Chapter 8: Organic Chemistry — Some Basic Principles and Techniques

Exercises — Exercises

Q1 What are the 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

SOLUTION

Hybridisation determines the geometry around each carbon based on the number of sigma bonds and lone pairs.

$CH_2=C=O$ (ketene):
C_1 ($=CH_2$): forms 1 C=C sigma + 2 C-H sigma bonds = 3 sigma bonds → sp^2
C_2 (=C=): forms sigma bonds to C_1 and O with two pi bonds (cumulated) → sp hybridised

$CH_3CH=CH_2$ (propene):
C_1 (CH_3^-): forms 3 C-H + 1 C-C sigma bonds = 4 sigma bonds → sp^3
C_2 (-CH=): forms 1 C=C (sigma+pi), 1 C-C sigma, 1 C-H sigma = 3 sigma bonds → sp^2
C_3 ($=CH_2$): forms 1 C=C (sigma+pi) + 2 C-H sigma = 3 sigma bonds → sp^2

$(CH_3)_2CO$ (acetone / propan-2-one):
C_1 (CH_3^-): 3 C-H + 1 C-C = 4 sigma bonds → sp^3
C_2 (>C=O): 2 C-C sigma + 1 C=O sigma = 3 sigma bonds → sp^2
C_3 (CH_3^-): same as C_1 → sp^3

$CH_2=CHCN$ (acrylonitrile):
C_1 ($=CH_2$): sp^2
C_2 ($=CH^-$): sp^2
C_3 (≡N carbon in CN): forms 1 C-C sigma + 1 C≡N (sigma+2pi) = 2 sigma bonds → sp

C_6H_6 (benzene ring): all 6 ring carbons form 2 C-C sigma + 1 C-H sigma = 3 sigma bonds → all sp^2

Answer: $CH_2=C=O$: C_1 sp^2, C_2 sp; $CH_3CH=CH_2$: C_1 sp^3, C_2 sp^2, C_3 sp^2; $(CH_3)_2CO$: carbonyl C sp^2, methyl carbons sp^3; $CH_2=CHCN$: C_1 sp^2, C_2 sp^2, C_3 (CN carbon) sp; C_6H_6: all ring carbons sp^2

Q2 Indicate the sigma and pi bonds in the following molecules: C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2=C=CH_2$, CH_3NO_2, $HCONHCH_3$

SOLUTION

Sigma (σ) bonds: all single bonds + the sigma component of every double/triple bond.
Pi (π) bonds: the extra bond(s) in each double bond (1π) or triple bond (2π).

C_6H_6 (benzene): 6 C-C σ (ring) + 6 C-H σ + 3 π (from the 3 formal double bonds in the Kekulé structure) → σ = 12, π = 3

C_6H_{12} (cyclohexane): 6 C-C σ (ring) + 12 C-H σ; no double bonds → σ = 18, π = 0

CH_2Cl_2 (dichloromethane): 2 C-H σ + 2 C-Cl σ → σ = 4, π = 0

$CH_2=C=CH_2$ (propadiene / allene): 4 C-H σ + 2 C-C σ (each C=C contributes 1 σ) + 2 π (one per cumulated double bond) → σ = 6, π = 2

CH_3NO_2 (nitromethane): 3 C-H σ + 1 C-N σ + 2 N-O σ (one N-O single, one N=O σ) + 1 π (from N=O) → σ = 6, π = 1

$HCONHCH_3$ (N-methylformamide): H-C σ, C=O (σ+π), C-N σ, N-H σ, N-CH_3 σ, and 3 C-H σ on the methyl → σ = 8, π = 1

Answer: C_6H_6: 12σ, 3π; C_6H_{12}: 18σ, 0π; CH_2Cl_2: 4σ, 0π; $CH_2=C=CH_2$: 6σ, 2π; CH_3NO_2: 6σ, 1π; $HCONHCH_3$: 8σ, 1π

Q3 Write bond line formulas for: Isopropyl alcohol, 2,3-Dimethylbutanal, Heptan-4-one.

SOLUTION

Bond-line (skeletal) formulas show carbon chains as zigzag lines; each vertex/end = C; H atoms on C are implied.

Isopropyl alcohol [$(CH_3)_2CHOH$]:
Draw a V-shape (2 C-C bonds meeting at central C) with -OH on the central carbon.
The end carbons are CH_3, central carbon carries -OH.
Bond-line: a V with -OH at the central vertex.

2,3-Dimethylbutanal [$CH_3CH(CH_3)CH(CH_3)CHO$]:
4-carbon chain (butanal backbone) with CHO at C_1, methyl at C_2 and C_3.
Bond-line: zigzag of 4 carbons, -CHO at one end, two methyl branches at C_2 and

C_3.

Heptan-4-one [$CH_3CH_2CH_2$-CO-$CH_2CH_2CH_3$]:
7-carbon chain with C=O at position 4.
Bond-line: zigzag of 7 carbons with a =O (ketone) at the 4th vertex.

Answer: Bond-line structures: Isopropyl alcohol = V-shape with -OH at central vertex; 2,3-Dimethylbutanal = 4-C zigzag with CHO at C_1 and methyl branches at C_2 and C_3; Heptan-4-one = 7-C zigzag with C=O at the 4th carbon

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Q4 Give the IUPAC names of the following compounds shown as bond-line formulas: (a) phenyl attached to a 3-carbon chain (b) a nitrile with a methyl branch (c) a branched alkane with two methyl branches (d) a 6-carbon chain bearing Cl and Br on the same (middle) carbon (e) a chloro-aldehyde chain (f) Cl_2CHCH_2OH.

SOLUTION

(a) C_6H_5-CH_2-CH_2-CH_3 (benzene ring bonded to a straight 3-carbon chain):
The parent is benzene with a propyl substituent → propylbenzene.
IUPAC name: Propylbenzene (1-phenylpropane).

(b) CH_3-CH_2-$CH(CH_3)$-CH_2-CN (nitrile carbon is C_1):
Longest chain containing the -CN carbon = 5 carbons → pentanenitrile; a methyl branch sits on C_3.
IUPAC name: 3-Methylpentanenitrile.

(c) The bond-line shows a 7-carbon chain with methyl branches at C_2 and C_5:
Parent = heptane; numbering to give the lowest locant set {2,5} (vs {3,6} from the other end).
IUPAC name: 2,5-Dimethylheptane.

(d) A 6-carbon chain with Cl and Br both on C_3 (CH_3-CH_2-$C(Cl)(Br)$-CH_2-CH_2-CH_3):
Parent = hexane; substituents cited alphabetically (bromo before chloro), both on C_3 (lower locant from the left end).
IUPAC name: 3-Bromo-3-chlorohexane.

(e) Cl-CH_2-CH_2-CHO (aldehyde carbon is C_1):
Parent = propanal; Cl on C_3.
IUPAC name: 3-Chloropropanal.

(f) Cl_2CHCH_2OH:

Parent = ethanol (2 carbons), -OH at C_1, two Cl on C_2.
IUPAC name: 2,2-Dichloroethanol.

Answer: (a) Propylbenzene (1-phenylpropane); (b) 3-Methylpentanenitrile; (c) 2,5-Dimethylheptane; (d) 3-Bromo-3-chlorohexane; (e) 3-Chloropropanal; (f) 2,2-Dichloroethanol.

