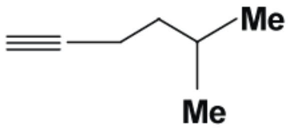
Date: 16/10/2021

Q1. Give IUPAC names:



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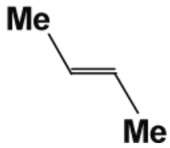

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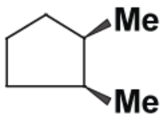

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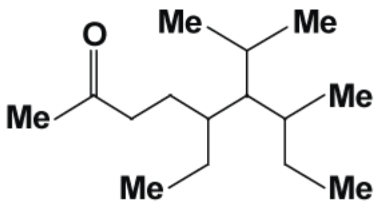

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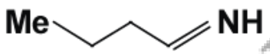

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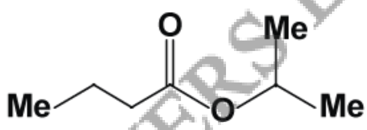

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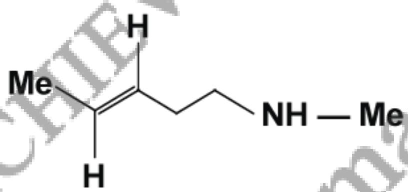

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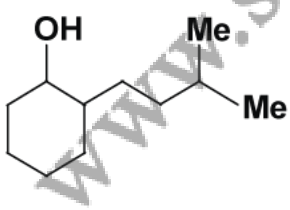

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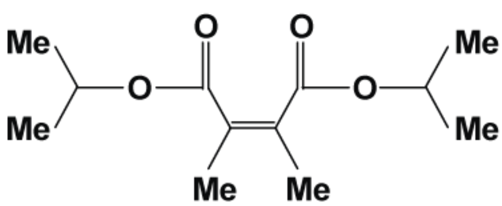

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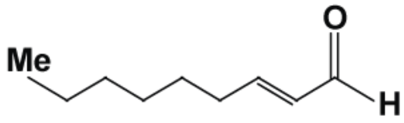

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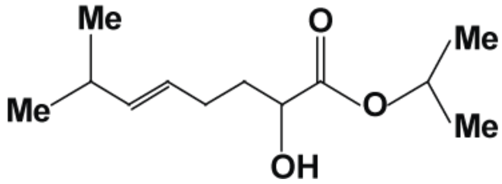

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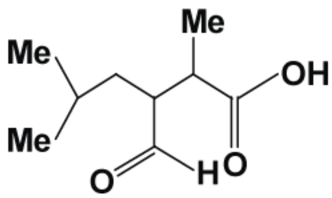

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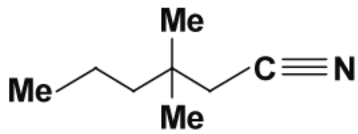

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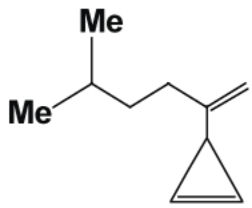

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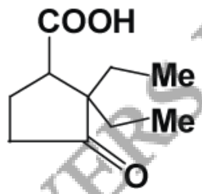

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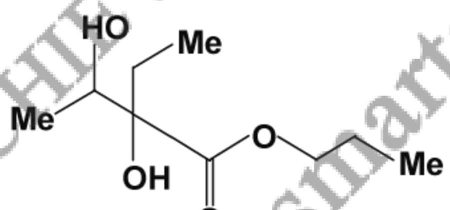

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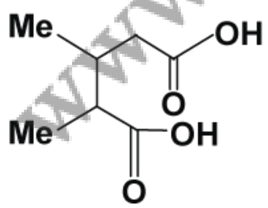

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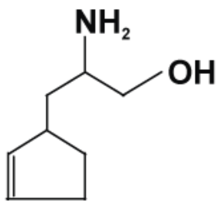

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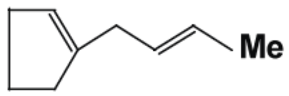

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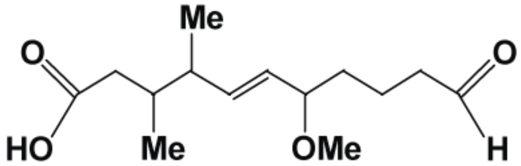

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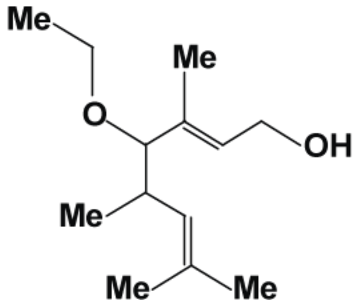

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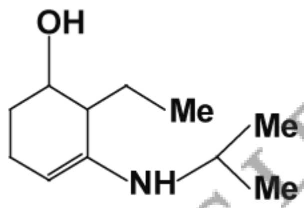

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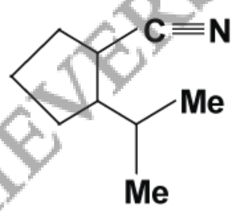

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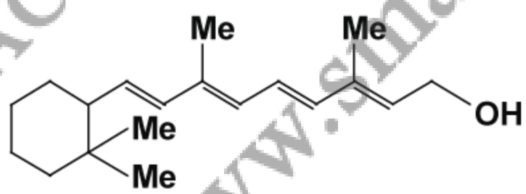

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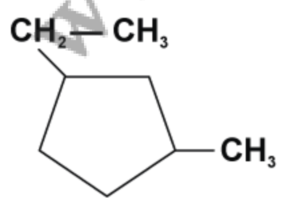

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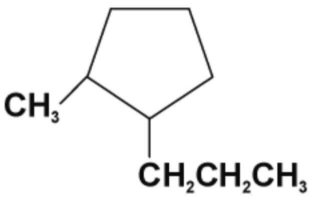

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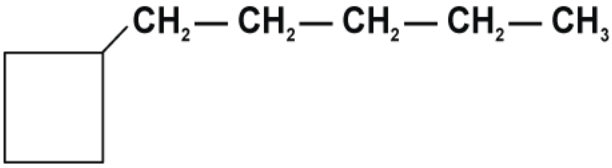

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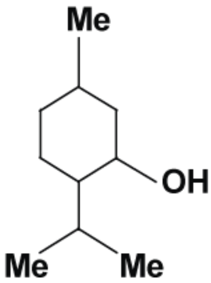

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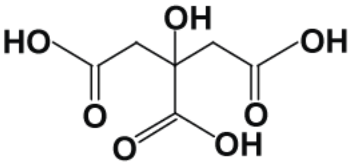

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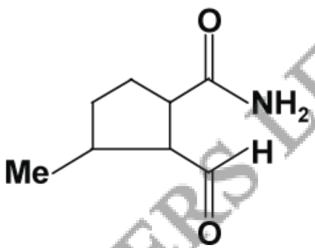

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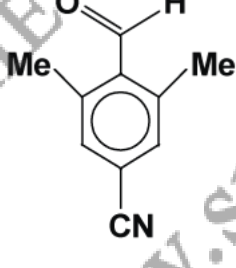

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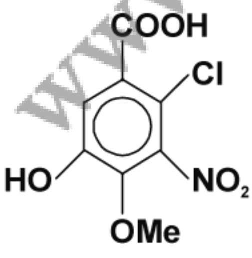

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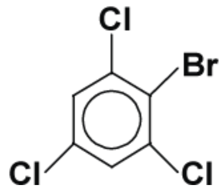

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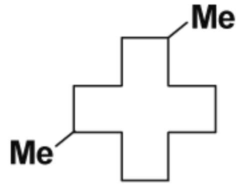

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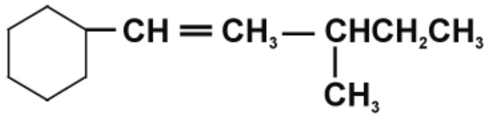

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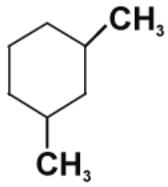

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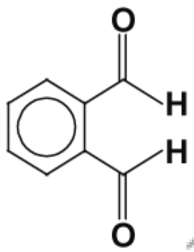

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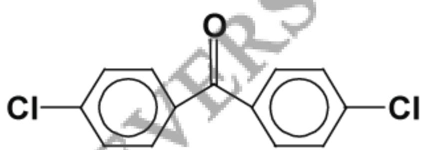

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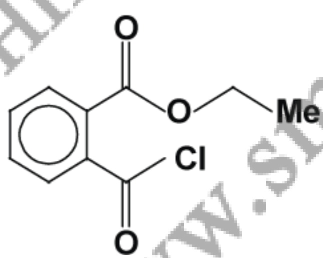

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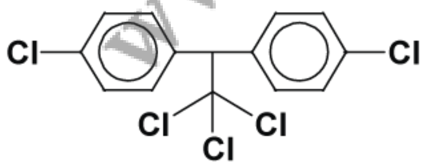

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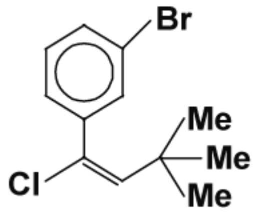

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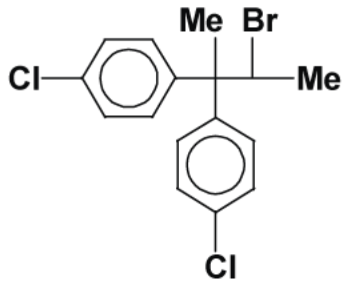

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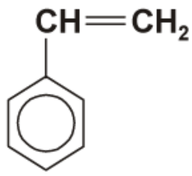

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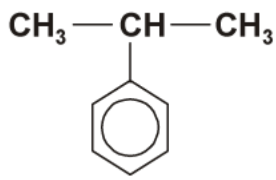

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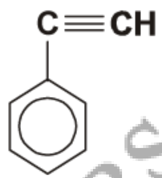

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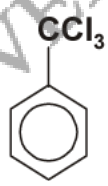

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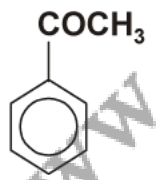

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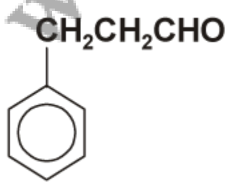

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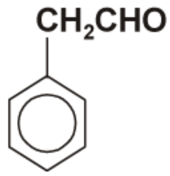

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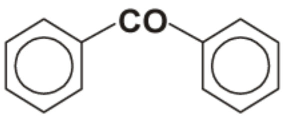

