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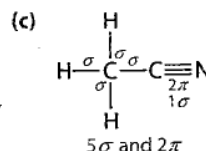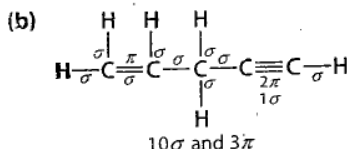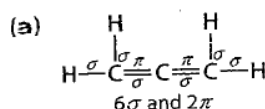
ORGANIC CHEMISTRY : SOME BASIC PRINCIPLES AND TECHNIQUES

12.2 TETRAVALENCE OF CARBON: SHAPES OF ORGANIC COMPOUNDS

Conceptual Questions

1. How many σ and π bonds are present in each of the following molecules?
   (a) $CH_2=C=CH_2$ (b) $CH_2=CH-CH_2-C\equiv CH$ (c) $CH_3C\equiv N$

Solution

(a) 6σ and 2π

(b) 10σ and 3π

(c) 5σ and 2π

2. What are hybridization states of each carbon atom in the following compounds?   (NCERT)
   $CH_2=C=O, CH_3CH=CH_2, (CH_3)_2CO, CH_2=CHCN, C_6H_6$

Solution

Each C is sp^2 hybridized
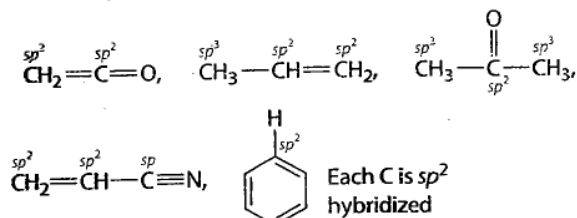
3. Indicate the σ and π bonds in the following molecules: $C_6H_6, C_6H_{12}, CH_2Cl_2, CH_2=C=CH_2, CH_3NO_2, HCONHCH_3$.   (NCERT)

Solution
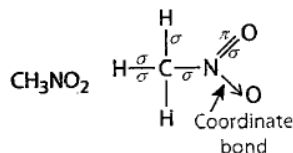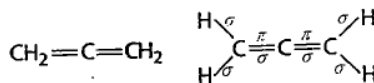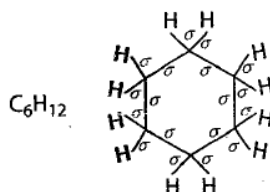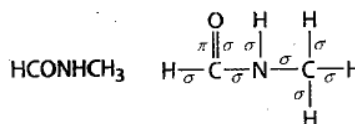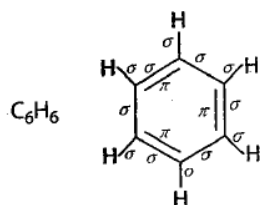
4. In the organic compound $CH_2=CH-CH_2-CH_2-C\equiv CH$, the pair of hybridized orbitals involved in the formation of C2–C3 bond is: (NCERT)

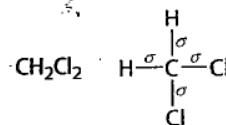   (a) $sp-sp^2$ (b) $sp-sp^3$ (c) sp^2-sp^3 (d) sp^3-sp^3

Solution

(b) $\overset{6}{C}H_2=\overset{5}{C}H-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}\equiv\overset{1}{C}H$. In the compound, C2 is sp and C3 is sp^3 hybridized.

2

12.3 STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS

Conceptual Questions

1. Rewrite each of the following condensed structural formulas, as dash structural (or dash) formulas and as bond-line formulas:

(a) $(CH_3)_3CCH_2CH_3$

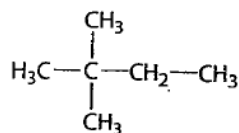(b) $CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH(CH_3)_2$

(c) $CH_3CH(OH)CH_2CH_2OH$

Solution

(a)   Dash formula   Bond-line formula
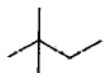
(b)
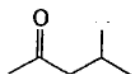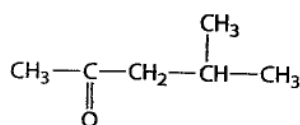
(c)
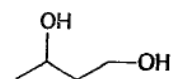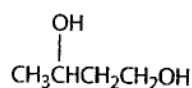
2. Write structural formulas for each of the following bond-line formulas:

(a)

(b)

(c)

Solution

(a)

$CH_3\overset{\overset{\displaystyle CH_3}{|}}{-}CH-CH_2-CH_2-OH$

(b) $CH_3-CH-CH_2-CH_2-CH_3$
       $\qquad\quad\;| \atop CH_3$
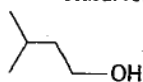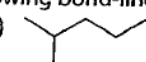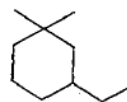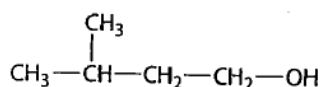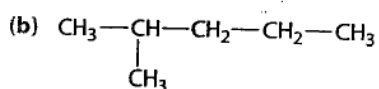
(c)
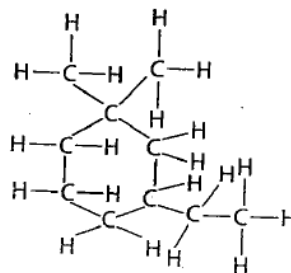
3. Write bond-line formulas for isopropyl alcohol, 2,3-Dimethylbutanal and heptan-4-one.

Solution   (NCERT)
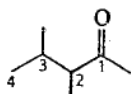
Isopropyl   2,3-Dimethyl   Heptan-4-one
alcohol   butanal
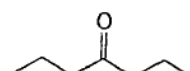
4. Give condensed and bond-line structural formulas and **identify the functional group(s) present, if any, for:**
   (a) 2,2,4-Trimethylpentane   (b) 2-Hydroxy-1,2,3-propanetricarboxylic acid   (c) Hexanedial

   (NCERT)

Solution

   (a) 2,2,4-Trimethylpentane
        Condensed formula: $(CH_3)_3CCH_2CH(CH_3)_2$

        Bond-line formula:

        No functional group present

   (b) 2-Hydroxy-1,2,3-propanetricarboxylic acid
        Condensed formula:

        $HOCCH_2C(OH)(COOH)CH_2COOH$

        Bond-line formula:

        Functional groups present:

        $-C-OH$ (carboxyl), $-OH$(hydroxyl)

   (c) Hexanedial
        Condensed formula: $CHO(CH_2)_4CHO$
        Bond-line formula:

        Functional group present:

        $-C-H$ (aldehyde)
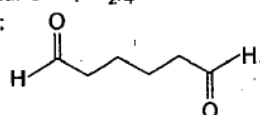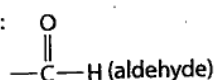
12.4 CLASSIFICATION OF ORGANIC COMPOUNDS and
12.5 NOMENCLATURE OF ORGANIC COMPOUNDS