Q5 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

(a) 2,2-Dimethylpentane vs 2-Dimethylpentane:
A carbon atom cannot have a single '2-dimethyl' designation — you need to specify each methyl's position.
Two methyl groups on C_2 → locants must be cited twice: 2,2-dimethylpentane.
CORRECT: 2,2-Dimethylpentane

(b) 2,4,7-Trimethyloctane vs 2,5,7-Trimethyloctane:
Methyloctane parent = 8 carbons. Numbering must give the lowest set of locants.
Numbering from the end that gives lower locants: 2,4,7 vs 2,4,7 (reverse gives 2,5,7).
Locant set {2,4,7} < {2,5,7}: CORRECT: 2,4,7-Trimethyloctane

(c) 2-Chloro-4-methylpentane vs 4-Chloro-2-methylpentane:
Principal chain: pentane. Number from end nearest the first branch.
Numbering from Cl end: Cl at C_1, methyl at C_3 → 1-chloro-3-methylpentane.
Numbering from methyl end: methyl at C_2, Cl at C_4 → 4-chloro-2-methylpentane.
Alphabetical order of substituents for citation: chloro (C) before methyl (M) alphabetically.
Using lowest set of locants {2,4} vs {2,4}: both equivalent; alphabetical principle: cite chloro first; gives 2-chloro-4-methylpentane.
CORRECT: 2-Chloro-4-methylpentane

(d) But-3-yn-1-ol vs But-4-ol-1-yne:
Numbering rule: give lower locant to the principal characteristic group (-OH) and then to the triple bond.
Numbering to give -OH the lower number: -OH at C_1, triple bond at C_3 →

But-3-yn-1-ol.
CORRECT: But-3-yn-1-ol

Answer: Correct IUPAC names: (a) 2,2-Dimethylpentane (b) 2,4,7-Trimethyloctane (c) 2-Chloro-4-methylpentane (d) But-3-yn-1-ol

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Q6 Draw the formulas for the first five members of each homologous series beginning with the following compounds: (a) H-COOH (b) CH_3COCH_3 (c) $H\text{-}CH{=}CH_2$.

SOLUTION

In a homologous series, successive members differ by a $-CH_2^-$ unit and share the same general formula.

(a) H-COOH — carboxylic acid series ($C_nH_{2n+1}COOH$ / -COOH group):
1. HCOOH (methanoic acid)
2. CH_3COOH (ethanoic acid)
3. CH_3CH_2COOH (propanoic acid)
4. $CH_3CH_2CH_2COOH$ (butanoic acid)
5. $CH_3CH_2CH_2CH_2COOH$ (pentanoic acid)

(b) CH_3COCH_3 — ketone series (>C=O group):
1. CH_3COCH_3 (propan-2-one)
2. $CH_3COCH_2CH_3$ (butan-2-one)
3. $CH_3COCH_2CH_2CH_3$ (pentan-2-one)
4. $CH_3COCH_2CH_2CH_2CH_3$ (hexan-2-one)
5. $CH_3COCH_2CH_2CH_2CH_2CH_3$ (heptan-2-one)

(c) $H\text{-}CH{=}CH_2$ (ethene) — alkene series (C_nH_{2n} / C=C group):
1. $CH_2{=}CH_2$ (ethene)
2. $CH_3CH{=}CH_2$ (propene)
3. $CH_3CH_2CH{=}CH_2$ (but-1-ene)
4. $CH_3CH_2CH_2CH{=}CH_2$ (pent-1-ene)
5. $CH_3CH_2CH_2CH_2CH{=}CH_2$ (hex-1-ene)

Answer: (a) Carboxylic acids: HCOOH, CH_3COOH, CH_3CH_2COOH, $CH_3CH_2CH_2COOH$, $CH_3CH_2CH_2CH_2COOH$. (b) Ketones: CH_3COCH_3, $CH_3COCH_2CH_3$, $CH_3COCH_2CH_2CH_3$, $CH_3COCH_2CH_2CH_2CH_3$, $CH_3COCH_2CH_2CH_2CH_2CH_3$ (propan-2-one → heptan-2-one). (c) Alkenes: $CH_2=CH_2$, $CH_3CH=CH_2$, $CH_3CH_2CH=CH_2$, $CH_3CH_2CH_2CH=CH_2$, $CH_3CH_2CH_2CH_2CH=CH_2$ (ethene → hex-1-ene).

Q7 Give condensed and bond-line structural formulas and identify the functional groups present, if any, for: (a) 2,2,4-Trimethylpentane (b) 2-Hydroxy-1,2,3-propanetricarboxylic acid (c) Hexanedial

SOLUTION

(a) 2,2,4-Trimethylpentane:
Condensed: $(CH_3)_3C\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$
Functional group: None — it is a pure alkane (saturated hydrocarbon)

(b) 2-Hydroxy-1,2,3-propanetricarboxylic acid:
Condensed: $HOOC\text{-}CH_2\text{-}C(OH)(COOH)\text{-}CH_2\text{-}COOH$
Functional groups: -OH (secondary alcohol) and -COOH (carboxylic acid, ×3)

(c) Hexanedial:
Condensed: $OHC\text{-}(CH_2)_4\text{-}CHO$
Functional group: -CHO (aldehyde) at C_1 and C_6

Answer: (a) $(CH_3)_3C\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$; no functional group. (b) $HOOC\text{-}CH_2\text{-}C(OH)(COOH)\text{-}CH_2\text{-}COOH$; groups: -OH and -COOH (×3). (c) $OHC\text{-}(CH_2)_4\text{-}CHO$; group: -CHO (×2)

Q8 Identify the functional groups in the following compounds: (a) a benzene ring bearing -CHO, $-OCH_3$ (OMe) and -OH (b) a benzene ring bearing $-NH_2$ and $-COOCH_2CH_2N(C_2H_5)_2$ (c) a benzene ring with a $-CH=CH-NO_2$ substituent.

SOLUTION

Functional groups are the reactive parts of organic molecules.

(a) A benzene ring carrying three substituents: -CHO, $-OCH_3$ and -OH.
Functional groups: aldehyde (-CHO), ether (methoxy, $-OCH_3$) and alcoholic/phenolic hydroxyl (-OH).

(b) A benzene ring carrying $-NH_2$ and $-C(=O)\text{-}O\text{-}CH_2CH_2N(C_2H_5)_2$ (this compound

is procaine).
Functional groups: primary amine (-NH_2, aromatic), ester (-COO^-) and tertiary amine (-$N(C_2H_5)_2$).

(c) A benzene ring bearing -CH=CH-NO_2 (β-nitrostyrene).
Functional groups: carbon-carbon double bond (C=C, alkene) and nitro group (-NO_2).

Answer: (a) Aldehyde (-CHO), ether (-OCH_3) and hydroxyl (-OH). (b) Primary amine (-NH_2), ester (-COO^-) and tertiary amine (-$N(C_2H_5)_2$). (c) C=C double bond (alkene) and nitro group (-NO_2).

Q9 Which of the two: O_2N-CH_2-CH_2-O^- or CH_3-CH_2-O^- is expected to be more stable and why?

SOLUTION

Both species are alkoxide anions (O^- at the end of a chain).

CH_3-CH_2-O^- (ethoxide ion):
The ethyl group (-CH_2CH_3) is electron-donating by inductive effect.
This INCREASES the electron density on the already negatively charged oxygen, making it less stable (destabilisation).

O_2N-CH_2-CH_2-O^- (2-nitroethoxide ion):
The nitro group (-NO_2) at the other end is strongly electron-withdrawing by inductive effect (-I).
This DECREASES the electron density on the O^- end, dispersing/delocalising the negative charge and STABILISING the anion.

The electron-withdrawing -NO_2 group stabilises the anion by pulling electron density away from the O^- through the inductive effect.

Therefore: O_2N-CH_2-CH_2-O^- is more stable than CH_3-CH_2-O^-.

Answer: O_2N-CH_2-CH_2-O^- is more stable. The -NO_2 (nitro) group is strongly electron-withdrawing (-I inductive effect), which disperses the negative charge and stabilises the anion. $CH_3CH_2O^-$ has an electron-donating ethyl group (+I) that intensifies the charge and destabilises the anion.