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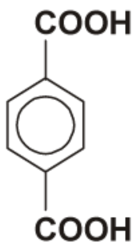

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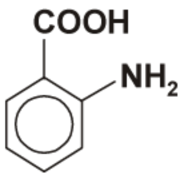

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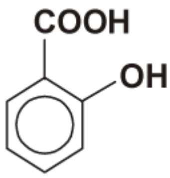

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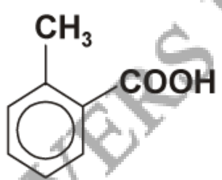

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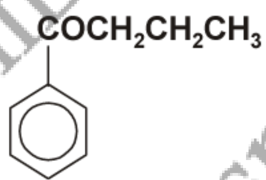

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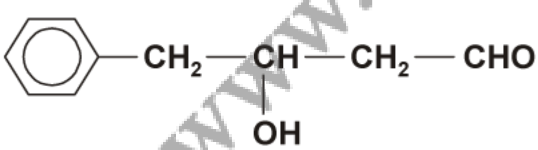

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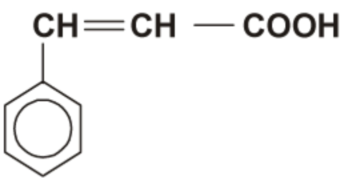

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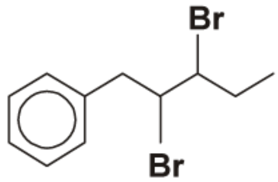

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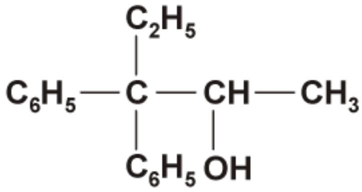

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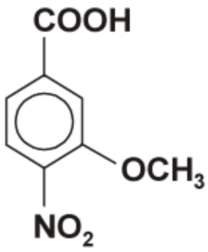

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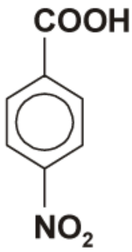

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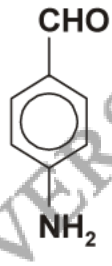

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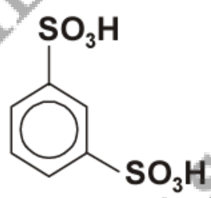

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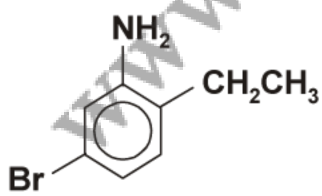

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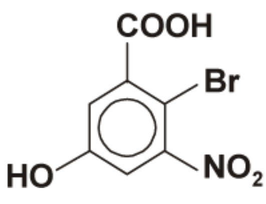

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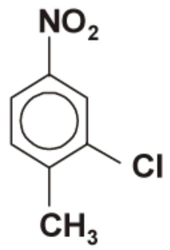

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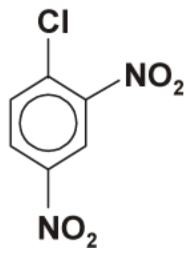

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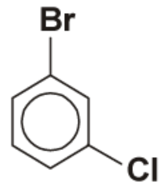

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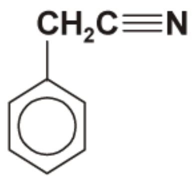

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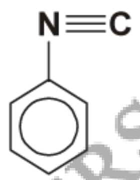

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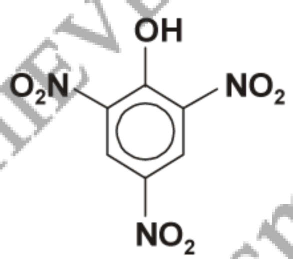


Q72. Draw structure for these compounds:

(a) 1, 6-hexanedioic acid
(b) Ethyl 2-ethyl-2 hydroxybutanoate
(c) 2-amino-3-cyclohexyl-1-propanol
(d) tert-butyl 2-hydroxy oct-5en-1-oate

Q73. Which of the following represents the correct IUPAC name for the compounds concerned:

(a) 2, 2-Dimethylpentane or 2-Dimethylpentane
(b) 2, 4, 7-Trimethylocatane 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.

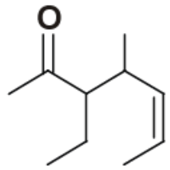
Q74. Write bond-line formulas for: Isopropyl alcohol 2, 3-dimethylbutanal, heptan-4-one.

Q75. **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-propanetri-carboxylic acid (c) Hexanedial.**

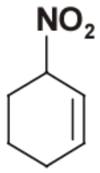
Q76. **Write down the structural formulae of the following:**

(a) 4-Methylpent-4-en-2-one (b) 3-Methylbut-1-yne (c) 2-Ethyl-3-methylpent-1-ene.

Q77. **Name the compounds whose line formulae are given below:**



Q78. **Name the compounds whose line formulae are given below:**



Date: 16/10/2021

S1. 5-Methyl hex-1-yne.

S2. *trans*-but-2-ene.

S3. *cis*-1, 2-Dimethyl cyclopentane.

S4. 5-Ethyl-6-isopropyl-7-methyl nonan-2-one.

S5. Butanal imine.

S6. Isopropyl butanoate.

S7. N-Methyl-5-amino-pent-2-ene.

S8. 2-(3′-Methylbutyl) cyclohexan-1-ol.

S9. bisopropyl-2,3-dimethyl but-2-en-1, 4-dioate.

S10. Non-2-en-1-al.

S11. Isopropyl-2-hydroxy-7-methyl oct-5-en-1-oate.

S12. 3-Formyl-5-methyl hexan-1-oic acid.

S13. 3,3-Dimethyl hexane nitrile

S14. 2-(Cycloprop-2-enyl)-5-methyl hex-1-ene.

S15. 2,2-Diethyl-3-oxo-cyclopentane-1-carboxylic acid.

S16. Propyl-2, 3-dihydroxy-2-methyl butanoate.

S17. 2,3-Dimethyl pentane-1, 5-dioic acid.

S18. 2-Amino-3-(cyclopent-2-enyl) propan-1-ol.

S19. 1-(But-2-enyl) cyclopent-1-ene.

S20. 10-Formyl-7-methoxy-3,4-dimethyldec-5-enoic-acid.

S21. 4-Ethoxy-3, 5,7-trimethyl oct-2, 6-diene-1-ol.

S22. 3-(N-Isopropyl) amino-2-ethyl cyclohex-3-en-1-ol.

S23. 2-Isopropyl cyclopentane carbonitrile.

S24. 3,7-Dimethyl-9-(2,2-dimethyl cyclohexyl) non-2,4,6,8-tetraen-1-ol.

S25. 1-Ethyl-3-methylcyclopentane.

S26. 1-Methyl-2-propylcyclopentane.

S27. 1-Cyclobutylpentane.

S28. 2-Isopropyl-5-methyl cyclohexan-1-ol.

S29. 2-Hydroxy propane 1,2,3-tricarboxylic acid (Common name: Citric acid).

S30. 2-Formyl-3-methyl cyclopentane carboxamide.

S31. 4-Cyano-2, 6-dimethylphenyl carbaldehyde.

S32. 2-Chloro-5-hydroxy-4-methoxy-3-nitro benzoic acid.

S33. 2,4,6-Trichloro-1-bromo benzene.

S34. 1, 5-Dimethyl cyclododecane.

S35. 1-cyclohexyl-3-methyl-1-pentene.

S36. 1, 3-dimethylcyclohexane.

S37. Benzene-1, 2-dicarbaldehyde.

S38. Bis-(4-chlorophenyl) methanone or Di-(*p*-chlorophenyl) ketone (common name).

S39. Ethyl-2-(chloro carbony) benzoate.

S40. 2,2-Bis(*p*-chloro phenyl)-1, 1, 1-trichloro ethane or D.D.T. (Dichlorodiphenyl trichloroethane) (common name); used as an insecticide.

S41. 1-(3-Bromo phenyl)-1-chloro-3, 3-dimethyl but-1-ene.

S42. 2-Bromo-3, 3-bis(4-chloro phenyl) butane.

S43. Ethenylbenzene (Styrene).

S44. Isopropyl benzene comerical Cumene.

S45. Ethynylbenzene (Phenylacetylene).

S46. Phenyltrichloromethane (Benzo chloride).

S47. 1-Phenylethan-1-one (Acetophenone).

S48. 3-Phenylpropanal (β-Phenylpropionaldehyde).

S49. 2-Phenylethanal (Phenyl acetaldehyde).

S50. Diphenyl ketone (Benzophenone) or diphenyl ketone.

S51. Benzene-1,4-dicarboxylic acid (Terephthalic acid).

S52. 2-Aminobenzoic acid.

S53. 2-Hydroxybenzoic acid (*o*-Salicylic acid or *o*-Hydroxy benzoic acid).

S54. 2-Methylbenzoic acid (*o*-oluic acid or *o*-methyl benzoic acid).

S55. 1-Phenylbutan-1-one.

S56. 4-Phenyl-3-hydroxybutanal.

S57. 3-Phenylprop-2-enoic acid.

S58. 2, 3-Dibromo-1-phenylpentane.

S59. 3, 3-Diphhenyl pentan-2-ol.

S60. 3-Methoxy-4-nitrobenzoic acid.

S61. 4-Nitrobenzoic aoicd.

S62. 4-Aminobenzaldehyde.

S63. Benzene-1, 3-disulphonic acid (*m*-Benzene disulphonic acid).

S64. 5-Bromo-2-ethylaniline.

S65. 2-Bromo-5-hydroxy 3-nitrobenzoic acid.

S66. 2-Chloro-2-methyl-4-nitrotoluene.

S67. 1-Chloro-2,4-dinitrobenene.

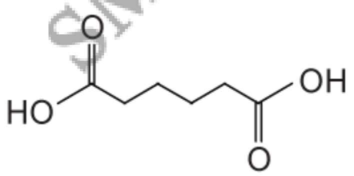
S68. 1-Bromo-3-chlorobenzene.

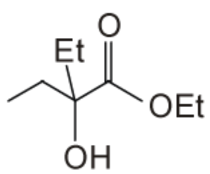
S69. Phenylethanenitrile (Benzyl cyanide or Phenyl acetonitrile).

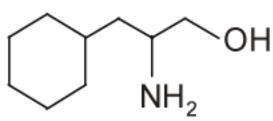
S70. Phenylisocyanide or Phenyl carblamine.

