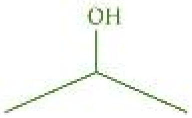
Answer 12.3:
The bond line formulae of the given compounds are:

(a) Isopropyl alcohol

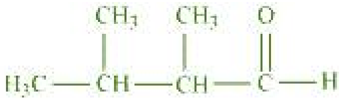


$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{OH}{|}}{C}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

→

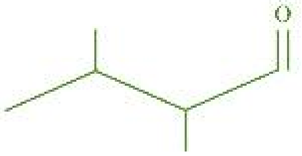


(b) 2, 3–dimethyl butanal

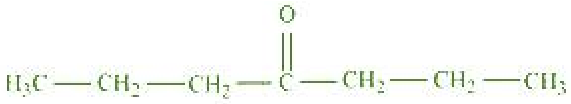


$$H_3C-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-H$$

→

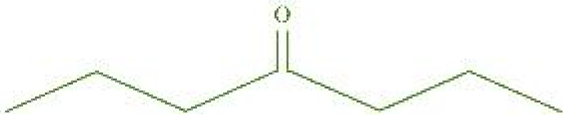


(c) Heptan–4–one



$$H_3C-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$$

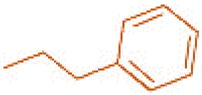
→



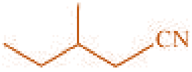
Question 12.4:

Give the IUPAC names of the following compounds:

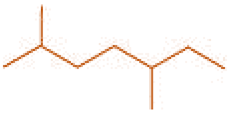
(a)



(b)

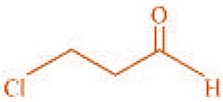


(c)



(d)

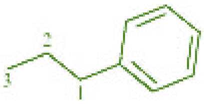
(e)



(f) Cl_2CHCH_2OH

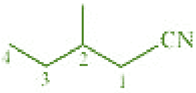
Answer 12.4:

(a)



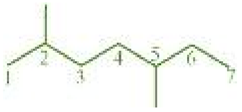
3–phenyl propane

(b)



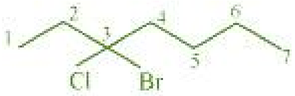
2–methyl–1–cyanobutane

(c)



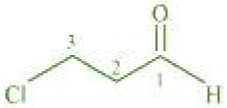
2, 5–dimethyl heptane

(d)



3–bromo–3–chloroheptane

(e)



3–chloropropanal

(f) Cl_2CHCH_2OH

1, 1–dichloro–2–ethanol

Question 12.5:

Which of the following represents the correct IUPAC name for the compounds concerned?

(a) 2,2-Dimethylpentane or 2-Dimethylpentane

(b) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane

(c) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane

(d) But-3-yn-1-ol or But-4-ol-1-yne

Answer 12.5:

(a) The prefix *di* in the IUPAC name indicates that two identical substituent groups are present in the parent chain. Since two methyl groups are present in the C–2 of the parent chain of the given compound, the correct IPUAC name of the given compound is 2, 2–dimethylpentane.

(b) Locant number 2, 4, 7 is lower than 2, 5, 7. Hence, the IUPAC name of the given compound is 2, 4, 7–trimethyloctane.

(c) If the substituents are present in the equivalent position of the parent chain, then the lower number is given to the one that comes first in the name according to the alphabetical order. Hence, the correct IUPAC name of the given compound is 2–chloro– 4–methylpentane.

(d) Two functional groups – alcoholic and alkyne – are present in the given compound. The principal functional group is the alcoholic group. Hence, the parent chain will be suffixed with *ol*. The alkyne group is present in the C–3 of the parent chain. Hence, the correct IUPAC name of the given compound is But–3–yn–1–ol.