Q10 Explain why alkyl groups act as electron donors when attached to a pi system.

SOLUTION

Alkyl groups donate electrons to adjacent pi systems through two effects:

1. Hyperconjugation (Baker-Nathan effect):
The C-H sigma bonding electrons in the alkyl group can overlap with the adjacent p-orbital (part of the pi system).
This is called hyperconjugation — the sigma electrons delocalise into the pi system.
For example, in propene (CH_3-CH=CH_2), the 3 C-H bonds of CH_3 can each donate electron density into the C=C pi bond.
Greater the number of alpha-C-H bonds → greater the hyperconjugation → greater electron donation.

2. Inductive effect:
Carbon is slightly less electronegative than the central sp^2/sp carbon of the pi system.
Alkyl groups push electrons toward the pi system through the sigma framework (weak inductive donation).

Result: Alkyl-substituted alkenes and carbocations are more stable than unsubstituted ones because the alkyl group donates electron density, stabilising the electron-deficient pi system or cation.

Answer: Alkyl groups donate electrons to adjacent pi systems via hyperconjugation (C-H sigma bond electrons overlap with the adjacent p-orbital) and inductive effect. The more C-H bonds adjacent to the pi system, the greater the electron donation and stabilisation.

Q11 Draw the resonance structures for the following compounds and show the electron shift using curved-arrow notation: (a) C_6H_5OH (b) $C_6H_5NO_2$ (c) $CH_3CH=CHCHO$ (d) C_6H_5-CHO (e) C_6H_5-CH_2^+ (benzyl cation) (f) $CH_3CH=CH$-CH_2^+ (allyl cation).

SOLUTION

Resonance structures are drawn by shifting pi electrons (and lone pairs) using curved arrows.

(a) C_6H_5OH (phenol):

Lone pairs on -OH oxygen can donate into the ring via resonance.
Structures: canonical benzene ring + three contributors with $-O^-$ and positive charges at ortho and para positions.
Curved arrows: lone pair on O → C-O pi bond → ring → carbons at ortho/para develop +ve charge.
Shows -OH is electron-donating to the ring (activating, ortho/para director).

(b) $C_6H_5NO_2$ (nitrobenzene):
The N=O groups in the $-NO_2$ withdraw electrons from the ring.
N-O has pi bonds; the ring pi system donates into the empty orbital on N.
Structures: ring carbons (ortho/para to NO_2) develop partial positive charge.
Curved arrows: ring pi bond → N, N=O lone pair out.
Shows $-NO_2$ is electron-withdrawing (deactivating, meta director).

(c) $CH_3CH=CHCHO$ (but-2-enal / crotonaldehyde):
Conjugated system: C=C-C=O.
Resonance contributors: $CH_3CH=CH-CH=O \leftrightarrow CH_3-CH(-)-CH=CH-O^+$ (from pi shift).
Also: $+CH_3-CH=CH-CH=O \leftrightarrow CH_3CH=CH-C^(-)-O^+$.
Main contributors show electron density alternating across the conjugated chain.

(d) C_6H_5CHO (benzaldehyde):
Ring donates into the C=O of the aldehyde, and the C=O withdraws from the ring.
Structures: ring with partial positive at ortho/para, C=O with partial negative on O.
Curved arrows: ring pi → C(CHO), O lone pairs alternate.

(e) $C_6H_5-CH_2^+$ (benzyl cation):
The empty p orbital on the CH_2^+ carbon overlaps with the ring pi system; the positive charge is delocalised onto the ortho and para ring carbons.
Curved arrows: a ring pi bond shifts toward the exocyclic carbon, placing + on the ring in turn.

(f) $CH_3CH=CH-CH_2^+$ (allyl cation):
The C=C pi bond is adjacent to the empty p orbital of CH_2^+; the positive charge is shared between the two terminal carbons.
Contributors: $CH_3CH=CH-CH_2^+ \leftrightarrow CH_3-CH+-CH=CH_2$ (the pi bond shifts and the + relocates).

Answer: Resonance structures show pi electron delocalisation: (a) Phenol: -OH lone pair donates into ring — ortho and para positions develop negative charge (with O becoming +). (b) Nitrobenzene: ring pi donates to -NO_2 — ortho and para carbons develop partial positive charge. (c) But-2-enal: pi electrons delocalise across the C=C-C=O conjugated system. (d) Benzaldehyde: ring and CHO conjugation creates electron-density alternation. (e) Benzyl cation: + charge delocalised onto the ortho/para ring carbons. (f) Allyl cation: + charge shared between the two terminal carbons.

Q12 What are electrophiles and nucleophiles? Explain with examples.

SOLUTION

Electrophiles (electron-loving / electron-deficient species):

An electrophile is a reagent that is electron-deficient and seeks electron-rich centres.

It accepts an electron pair from a nucleophile.

Can be cations or neutral molecules with incomplete octets or partial positive charges.

Examples of electrophiles:

- H^+ (proton) — most common; accepts lone pair from nucleophile
- NO_2^+ (nitronium ion) — in nitration of benzene
- Cl^+ , Br^+ (halonium ions) — in halogenation
- BF_3, $AlCl_3$, $FeBr_3$ — Lewis acids with incomplete octets
- Carbocations (R^+) — e.g., $(CH_3)_3C^+$
- Carbonyl carbon in RCHO, RCOR' — partial positive due to C=O polarisation

Nucleophiles (nucleus-loving / electron-rich species):

A nucleophile is a reagent that is electron-rich and donates an electron pair to an electrophile.

Can be anions or neutral molecules with lone pairs or pi electrons.

Examples of nucleophiles:

- OH^- (hydroxide) — lone pairs on O
- CN^- (cyanide) — lone pair on C
- NH_3 — lone pair on N
- H_2O — lone pairs on O
- Halide ions: Cl^-, Br^-, I^-
- Alkoxide ions: RO^-

• Enolate ions and carbanions

Answer: Electrophiles are electron-deficient species that accept electron pairs (e.g., H^+, NO_2^+, BF_3, R^+, $AlCl_3$). Nucleophiles are electron-rich species that donate electron pairs (e.g., OH^-, CN^-, NH_3, H_2O, RO^-). Electrophiles attack electron-rich centres; nucleophiles attack electron-deficient centres.

Q13 Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles: (a) $CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$ (b) $CH_3COCH_3 + CN^- \rightarrow (CH_3)_2C(CN)OH$ (c) $C_6H_5 + CH_3CO^+ \rightarrow C_6H_5COCH_3$

SOLUTION

(a) $CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$
The reagent in bold is HO^- (hydroxide ion).
HO^- has lone pairs on oxygen and acts as an electron-pair donor.
It abstracts the proton (H^+) from the carboxylic acid — acting as a BASE.
From Lewis perspective, HO^- donates electrons → it is a NUCLEOPHILE.
Answer: HO^- is a nucleophile (base).

(b) $CH_3COCH_3 + CN^- \rightarrow (CH_3)_2C(CN)OH$
The reagent in bold is CN^- (cyanide ion).
CN^- donates its lone pair (on carbon) to the electrophilic carbonyl carbon of acetone (C=O).
It is an electron-pair donor attacking an electron-deficient centre.
Answer: CN^- is a nucleophile.

(c) $C_6H_5 + CH_3CO^+ \rightarrow C_6H_5COCH_3$
The reagent in bold is CH_3CO^+ (acetyl cation / acylium ion).
CH_3CO^+ is electron-deficient (positive charge on carbon).
It attacks the electron-rich benzene ring (electrophilic aromatic substitution).
Answer: CH_3CO^+ is an electrophile.