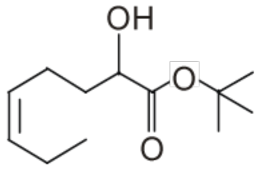
S71. 2, 4, 6-Trinitrophenol (Picric acid).

S72.

(a) 

(b) 

(c) 

(d) 

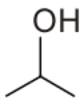
S73. (a) 2, 2-Dimethylpentane.

(b) 2, 4, 7-Trimethylocatane. For two alkyl groups on the same carbon its locant is repeated twice, 2, 4, 7-locant set is lower than 2, 5, 7.

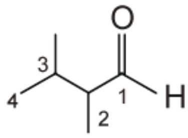
(c) 2-chloro-4-methylpentane. Alphabetical order of substituents.

(d) But-3-yn-1-ol. Lower locant for the principal functional group, *i.e.*, alcohol.

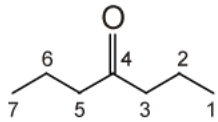
S74. The bond-line formulas of the above molecules are:



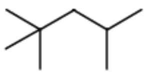
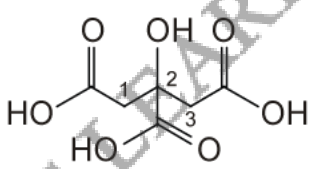
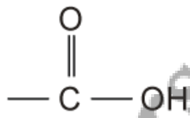
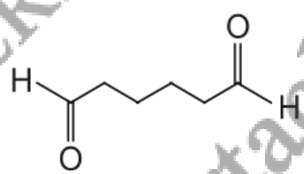
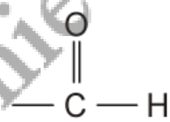
Isopropyl alcohol ;

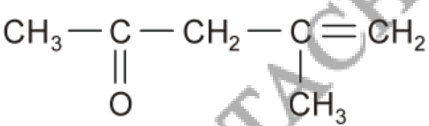


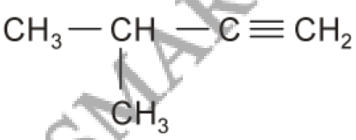
2, 3-Dimethylbutanal ;

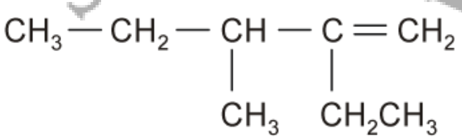


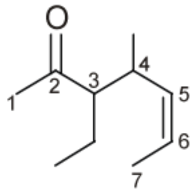
Heptan-4-one

S75.	**Condensed formula**	**Bond line**	**Functional group**
(a)	$(CH_3)_3CCH_2CH(CH_3)_2$		
(b)	$(COOH)CH_2(OH)C(COOH)CH_2COOH$		 (Carboxyl) and —OH (Hydroxyl)
(c)	$OHC(CH_2)_4CHO$		 (Aldehyde)

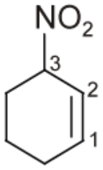
S76. (a) 

(b) 

(c) 

S77. 

3-Ethyl-4-methylhept-5-en-2-one.

S78. 

3-Nitrocyclohexene.

Date: 16/10/2021

Q1. Draw resonance structures for the following: C_6H_5OH.

Q2. Which of the following resonance structure for propenal is more stable?

Q3. In which C — C bond $CH_3CH_2CH_2Br$, the inductive effect is expected to be least?

Q4. Show the polarisation of carbon-magnesium bond in the following structure:

$$CH_3CH_2 — CH_2MgX.$$

Q5. What is the hybridisation of each carbon in $CH_2 = C = CH_2$?

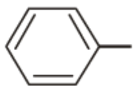
Q6. Draw resonance structures for the following: C_6H_5CHO.

Q7. Draw resonance structures for the following: $C_6H_5 — CH_2^+$.

Q8. List the following carbocations in the order of decreasing stability:

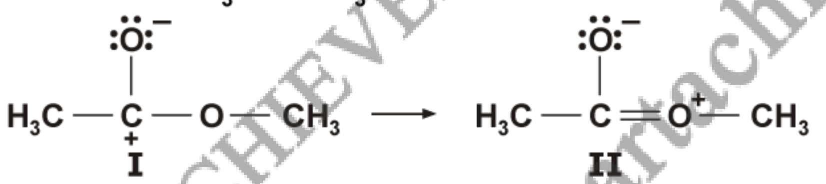
$$CH_3\underset{\underset{Cl}{|}}{C}HCH_2CH_2^+, \quad CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2^+, \quad CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_2^+,$$

Q9. Arrange the following free radicals in decreasing order of stability:

$(CH_3)_3\dot{C}$, $CH_3\dot{C}H_2$,  $—\dot{C}H_2$, $CH_2 = CH — \dot{C}H_2$, $(CH_3)_2\dot{C}H$

Q10. Write resonance structures of the following showing the movement of electrons by curved arrows: Acetate ion, CH_3COO^-.

Q11. Give reasons why the following two structures **I** and **II** cannot be the major contributors to the real structures of CH_3COOCH_3.



Q12. Draw the resonance structure of $CH_3CH = CHCHO$ compound. Show the electron shift using curved-arrow notation.

Q13. Draw the resonance strucure of $C_6H_5NO_2$ compound. Show the electron shift using curved-arrow notation.

Q14. Explain why alkyl groups act as electron donors when attached to a π-system.

Q15. Which is expected to be more stable: $O_2NCH_2CH_2O^-$ and $CH_3CH_2O^-$ and why?

Q16. Which hybrid orbitals are used by underlined carbon in the following molecules?

(a) $CH_3 — \underline{C}HO$ (b) $CH_3 — CH = \underline{C}H_2$

Q17. Write the structural formula of 4-chloro-pent-2-ene.

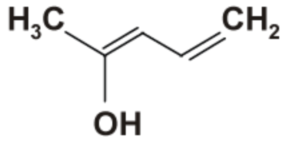
Q18. Arrange ethyne, ethene and ethane in the order of increasing acidity

Q19. Calculate number of sigma and pi bonds in 1,3-butadiene.

Q20. Identify the electrophilic centre in the following:

(a) CH_3CN (b) $CH_3 - I$

Q21. Write resonance structures of given compound.



Q22. Draw the resonance structure of $CH_3CH = CHC^+H_2$ compound. Show the electron shift using curved-arrow notation.

Q23. Write the resonance structures of diazomethane (CH_2N_2).

Q24. What is the type of hybridisation of each carbon in the following compounds:

(a) $CH_3CH = CHCN$ (b) $(CH_3)_2C = O$

Q25. Which bond is more polar in the following pairs of molecules:

(a) $H_3C - H$ or $H_3C - Br$ (b) $H_3C - NH_2$ or $H_3C - OH$

(c) $H_3C - OH$ or $H_3C - SH$

Q26. Write resonating structures for $CH_2 = CHCHO$. Indicate relative stability of the contributing structures:

Q27. Write resonance structures of

Q28. Explain why $(CH_3)_3C^+$ is more stable than $CH_3CH_2^+$ and CH_3^+ is the least stable cation.

Q29. Identity the most stable species in the folowing sets of ions giving reasons:

(a) $\bar{C}H_3$, $\bar{C}H_2Cl$, $\bar{C}HCl_2$, $\bar{C}Cl_3$ (b) $\overset{+}{C}H_3$, $\overset{+}{C}H_2Br$, $\overset{+}{C}HBr_2$, $\overset{+}{C}Br_3$

Q30. Write structures of various carbocations that can be obtained from 2-methylbutane. Arrange these carbocations in order of increasing stability.

Q31. Classify the following molecules/ions as nucleophiles or electrophiles:

HS^-, BF_3, $CH_3CH_2O^-$, $(CH_3)_3N$, Cl^+, $CH_3C = O$, $H_2N^-:$, NO_2^+

Q32. Classify the following reactions according to the reaction type:

(a) $CH_3 - C(C_6H_5) = NOH \longrightarrow CH_3 - C(NHC_6H_5) = O$

(b) $(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_2C = CH_2 + H_2O + Cl^-$

(c) $(CH_3)_3C - CH_2OH + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3 + H_2O$

Q33. Classify the following reactions according to the reaction type:

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

(b) $(CH_3)_2C = CH_2 + \dot{H}Cl \longrightarrow (CH_3)_2C(Cl) - CH_3$

(c) $CH_3CH_2Br + HO^- \longrightarrow CH_2 = CH_2$

(d) $H_2C = CHCH_2CH_3 \longrightarrow H_3CCH = CHCH_3$

Q34. Which of the following carbocation is most stable? Explain.

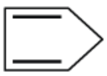
(a) $(CH_3)_3C\overset{+}{C}H_2$ (b) $(CH_3)_3\overset{+}{C}$

(c) $CH_3CH_2\overset{+}{C}H_2$ (d) $CH_3\overset{+}{C}HCH_2CH_3$

Q35. Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.

(a) $C_6H_5 - CHO$ (b) $CH_3CH = CHNO_2$

Q36. (a) Draw *cis*- and *trans*-structures for Hex-2ene, which isomer will have higher boiling point and why?

(b) Explain why  is not aromatic.

Q37. Which of the following pairs of structures do not constitute reasonance structures:

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

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

(c) $(CH_3)_2CO$ and $CH_3 - C(-OH)=CH_2$

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

Q38. Classify the reagents shown in bold in the following equations as nucleophiles or electrophiles:

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

(b) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$

(c) $C_6H_5 + CH_3CO^+ \longrightarrow C_6H_5COCH_3$

(d) $CH_3COCH_3 + CN^- \longrightarrow CH_3C(OH)(CN) - CH_3$

Q39. Arrange the following:

(a) $(CH_3)_3\overset{\oplus}{C}$, $CH_3CH_2\overset{\oplus}{C}H(CH_3)$, $CH_3CH_2CH_2\overset{\oplus}{C}H_2$

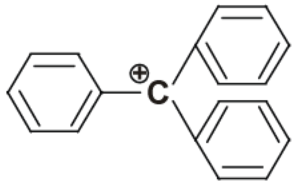
[Increasing order of stability]

(b) $-I$, $-Br$, $-Cl$, $-F$

[Decreasing order of $-I$ effect]

Q40. Write structures of varius carbocations that can be obtained from 2-methylbutane. Arrange these carbocations in order of increasing stability.

Q41. The structure of triphenylmethyl cation is given below. This is very stable and some of its salts can be stored for months. Explain the use of high stabiliy of this cation.