Question 12.6:
Draw formulas for the first five members of each homologous series beginning with the following compounds.
(a) H–COOH
(b) CH_3COCH_3
(c) $H–CH=CH_2$

Answer 12.6:
The first five members of each homologous series beginning with the given compounds are shown as follows:

(a)
H–COOH : Methanoic acid

$CH_3–COOH$: Ethanoic acid
$CH_3–CH_2–COOH$: Propanoic acid

$CH_3–CH_2–CH_2–COOH$: Butanoic acid

$CH_3–CH_2–CH_2–CH_2–COOH$: Pentanoic acid

(b)

CH_3COCH_3 : Propanone $CH_3COCH_2CH_3$

: Butanone

$CH_3COCH_2CH_2CH_3$: Pentan-2-one

$CH_3COCH_2CH_2CH_2CH_3$: Hexan-2-one

$CH_3COCH_2CH_2CH_2CH_2CH_3$: Heptan-2-one

(c)

$H–CH=CH_2$: Ethene

$CH_3–CH=CH_2$: Propene

$CH_3–CH_2–CH=CH_2$: 1-Butene

$CH_3–CH_2–CH_2–CH=CH_2$: 1-Pentene

$CH_3–CH_2–CH_2–CH_2–CH=CH_2$: 1-Hexene

Question 12.7:
Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for:

(a) 2,2,4-Trimethylpentane

(b) 2-Hydroxy-1,2,3-propanetricarboxylic acid

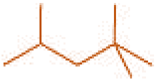
(c) Hexanedial

Answer 12.7:
(a) 2, 2, 4–trimethylpentane

Condensed formula

$(CH_3)_2CHCH_2C\ (CH_3)_3$

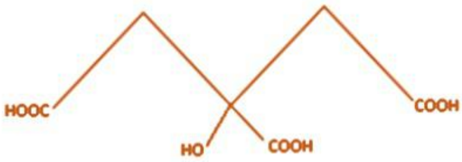
Bond line formula



(b) 2–hydroxy–1, 2, 3–propanetricarboxylic acid

Condensed Formula

$(COOH)CH_2C(OH)\ (COOH)CH_2(COOH)$
Bond line formula:



The functional groups present in the given compound are carboxylic acid (–COOH) and alcoholic (–OH) groups.

(c) Hexanedial

Condensed Formula

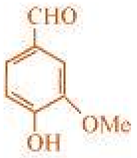
$(CHO)\ (CH_2)_4\ (CHO)$

Bond line Formula

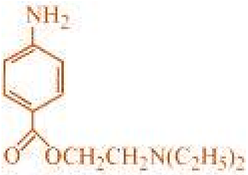
The functional group present in the given compound is aldehyde (–CHO).

Question 12.8:
Identify the functional groups in the following compounds

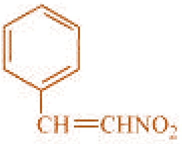
(a)



(b)



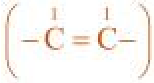
(c)



Answer 12.8:
The functional groups present in the given compounds are:

(a) Aldehyde (–CHO), Hydroxyl (–OH),

Methoxy (–OMe),

C=C double bond  $\left(-\overset{|}{C}=\overset{|}{C}-\right)$

(b) Amino ($-NH_2$),

Ketone (C = O),

Diethylamine ($N(C_2H_5)_2$)

(c) Nitro ($-NO_2$),

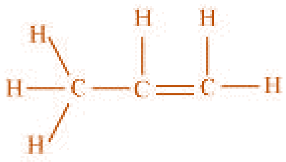
C=C double bond $\left(-C=C-\right)$

Question 12.9:
Which of the two: $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why?

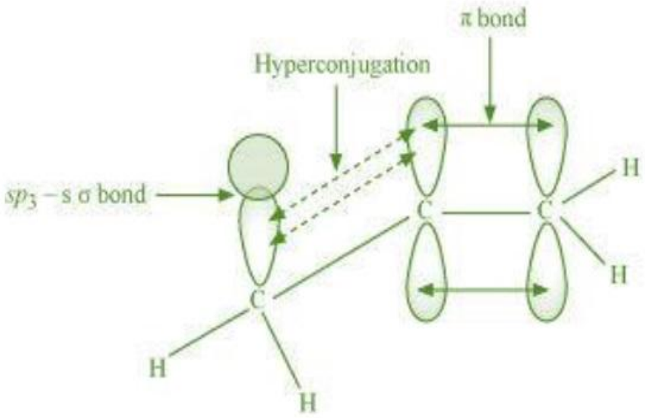
Answer 12.9:
NO_2 group is an electron-withdrawing group. Hence, it shows –I effect. By withdrawing the electrons toward it, the NO_2 group decreases the negative charge on the compound, thereby stabilising it. On the other hand, ethyl group is an electron-releasing group. Hence, the ethyl group shows +I effect. This increases the negative charge on the compound, thereby destabilising it. Hence, $O_2NCH_2CH_2O^-$ is expected to be more stable than $CH_3CH_2O^-$.