Answer: (a) HO^- is a nucleophile (donates lone pair, acts as base toward H^+). (b) CN^- is a nucleophile (donates lone pair to electrophilic carbonyl carbon). (c) CH_3CO^+ (acylium ion) is an electrophile (electron-deficient, attacks electron-rich benzene ring).

Q14 Classify the following reactions in one of the reaction types studied in this unit: (a) $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$ (b) $(CH_3)_2C=CH_2 + HCl \rightarrow (CH_3)_2ClC\text{-}CH_3$ (c) $CH_3CH_2Br + HO^- \rightarrow CH_2=CH_2 + H_2O + Br^-$ (d) $(CH_3)_3C\text{-}CH_2OH + HBr \rightarrow (CH_3)_2CBrCH_2CH_2CH_3 + H_2O$

SOLUTION

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

A nucleophile (HS^-) replaces the leaving group (Br^-).

Type: Nucleophilic Substitution (SN reaction)

(b) $(CH_3)_2C=CH_2 + HCl \rightarrow (CH_3)_2ClC\text{-}CH_3$

HCl adds across the C=C double bond; the double bond is broken and H and Cl add to the two carbons.

Type: Electrophilic Addition reaction

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

HO^- (base) removes a beta-hydrogen and Br^- leaves simultaneously, forming the C=C of ethene.

Type: Elimination reaction (dehydrohalogenation)

(d) $(CH_3)_3C\text{-}CH_2OH + HBr \rightarrow (CH_3)_2CBr\text{-}CH_2\text{-}CH_2\text{-}CH_3 + H_2O$

The -OH is replaced by -Br. The change in the carbon skeleton (neopentyl alcohol → a tertiary bromide) shows a carbocation rearrangement (1,2-methyl shift) accompanies the reaction.

The reagent HBr protonates -OH; water leaves; the resulting carbocation rearranges and captures Br^-.

Type: Nucleophilic Substitution (replacement of -OH by -Br, with rearrangement)

Answer: (a) Nucleophilic substitution (HS^- replaces Br^-). (b) Electrophilic addition (HCl adds to C=C). (c) Elimination (loss of HBr to give ethene). (d) Nucleophilic substitution (HBr replaces -OH with -Br, with a carbocation rearrangement).

Q15 What is the relationship between the members of the following pairs of structures? Are they structural or geometrical isomers or resonance contributors? (a) two ketones — one with the C=O at the middle of a 5-carbon chain and one with the C=O next to the end (b) two C=C structures differing only in the D/H arrangement about the double bond (c) H-C(=O+H)-OH and H-C+(OH)-OH.

SOLUTION

(a) The two ketones are pentan-3-one (CH_3CH_2-CO-CH_2CH_3) and pentan-2-one (CH_3-CO-$CH_2CH_2CH_3$).

Both have the molecular formula $C_5H_{10}O$ but differ in the POSITION of the carbonyl group along the chain — i.e. different connectivity.

Answer: Structural isomers (position/functional isomers).

(b) The two structures show the same C=C with D and H atoms arranged differently about the double bond (one has D and H cis on each carbon, the other trans).

Same connectivity of atoms, but different spatial arrangement about the rigid C=C.

Answer: Geometrical (cis-trans) isomers.

(c) H-C(=O+H)-OH and H-C+(OH)-OH (canonical forms of protonated formic acid):

Same atomic connectivity — they differ only in the distribution of electrons/charge (electrons shift, atoms do not move).

Answer: Resonance contributors (canonical structures of the same species).

Answer: (a) Structural (position) isomers — pentan-3-one vs pentan-2-one, same formula, different carbonyl position. (b) Geometrical (cis-trans) isomers — same connectivity, different arrangement of D/H about C=C. (c) Resonance contributors — same connectivity, differ only in electron distribution.

Q16 For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify the reactive intermediate produced as free radical, carbocation, or carbanion: (a) CH_3-O-CH_3 → CH_3-O^ + ^CH_3 (b) $(CH_3)_2C{=}O + HO^-$ → (c) $(CH_3)_3C$-Br → $(CH_3)_3C^+ + Br^-$ (d) benzene ring + E^+ →

SOLUTION

Homolysis: bond breaks with one electron going to each fragment → free radicals (neutral species with unpaired electrons).
Heterolysis: bond breaks with both electrons going to one fragment → ions (cation and anion).

(a) CH_3-O-CH_3 → CH_3-O^• + ^•CH_3 (the ether C-O bond cleaves homolytically):
Curved arrows: a single-barbed (fishhook) arrow from C-O bond → one electron to O, another to C.
Each fragment gets one electron.
Type: Homolysis
Reactive intermediate: Free radicals (CH_3O^• and ^•CH_3)

(b) C=O + HO^- → alcohol product (addition to carbonyl):
HO^- attacks the electrophilic carbonyl carbon. The C=O pi bond breaks heterolytically; both pi electrons go to O.
Curved arrows: lone pair on O of HO^- → C of C=O; C=O pi bond → O (two electrons).
Type: Heterolysis (of the C=O pi bond)
Reactive intermediate: an alkoxide (the carbonyl carbon becomes tetrahedral and the negative charge resides on oxygen).

(c) $(CH_3)_3C$-Br → $(CH_3)_3C^+ + Br^-$ (ionisation of tert-butyl bromide):
The C-Br bond breaks with BOTH bonding electrons going to bromine, leaving the carbon electron-deficient.
Curved arrows: a two-barbed (double-headed) arrow from the C-Br bond → to Br (both electrons to Br).
Type: Heterolysis
Intermediate: Carbocation (tert-butyl cation, $(CH_3)_3C^+$) plus the bromide ion Br^-

(d) Benzene ring + E^+ → (electrophilic aromatic substitution):
The electrophile E^+ attacks the electron-rich benzene ring; a pair of pi electrons attacks E^+.
Curved arrows: pi bond of ring → E^+ (two-barbed, heterolytic).

Type: Heterolysis

Intermediate: Carbocation (arenium ion / sigma complex)

Answer: (a) Homolysis → free radicals ($CH_3O^{\wedge}\bullet$ and $^{\wedge}\bullet CH_3$). (b) Heterolysis of the C=O pi bond → tetrahedral alkoxide intermediate (nucleophilic addition of HO^-). (c) Heterolysis of the C-Br bond in $(CH_3)_3C\text{-}Br$ → carbocation ($(CH_3)_3C^+$) + Br^-. (d) Heterolysis → carbocation intermediate (arenium ion / sigma complex in EAS).

Q17 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) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

SOLUTION

Inductive Effect (I effect):

The displacement of electron density in a sigma bond due to the difference in electronegativity between bonded atoms or groups.

It operates through the sigma bond framework and decreases with distance.

Electron-withdrawing groups (e.g., -F, -Cl, $-NO_2$, -CN) have -I effect: pull electrons toward themselves.

Electron-donating groups (e.g., alkyl -R) have +I effect: push electrons toward the chain.

Electromeric Effect (E effect):

A temporary intramolecular electron displacement in a pi bond system occurring under the influence of an attacking reagent.

The pi electron pair is completely transferred to one atom.

E^+ effect: pi electrons shift toward the attacking electrophile.

E^- effect: pi electrons shift away from the attacking electrophile.

This effect is temporary and occurs on demand of the reagent.

Acidity order (a): $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

Inductive effect explains this. Cl is strongly electron-withdrawing (-I effect).

More Cl atoms → greater withdrawal of electrons from the carboxylate O-H → weaker O-H bond → greater acidity.

Three Cl groups pull more electron density than two, which pulls more than one.

This stabilises the conjugate base (COO^-) more effectively.