Q42. Identify the most stable species in the following set of ions giving reasons:

(a) $\overset{+}{C}H_3$, $\overset{+}{C}H_2Br$, $\overset{+}{C}HBr_2$, $\overset{+}{C}Br_3$ (b) $\overset{\ominus}{C}H_3$, $\overset{\ominus}{C}H_2Cl$, $\overset{\ominus}{C}HCl_2$, $\overset{\ominus}{C}Cl_3$

Q43. Classify the following reactions in one of the reaction type:

(a) $CH_3CH_2Br + :^{-}OCH_3 \longrightarrow CH_3CH_2OCH_3 + :Br^{-}$

(b) $CH_3-C(CH_3)=C(CH_3)-CH_3 + HBr \longleftrightarrow CH_3-C(H)(CH_3)-C(Br)(CH_3)-CH_3$

(c) $CH_3CH(Br)CH_3 + :^{-}OH \longleftrightarrow CH_3CH=CH_2 + H_2O + Br^{-}$

(d) $2CH_3CH_2CHO \xrightarrow{^{-}OH} CH_3-CH_2-CH(OH)-CH(CH_3)-CHO$

Q44. Which is expected to be more stable, $O_2N-CH_2-COO^{-}$ or $CH_3CH_2COO^{-}$ and why?

Q45. Explain why alkyl groups act as electron donors when attached to a π-system.

Q46. Which of the two structures (A) and (B) given below is more stabilised by resonance? Explain.

CH_3COOH (A) and $CH_3CO\overset{\ominus}{O}$ (B)

Q47. Write various contributing structures of $CH_2=CH-CHO$, and indicate what is the relative stability of these structures? Which strucure makes maximum contributation towards the resonance hybrid?

Q48. Explain the following giving example:

(a) Inductive effect (b) Electrophile

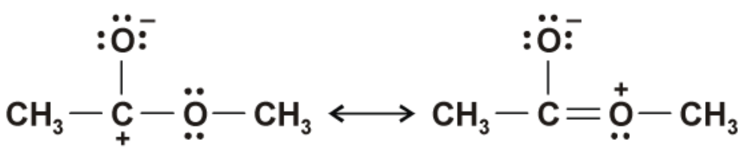
Q49. Indicate the σ- and π-bond in the following molecules:

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

Q50. What are hybridisation states of each carbon atom in the following compounds?

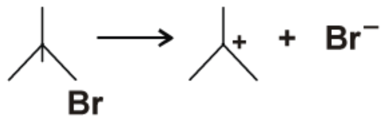
$CH_2=C=O$, $CH_3CH=CH_2$, $(CH_3)_2CO$, $CH_2=CHCN$, C_6H_6.

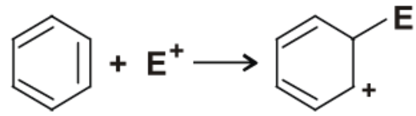
Q51. Explain why the following two structures **I** and **II** cannot be major contributors to the real structure CH_3COOCH_3



I **II**

Q52. 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) 

(b) 

Q53. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(b) $CH_3CH_2COOH > (CH_3)_3CHCOOH > (CH_3)_3CCOOH$

Q54. Using curved arrows notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage:

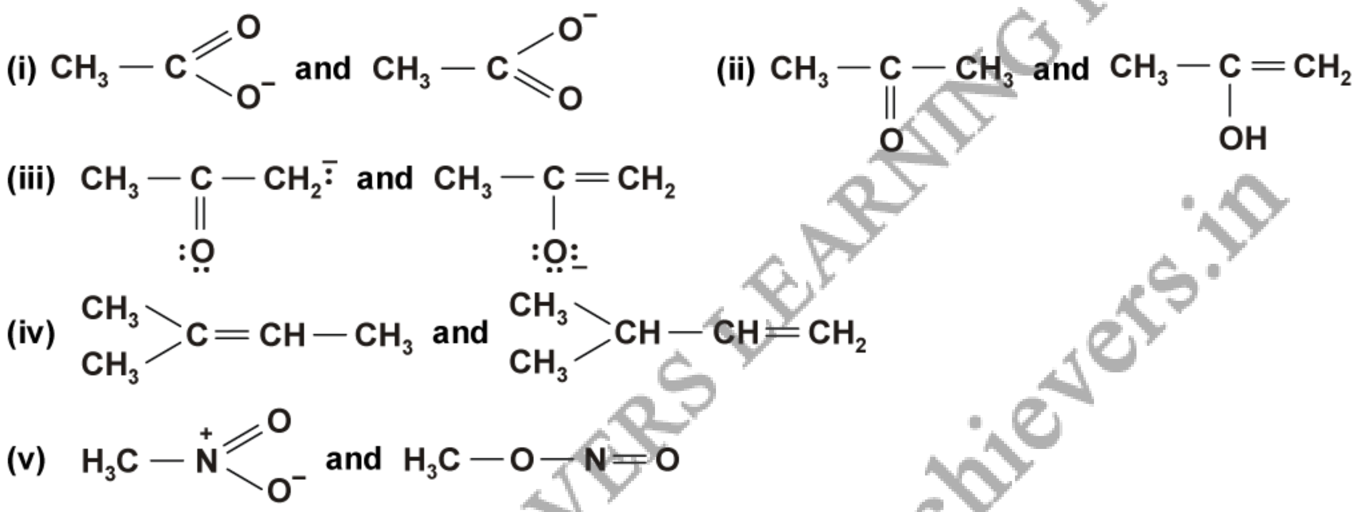
(a) $CH_3 — SCH_3$ (b) $CH_3 — CN$ (c) $CH_3 — Cu$

Q55. What are nucleophiles and electrophiles? Explain with examples.

Q56. With proper justification, arrange the following in order of inreasing stability

$CH_3CH_2^-$, $CH \equiv C^-$, $CH_2 = CH^-$.

Q57. Which of the following pairs of structures do not constitute resonance structures?



Q58. Draw resonance structures for the following compounds:

(a) $CH_3 = CH — C(H) = O$ (b) $CH_2 = CH — \ddot{C}l:$ (c) $CH_2 = CH — CH = CH_2$

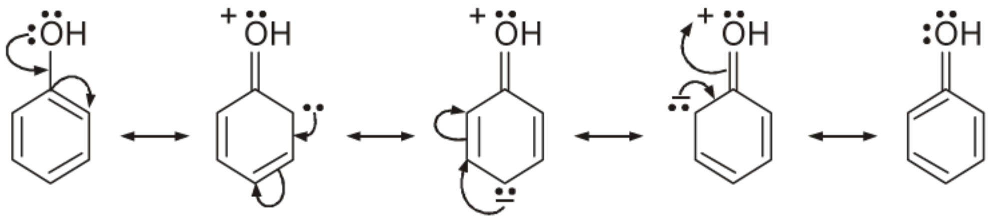
Q59. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

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

Q60. Discuss the hybridization of carbon atoms in allene (C_3H_4) and show the π-orbital overlaps.

Date: 16/10/2021

S1. 

S2. $CH_2 = CH - CH = O \longleftrightarrow \overset{+}{C}H_2 - CH = CH - \bar{O}$.

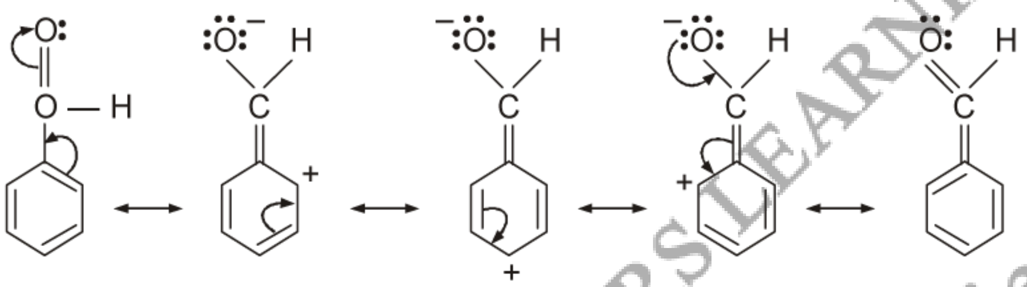
(A) (B)

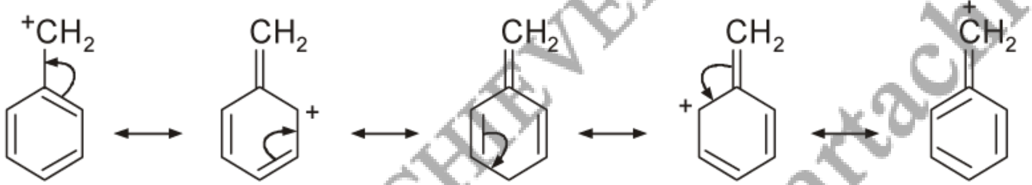
A is more stable than B.

S3. The inductive effect is least in $C_2 - C_3$ bond because the magnitude of inductive effect decreases as the number of intervening bonds increase.

S4. $CH_3CH_2\overset{\delta-}{C}H_2 - \overset{\delta+}{Mg} - X$

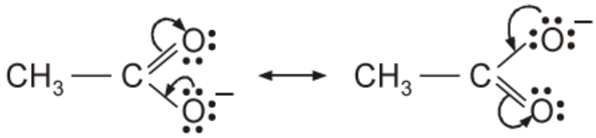
S5. sp^2, sp and sp^2.

S6. 

S7. 

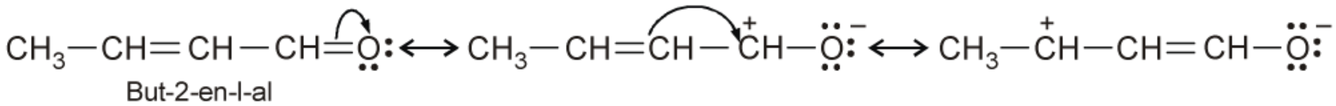
S8. $CH_3CH(CH_3)CH_2CH_2^+ > CH_3CH(Cl)CH_2CH_2^+ > CH_3CH_2CH(Cl)CH_2^+$

S9. $C_6H_5-\dot{C}H_2 > CH_2{=}CH-\dot{C}H_2 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2$

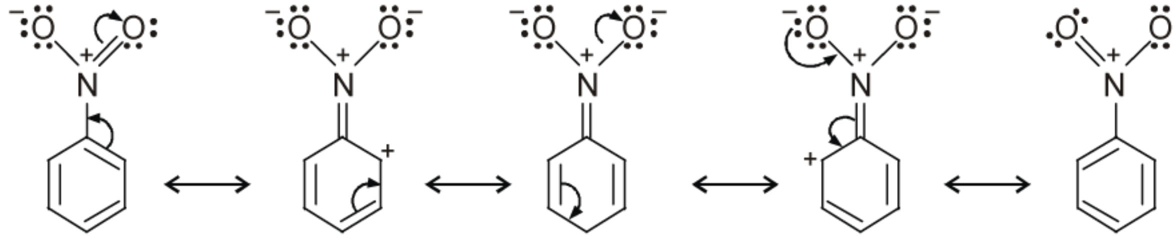
S10. 