Conceptual Questions

1. Give IUPAC names for the following hydrocarbons:

   (a) $CH_3-CH-CH-CH_3$
               C_2H_5 C_2H_5

   (b) $CH_3-CH_2-CH_2-CH$
               $CH_3-C-CH_2-CH_3$
               $CH-CH_2-CH_3$
               $CH_2-CH_2-CH_3$

   (c) CH_3
        CH
        H_2C CH_2
        H_2C CH_2

   (d) CH_2-CH_3
        H_3CH_2C CH_2CH_3

   (e) $CH_3-CH-CH_2-CH_2-CH-CH-CH_2-CH_3$
               CH_3 CH_3 CH_3
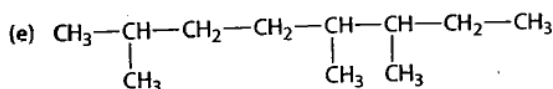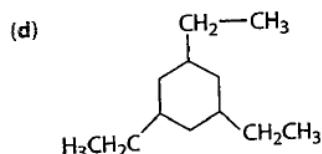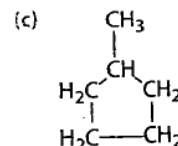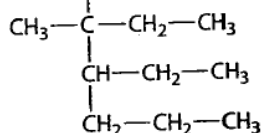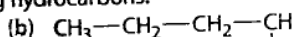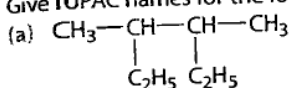
Solution

   (a) 3,4-Dimethylhexane   (b) 4,5-Diethyl-5-methylnonane   (c) Methylcyclopentane
   (d) 1,3,5-Triethylcyclohexane   (e) 2,5,6-Trimethyloctane

2. Draw the structure of the functional group corresponding to
   (a) aldehyde.   (b) nitro compound.   (c) carboxylic acid.   (d) ether.

Solution

   (a) $-C-H$ (b) $-N\overset{O}{\underset{O}{}}$ (c) $-C-OH$ (d) $-O-$

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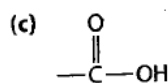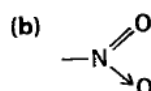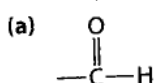
3. Write the structure of the first member of the ketone homologous series. Give its IUPAC name.

Solution

The first number of the ketone homologous series is

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$
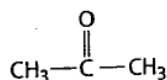
Its IUPAC name is propanone.

4. Write the IUPAC name of
(a) $CH_3-\overset{\overset{\displaystyle }{|}}{\underset{Cl}{C}}=CHCOOCH_3$

(b) [structure of methylcyclohexyne]
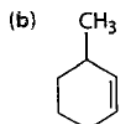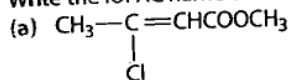
Solution

(a) Methyl-3-chlorobut-2-en-1-oate

(b) 3-Methylcyclohexyne

(NCERT)

5. Give the IUPAC names of the following compounds:
(a) [structure]

(b) [structure with CN]

(c) [structure]

(d) [structure with Cl, Br]

(e) [structure with Cl and O]

(f) Cl_2CHCH_2OH

Solution

(a) [benzene structure, positions 1-6]

Propylbenzene

(b) [structure with CN, positions 5 4 3 2 1]

3-Methylpentanenitrile

(c) [structure, positions 1-7]

2,5-Dimethylheptane

(d) [structure with Cl, Br, positions 1-7]

3-Bromo-3-chloroheptane

(e) [structure with Cl, positions 3 2 1, O, H]

3-Chloropropanal

(f) $\overset{2}{C}l_2CH\overset{1}{C}H_2OH$

2,2-Dichloroethanol

6. Identify the functional groups in the following compounds
(a) [structure with CHO, OMe, OH]

(b) [structure with NH₂, O, OCH₂CH₂N(C₂H₅)₂]

(c) [structure with CH=CHNO₂]
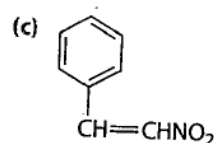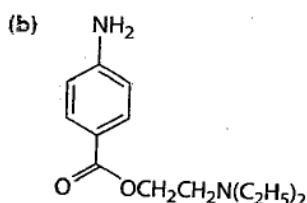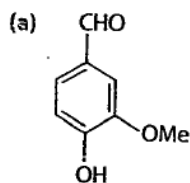
(NCERT)

Solution

(a) CHO (aldehyde), OMe (phenolic ether), OH (phenolic alcohol)
(b) NH_2 (1° amino), COO (ester), $N(C_2H_5)_2$ (3° amino)
(c) CH=CH (ethylenic double bond), NO_2 (nitro)

7. 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

Solution

(NCERT)

(a) 2,2-Dimethylpentane because two alkyl groups on the same carbon, so its locant is repeated twice.
(b) 2,4,7-Trimethyloctane because 2,4,7-locant set is lower than 2,5,7.
(c) 2-Chloro-4-methylpentane because alphabetical order of substituents is followed.
(d) But-3-yn-1-ol because lower locant for the principal functional group, that is, alcohol.

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

Solution

(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)

(c) $H–CH=CH_2$ (Ethene)
$H_3C–CH=CH_2$ (Propene)
$CH_3–CH_2–CH=CH_2$ (But-1-ene)
$CH_3–CH=CH–CH_3$ (But-2-ene)
$CH_3–CH_2–CH_2–CH=CH_2$ (Pent-1-ene)

(b) CH_3COCH_3 (Propanone)
$CH_3COCH_2CH_3$ (Butan-2-one)
$CH_3COCH_2CH_2CH_3$ (Pentan-2-one)
$CH_3CH_2COCH_2CH_3$ (Pentan-3-one)
$CH_3COCH_2CH_2CH_2CH_3$ (Hexan-2-one)

12.6 ISOMERISM IN ORGANIC COMPOUNDS

Conceptual Questions

1. How many isomers are possible for monosubstituted and disubstituted benzene ?

Solution

There is one monosubstituted benzene:

Monosubstituted
benzene
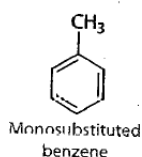
There are three disubstituted benzenes:

o   m   p

Disubstituted benzene
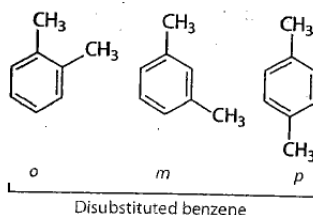
2. Draw all the acyclic and cyclic isomers having the molecular formula C_3H_6O.

Solution

Acyclic isomers are

(a) $CH_3—\overset{O}{\overset{\|}{C}}—CH_3$
Acetone

(b) $CH_3—\overset{OH}{\overset{|}{C}}=CH_2$
(Tautomer of acetone)

(c) $CH_3CH_2—\overset{O}{\overset{\|}{C}}—H$
Propionaldehyde

(d) $CH_3CH=CH—OH$
(Tautomer of propionaldehyde)

(e) $CH_2=CH—CH_2OH$
Prop-2-en-1-ol

(f) $CH_2=CH—OCH_3$
Methoxyethane

Cyclic isomers are

Cyclopropanol   Propylene oxide   Oxetane
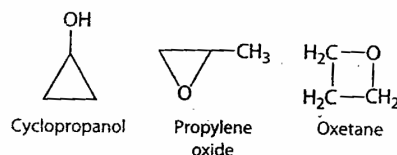
3. Which of the following compounds shows geometrical isomerism?
   (a) Pent-1-ene
   (b) 2-Methylbut-2-ene
   (c) Pent-2-ene

Solution

Only pent-2-ene will show geometrical isomerism because the groups attached on either side of the double bond are different while in (a) and (b), the groups attached on either side of the double bond are the same. The two geometrical isomers of pent-2-ene are

cis-Pent-2-ene   trans-Pent-2-ene

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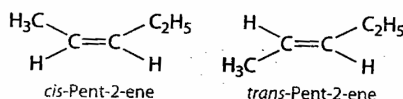
4. What is the minimum number of carbon atom that an alkane must contain to have isomers?