Effect: -I effect of Cl is cumulative and increases acid strength.

Acidity order (b): $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

Inductive effect explains this too, via the electron-DONATING +I effect of alkyl groups.

Alkyl groups push electron density toward the -COOH; this intensifies the negative charge on the conjugate base ($RCOO^-$), destabilising it → weaker acid.

Going from $CH_3CH_2^-$ (one alkyl branch at the alpha carbon) to $(CH_3)_2CH^-$ (two) to $(CH_3)_3C^-$ (three), the cumulative +I effect increases.

More alkyl groups → greater +I donation → weaker acid. Hence $(CH_3)_3C.COOH$ is the weakest of the three.

Answer: Inductive effect: permanent electron displacement through sigma bonds due to electronegativity differences; decreases with distance. Electromeric effect: temporary complete pi electron shift under the influence of an attacking reagent. Both orders are explained by the INDUCTIVE effect. (a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$: cumulative -I (electron-withdrawing) effect of Cl atoms stabilises the carboxylate and increases acidity. (b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$: the +I (electron-donating) effect of alkyl groups destabilises the carboxylate — more alkyl groups = weaker acid.

Q18 Give a brief description of the principles of the following techniques taking an example in each case: (a) Crystallisation (b) Distillation (c) Chromatography

SOLUTION

(a) Crystallisation:

Principle: Based on the difference in solubilities of the compound and impurities in a suitable solvent at different temperatures. The compound dissolves in the hot solvent; on cooling, the pure compound crystallises out (since its solubility is lower at room temperature) while impurities remain in solution.

Example: Impure acetanilide (aniline acetate) is dissolved in minimum hot water; on slow cooling, pure acetanilide crystals separate out.

(b) Distillation:

Principle: Based on the difference in boiling points of miscible liquids in a mixture. The mixture is heated; the more volatile component (lower boiling point) vapourises first and is condensed separately.

Example: A mixture of water (b.p. 100°C) and acetone (b.p. 56°C) can be separated by distillation — acetone distils over first.

(c) Chromatography:

Principle: Based on the difference in rates at which the components of a mixture move through a stationary phase under the influence of a mobile phase. The component with greater affinity for the stationary phase moves slower; that with lesser affinity moves faster.

Example: Paper chromatography of ink dyes — a spot of ink is placed on paper (stationary phase) and water or solvent (mobile phase) moves up the paper; different dye pigments travel different distances and separate as distinct spots.

Answer: (a) Crystallisation: difference in solubility at different temperatures; impure acetanilide dissolved in hot water, pure crystals separate on cooling. (b) Distillation: difference in boiling points; acetone-water mixture separated by heating (acetone distils first). (c) Chromatography: differential migration through stationary vs mobile phase; ink pigments separated on paper by solvent movement.

Q19 Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

SOLUTION

The method is Fractional Crystallisation (or simple crystallisation applied sequentially).

Procedure:

1. Dissolve both compounds in the minimum amount of hot solvent S (both are soluble when hot).
2. Allow the solution to cool slowly. The compound with lower solubility in S crystallises out first (it becomes supersaturated earlier).
3. Filter the crystals of the less-soluble compound.
4. The filtrate still contains the more-soluble compound. Evaporate the filtrate further and cool again.
5. The more-soluble compound now crystallises out.
6. Repeat as necessary to obtain pure samples of both.

Example: A mixture of potassium nitrate (high solubility, especially at high T) and sodium chloride (less variation in solubility with temperature) can be separated by fractional crystallisation from water — KNO_3 crystallises preferentially on cooling a hot concentrated solution.

Answer: Fractional crystallisation: dissolve both compounds in minimum hot solvent S; cool slowly — the less-soluble compound crystallises first; filter; evaporate filtrate and cool again to recover the more-soluble compound. Repeat to obtain pure samples of each.

Q20 What is the difference between distillation, distillation under reduced pressure, and steam distillation?

SOLUTION

Distillation (Simple/Fractional):
Used for miscible liquids with different boiling points.
Performed at normal atmospheric pressure (1 atm).
The mixture is heated and the more volatile component distils over first.
Suitable for thermally stable liquids.

Distillation under Reduced Pressure (Vacuum Distillation):
Used for compounds that decompose or undergo chemical change at or below their normal boiling point.
The pressure above the liquid is reduced (using a vacuum pump) which lowers the boiling point significantly.
The compound distils at a lower temperature, avoiding decomposition.
Example: Glycerol (b.p. 290°C at 1 atm) can be distilled at a much lower temperature under vacuum.

Steam Distillation:
Used for separating substances that are:
(i) immiscible with water,
(ii) volatile in steam (have appreciable vapour pressure at 100°C),
(iii) thermally unstable at their own boiling points.
Steam is passed through the mixture; the compound distils with steam at a temperature below 100°C (below both boiling points separately).
The compound co-distils with water and is separated from the distillate.
Example: Aniline (b.p. 184°C) is purified by steam distillation — it co-distils with water at about 98°C.

Answer: Distillation: separates miscible liquids at normal pressure by boiling point difference. Distillation under reduced pressure (vacuum distillation): lowers boiling point by reducing pressure — used for thermally unstable compounds (e.g., glycerol). Steam distillation: water-immiscible, steam-volatile substances co-distil with steam below 100°C — used for heat-sensitive, high-boiling compounds (e.g., aniline).

Q21 Discuss the chemistry of Lassaigne's test.

SOLUTION

Lassaigne's test (Sodium fusion test) is used for the qualitative detection of nitrogen, sulphur, and halogens in organic compounds.

Principle:
The organic compound is fused with excess sodium metal in a fusion tube. The covalently bonded elements (N, S, X) are converted into their water-soluble ionic forms:
N → NaCN
S → Na_2S
Cl/Br/I → NaCl/NaBr/NaI
If both N and S are present: NaSCN (sodium thiocyanate)

The fusion mass is extracted with distilled water to give the Lassaigne's extract (sodium fusion extract), which is then tested:

Test for Nitrogen:
The extract + $FeSO_4$ solution → boil → acidify with dil. H_2SO_4.
Prussian blue (ferric ferrocyanide) precipitate indicates N.
Reactions: Na + C + N → NaCN (fusion)
$FeSO_4$ → Fe^{2+} ions; on heating: Fe^{2+} oxidises to Fe^{3+}
$Fe^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-}$ (ferrocyanide)
$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_6]_3$ (Prussian blue)

Test for Sulphur:
(i) Sodium nitroprusside test: extract + $Na_2[Fe(CN)_5NO]$ → violet/purple colour (Na_2S present).
(ii) Lead acetate test: acidified extract + lead acetate paper → black ppt of PbS.

Test for Halogens:
Acidify the extract with dil. HNO_3, add $AgNO_3$ solution.

White ppt (AgCl) — Chlorine; soluble in $NH_3(aq)$.
Pale yellow ppt (AgBr) — Bromine; sparingly soluble in NH_3.
Yellow ppt (AgI) — Iodine; insoluble in NH_3.

Answer: Lassaigne's test: organic compound fused with Na metal converts N→NaCN, S→Na_2S, halogens→NaX. The aqueous extract is tested: (i) N: $FeSO_4$ + heating + H_2SO_4 → Prussian blue [$Fe_4[Fe(CN)_6]_3$]; (ii) S: $Na_2[Fe(CN)_5NO]$ → violet colour; (iii) Halogens: $AgNO_3$ in HNO_3 → white (Cl), pale yellow (Br), yellow (I) precipitate.

Q22 Differentiate between the principle of estimation of nitrogen in an organic compound by (i) Dumas method and (ii) Kjeldahl's method.