S11. The structures I and II are important contributors because they involve charge separation. Therefore, they do not contribute substantially towards the resonance hybrid. Further, structures I also contains a carbon atom with an incomplete octet (sextet of electrons) and therefore, the contribution is lower than that of structure II.

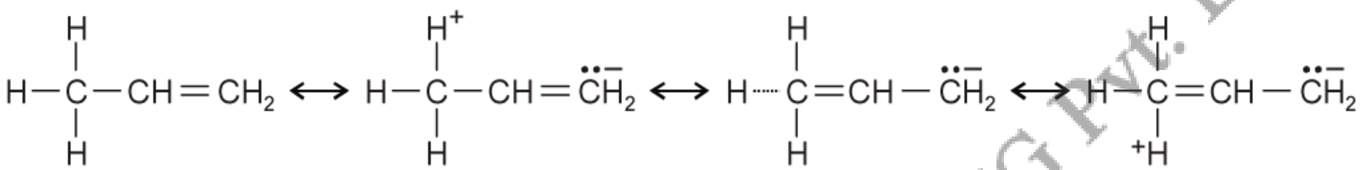
S12.



S13.



S14. Due to hyperconjugation, alkyl groups act as electron donors when attached to a π-system.



It should be noted that the H atom shown by dotted line is firmly attached.

S15. $O_2NCH_2CH_2O^-$ is more stable than $CH_3CH_2O^-$ because $^-NO_2$ group has – I inductive effect and tends to disperse the – ve charge on the O-atom. This results into stability. However, CH_3CH_2 – group + I effect and tends to intensify the – ve charge and therefore, destabilizes it.

S16.

(a) $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$
sp^2-hybidrized

(b) $CH_3-CH=CH_2$
sp^2-hybidrized

S17. $CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH=CH-CH_3$

S18. $CH\equiv CH > CH_2=CH_2 > CH_3-CH_3$

S19. $CH_2=CH-CH=CH_2$

π bonds = 2

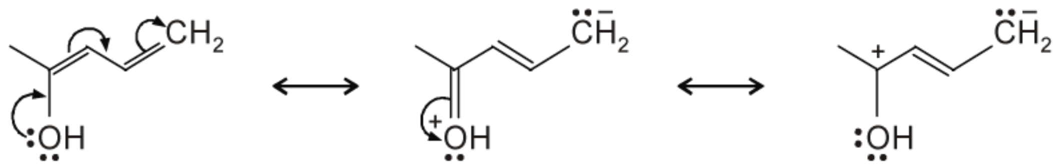
σ bonds = 9

S20. The electrophilic centres are shown by shared carbon (C*) because these will acquire partial positive charge due to the polarity of the bond:

(a) $H_3CC^*\equiv N$

(b) H_3C^*-I

S21. The following three resonance structures can be written for the given compound.

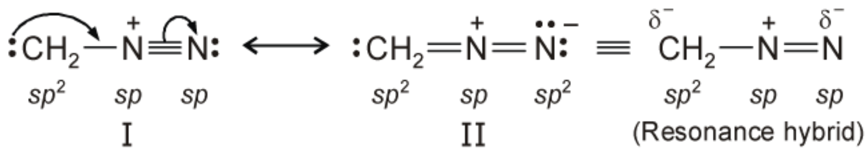


S22.

$$CH_3-CH=CH-\overset{+}{C}H_2 \longleftrightarrow CH_3-\overset{+}{C}H-CH=CH_2$$

But-2-en-l-yl carbocation

S23.



S24.

(a) $\overset{sp^3}{CH_3}-\overset{sp^2}{CH}=\overset{sp^2}{CH}-\overset{sp}{C}\equiv N$: sp^3, sp^2, sp^2, sp

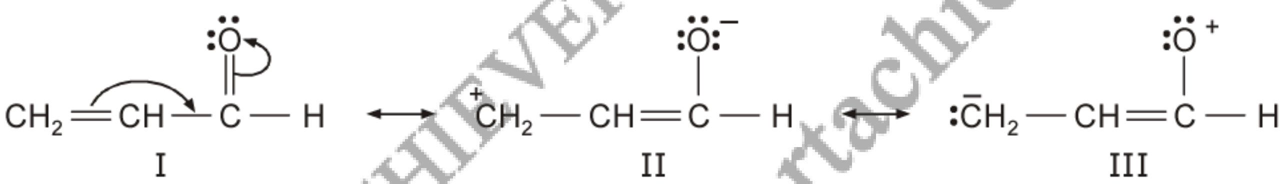
(b) $\overset{sp^3}{CH_3}-\overset{sp^2}{C}(\underset{sp^3}{CH_3})=O$: sp^3, sp^2, sp^3

S25. (a) C — Br because Br is more electronegative than H.

(a) C — O because O is more electronegative than N.

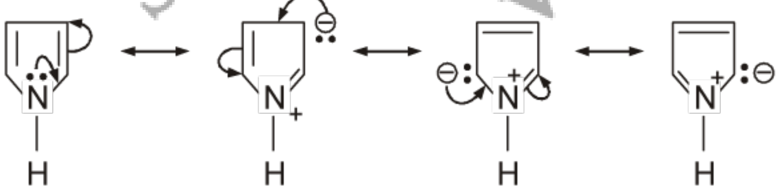
(a) C — O because O is more electronegative than S.

S26. The resonating structures for $CH_2=CHCHO$ are:



I is most stable because it has more number of covalent bonds and each carbon and oxygen atoms has an octet and no carbon or oxygen atom has a charge. Structure III is least stable because more electronegative O-atom has positive charge and electropositive carbon has negative charge. In structure II, there is positive cvharge on electropositive C atom and negative charge on electronegative O-atom. But both structures II and III have charge separation. Thus, decreasing order of stability is: I > II > III.

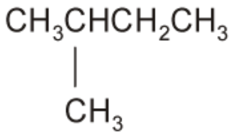
S27.



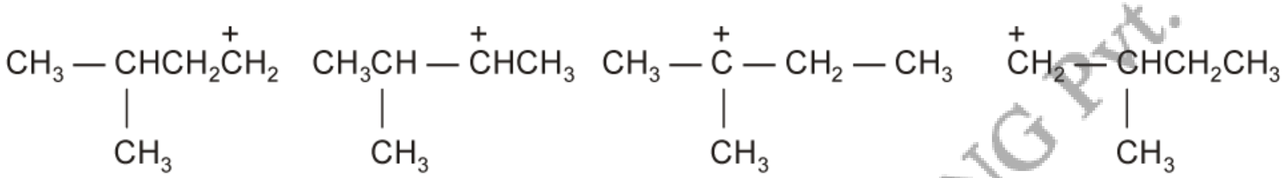
S28. Hyperconjugation interaction in carbocations depends upon the number of α-hydrogen atoms. It is greater in $(CH_3)_3C^+$ than in $(CH_3)_2CH^+$ because $(CH_3)_3C^+$ has nine C — H bonds while $(CH_3)_2CH^+$ has only six C — H bonds. Greater hyperconjugation means greater stability of the cation and hence $(CH_3)_3C^+$ is more stable than $(CH_3)_2CH^+$. In CH_3^+, the vacant *p*-orbital is perpendicular to the plane in which C — H bonds lie and hence there is no possibility of overlapping. Thus CH_3^+ lacks hyperconjugation stability and is the least stable carbocation.

S29. (a) $\bar{C}-Cl_3$ is most stable because Cl is more electronegative than hydrogen. On replacing hydrogen by chlorine, negative charge on C is reduced and the species becomes stable.

(b) $\overset{+}{C}H_3$ is most stable. The replacement of H by Br increases positive charge on carbon atom because Br is more electronegative than H and consequently the species becomes less stable.

S30. 

The possible carbocations ae:



I (1°) II (2°) III (3°) IV (1°)

Order of increasing stability I < IV < II < III.

S31. **Electrophiles:** BF_3, Cl^+, $CH_3C^+=O$, NO_2^+

In these the reactive sites have only six valence electrons and therefore can accept electron pairs from a nucleophile.

Nucleophiles: HS^-, $CH_3CH_2O^-$, $(CH_3)_3N$, H_2N^-:

These species have unshared pair of electron which can be donated and shared with an electrophile.

S32. (a)  Rearrangement reaction

(b) $(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_2C=CH_2 + H_2O + Cl^-$ Elimination reaction

(c) $(CH_3)_3C-CH_2OH + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3 + H_2O$ Substitution with rearrangement reaction

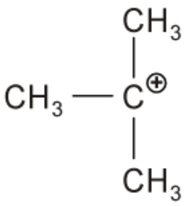
S33. (a) $CH_3CH_2Br + HO^- \longrightarrow CH_3CH_2CH + Br^-$ Substitution reaction

(b) $(CH_3)_2C=CH_2 + HCl \longrightarrow (CH_3)_2C(Cl)-CH_3$ Addition reaction

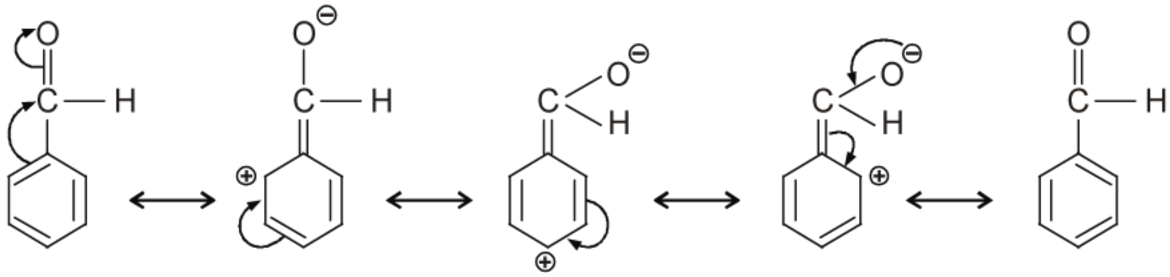
(c) $CH_3CH_2 + OH^- \longrightarrow CH_2=CH_2$ Elimination reaction

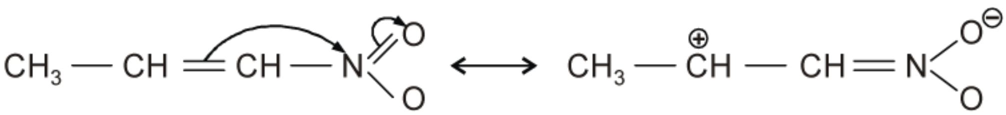
(d) $H_2C=CHCH_2CH_3 \longrightarrow H_3CCH=CHCH_3$ Isomerisation reaction

S34.