Solution

Alkane must contain a minimum of four carbon atoms in order to show isomerism.

5. Name and draw the functional isomer of propan-1-ol.

Solution

The functional isomer of propan-1-ol is $CH_3-O-CH_2CH_3$ and its name is methoxyethane.

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

Methoxyethane
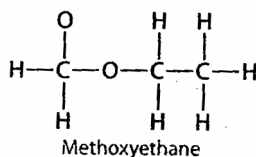
6. What is the relationship between the members of following pairs of structures? Are they structural or geometrical isomers or resonance contributors? **(NCERT)**

(a)

(b)

(c)
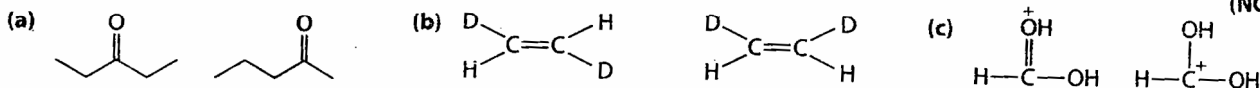
Solution

(a) They are structural isomers (position isomers as well as metamers).

(b) They are geometrical isomers (*trans* and *cis*).

(c) They are resonance contributors because they differ in the position of electrons but not atoms.

12.7 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

Conceptual Questions

1. Classify the following transformations according to the reaction type.

(a) $H_3C-CH=CH-CH_3 + Br_2 \longrightarrow H_3C-CHBr-CHBr-CH_3$ (b) $(H_3C)_2C=C(CH_3)_2 + Br_2 \longrightarrow (H_3C)_2C=C(CH_3)CH_2Br + HBr$

(c) $H_2C=CH-CH_2CH_3 \longrightarrow H_3C-CH=CH-CH_3$ (d) $C_6H_5CHO + CH_3COCH_3 \longrightarrow C_6H_5CH(OH)CH_2COCH_3$

(e) $(CH_3)_3CCl + HO^- \longrightarrow (CH_3)_2C=CH_2$ (f) $CH_3-\underset{\underset{Ph}{|}}{C}=N-OH + H_3O^+ \longrightarrow CH_3-\underset{\underset{NHPh}{|}}{C}=O$
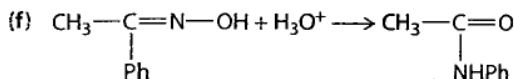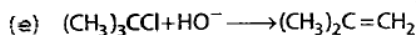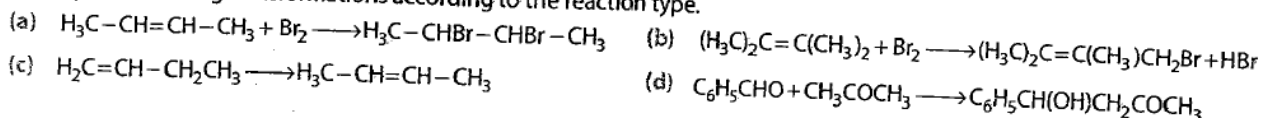
Solution

(a) Electrophilic addition   **(b)** Free radical substitution   **(c)** Isomerization

(d) Condensation   **(e)** β-elimination reaction   **(f)** Rearrangement

2. Which of the following pairs do not constitute resonance structures?

(a) $H_3C-\overset{+}{N}\underset{O^-}{\overset{O}{\diagdown}}$ and $H_3C-O-N=O$

(b) $CH_3-C\underset{CH_2^-}{\overset{O:}{\diagup}}$ and $CH_3-C\underset{CH_2}{\overset{\ddot{O}:^-}{\diagup}}$

(c) $(CH_3)_2CO$ and $CH_3-C\underset{CH_2}{\overset{OH}{\diagup}}$

(d) $CH_3CH=CHCH_3$ and $CH_3CH_2CH=CH_2$
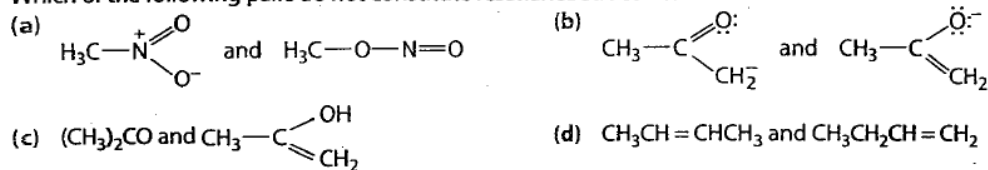
Solution

(a) The two structures differ in the position of **atoms**, and hence they are not resonance structures. In fact, these are functional isomers.

(b) Yes, it contributes to the resonance structures because here the position of atoms remains the same while the position of electrons changes.

$$CH_3-C\underset{CH_2^-}{\overset{\ddot{O}}{\diagup}} \longleftrightarrow CH_3-C\underset{CH_2}{\overset{\ddot{O}:^-}{\diagup}}$$

7
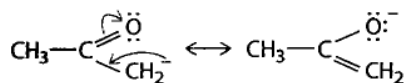
(c) No, it does not contribute to resonance **structures** because here the position of atoms has been changed. They are tautomers.

(d) No, it does not contribute to resonance **structures** because these differ in the **position** of the double bond. They are position isomers.

3. Write resonance structure of CH_3-CO^+ and **identify** the most stable structure. Give reasons also.

Solution

CH_3CO^+ has two resonance structures. Structure (II) is more stable than structure (I) because in this the octet of each atom is complete.

$$CH_3-\overset{:\overset{\cdot\cdot}{O}}{\underset{I}{\overset{\|}{C}}}{}^+ \longleftrightarrow CH_3-\overset{:\overset{+}{O}}{\underset{II}{\overset{\||}{C}}}$$
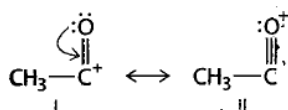
4. What is the correct order of stability of the carbocations: $(CH_3)_3C^+$, $CH_3CH_2^+$, CH_3^+, $(CH_3)_2CH^+$?

Solution

The decreasing order of stability of the carbocations is $(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$.

5. Using curved arrows notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage: (a) CH_3-SCH_3, (b) CH_3-CN and (c) CH_3-**Cu.**

Solution

(a) $CH_3\!\!\overset{\frown}{-}\!\!SCH_3 \longleftrightarrow \overset{+}{C}H_3 + \overset{-}{S}CH_3$ (b) $CH_3\!\!\overset{\frown}{-}\!\!CN \longleftrightarrow \overset{+}{C}H_3 + CN^-$ (c) $\overset{\frown}{CH_3}\!\!-\!\!Cu \longleftrightarrow \overset{-}{C}H_3 + Cu^+$

Carbocation   Carbocation   Carbanion
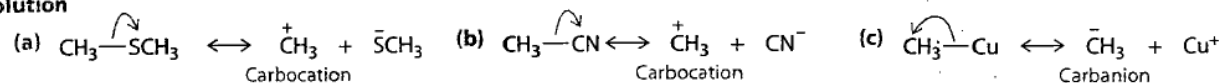
6. Give reason why the following two structures (I) and (II) cannot be the major contributors to the real structure of CH_3COOCH_3.

$$CH_3\!\!-\!\!\overset{:\overset{\cdot\cdot}{O}{}^-}{\underset{\overset{+}{I}}{C}}\!\!-\!\!\overset{\cdot\cdot}{O}\!\!-\!\!CH_3 \longleftrightarrow CH_3\!\!-\!\!\overset{:\overset{\cdot\cdot}{O}{}^-}{\underset{II}{C}}\!\!=\!\!\overset{+}{\overset{\cdot\cdot}{O}}\!\!-\!\!CH_3$$
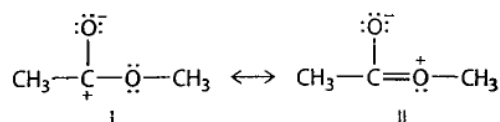
Solution

The two structures are less important contributors as they contain charge separation. Also, structure (I) contains a carbon atom with an incomplete octet.