SOLUTION

Dumas Method:
Principle: The organic compound is heated with excess CuO (copper oxide) in an atmosphere of CO_2.
Carbon → CO_2, Hydrogen → H_2O, Nitrogen → N_2 (gaseous).
The gaseous products are passed over heated copper (to reduce any nitrogen oxides to N_2) and then through KOH solution (absorbs CO_2).
The volume of N_2 collected over KOH at known temperature and pressure is measured.
The percentage of nitrogen is calculated from the volume of N_2.

Equation: N_2 volume (at STP) → moles of N_2 → % N

Kjeldahl's Method:
Principle: The organic compound is heated with concentrated H_2SO_4 in a Kjeldahl flask with K_2SO_4 and $CuSO_4$ (catalyst).
Nitrogen in the compound is converted to ammonium sulphate [$(NH_4)_2SO_4$].
The mixture is then treated with excess NaOH; NH_3 gas is liberated.
NH_3 is distilled into a known volume of standard acid (e.g., H_2SO_4 or HCl) and the excess acid is back-titrated with standard NaOH.
From the amount of acid neutralised by NH_3, the % N is calculated.

Key Difference:
Dumas method: N is collected as gaseous N_2 and measured volumetrically. Applicable to all nitrogen-containing compounds (including heterocyclic, nitro, azo, etc.).

Kjeldahl's method: N is converted to NH_3 and measured titrimetrically. NOT applicable to compounds where nitrogen is in nitro ($-NO_2$), azo ($-N=N^-$), or heterocyclic rings (pyridine etc.) — these are not readily converted to $(NH_4)_2SO_4$.

Answer: Dumas: compound heated with CuO → N_2 gas collected and measured volumetrically. Applicable to all N-compounds. Kjeldahl: compound digested with conc. H_2SO_4 → $(NH_4)_2SO_4$; NaOH liberates NH_3; NH_3 absorbed in standard acid and back-titrated. Not applicable to nitro/azo/heterocyclic N compounds.

Q23 Discuss the principle of estimation of halogens, sulphur, and phosphorus present in an organic compound.

SOLUTION

Estimation of Halogens (Carius Method):
The organic compound is heated with fuming nitric acid (HNO_3) in the presence of silver nitrate ($AgNO_3$) in a sealed Carius tube.
Carbon → CO_2, Hydrogen → H_2O, Halogen (X) → AgX (silver halide precipitate).
The AgX precipitate is filtered, dried, and weighed.
% X = (atomic mass of X × mass of AgX × 100) / (molar mass of AgX × mass of compound)

Estimation of Sulphur (Carius Method):
The compound is heated with fuming nitric acid in a Carius tube.
Sulphur → H_2SO_4 → precipitated as $BaSO_4$ by adding excess $BaCl_2$ solution.
$BaSO_4$ is filtered, dried, and weighed.
% S = (32 × mass of $BaSO_4$ × 100) / (233 × mass of compound)
where 233 = molar mass of $BaSO_4$.

Estimation of Phosphorus:
The compound is heated with fuming HNO_3 in a Carius tube.
Phosphorus → H_3PO_4 → treated with ammonium molybdate $[(NH_4)_2MoO_4]$ in HNO_3 to precipitate ammonium phosphomolybdate $[(NH_4)_3PO_4 \cdot 12MoO_3]$.
The precipitate is filtered, dried, and weighed.
Alternatively, phosphorus can be estimated by precipitating as $MgNH_4PO_4$ and igniting to $Mg_2P_2O_7$.
% P = (62 × mass of $Mg_2P_2O_7$ × 100) / (222 × mass of compound)

Answer: Halogens (Carius): compound + fuming HNO_3 + $AgNO_3$ in sealed tube → AgX precipitate; % X = (at. mass X × mass AgX × 100) / (M_AgX × mass compound). Sulphur (Carius): compound + HNO_3 → H_2SO_4; precipitate as $BaSO_4$; % S = (32 × mass $BaSO_4$ × 100) / (233 × mass compound). Phosphorus: compound + HNO_3 → H_3PO_4; precipitate as ammonium phosphomolybdate or $Mg_2P_2O_7$; calculate % P from mass of precipitate.

Q24 Explain the principle of paper chromatography.

SOLUTION

Paper chromatography is a type of partition chromatography.

Stationary Phase: Paper (cellulose) with adsorbed water molecules. Water held in the fibers of the paper acts as the stationary phase.

Mobile Phase: An organic solvent or a mixture of solvents that moves up the paper by capillary action.

Principle: The mixture to be separated is spotted near the bottom of the paper. When the mobile phase (solvent) moves up the paper, the components of the mixture distribute themselves between the stationary (water) and mobile (solvent) phases. Components more soluble in the mobile phase move faster (travel farther); those more soluble in the stationary phase (water) move slower (stay near the bottom).

This differential partitioning between the two phases separates the components into distinct spots.

Rf (Retardation Factor) value: Rf = (distance travelled by compound) / (distance travelled by solvent front).
Each pure compound has a characteristic Rf value under defined conditions; this is used for identification.

Application: Separation and identification of amino acids, pigments, drugs, and plant dyes.

Answer: Paper chromatography is partition chromatography. Stationary phase = water held in paper fibres; mobile phase = organic solvent moving up by capillary action. Components partition between the two phases — those more soluble in mobile phase travel farther. Separated as spots; identified by Rf = (distance by compound) / (distance by solvent front).

Q25 Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

SOLUTION

The sodium fusion (Lassaigne's) extract contains not only NaX (halide ions) but also NaCN (if N is present), Na_2S (if S is present), and NaSCN (if both N and S are present).

If silver nitrate were added directly to the alkaline extract:
• AgCN would precipitate (white) — could be confused with AgCl
• Ag_2S would precipitate (black) — would interfere with halide detection

Dilute HNO_3 (nitric acid) is added first to:
1. Neutralise the NaOH alkalinity of the extract (since the extract is boiled with alkali).
2. Decompose NaCN → HCN (gas, driven off) → removes cyanide ions that would form AgCN.
3. Decompose Na_2S → H_2S (gas, driven off) → removes sulphide ions that would form Ag_2S.
4. Prevent precipitation of Ag_2CO_3 (from carbonate if present).

After treatment with HNO_3, only the halide ions (Cl^-, Br^-, I^-) remain in solution. Addition of $AgNO_3$ then gives characteristic precipitates: AgCl (white), AgBr (pale yellow), AgI (yellow) — unambiguous identification.

Answer: HNO_3 is added to decompose and drive off interfering ions: CN^- → HCN (gas) and S^{2-} → H_2S (gas), which would otherwise form AgCN and Ag_2S precipitates and interfere with halide detection. Only halide ions remain after acidification, giving characteristic AgX precipitates on $AgNO_3$ addition.

Q26 Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur, and halogens.

SOLUTION

In organic compounds, the elements nitrogen, sulphur, and halogens are covalently bonded to carbon.

Covalent compounds do not ionise in water; therefore, the usual ionic tests for N^{3-}, S^{2-}, and X^- cannot be applied directly.

Fusion with sodium metal (Na) serves to:

1. Convert covalently bonded N, S, and halogens into their water-soluble, ionic sodium salts:
   N (covalent) + Na/C → NaCN (ionic, water-soluble)
   S (covalent) + Na → Na_2S (ionic, water-soluble)
   Cl/Br/I (covalent) + Na → NaCl/NaBr/NaI (ionic, water-soluble)

2. These ionic salts dissolve in water to give ions (CN^-, S^{2-}, X^-) that can be detected by standard qualitative tests.

Without sodium fusion, the covalent bonds holding N, S, and X in the organic compound prevent their detection.
The fusion provides the drastic reducing/ionic conversion conditions needed to break these strong C-N, C-S, and C-X covalent bonds.