Ans. (b).  carbocation is most stable because of maximum (10) Hyperconjugation contribution.

S35.

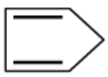
(a) 

(b) 

S36. (a) 

trans *cis*

Trans-isomer boilin point is higher than *cis*-isomer.

(b)  is not aromatic because if not follow (i) un + 2π electron, rule. (ii) structure is not in plane *i.e.*, one carbon is sp^3-hybidrized.

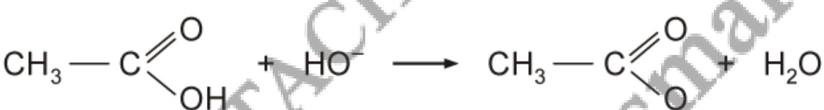
S37. (a) The two structures differ in the position of atoms and therefore, do not constitute resonance structures.

(b) These constitutes a pair of resonance structures.

(c) Thes are not resonance structures because these differ in the position of atoms.

(d) These are not resonance structures because these differ in the position of atoms.

S38.

(a) 

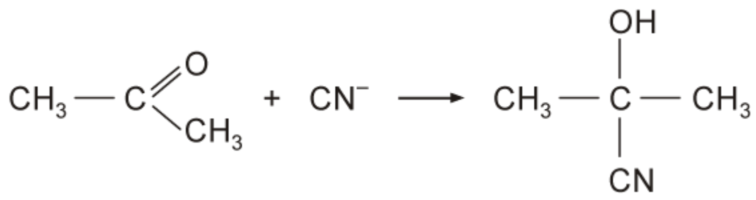
OH^- is nucleophile

(b) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$

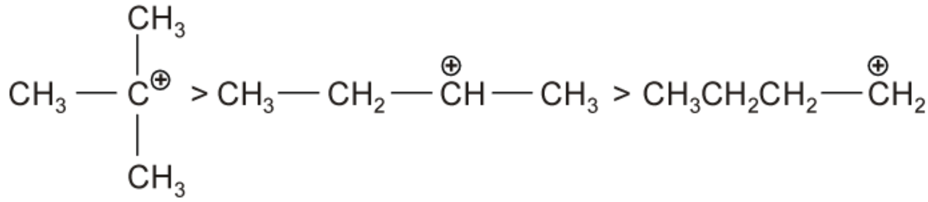
SH^- is nucleophile

(c) $C_6H_6 + CH_3CO^+ \longrightarrow C_6H_5COCH_3$

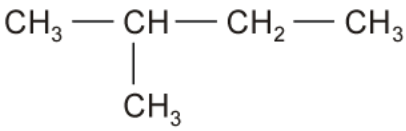
CH_3CO^+ acts as electrophile

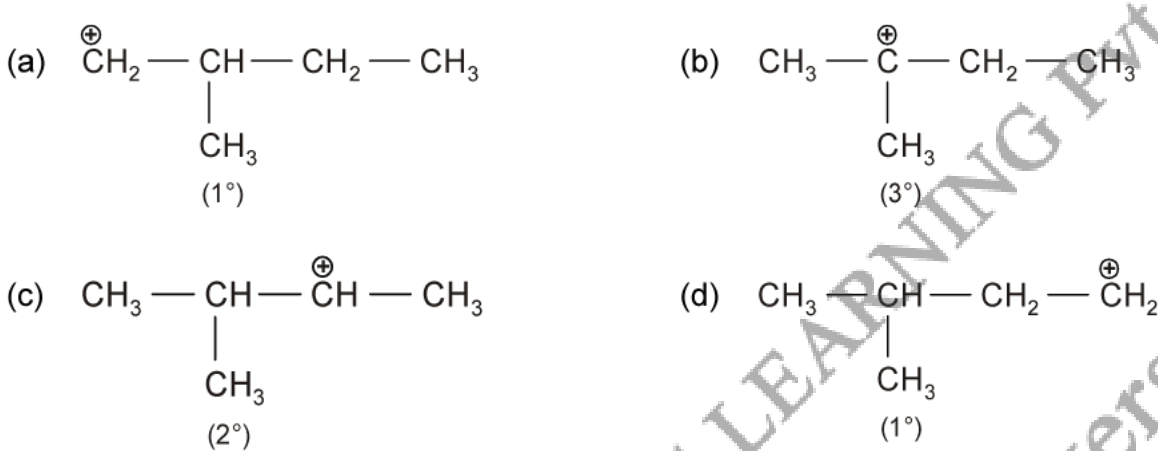
(d) 

CN^- is nucleophile

S39. (a) 

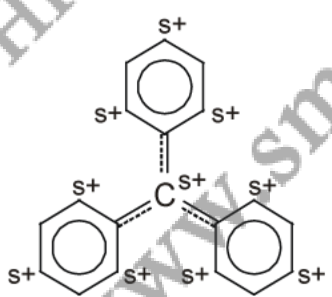
(b) — F > — Cl > — Br > — I

S40. 



Stability order: (b) > (c) > (a) > (d).

S41. Triphenylmethyl cation is more stable because of resonance contribution in three phenyl group the charge distribute by forming ten resonance structure.



S42. $\overset{\oplus}{C}H_3$ is more stable in (a) and (b), because of — I effect of Br and Cl, remaining carbocations are unstable (because of decreasing electron-density).

S43. (a) Substitution (Nucleophilic) (b) Addition (electrophilic)

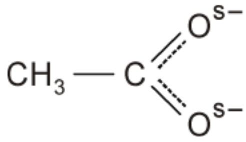
(c) β-Elimination (d) Condensation

S44. $O_2NCH_2 - COO^-$ is more stable thant $CH_3CH_2COO^-$ because the presence of electron withdrawing NO_2 reduces the charge density. On the contrary electron releasing alkyl group in $CH_3CH_2COO^-$ increases the charge density and hence decreases the stability. It is for this reason that α-nitroacetic acid (O_2NCH_2COOH) is more acidic than propionic acid (CH_3CH_2COOH).

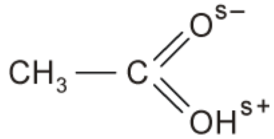
S45. Because alkyl group carbon is *sp*^{3}-hybidrized carbon, which is respectively electropositive than *sp*^{2}-hybidrized carbon of π system

$$\underset{sp^3}{CH_3} - \underset{sp^2}{CH} = CH_2$$

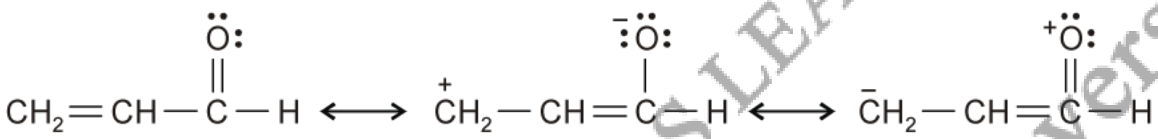
S46. $CH_3 - \overset{\overset{O}{\|}}{C} - O^{\ominus}$ give more stabilize resonance structure, because –ve charge distribute on electronegative oxygen.



while in $CH_3 - \overset{\overset{O}{\|}}{C} - OH$, +ve charge create on electronegative oxygen.



S47.



I II III

The order of stability of these structures is

$$I > II > III$$

Structure III is least stable because it contains an oxygen atom with incomplete octed and also carries positive charge on highly electronegative atom, oxygen.

Structure II is less stable than I because it involves charge separation.

Structure I is the most stable structure and makes maximum contribution towards the resonance hybrid.

S48. (a) **Inductive effect:** Shifting of σ electrondensity of electropositive chain (alkyl group) towards. Electroneative (functiional group) called **inductive effect**.

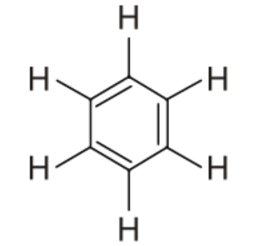
eg., $\overset{sss+}{CH_3} \rightarrow \overset{ss+}{CH_2} \rightarrow \overset{s+}{CH_2} \rightarrow \overset{s-}{Cl}$

(b) Electrophile: Electron deficent species called, electrophile

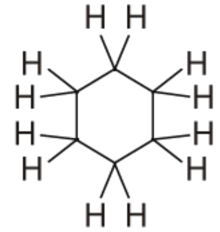
eg., cations $\overset{\oplus}{C}H_3$, $Cl^{\oplus}$ $\overset{\oplus}{N}O_2$

Lewis acid $AlCl_3$, BCl_3 etc.

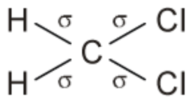
S49.



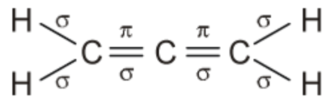
(12 and 3 bonds)



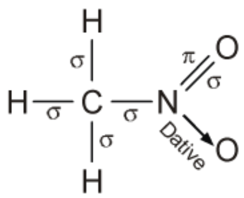
(18 bonds)



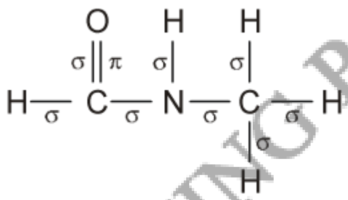
(4 σ bonds)



(6 σ and 2π bonds)



(6 σ and 1π bonds)

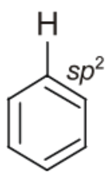


(8 σ and 1π bonds)

S50. The hybridisation of each carbon is written as superscript on the carbon atom in the molecule.

$\overset{sp^2}{CH_2} = \overset{sp}{C} = O$; $\overset{sp^3}{CH_3} - \overset{sp^2}{CH} = \overset{sp^2}{CH_2}$; $\overset{sp^3}{CH_3} - \underset{sp^2}{\overset{O}{\overset{\|}{C}}} - \overset{sp^3}{CH_3}$

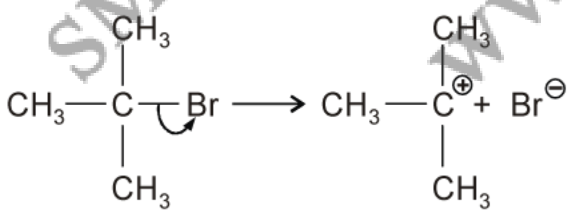
$\overset{sp^2}{CH_2} = \overset{sp^2}{CH} - \overset{sp}{C} \equiv N$;

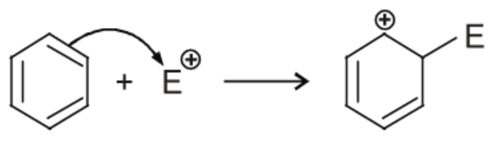


Each C in benzene is sp^2-hybridized.