7. Spectroscopic measurements indicate that the **two** oxygen atoms of sodium acetate are equivalent. Both the C–O bonds have the same length (126 pm). Explain.

Solution

According to the spectroscopic measurements, the two oxygen atoms are equivalent because they are involved in resonance as a result of which they have same bond length.

8. Which of the two: $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be **more** stable and why? (NCERT)

Solution

$NO_2CH_2CH_2O^-$ is more stable than $CH_3CH_2O^-$ because of the presence of NO_2 group (–I effect). It results in the dispersal of negative charge on the oxygen atom. In contrast, CH_3CH_2 has +I effect. It, therefore, tends to intensify the negative charge and hence desta-bilizes it.

$$O_2N \overset{\longleftarrow}{} CH_2 \overset{\longleftarrow}{} CH_2 \overset{\longleftarrow}{} O^-$$
I

$$CH_3 \overset{\longrightarrow}{} CH_2 \overset{\longrightarrow}{} O^-$$
II
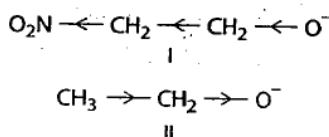
9. Explain why alkyl groups act as electron donors when attached to a π system. (NCERT)

Solution

Due to hyperconjugation, which involves delocalization of π electrons, alkyl groups act as electron donors when attached to a π system.

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-C=CH_2 \longleftrightarrow H-\underset{\underset{H}{|}}{\overset{\overset{H^+}{|}}{C}}=CH-\overset{\cdot\cdot}{C}H_2$$

$$\updownarrow$$

$$H-\underset{\underset{H^+}{|}}{\overset{\overset{H}{|}}{C}}=CH-\overset{\cdot\cdot}{C}H_2 \longleftrightarrow H^+\,\overset{\overset{H}{|}}{C}=CH-\underset{\underset{H}{|}}{\overset{}{\overset{\cdot\cdot}{C}H_2}}$$
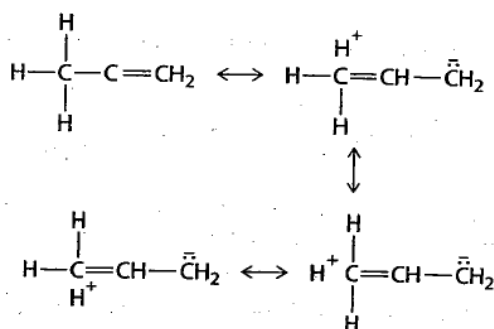
10. Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation. **(NCERT)**

    (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) $CH_3\overset{+}{C}H=CHCH_2$

Solution

(c) $CH_3-CH=CH-CH=\ddot{O} \longleftrightarrow CH_3-CH=CH-\overset{+}{C}H-\ddot{O}^- \longleftrightarrow CH_3-\overset{+}{C}H-CH=CH-\ddot{O}^-$

(f) $CH_3-CH=CH-\overset{+}{C}H_2 \longleftrightarrow CH_3-\overset{+}{C}H-CH=CH_2$
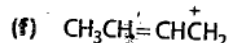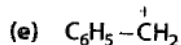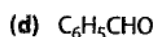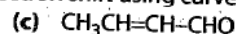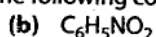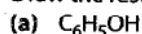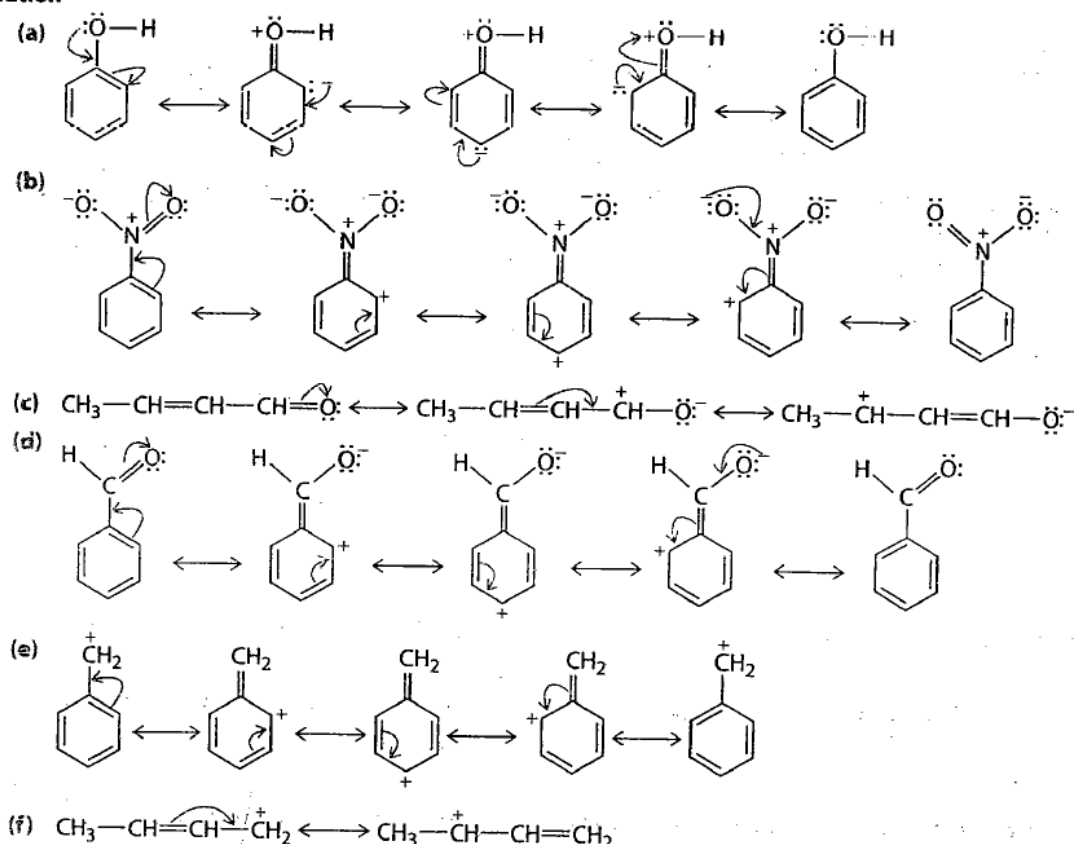
11. What are electrophiles and nucleophiles? Explain with examples. **(NCERT)**

Solution

Electrophiles are electron-loving chemical species. They are electron-deficient species and may be either positively charged or electrically neutral. For example, H^+, Cl^+, Br^+, SO_3, BF_3, etc.

Nucleophiles are nucleus-loving chemical species. They are electron-rich species and may be either negatively charged or neutral. For example, OH^-, CN^-, NH_3, Cl^-, etc.

12. Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:

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

    (b) $CH_3COCH_3 + \textbf{CN}^- \longrightarrow (CH_3)_2C(CN)(OH)$

    (c) $C_6H_5 + \textbf{CH}_3\overset{+}{\textbf{C}}\textbf{O} \longrightarrow C_6H_5COCH_3$ **(NCERT)**
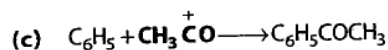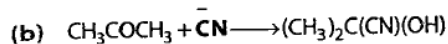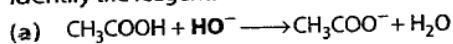
Solution

    (a) Nucleophile   (b) Nucleophile   (c) Electrophile.

13. Classify the following reactions in one of the reaction type studied in this unit.

    (a) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$ (b) $(CH_3)_2C=CH_2 + HCl \longrightarrow (CH_3)_2ClC-CH_3$

    (c) $CH_3CH_2Br + HO^- \longrightarrow CH_2=CH_2 + H_2O + Br^-$ (d) $(CH_3)_3C-CH_2OH + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3 + H_2O$ **(NCERT)**
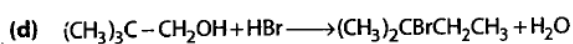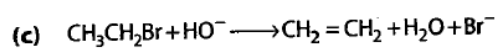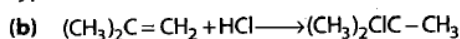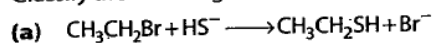
Solution

    (a) Nucleophilic substitution   (b) Electrophilic substitution

    (c) Bimolecular elimination   (d) Nucleophilic substitution with rearrangement.

9

14. 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) $CH_3O-OCH_3 \longrightarrow CH_3\overset{.}{O} + \overset{.}{O}CH_3$

(b) $\overset{}{>}=O + ^-OH \longrightarrow \overset{}{>}=O + H_2O$

(c)

(d)

(NCERT)

Solution

(a) $CH_3\overset{\frown\frown}{O}OCH_3 \xrightarrow{\text{Homolysis}} CH_3O^. + {}^.OCH_3$
Free radicals

(b) $\xrightarrow{\text{Heterolysis}}$ $>=O + H_2O$
Carbanion

(c) $\xrightarrow{\text{Heterolysis}}$ $+ Br^-$
Carbocation

(d) $\xrightarrow{\text{Heterolysis}}$
Carbocation
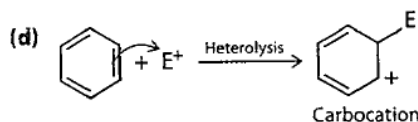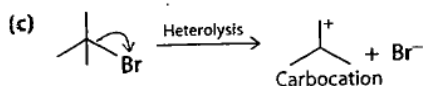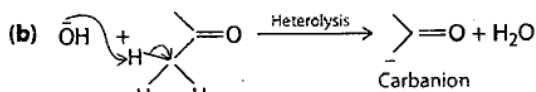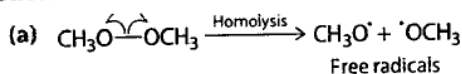
15. Explain the terms inductive and electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$
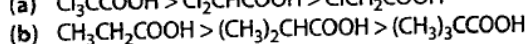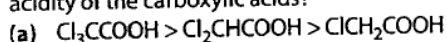
(NCERT)

Solution

Whenever a covalent bond is formed between two different atoms, out of which one is highly electronegative (say halogens) then the electron density is more towards the electronegative atom of the bond. As a result of this, the electronegative atom (Cl in Fig. 12.1) acquires a partial negative charge and the other atom acquires partial positive charge (C_1 in Fig. 12.1). The small positive charge set up on C_1 attracts the σ electrons of the C_2 and thus C_2 acquires a small positive charge, smaller than that on C_1. Similarly, C_3 acquires a small positive charge, that is still smaller than that on C_2. This type of displacement of the σ electrons along a saturated carbon chain whenever an electron withdrawing group (or electron donating) group is present at the end of the chain is called the inductive effect or the I effect.

$$C_4 \rightarrow \overset{\delta\delta\delta+}{C_3} \rightarrow \overset{\delta\delta+}{C_2} \rightarrow \overset{\delta+}{C_1} \rightarrow \overset{\delta-}{Cl}$$
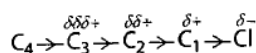
Figure 12.1 Inductive effect.

Electromeric effect involves the complete transfer of electrons of a multiple bond (double or triple bond) to one of the bonded atoms (usually more electronegative) in presence of an attacking reagent. It is called E effect.
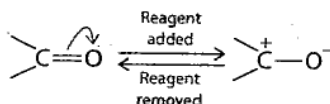
(a) –I effect explains this because as the number of chlorine atoms decreases, the overall –I effect decreases and the acid strength decreases accordingly.

(b) +I effect explains this because as the number of alkyl groups increases, the +I effect increases and the acid strength decreases.

16. Which of the following carbocations is most stable?

(NCERT)

(a) $(CH_3)_3C\overset{+}{C}H_2$

(b) $(CH_3)_3\overset{+}{C}$

(c) $CH_3CH_2\overset{+}{C}H_2$

(d) $CH_3\overset{+}{C}HCH_2CH_3$
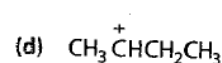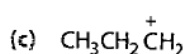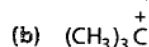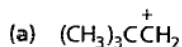
Solution

The order of stability of carbocation is 3° > 2° > 1°. Therefore, option (b) is correct.

17. The reaction: $CH_3CH_2I + KOH (aq) \longrightarrow CH_3CH_2OH + KI$ is classified as

(a) electrophilic substitution.
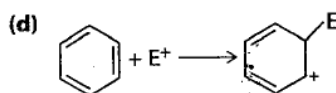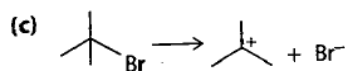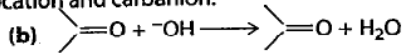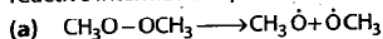
(b) nucleophilic substitution.

(c) elimination.

(d) addition.

(NCERT)

Solution

(b) This is an example of nucleophilic substitution reaction since I^- is replaced by the nucleophile OH^- ion. Thus option (b) is correct.

12.8 METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

Conceptual Questions

1. When do we use a fluted filter paper or hot water funnel for filtration?

Solution

Fluted filter paper is used when the volume of the solution to be filtered is small and hot water funnel is used when the volume is large.

2. How will you purify essential oils?

Solution

Steam distillation

3. How will you purify a liquid having non-volatile impurities?

Solution

Simple distillation is used to purify a liquid having non-volatile impurities.

4. A mixture contains two components A and B. The solubilities of A and B in water near their boiling point are, respectively, 10 g per 100 mL and 2 g per 100 mL. How will you separate A and B from this mixture?

Solution

A and B are separated using fractional crystallization. When the saturated solution of this mixture is allowed to cool, the less soluble component B crystallizes out first leaving the more soluble component A in the mother liquor. The mother liquor is again concentrated, the hot solution again allowed to cool and the crystals of component A are obtained.

5. The R_f value of A and B in a mixture determined by TLC in a solvent mixture are 0.65 and 0.42, respectively. If the mixture is separated by column chromatography using the same solvent mixture as a mobile phase, which of the two components A or B will elute first? Explain.

Solution

A will elute first because the R_f value of A is more than B, which means that it is less strongly adsorbed as compared to B.

6. Is it possible to get pure benzoic acid from a mixture of benzoic acid and naphthalene through the process of recrystallization, using benzene as a solvent? Give reasons.