Answer: Organic compounds contain N, S, and halogens covalently bonded to C; they are not ionisable and cannot be detected directly. Fusion with Na metal converts them to ionic, water-soluble salts: NaCN (from N), Na_2S (from S), NaX (from halogens). These ions then undergo standard qualitative tests.

Q27 Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

SOLUTION

Calcium sulphate ($CaSO_4$) is a non-volatile, high-melting ionic solid that does not sublime.
Camphor is an organic compound that readily sublimes (converts directly from solid to vapour on heating without melting).

The suitable technique is Sublimation.

Procedure:
The mixture is placed in a china dish. An inverted funnel (with the stem plugged with cotton wool) is placed over the dish.
The dish is gently heated.
Camphor sublimes, and its vapour condenses on the cooler inner walls of the funnel as pure camphor crystals.
$CaSO_4$ (non-volatile) remains in the dish.
The two components are thus separated completely.

Answer: Sublimation. Camphor sublimes on gentle heating and is collected on the cool walls of an inverted funnel, while non-volatile $CaSO_4$ remains behind.

Q28 Explain why an organic liquid vaporises at a temperature below its boiling point in its steam distillation.

SOLUTION

In steam distillation, the organic liquid and water are immiscible (they do not mix).

Dalton's Law of partial pressures: For immiscible liquids, the total vapour pressure of the mixture equals the sum of the vapour pressures of the individual components at that temperature:
$P_{total} = P_{water} + P_{organic}$

The mixture will boil when P_{total} = atmospheric pressure (P_{atm} = 1 atm).

Since the total pressure is the sum of the two individual vapour pressures, P_{total} reaches 1 atm at a temperature LOWER than the boiling point of either component alone.

Therefore, the organic compound distils over at a temperature below 100°C (below its own boiling point and below water's boiling point).

This is particularly useful for high-boiling, thermally unstable organic compounds that would otherwise decompose at their normal boiling points.

Answer: Because the mixture of immiscible liquids obeys Dalton's law: $P_{total} = P_{water} + P_{organic}$. The total pressure reaches 1 atm at a temperature lower than the boiling point of either component. Hence the organic liquid co-distils with water well below its own boiling point.

Q29 Will CCl_4 give a white precipitate of AgCl on heating with $AgNO_3$? Hint: CCl_4 does not give silver chloride precipitate with $AgNO_3$ whereas CH_3Cl does. Give reason for your answer.

SOLUTION

CCl_4 does NOT give a white precipitate of AgCl with $AgNO_3$.

Reason:
In CCl_4 (carbon tetrachloride), the C-Cl bonds are very strong covalent bonds and are non-polar (the symmetric tetrahedral geometry makes the molecule non-polar overall).

CCl_4 does not ionise in solution; it cannot produce free Cl^- ions.
Since there are no Cl^- ions in solution, no AgCl precipitate forms.

In CH_3Cl (chloromethane), the C-Cl bond is polar (C is less electronegative than Cl), and CH_3Cl can undergo hydrolysis (or react directly) to produce Cl^- ions:
$CH_3Cl + H_2O \rightarrow CH_3OH + HCl \rightarrow H^+ + Cl^-$
These Cl^- ions react with $Ag^+ \rightarrow AgCl\downarrow$ (white precipitate).

Additionally, CH_3Cl can undergo nucleophilic substitution with $AgNO_3$ directly:
$CH_3Cl + AgNO_3 \rightarrow CH_3NO_3 + AgCl\downarrow$

Summary: CCl_4 is fully covalent and non-ionisable; CH_3Cl can ionise/hydrolyse to give Cl^- ions.

Answer: No, CCl_4 does not give AgCl precipitate. In CCl_4, C-Cl bonds are strong, symmetric, and non-ionisable — no Cl^- ions are released. CH_3Cl has a polar, labile C-Cl bond that can undergo hydrolysis or SN_2 with $AgNO_3$ to release Cl^-, giving $AgCl\downarrow$.

Q30 Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

SOLUTION

In the estimation of carbon by combustion (Liebig method), the organic compound is burned in excess O_2.
The products are CO_2 (from C) and H_2O (from H).
Both CO_2 and H_2O pass through the absorption train.

KOH (potassium hydroxide) solution absorbs CO_2 selectively and quantitatively:
$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$

Why KOH specifically:
1. KOH reacts completely and irreversibly with CO_2, ensuring quantitative absorption.
2. KOH solution (aqueous or in the form of KOH pellets) does not absorb other products such as H_2O, O_2, or N_2.
3. Water is absorbed separately in anhydrous $CaCl_2$ or $Mg(ClO_4)_2$ tubes (placed before the CO_2 absorber).
4. The increase in mass of the KOH absorber = mass of CO_2 = used to calculate % C.

The specific sequence is: water absorber first, then KOH absorber for CO_2 — this ensures accurate separation of the two products.

Answer: KOH absorbs CO_2 quantitatively: $CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$. The increase in mass of the KOH tube = mass of CO_2, which is used to calculate % C. KOH selectively absorbs CO_2 without interfering with H_2O (absorbed separately in $CaCl_2$).

Q31 Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

SOLUTION

The sodium fusion extract is tested for sulphur using the lead acetate test:
$S^{2-} + Pb^{2+} \rightarrow PbS\downarrow$ (black precipitate)

If H_2SO_4 (sulphuric acid) were used for acidification:
H_2SO_4 itself contains sulphate (SO_4^{2-}), which would react with lead acetate:
$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4\downarrow$ (white precipitate)
This would create a false positive or interfere with the black PbS test, making the result ambiguous.
Additionally, excess H_2SO_4 would precipitate $PbSO_4$ regardless of whether S is present in the original compound.

Acetic acid (CH_3COOH) is used instead because:
1. It provides the acidic conditions needed to acidify the extract.
2. It does not contain sulphate ions — no interference with the lead acetate test.
3. Lead acetate remains soluble in acetic acid, so the black PbS precipitate (if S is present) is clearly visible.

Therefore, CH_3COOH is the correct choice for acidification in the sulphur test.

Answer: H_2SO_4 contains SO_4^{2-} ions which react with Pb^{2+} to form $PbSO_4$ (white precipitate), interfering with the PbS (black) test. Acetic acid provides acidification without sulphate ions, so only PbS (black) forms if S^{2-} is present.

Q32 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.

SOLUTION

Given: Organic compound with 69% C, 4.8% H; remainder = O
% O = 100 - 69 - 4.8 = 26.2%

Mass of compound taken = 0.20 g

Step 1: Find mass of C and H in 0.20 g
Mass of C = (69/100) × 0.20 = 0.138 g
Mass of H = (4.8/100) × 0.20 = 0.0096 g

Step 2: Calculate mass of CO_2 produced
Complete combustion: $C + O_2 \rightarrow CO_2$
12 g C produces 44 g CO_2
0.138 g C produces: (44/12) × 0.138 = 0.506 g CO_2

Step 3: Calculate mass of H_2O produced
Complete combustion: $2H_2 + O_2 \rightarrow 2H_2O$ (i.e., 4 g H → 36 g H_2O, or 2 g H → 18 g H_2O)
2 g H produces 18 g H_2O
0.0096 g H produces: (18/2) × 0.0096 = 0.0864 g H_2O

Answer: Mass of CO_2 produced = 0.506 g; Mass of H_2O produced = 0.0864 g

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Q33 A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5 M NaOH solution for neutralisation. Find the percentage composition of nitrogen in the compound.