S51. The two structures are less important contributors as they involve Charge separation. In addition to this structure I contains C atom with incomplete octed.

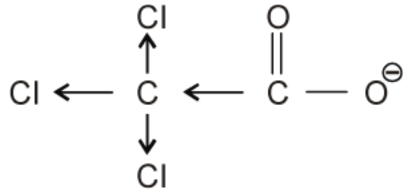
S52.

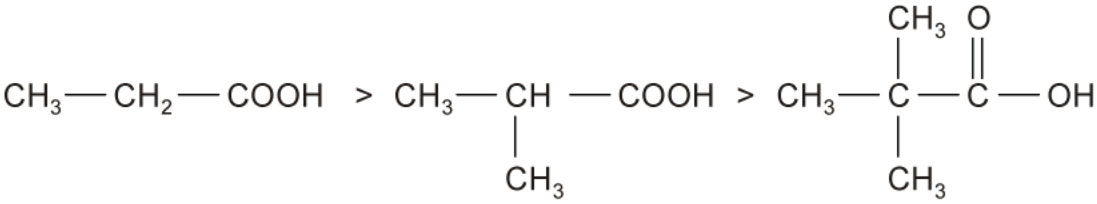
(a) 

(b) 

S53. (a) $CCl_3 - COOH > Cl_2 - CH - COOH > Cl - CH_2 - COOH$,

because of — I effect increase on increase — Cl at α-position, which increase stability of conjugate base on decreasing



(b) 

because on increasing degree of α-carbon, +I effect increase. Which decrease stability on conjugate base on increasing electrondensity.

S54. (a) 

(SCH_3 is more electronegative than CH_3)

(b) 

(CN is more electronegative than CH_3)

(c) 

(Cu is more electropositive than CH_3)

S55. **Nucleophille:** Electron rich species which attack on electron-deficent species called **nucleophille**.

Nucleophille are two in types:

(a) Anion: $Cl^{\ominus}$ $^{\ominus}OH$ $CH_3^{\ominus}$

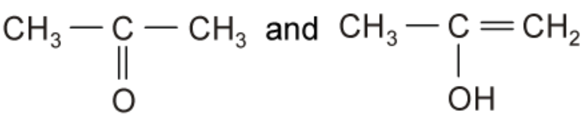
(b) Neutral having lone pair (Lewis base)

$$NH_3,\ H\ddot{\underset{..}{O}}H,\ CH_3 - \ddot{N}H_2$$

S56. In acetylide ion $CH \equiv C^-$, the carbon atom carrying the – ve charge is *sp*-hybridized and has 50% *s*-character, in $CH_2 = CH^-$ ion. the carbon atom is sp^2-hybridized and has 33.3% *s*-character while in $CH_3CH_2^-$ ion, the carbon atom bearing the – ve charge is sp^3-hybridized and has 25% *s*-character.

Since *s*-electrons, on the average, are closer to the nucleus than *p*-electrons, therefore, a carbon atom with greater *s*-character can accommodate or stabilize the negative charge better than a carbon atom with smaller *s*-character. In other words, the stability of the carbanion increases as the *s*-character of the carbon atom carrying the negative charge increases. Now since the *s*-character of the carbon decrease as we move from *sp* to sp^2 to sp^3-carbon, therefore, the relative stabilities of the three carbanions follows the sequence:

$$CH \equiv C^- > CH_2 = CH^- > CH_3CH_2^-.$$

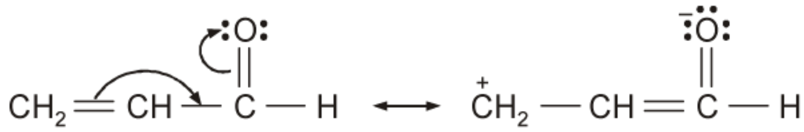
S57. (ii) 

do not constitute resonance structures because they have different arrangement of atoms whereas resonance structures must have same arrangement of atoms.

(iv) $(CH_3)_2C=CH-CH_3$ and $(CH_3)_2CH-CH=CH_2$ also do not constitute resonance structures because they have different arrangement of atoms.

(v) The given structures are functional isomers of each other.

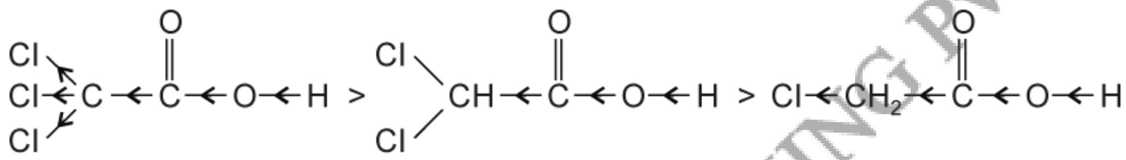
S58.

(a) 

(b) 

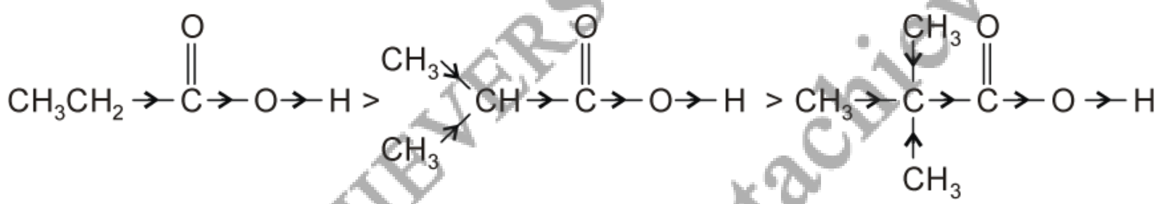
(c) 

S59. (a) The given order of acidic character is explanable on the basis of – **I-effect** as shown below:



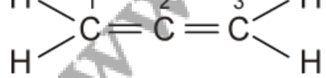
More is the number of halogen atoms greater is the – I-effect and hene more polar is the O — H bond *i.e.*, is more. As the number of halogen atoms decrease the polarity of O — H bond decreases and hence the acidic character.

(b) The given order of acidic character is explanable on the basis of – **I-effect** as shown below:

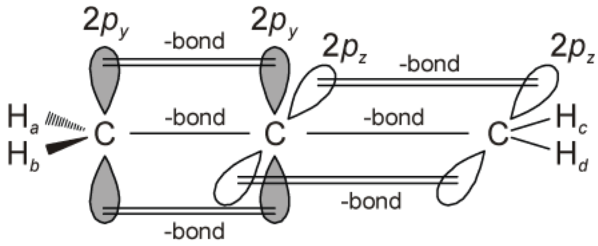


As the number of alkyl groups increases, the +I-effect increases and the acid strength decreases accordingly.

S60. The structure of allene (C_3H_4) is



The carbon atoms 1 and 3 are sp^2-hybridized since each one of them is joined by a double bond. In contrast, carbon atom 2 is sp-hybridized since it has two double bonds. Thus, the two π-bonds in allene like in acetylene are perpendicular to each other as shown beneath:



Where H_c and H_d lie in the plane of the paper while H_a and H_b lie in a plane perpendicular to the plane of the paper.

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Q1. A mixture contains 71 per cent of calcium sulphate and 29 per cent of camphor. Name a suitable technique of separation of the components of the mixture.

Q2. Name a method suitable for separating the mixture of iodine and sodium chloride.

Q3. What conclusions would you draw if the Lassaigne's extact gives a blood red colouration with $FeCl_3$?

Q4. What is the basic principle of chromatography?

Q5. Name two compounds which are purified by sublimation.

Q6. Will a precipitate of AgCl be formed on treating $CHCl_3$ with $AgNO_3$? Explain.

Q7. How will you separate benzoic acid from a mixture of naphthalene and benzoic acid?

Q8. How will you separate a mixture of *o*-nitrophenol and *p*-nitrophenol?

Q9. Suggest methods for the separation of the following mixtures:
(a) a mixture of liquid A (b.p. 365 K) and liquid B (b.p. 355 K)
(b) a mixture of liquid C (b.p. 348 K) and liquid D (b.p. 478 K).

Q10. Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium exract for testing sulphur by lead acetate test?

Q11. Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

Q12. 0.50 g of an organic substance was Kjeldahlised and the ammonia obtained was passed into 100 cm^3 of M/10-H_2SO_4. The excess of acid required 154 cm^3 of M/10-NaOH of neutralisation. Calculate the percentage of nitrogen in the compound.

Q13. 0.25 g of an organic compound gave 30 cm^3 of moist dinitrogen at 288 K and 745 mm pressure. Calculate the percentage of nitrogen. (Aq tension at 288 K = 12.7 mm)

Q14. An organic compound contains 69% C and 4.8% hydrogen the remainder being oxygen. Calculate the masses of carbon dioxide and water formed by the complete combustion of 0.20 g of the substance.

Q15. Why is nitric acid added to sodium extract before adding silver nitrate solution for testing halogens?

Q16. 0.246 g of an organic acid gave on combustion 0.198 g of carbon dioxide and 0.1014 g of water vapours. Calculate the percentage of C and H.

Q17. During nitrogen estimation in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound neutralised 10 mL of 1 M H_2SO_4. What is the % of N in the organic compound?

Q18. 0.40 g of an organic compound gave 0.3 g of silver bromide by Carius method. Find the percentage of bromine in the compound.

Q19. (a) In sulphur estimation, 0.57 g of organic compound gave 0.4813 g of $BaSO_4$. What is the percentage of sulphur in organic compound?

(b) 0.092 g of organic compound on heating in carius tube and subsequent ignition gave 0.111 g of $Mg_2P_2O_7$. Calculate the percentage of phosphorus in organic compound.

Q20. 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 solution of NaOH for neutralisation. Find the perentage composition of nitrogen in the compound.

Q21. 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.

Q22. 0.25 g of an organic compound containing carbon, hydrogen and oxygen was analysed by the combustion method. The increase in the mass of calcium chloride tube and the potash bulbs at the end of the operation was found to be 0.15 g and 0.1837 g respectively. Calculate the percentage composition of the compound.