Solution

No, it is not possible because both benzoic acid and naphthalene are quite soluble in benzene.

7. Which method is most appropriate in the separation of ether from toluene?

Solution

Simple distillation is used to separate ether from toluene.

8. What is the criterion of determining purity of an organic compound?

Solution

The criteria for determining the purity of an organic compound is its melting point, boiling point, refractive index, etc. This is because each pure compound possesses a distinct set of physical properties which differentiates it from the other compounds.

9. Give a brief description of the principles of the following techniques taking an example in each case: (a) crystallization, (b) distillation and (c) chromatography.   (NCERT)

Solution

    (a) Crystallization: This method is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. For example, crystallization of sugar.

    (b) Distillation: This method is used to separate volatile liquids from non-volatile impurities and to separate the liquids having large difference in their boiling points. For example, a mixture of chloroform and benzene.

    (c) Chromatography: This method is used for separation, purification, identification and characterization of the components of a mixture. In this method, a mixture is applied onto a stationary phase (may be liquid or solid). A pure solvent (mixture of solvents or a gas) is allowed to move slowly over the stationary phase and the components of the mixture get gradually separated from one another. For example, a mixture of naphthalene and benzophenone.

10. Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.   (NCERT)

Solution

The method used to separate two compounds with different solubilities in a solvent S is fractional crystallization. In this method, a hot saturated solution of the two components is first allowed to cool. The less soluble compound crystallizes out first, while the more soluble remains in the solution. After that the crystals are separated from the mother liquor. This mother liquor is concentrated again, and again the hot solution is allowed to cool to obtain the crystals of the more soluble compound, which are again filtered and dried.

11. What is the difference between distillation, distillation under reduced pressure and steam distillation?　　　　**(NCERT)**

Solution

(a) **Distillation:** This method is used to separate volatile liquids from non-volatile impurities and to separate the liquids having large differences in their boiling points. For example, a mixture of chloroform and benzene.

(b) **Distillation under reduced pressure:** This method is used to purify liquids having very high boiling points and those which decompose at or below their boiling points. For example, concentration of sugarcane in sugar industry.

(c) **Steam distillation:** This method is used to purify such liquids which are steam volatile, insoluble in water, possess a vapor pressure of 10–15 mm Hg and contain non-volatile impurities.

12. Explain the principle of paper chromatography.　　　　**(NCERT)**

Solution

It works on the principle of partition, that is, it is based upon continuous differential partitioning of the various components of the mixture between the stationary and the mobile phases.

13. Name a suitable technique for separation of the components from a mixture of calcium sulphate and camphor.　　　　**(NCERT)**

Solution

A suitable technique for this separation is by sublimation because camphor can undergo is sublimation, while $CaSO_4$ is not.

14. Explain, why an organic liquid vaporizes at a temperature below its boiling point in its steam distillation?　　　　**(NCERT)**

Solution

In steam distillation, the mixture of the organic liquid and water boils only when the sum of their vapor pressures becomes equal to the atmospheric pressure. Since, the vapor pressure of water is quite high and that of the liquid is low, therefore, the organic liquid vaporizes at a temperature much lower than its normal boiling point.

15. The best and latest technique for isolation, purification and separation of organic compounds is

(a) crystallization.　　(b) distillation.　　(c) sublimation.　　(d) chromatography.　　　　**(NCERT)**

Solution

(d) Chromatography is the best and the latest technique.

12.9 QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Conceptual Questions

1. How will you detect the presence of carbon and hydrogen in an organic compound?

Solution

The presence of carbon and hydrogen in an organic compound can be detected by heating the compound with copper(II) oxide in a hard glass tube. Carbon present in the organic compound is oxidized to carbon dioxide and hydrogen is oxidized to water. Carbon dioxide turns lime water milky, while water condenses on the cooler parts of the test tube and turns anhydrous copper sulphate blue. The equations involved are

$$C + 2CuO \xrightarrow{Heat} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{Heat} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow \underset{\text{Milkiness}}{CaCO_3} + H_2O$$

$$5H_2O + \underset{\text{(White)}}{CuSO_4} \longrightarrow \underset{\text{(Blue)}}{CuSO_4} + 5H_2O$$
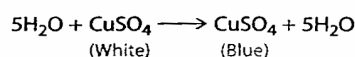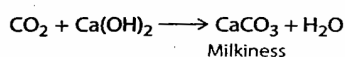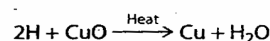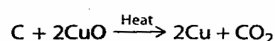
2. Write chemical equations involved in the detection of sulphur and phosphorus in organic compounds.

Solution

(a) **Detection of sulphur:**
(i) Lassaigne's test

$$2Na + S \xrightarrow{Heat} Na_2S$$
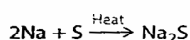
(ii) Sodium nitroprusside test

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{(Violet)}}{Na_4[Fe(CN)_5NOS]}$$

(iii) Lead acetate test

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{(Black ppt.)}}{PbS} + 2CH_3COONa$$

12
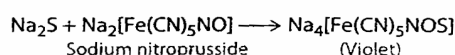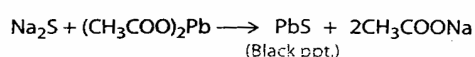
(b) Detection of phosphorus:

$$5Na_2O_2 + 2P \xrightarrow{Heat} 2Na_3PO_4 + 2Na_2O$$
(From organic compound)

$$Na_3PO_4 + 3HNO_3 \xrightarrow{Heat} H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \xrightarrow{Heat} (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$$
Ammonium molybdate   Ammonium polyphosphomolybdate (Yellow ppt.)
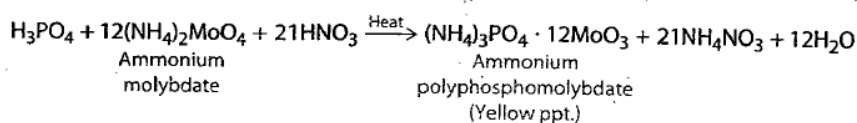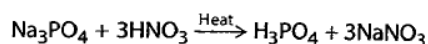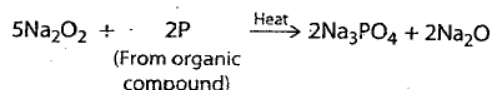
3. Discuss the chemistry of Beilstein test for the detection of halogens. Why is this test not dependable?

Solution

In Beilstein test, a (clean) copper wire is heated in the non-luminous flame of the Bunsen burner until it ceases to impart any green or bluish green color to the flame. The heated end of the wire is dipped into the organic compound and is again introduced into the Bunsen flame. The appearance of a bluish green or green flame due to the formation of volatile cupric halides shows the presence of halogens in the given organic compound. This test is not dependable because some compounds like urea, thiourea which do not contain halogens respond to this test due to the formation of volatile cupric cyanide. Moreover, it does not actually tell us which halogen is actually present in the organic compound.

4. Why is a freshly prepared saturated solution of ferrous sulphate used in the Lassaigne's test for nitrogen?

Solution

On keeping aqueous $FeSO_4$ solution, it undergoes oxidative hydrolysis to form basic ferric sulphate.

$$4FeSO_4 + 2H_2O + O_2 \longrightarrow 4Fe(OH)SO_4$$
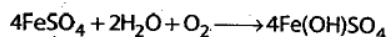
The pale yellow color of Fe^{3+} ions interferes with the light green color usually obtained in Lassaigne's test.