Question 12.10:
Explain why alkyl groups act as electron donors when attached to a π system.

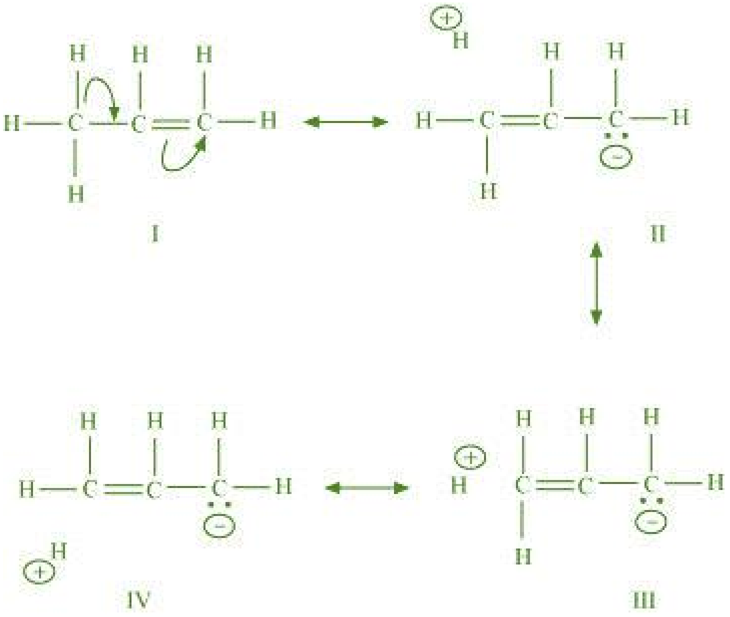
Answer 12.10:
When an alkyl group is attached to a π system, it acts as an electron-donor group by the process of hyperconjugation. To understand this concept better, let us take the example of propene.



In hyperconjugation, the sigma electrons of the C–H bond of an alkyl group are delocalised. This group is directly attached to an atom of an unsaturated system. The delocalisation occurs because of a partial overlap of a sp^3 –*s* sigma bond orbital with an empty *p* orbital of the π bond of an adjacent carbon atom.
The process of hyperconjugation in propene is shown as follows:



This type of overlap leads to a delocalisation (also known as no-bond resonance) of the π electrons, making the molecule more stable.

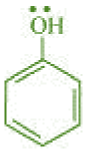


Question 12.11:
Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.

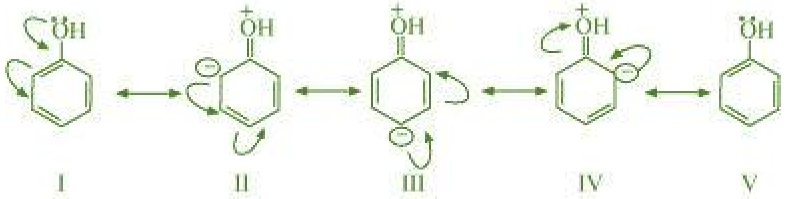
(a) C_6H_5OH **(b)** $C_6H_5NO_2$ **(c)** $CH_3CH = CH - CHO$

(d) C_6H_5CHO **(e)** $C_6H_5-\overset{+}{C}H_2$ **(f)** $CH_3CH=CH\overset{+}{C}H_2$

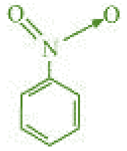
Answer 12.11:
(a) The structure of C_6H_5OH is:



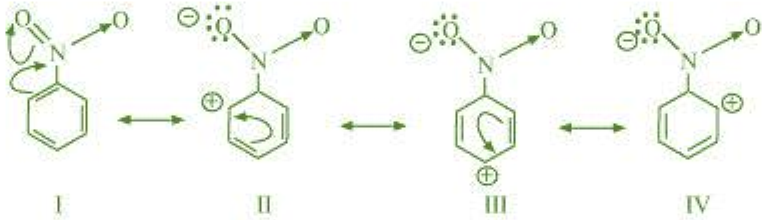
The resonating structures of phenol are represented as:



(b) The structure of $C_6H_5NO_2$ is:

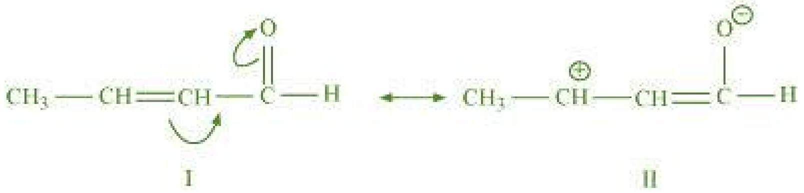


The resonating structures of nitro benzene are represented as:

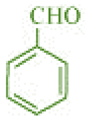


(c) $CH_3CH = CH - CHO$

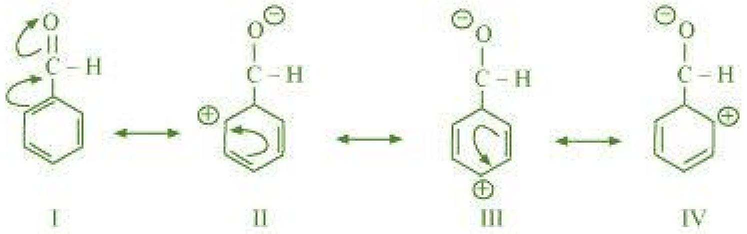
The resonating structures of the given compound are represented as:



(d) The structure of C_6H_5CHO is:

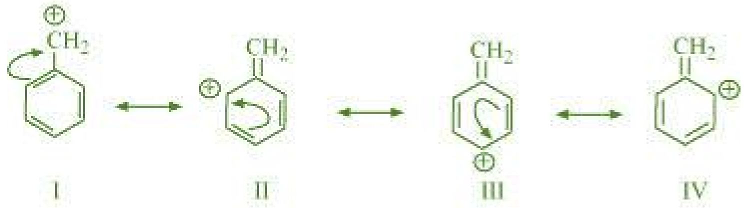


The resonating structures of benzaldehyde are represented as:



(e) $C_6H_5CH_2^{\oplus}$

The resonating structures of the given compound are:



(f) $CH_3\,CH = CH\,CH_2^{\oplus}$

The resonating structures of the given compound are:

Question 12.12:
What are electrophiles and nucleophiles? Explain with examples.

Answer 12.12:
An electrophile is a reagent that takes away an electron pair. In other words, an electron-seeking reagent is called an electrophile (E^+). Electrophiles are electrondeficient and can receive an electron pair.

Carbocations $\left(CH_3CH_2^+\right)$ and neutral molecules having functional groups such as carbonyl group ($>C=O$) are examples of electrophiles.

A nulceophile is a reagent that brings an electron pair. In other words, a nucleus-seeking reagent is called a nulceophile (Nu:).
For example: OH^-, NC^-, carbanions (R_3C^-), etc.

Neutral molecules such as $H_2\ddot{O}$ and ammonia also act as nulceophiles because of the presence of a lone pair.

Question 12.13:
Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:

(a) $CH_3COOH + \mathbf{HO^-} \longrightarrow CH_3COO^- + H_2O$

(b) $CH_3COCH_3 + \bar{\mathbf{C}}\mathbf{N} \longrightarrow (CH_3)_2C(CN) + (OH)$

(c) $C_6H_5 + \mathbf{CH_3\overset{+}{C}O} \longrightarrow C_6H_5COCH_3$

Answer 12.13:
Electrophiles are electron-deficient species and can receive an electron pair. On the other hand, nucleophiles are electron-rich species and can donate their electrons.

(a) $CH_3COOH + \mathbf{HO^-} \longrightarrow CH_3COO^- + H_2O$

Here, HO^- acts as a nucleophile as it is an electron-rich species, i.e., it is a nucleusseeking species.

(b) $CH_3COCH_3 + \bar{\mathbf{C}}\mathbf{N} \longrightarrow (CH_3)_2C(CN) + (OH)$

Here, ^-CN acts as a nucleophile as it is an electron-rich species, i.e., it is a nucleusseeking species.

(c) $C_6H_5 + \mathbf{CH_3\overset{+}{C}O} \longrightarrow C_6H_5COCH_3$

Here, $CH_3\overset{+}{C}O$ acts as an electrophile as it is an electron-deficient species.

Question 12.14:
Classify the following reactions in one of the reaction type studied in this unit.