SOLUTION

Given:
Mass of organic compound = 0.50 g
H_2SO_4 taken: 50 mL of 0.5 M = 50 × 0.5 = 25 mmol
NaOH for residual acid: 60 mL of 0.5 M = 60 × 0.5 = 30 mmol

Step 1: Moles of H_2SO_4 neutralised by residual NaOH
$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$
Moles of H_2SO_4 (residual) = 30 mmol NaOH ÷ 2 = 15 mmol

Step 2: Moles of H_2SO_4 consumed by NH_3
H_2SO_4 consumed by NH_3 = 25 - 15 = 10 mmol

Step 3: Moles of NH_3 (= moles of N)
$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$
1 mol H_2SO_4 reacts with 2 mol NH_3
Moles of NH_3 = 2 × 10 = 20 mmol

Step 4: Mass of N
Mass of N = 20 mmol × 14 mg/mmol = 280 mg = 0.280 g

Step 5: % N
% N = (0.280 / 0.50) × 100 = 56%

Answer: Percentage of nitrogen in the compound = 56%

Q34 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine in the compound.

SOLUTION

Given:
Mass of organic compound = 0.3780 g
Mass of AgCl formed = 0.5740 g
Molar mass of AgCl = 108 + 35.5 = 143.5 g/mol
Atomic mass of Cl = 35.5 g/mol

Calculation:
% Cl = (atomic mass of Cl × mass of AgCl × 100) / (molar mass of AgCl × mass of compound)
% Cl = (35.5 × 0.5740 × 100) / (143.5 × 0.3780)
% Cl = (2037.7) / (54.243)
% Cl = 37.57%

Answer: Percentage of chlorine in the compound = 37.57%

Q35 In the 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.

SOLUTION

Given:
Mass of organic compound = 0.468 g
Mass of $BaSO_4$ formed = 0.668 g
Molar mass of $BaSO_4$ = 137 + 32 + 64 = 233 g/mol
Atomic mass of S = 32 g/mol

Calculation:
% S = (atomic mass of S × mass of $BaSO_4$ × 100) / (molar mass of $BaSO_4$ × mass of compound)
% S = (32 × 0.668 × 100) / (233 × 0.468)
% S = (2137.6) / (109.044)
% S = 19.60%

Answer: Percentage of sulphur in the compound = 19.60%

Q36 In the organic compound $CH_2=CH-CH_2-CN$, the pair of hybridised orbitals involved in the formation of the C_2-C_3 bond is: (a) sp-sp^2 (b) sp^2-sp^3 (c) sp^3-sp^2 (d) sp^3-sp

SOLUTION

Structure: $CH_2=CH-CH_2-CN$
C_1 = CH_2= (double bond end): sp^2 hybridised
C_2 = $=CH^-$ (other end of double bond): sp^2 hybridised
C_3 = $-CH_2^-$ (methylene group adjacent to CN): sp^3 hybridised
C_4 = C in CN (triple bond C≡N): sp hybridised

The C_2-C_3 bond:
C_2 is sp^2 (part of the C=C double bond)
C_3 is sp^3 (saturated CH_2 group)

The C_2-C_3 sigma bond is formed by overlap of sp^2 orbital (from C_2) and sp^3 orbital (from C_3).

Answer: (b) sp^2-sp^3

Answer: (b) sp^2-sp^3. C_2 (part of C=C, sp^2) and C_3 ($-CH_2^-$, sp^3) form the C_2-C_3 sigma bond by sp^2-sp^3 orbital overlap.

Q37 In the Lassaigne's test for an organic compound, the Prussian blue colour is obtained due to the formation of: (a) $Na_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$ (c) $Fe_3[Fe(CN)_6]$ (d) $Fe_4[Fe(CN)_6]$

SOLUTION

In Lassaigne's test for nitrogen, the following sequence of reactions occurs:

Step 1: Sodium fusion converts organic N → NaCN

Step 2: The extract is boiled with $FeSO_4$:
$Fe^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-}$ (ferrocyanide ion)

Step 3: On acidification with H_2SO_4, some Fe^{2+} is oxidised to Fe^{3+}:
$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_6]_3$ (Prussian blue)

Prussian blue = ferric ferrocyanide = $Fe_4[Fe(CN)_6]_3$

Answer: (b) $Fe_4[Fe(CN)_6]_3$

Answer: (b) $Fe_4[Fe(CN)_6]_3$ — ferric ferrocyanide (Prussian blue), formed by $4Fe^{3+} + 3[Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_6]_3$.

Q38 Which of the following carbocations is most stable? (a) $(CH_3)_3C^+$ (b) $CH_3CH_2^+$ (c) $CH_3CH_2CH_2^+$ (d) $(CH_3)_2CH^+$

SOLUTION

Stability of carbocations increases with the number of alkyl groups attached to the positive carbon:
Tertiary > Secondary > Primary > Methyl

(a) $(CH_3)_3C^+$ — tertiary carbocation (3 methyl groups on C^+)
(b) $CH_3CH_2^+$ — primary carbocation (1 alkyl group)
(c) $CH_3CH_2CH_2^+$ — primary carbocation (1 alkyl group, n-propyl)
(d) $(CH_3)_2CH^+$ — secondary carbocation (2 methyl groups on C^+)

Stabilisation is due to:
1. Hyperconjugation: more alpha-C-H bonds → more sigma electron donation into the empty p orbital.
2. Inductive effect: alkyl groups (+I) push electrons toward the positive carbon.

Most stable = $(CH_3)_3C^+$ (tertiary, with 9 alpha-C-H bonds available for hyperconjugation).

Answer: (a) $(CH_3)_3C^+$

Answer: (a) $(CH_3)_3C^+$ is the most stable carbocation — tertiary cation stabilised by hyperconjugation (9 alpha C-H bonds) and +I inductive effect of three methyl groups.

Q39 The best and latest technique for isolation, purification, and separation of organic compounds is: (a) Crystallisation (b) Distillation (c) Sublimation (d) Chromatography

SOLUTION

Chromatography is the most modern, versatile, and widely applicable technique for separation, purification, and identification of organic compounds.

Advantages of chromatography over other techniques:
• Can separate very small quantities of substances (nanogram scale).
• Can separate compounds with very similar physical properties (e.g., similar boiling points or solubilities) that cannot be resolved by distillation or crystallisation.
• Multiple types available: paper, thin-layer (TLC), column, gas chromatography (GC), high-performance liquid chromatography (HPLC).
• Allows simultaneous separation and identification.
• Very high sensitivity and resolution.

The other techniques (crystallisation, distillation, sublimation) are older, less precise, and require larger quantities or involve thermal treatment that may damage sensitive compounds.

Answer: (d) Chromatography

Answer: (d) Chromatography — the most modern, sensitive, and versatile technique for isolation, purification, and separation of organic compounds, applicable even to minute quantities and closely related substances.

Q40 The reaction: $CH_3CH_2I + OH^- \rightarrow CH_3CH_2OH + I^-$ is classified as: (a) electrophilic substitution (b) nucleophilic substitution (c) elimination (d) addition

SOLUTION

In the reaction $CH_3CH_2I + OH^- \rightarrow CH_3CH_2OH + I^-$:

Analysis:
• CH_3CH_2I: iodoethane; I is attached to carbon, making that C slightly electrophilic

(C-I polar bond, C is delta+).

• OH^- (hydroxide): has lone pairs on oxygen; it is electron-rich → nucleophile.

• OH^- attacks the electrophilic C (bearing I), donates its lone pair to C.

• I^- is displaced (leaves as the leaving group).

• The OH group replaces I in the same position.

This is a substitution reaction where a nucleophile (OH^-) replaces the leaving group (I^-).

Type: Nucleophilic Substitution (SN reaction).

Answer: (b) Nucleophilic substitution

Answer: (b) Nucleophilic substitution. OH^- (nucleophile) attacks the electrophilic carbon bearing I^- (leaving group), replacing it in a substitution reaction.