5. Discuss the chemistry of Lassaigne's test.

Solution

In Lassaigne's test, a small piece of freshly cut sodium is heated in a fusion tube till it forms a shining globule. The tube is removed from the flame, then a small amount of the organic compound is added and the tube is heated strongly till it becomes red hot. The red hot tube is then plunged into a china dish containing 10–15 mL of distilled water. The contents of the china dish are boiled, cooled and then filtered. This filtrate is known as Lassaigne's extract.

During fusion, carbon and nitrogen of the organic compound combine to form sodium cyanide

$$Na + C + N \xrightarrow{Heat} NaCN$$
(From organic compound)
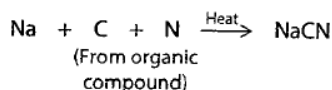
On heating the filtrate with ferrous sulphate solution, sodium ferrocyanide, that is, sodium hexacyanoferrate(II) is formed and also some of the ferrous (Fe^{2+}) ions are oxidized to ferric (Fe^{3+}) ions. These Fe^{3+} ions reacts with sodium hexacyanoferrate(II) to give iron(III) hexacyanoferrate(II) which is Prussian blue in color.

$$2NaCN + FeSO_4 \longrightarrow Na_2SO_4 + Fe(CN)_2$$

$$Fe(CN)_2 + 4NaCN \longrightarrow Na_4[Fe(CN)_6]$$
Sodium hexacyanoferrate (II)

$$3Na_4[Fe(CN)_6] + 4Fe^{3+} \longrightarrow Fe_4[Fe(CN)_6]_3 + 12Na^+$$
Iron (III) hexacyanoferrate (II) (Prussian blue)
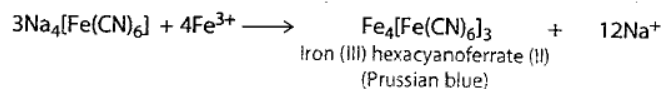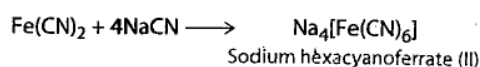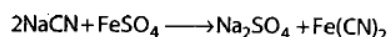
However, if both sulphur and nitrogen are present in the organic compound, they may combine during fusion to form sodium thiocyanate due to insufficient sodium. This when heated with ferrous sulphate produces a blood red coloration due to ferric thiocyanate by reaction with ferric ions formed by oxidation of ferrous ions.

$$Na + C + S + N \xrightarrow{Heat} NaSCN$$

$$Fe^{3+} + 3NaSCN \longrightarrow Fe(SCN)_3 + 3Na^+$$
Ferric thiocyanate (Blood red coloration)
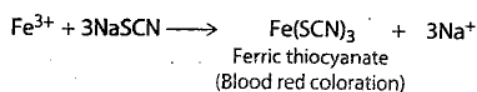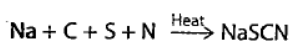
6. Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens? (NCERT)

Solution

Sodium extract is boiled with nitric acid is added to decompose NaCN and Na_2S, if present,

$$NaCN + AgNO_3 \longrightarrow NaNO_3 + HCN$$

$$Na_2S + 2AgNO_3 \longrightarrow 2NaNO_3 + H_2S$$
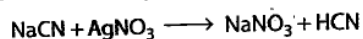
otherwise these will react with $AgNO_3$ and hence interfere with the test for halogens as shown below.

$$NaCN + AgNO_3 \longrightarrow \underset{\text{(White ppt.)}}{AgCN} + NaNO_3$$

$$Na_2S + 2AgNO_3 \longrightarrow \underset{\text{(Black ppt.)}}{Ag_2S} + 2NaNO_3$$

7. Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens. (NCERT)

Solution

As the elements present in the organic compound are in their covalent form, so they have to be fused with sodium metal so as to convert them to ionic form.

8. Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

Solution

No, white precipitate is not formed because CCl_4 is a covalent compound. It does not ionize to give Cl^- ion which is required for the formation of ppt. of AgCl.

9. Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test? (NCERT)

Solution

For testing sulphur, the sodium extract is acidified with acetic acid because lead acetate is soluble in it, and therefore, does not interfere with the test. However, if H_2SO_4 is used lead acetate will react with H_2SO_4 to form white precipitate of lead sulphate which will interfere with the test.

10. In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue color is obtained due to the formation of (NCERT)
(a) $Na_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$ (c) $Fe_2[Fe(CN)_6]$ (d) $Fe_3[Fe(CN)_6]_4$

Solution

(b) Refer to Question 5 of this section.

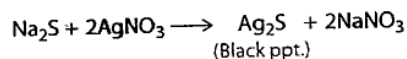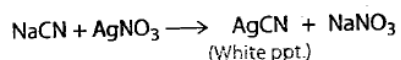# 12.10 QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Conceptual Questions

1. For which type of compounds, Kjeldahl's method is not applicable?

Solution

Kjeldahl's method is not applicable to compounds containing nitrogen in the ring (e.g., pyridine, quinoline, etc.) and compounds containing nitrogen directly linked to oxygen atom (e.g., NO_2) or another nitrogen atom, that is, azo compounds.

2. If 0.35 g of an organic compound on Kjeldahl's method gave enough ammonia to just neutralize 30 cm³ of 0.10 M HCl, calculate the percentage of nitrogen in the organic compound.

Solution

The percentage of nitrogen is found as

$$\% \text{ of } N = \frac{1.4 \times \text{Molarity of the acid} \times \text{Basicity of acid} \times \text{Volume of acid used}}{\text{Mass of organic substance taken}}$$

$$= \frac{1.4 \times 1 \times 0.1 \times 30}{0.35} = 12\%$$

3. In what form we estimate phosphorus present in the organic compound?

Solution

Phosphorus is precipitated as ammonium phosphomolybdate or as magnesium pyrophosphate depending upon the reagent used.

4. If 0.2570 g of an organic compound in quantitative analysis gave 0.3500 g of barium sulphate, calculate the percentage of sulphur in the organic compound.

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Solution

The percentage of sulphur is obtained as

$$\% \text{ of } S = \frac{32}{233} \times \frac{\text{Mass of barium sulphate formed}}{\text{Mass of organic substance taken}} \times 100 = \frac{32}{233} \times \frac{0.35}{0.257} \times 100 = 18.7\%$$

5. In what form do we estimate nitrogen in Dumas method?

Solution

In Dumas method, we estimate nitrogen present in the organic compound as dinitrogen at STP.

6. In Dumas method for estimation of nitrogen, which solution is taken in Schiff's nitrometer? Why water cannot be used?

Solution

In Dumas method, 40% KOH solution is taken in Schiff's nitrometer. KOH absorbs CO_2 and H_2O vapors produced during combustion and the nitrogen thus formed is collected over it. Water cannot be used because it is produced in the Dumas method.

7. Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound. (NCERT)
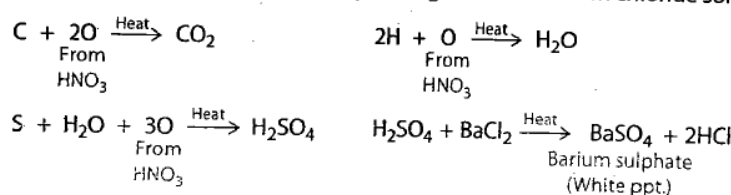
Solution

In Carius method, a known amount of organic compound is heated with fuming nitric acid and with a few crystals of silver nitrate in a sealed hard glass tube called Carius tube in a furnace. Under the conditions, carbon and hydrogen are oxidized to carbon dioxide and water, respectively, while halogen is converted to silver halide. The precipitates of silver halide are filtered, washed, dried and weighed. Knowing the mass of the substance taken and the mass of the precipitate formed, the percentage of halogen is calculated as follows:

$$\% \text{ of Halogen} = \frac{\text{Atomic mass of halogen}}{108 + \text{Atomic mass of halogen}} \times \text{Mass of silver halide formed} \times \frac{100}{\text{Mass of the substance taken}}$$
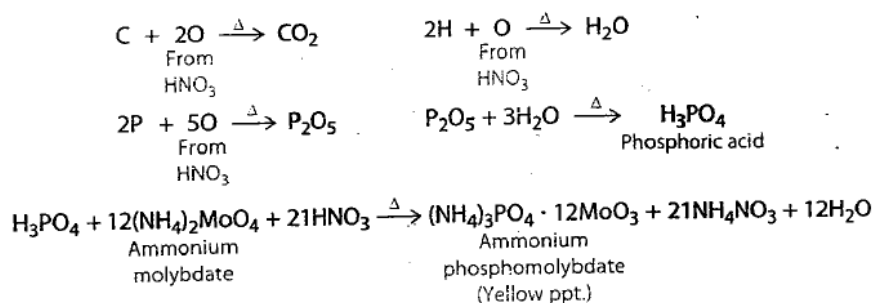
For estimating sulphur, a known mass of the substance is heated with sodium peroxide or fuming nitric acid in a sealed tube (Carius tube). Carbon and hydrogen are oxidized to CO_2 and H_2O, respectively, while sulphur present in the organic compound is oxidized to sulphuric acid which is then precipitated as barium sulphate by adding excess of barium chloride solution.

$$C + 2O \xrightarrow[\text{From HNO}_3]{\text{Heat}} CO_2 \qquad 2H + O \xrightarrow[\text{From HNO}_3]{\text{Heat}} H_2O$$

$$S + H_2O + 3O \xrightarrow[\text{From HNO}_3]{\text{Heat}} H_2SO_4 \qquad H_2SO_4 + BaCl_2 \xrightarrow{\text{Heat}} \underset{\substack{\text{Barium sulphate} \\ \text{(White ppt.)}}}{BaSO_4} + 2HCl$$

The ppt. of $BaSO_4$ is filtered, washed, dried and weighed. Knowing the mass of the substance taken and the mass of $BaSO_4$ ppt. formed, the percentage of sulphur can be calculated as

$$\% \text{ of } S = \frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \text{ formed}}{\text{Mass of organic substance taken}} \times 100$$

For estimating phosphorus, a known amount of organic substance is heated with fuming HNO_3 in a sealed tube (Carius tube). Under these conditions, carbon and hydrogen present in the organic compound are oxidized to CO_2 and H_2O, respectively, while phosphorus present in the organic compound is oxidized to phosphoric acid which is precipitated as ammonium phosphomolybdate by heating it with conc. HNO_3 and then adding ammonium molybdate.

$$C + 2O \xrightarrow[\text{From HNO}_3]{\Delta} CO_2 \qquad 2H + O \xrightarrow[\text{From HNO}_3]{\Delta} H_2O$$

$$2P + 5O \xrightarrow[\text{From HNO}_3]{\Delta} P_2O_5 \qquad P_2O_5 + 3H_2O \xrightarrow{\Delta} \underset{\text{Phosphoric acid}}{H_3PO_4}$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \xrightarrow{\Delta} \underset{\substack{\text{Ammonium} \\ \text{phosphomolybdate} \\ \text{(Yellow ppt.)}}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O$$

$\underset{\substack{\text{Ammonium} \\ \text{molybdate}}}{}$

The precipitates of ammonium phosphomolybdate thus formed are filtered, washed, dried and weighed. Knowing the mass of the organic compound taken and the mass of ammonium phosphomolybdate formed, the percentage of phosphorus can be calculated as:

$$\% \text{ of } P = \frac{31}{1877} \times \frac{\text{Mass of ammonium phosphomolybdate}}{\text{Mass of organic substance}} \times 100$$

8. Differentiate between the principle of estimation of nitrogen in an organic compound by (a) Dumas method and (b) Kjeldahl's method. **(NCERT)**

Solution

(a) The organic compound containing nitrogen is heated with copper oxide in an atmosphere of CO_2 when nitrogen present in the organic compound is converted into N_2 gas. The volume of N_2 thus obtained is converted into NTP and the percentage of nitrogen is estimated as:

$$\% \text{ of } N = \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at NTP}}{\text{Mass of organic substance}} \times 100$$

(b) The organic compound containing nitrogen is heated with conc. H_2SO_4 in presence of K_2SO_4 and some $CuSO_4$ or Hg in a long-necked flask called Kjeldahl's flask. The nitrogen present in the compound gets converted into ammonium sulphate. This ammonium sulphate thus obtained is boiled with excess of NaOH solution to liberate NH_3 gas which is absorbed in a known excess of a standard acid such as H_2SO_4 or HCl. The volume of acid left unused is found by titration against a standard alkali solution. From the volume of acid used, the percentage of nitrogen is determined by applying the equation

$$\% \text{ of } N = \frac{1.4 \times \text{Molarity of the acid} \times \text{Basicity of acid} \times \text{Volume of acid used}}{\text{Mass of organic substance taken}}$$

9. An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion. **(NCERT)**

Solution

Mass of organic compound (given) = 0.20 g
Percentage of carbon = 69, percentage of hydrogen = 4.8

$$\% \text{ of } C = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of organic compound}} \times 100$$

Therefore, mass of CO_2 formed $= \frac{44}{12} \times \frac{69 \times 0.20}{100} = 0.506 \text{ g}$

Similarly,

$$\% \text{ of } H = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of organic compound}} \times 100$$

Therefore, mass of H_2O formed $= \frac{18 \times 4.8 \times 0.20}{2 \times 100} = 0.0864 \text{ g}$

10. Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound? **(NCERT)**

Solution

CO_2 is acidic in nature; therefore, it reacts with the strong base KOH to form K_2CO_3. The increase in the mass of U-tube containing KOH then gives the mass of CO_2 produced and from its mass, the percentage of carbon in the organic compound can be estimated by using the equation:

$$\% \text{ of } C = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of organic compound}} \times 100$$

11. If 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation, calculate the percentage of chlorine present in the compound. **(NCERT)**

Solution

Mass of AgCl formed = 0.5740 g, mass of organic compound = 0.3780 g

1 mol of AgCl = 1 g atom of Cl

Thus, 143.5 g of AgCl = 35.5 g of AgCl. Now, applying the relation to obtain percentage of Cl

$$\% \text{ of } Cl = \frac{35.5}{143.5} \times \frac{\text{Mass of silver chloride formed}}{\text{Mass of organic compound taken}} \times 100 = \frac{35.5}{143.5} \times \frac{0.5740}{0.3780} \times 100 = 37.566 \%$$

12. In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

(NCERT)

Solution

Mass of organic compound = 0.468 g, mass of barium sulphate formed = 0.668 g

1 mol of $BaSO_4$ = 1 g atom of S or 233 g of $BaSO_4$ = 32 g of S

Applying the relation, we get the percentage of S as

$$\% \text{ of S} = \frac{32}{233} \times \frac{\text{Mass of barium sulphate formed}}{\text{Mass of organic substance taken}} \times 100 = \frac{32}{233} \times \frac{0.668}{0.468} \times 100 = 19.6\,\%$$