(a) $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$

(b) $(CH_3)_2 C = CH_2 + HCl \rightarrow (CH_3)_2 ClC{-}CH_3$

(c) $CH_3CH_2Br + HO^- \rightarrow CH_2 = CH_2 + H_2O + Br^-$

(d) $(CH_3)_3 C - CH_2 OH + HBr \rightarrow (CH_3)_2 CBrCH_2CH_3 + H_2O$

Answer 12.14:
(a) It is an example of substitution reaction as in this reaction the bromine group in bromoethane is substituted by the –SH group.

(b) It is an example of addition reaction as in this reaction two reactant molecules combine to form a single product.

(c) It is an example of elimination reaction as in this reaction hydrogen and bromine are removed from bromoethane to give ethene.

(d) In this reaction, substitution takes place, followed by a rearrangement of atoms and groups of atoms.

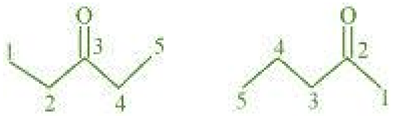
Question 12.15:
What is the relationship between the members of following pairs of structures? Are they structural or geometrical isomers or resonance contributors?

(a)

(b)

(c)

Answer 12.15:
(a) Compounds having the same molecular formula but with different structures are called structural isomers. The given compounds have the same molecular formula but they differ in the position of the functional group (ketone group).



In structure I, ketone group is at the C-3 of the parent chain (hexane chain) and in structure II, ketone group is at the C-2 of the parent chain (hexane chain). Hence, the given pair represents structural isomers.

(b) Compounds having the same molecular formula, the same constitution, and the sequence of covalent bonds, but with different relative position of their atoms in space are called geometrical isomers.

In structures I and II, the relative position of Deuterium (D) and hydrogen (H) in space are different. Hence, the given pairs represent geometrical isomers.

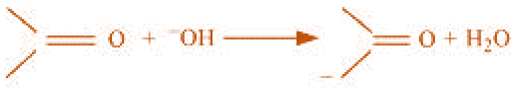
(c) The given structures are canonical structures or contributing structures. They are hypothetical and individually do not represent any real molecule. Hence, the given pair represents resonance structures, called resonance isomers.

Question 12.16:
For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

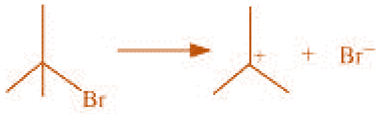
(a)

$$CH_3O-OCH_3 \longrightarrow CH_3\dot{O} + \dot{O}CH_3$$

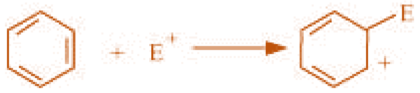
(b)



(c)

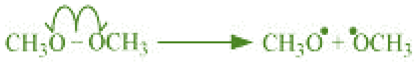


(d)



Answer 12.16:

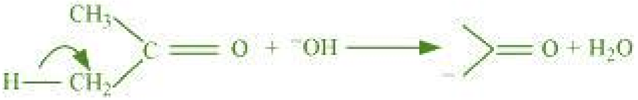
(a) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



$$CH_3\ddot{O}-\ddot{O}CH_3 \longrightarrow CH_3\dot{O} + \dot{O}CH_3$$

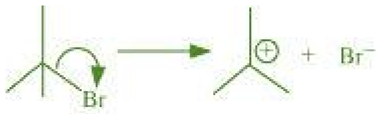
It is an example of homolytic cleavage as one of the shared pair in a covalent bond goes with the bonded atom. The reaction intermediate formed is a free radical.

(b) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



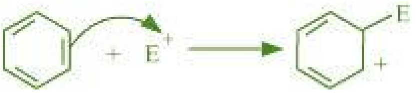
It is an example of heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with the carbon of propanone. The reaction intermediate formed is carbanion.

(c) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



It is an example of heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with the bromine ion. The reaction intermediate formed is a carbocation.

(d) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



It is a heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with one of the fragments. The intermediate formed is a carbocation.

Question 12.17:
Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

Answer 12.17:

Inductive effect
The permanent displacement of sigma (σ) electrons along a saturated chain, whenever an electron withdrawing or electron donating group is present, is called inductive effect. Inductive effect could be + I effect or – I effect. When an atom or group attracts electrons towards itself more strongly than hydrogen, it is said to possess – I effect.
For example,

$$F \leftarrow CH_2 \leftarrow CH_2 \leftarrow CH_2 \leftarrow CH_3$$

When an atom or group attracts electrons towards itself less strongly than hydrogen, it is said to possess + I effect.
For example,

$$CH_3 \rightarrow CH_2 \twoheadrightarrow Cl$$

Electrometric effect
It involves the complete transfer of the shared pair of π electrons to either of the two atoms linked by multiple bonds in the presence of an attacking agent. For example,

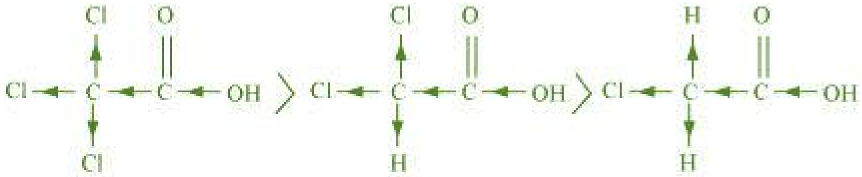
Electrometric effect could be + E effect or – E effect.

+ E effect: When the electrons are transferred towards the attacking reagent

– E effect: When the electrons are transferred away from the attacking reagent

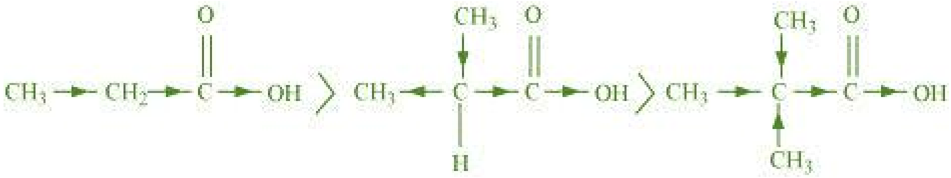
(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

The order of acidity can be explained on the basis of Inductive effect (– I effect). As the number of chlorine atoms increases, the – I effect increases. With the increase in – I effect, the acid strength also increases accordingly.



(b) $CH_3CH_2COOH > (CH_3)_2\ CHCOOH > (CH_3)_3\ C.COOH$

The order of acidity can be explained on the basis of inductive effect (+ I effect). As the number of alkyl groups increases, the + I effect also increases. With the increase in + I effect, the acid strength also increases accordingly.



Question 12.18:
Give a brief description of the principles of the following techniques taking an example in each case.

(a) Crystallisation

(b) Distillation

(c) Chromatography

Answer 12.18:

(a) Crystallisation

Crystallisation is one of the most commonly used techniques for the purification of solid organic compounds.

Principle: It is based on the difference in the solubilites of the compound and the impurities in a given solvent. The impure compound gets dissolved in the solvent in which it is sparingly soluble at room temperature, but appreciably soluble at higher temperature. The solution is concentrated to obtain a nearly saturated solution. On cooling the solution, the pure compound crystallises out and is removed by filtration.

For example, pure aspirin is obtained by recrystallising crude aspirin. Approximately 2 – 4 g of crude aspirin is dissolved in about 20 mL of ethyl alcohol. The solution is heated (if necessary) to ensure complete dissolution. The solution is then left undisturbed until some crystals start to separate out. The crystals are then filtered and dried.

(b) Distillation

This method is used to separate volatile liquids from non-volatile impurities or a mixture of those liquids that have a sufficient difference in their boiling points.

Principle: It is based on the fact that liquids having different boiling points vapourise at different temperatures. The vapours are then cooled and the liquids so formed are collected separately.

For example, a mixture of chloroform (b.p = 334 K) and aniline (b.p = 457 K) can be separated by the method of distillation. The mixture is taken in a round bottom flask fitted with a condenser. It is then heated. Chloroform, being more volatile, vaporizes first and passes into the condenser. In the condenser, the vapours condense and chloroform trickles down. In the round bottom flask, aniline is left behind.

(c) Chromatography

It is one of the most useful methods for the separation and purification of organic compounds.

Principle: It is based on the difference in movement of individual components of a mixture through the stationary phase under the influence of mobile phase.

For example, a mixture of red and blue ink can be separated by chromatography. A drop of the mixture is placed on the chromatogram. The component of the ink, which is less adsorbed on the chromatogram, moves with the mobile phase while the less adsorbed component remains almost stationary.