Q23. 0.3780 g of an oganic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

Q24. Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

Q25. Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

Q26. Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

Q27. Explain, why an organic liquid vapourises at a temperature below its boiling point in its steam distillation?

Q28. Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and phosphorus.

Q29. Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

Q30. In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find the percentage of sulphur in the given compound.

Q31. Discuss the Chemistry of Lassaigne's test.

Q32. Differentiate between the principle of estimation of nitrogen in an organic compound by (a) Dumas method (b) Kjeldahl's method.

Q33. What is the difference between distillation, distillation under reduced pressure and steam distillation?

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S1. The mixture can be separated by the process of sublimation. Camphor will sublimate whereas calcium sulphate will be left behind.

S2. Sublimation is used to separate the mixture of iodine and sodium chloride because iodine sublimes readily.

S3. It indicates that the compound contains both N and S. During fusion, sodium thiocyanate is formed which gives blood red colouration.

$$3NaSCN + FeCl_3 \longrightarrow \underset{\text{Blood red}}{Fe(SCN)_3} + 3NaCl$$

S4. The method of chromatography is based on the difference in the rates at which the components of a mixture are adsorbed on a suitable adsorbent.

S5. Camphor, Naphthalene.

S6. The precipitate of AgCl will not be formed because $CHCl_3$ is a covalent compound and does not ionize to give Cl^- ions. Therefore, $CHCl_3$ does not react with Ag^+ ions (from $AgNO_3$) to form ppt. of AgCl.

S7. Benzoic acid can be separated from nahthalene by treating the mixture with hot water. Benzoic acid dissolves but naphthalene remains insoluble. On cooling pure benzoic acid crystallises out.

S8. A mixture of *o*-nitrophenol and *p*-nitrophenol can be separated by steam distillation. *o*-nitrophenol being less volatile distils over along with water while *p*-nitrophenol being non-volatile remains in the flask.

S9. (a) Fractional distillation because the boiling points of the two liquids differ by only 10°.

(b) Simple distillation because the boiling points of the two liquids differ much.

S10. For testing sulphur, the sodium extract is acidified with acetic acid because lead acetate is soluble and does not interfere with the test. If H_2SO_4 were used, lead acetate will react with it forming white precipitate of lead sulphate.

$$(CH_3COO)_2Pb + H_2SO_4 \longrightarrow \underset{\text{White ppt.}}{PbSO_4} + 2CH_3COOH$$

S11. When CCl_4 is heated with $AgNO_3$ solution, white ppt. of AgCl will not be formed. The reason being that CCl_4 is a covalent compound, therefore, it does not ionize to give Cl^- ions needed for the formation of ppt. of AgCl.

S12. Mass of the organic compound = 0.50 g

Volume of standard H_2SO_4 taken = 100 cm^3 of M/10 solution

Let, Volume of unused $H_2SO_4 = v_1$

Volume NaOH required for the excess acid = 154 cm^3 of M/10 solution

Chemical reaction for titration is

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$$

According to molarity relationship,

$$v_1 \times \frac{1}{10} = 154 \times \frac{1}{10} \times \frac{1}{2}$$

$$\text{Volume of } \frac{M}{10}\ H_2SO_4 \text{ unused } (v_1) = \frac{154}{2} = 77\ cm^3$$

$$\text{Volume of } \frac{M}{10}\ H_2SO_4 \text{ used by } NH_3 = 100 - 77 = 23.0\ cm^3$$

$$\text{Millimoles of } H_2SO_4 \text{ used by } NH_3 = \frac{1}{10} = 2.3$$

$$\text{Millimoles of } NH_3 = 2 \times \text{Millimoles of } H_2SO_4$$

$$= 2 \times 2.3 = 4.6 \quad [\because\ 2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4]$$

$$\text{Mass of } NH_3 \text{ formed} = \text{Moles} \times \text{Molar mass}$$

$$= 4.6 \times 10^{-3} \times 17\,g$$

$$\text{Mass of nitrogen} = \frac{4.6 \times 10^{-3} \times 17 \times 14}{17}$$

$$= 14 \times 4.6 \times 10^{-3}\,g$$

Hence, $$\text{Percentage of nitrogen} = \frac{14}{1000} \times 4.6 \times \frac{100}{0.50} = \mathbf{12.88\%}.$$

S13. Mass of the substance = 0.25 g

Volume of moist dinitrogen = 30 cm^3

Temperature = 288 K

Pressure = 745 – 12.7 = 732.3 mm

Step - I: *To reduce the volume of N_2 at S.T.P.*

We know, $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

(P_2, T_2, V_2 refer to S.T.P. conditions)

$$\therefore \quad V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} = \frac{732.3 \times 30 \times 273}{288 \times 760} = \mathbf{27.4\ cm^3}.$$

Step - II: *Calculation of percentage of nitrogen.*

22400 cm^3 of dinitrogen at S.T.P. weighs

= 28 g

27.4 cm^3 of dinitrogen at S.T.P. weighs

$$= \frac{28 \times 274}{22400} = 0.034\text{ g}$$

Percentage of nitrogen in organic compound

$$= \frac{0.034}{0.25} \times 100 = \mathbf{13.6}.$$

S14.

$$\% C = \frac{12 \times W_{CO_2} \times 100}{44 \times W_{Substance}}$$

$$\therefore \quad W_{CO_2} = \frac{\% C \times 44 \times W_{Substance}}{12 \times 100}$$

$$= \frac{69 \times 44 \times 0.20}{12 \times 100} = \mathbf{0.506\ g.}$$

$$\% H = \frac{2 \times W_{H_2O} \times 100}{18 \times W_{Substance}}$$

$$\therefore \quad W_{H_2O} = \frac{\% H \times 18 \times W_{Substance}}{2 \times 100}$$

$$= \frac{4.8 \times 18 \times 0.2}{2 \times 100} = \mathbf{0.0864\ g}.$$

S15. Sodium extract is boiled with nitric acid to decompose NaCN and Na_2S if present.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$

$$Na_2S + HNO_3 \longrightarrow 2NaNO_3 + H_2S\uparrow$$

If cyanide and sulphide ions are not decomposed, they will interfere with the test by forming precipitate of AgCN and Ag_2S.

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

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

S16. Mass of organic compound = 0.246 g

Mass of CO_2 formed = 0.198 g

Mass of H_2O formed = 0.1014 g

(a) **Percentage of Carbon:**

$$44\text{ g of } CO_2 \text{ contains carbon} = 12\text{ g}$$

$$0.198\text{ g of } CO_2 \text{ contains carbon} = \frac{12}{44} \times 0.198$$

$$\text{Percentage of carbon} = \frac{0.054}{0.246} \times 100 = \mathbf{21.95\%}.$$

(b) **Percentage of Hydrogen:**

$$18\text{ g of } H_2O \text{ contains hydrogen} = 2\text{ g}$$

$$0.1014\text{ g of } H_2O \text{ contains hydrogen} = \frac{2}{18} \times 0.1014 = 0.011\text{ g}$$

$$\text{Percentage of hydrogen} = \frac{0.011}{0.246} \times 100 = \mathbf{4.58\%}.$$

S17. Volume of 1 M H_2SO_4 used by NH_3 = 10 mL

Millimoles of H_2SO_4 used = $10 \times 1 = 10$

Millimoles of NH_3 produced = $2 \times$ millimoles of H_2SO_4

$= 2 \times 10 = 20$ [2 mol of NH_3 neutralise 1 mol of H_2SO_4]

Mass of NH_3 formed = Mol $\times$ Molar mass = $20 \times 10^{-3} \times 17$ g

$$\text{Mass of N} = \frac{20 \times 10^{-3} \times 17 \times 14}{17} = 0.28\text{ g}$$

$$\text{\% of N} = \frac{0.28 \times 100}{0.5} = \mathbf{56.0\%}.$$

The % of N can also be found directly by aplying the formula,

$$\% = \frac{1.4 \times M_{H_2SO_4} \times \text{Basicity of } H_2SO_4 \times V_{H_2SO_4}}{W_{\text{Substance}}}$$

$$= \frac{1.4 \times 1 \times 2 \times 10}{0.5} = 56\%$$

S18. Mass of compound = 0.40 g

188 g of AgBr contains Br = 80 g

$\therefore$ 0.3 g of AgBr contains Br = $\frac{80}{188} \times 0.3 = 0.127$ g

The percentage of Br in the organic compound

$$= \frac{0.127}{0.40} \times 100 = \mathbf{31.75\%}.$$

Alternatively, the result can be directly obtained by the application of the formula

$$\% \text{ Br} = \frac{80 \times W_{AgBr} \times 100}{188 \times w_{Substance}}$$

$$= \frac{80 \times 0.3 \times 100}{188 \times 0.40} = \mathbf{31.75\%}.$$

S19. (a) Mass of $BaSO_4$ = 0.4813 g

Mass of organic compound = 0.157 g

$$\% \text{ S} = \frac{32 \times W_{BaSO_4} \times 100}{233 \times W_{Substance}}$$

$$= \frac{32 \times 0.4813 \times 100}{233 \times 0.157} = \mathbf{42.10\%}.$$

(b) Mass of organic compound = 0.092 g

Mass of $Mg_2P_2O_7$ = 0.111 g

$$\% \text{ of P} = \frac{62 \times W_{Mg_2P_2O_7} \times 100}{222 \times W_{Substance}}$$

$$= \frac{62 \times 0.111 \times 100}{222 \times 0.092} = \mathbf{33.69\%}.$$

S20. **Step - I:** *To determine the volume of H_2SO_4 used.*

Volume of acid taken = 50 ml of 0.5 M H_2SO_4 = 25 ml of 1 M H_2SO_4.

Volume of alkali used for neutralization of excess acid

= 60 ml of 0.5 M NaOH

= 30 ml of 1 M NaOH

Now 1 mole of H_2SO_4 neutralizes 2 moles of NaOH (*i.e.*, $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$)

∴ 30 ml of 1 M NaOH = 15 ml of 1 M H_2SO_4

∴ Volume of acid used by ammonia

= 25 – 15 = **10 ml**.

Step - II: *To determine percentage of nitrogen.*

1 mole of H_2SO_4 neutralizes 2 moles of NH_3

10 ml of 1 M H_2SO_4 = 20 ml of 1 M NH_3

But 1000 ml of 1 M NH_3 contain nitrogen = 14 g

∴ 20 ml of 1 M NH_3 will contain nitrogen

$$= \frac{14}{1000} \times 20\ g$$

But this much amount of nitrogen is present in 0.5 g of the organic compound.

$\therefore$ Percentage of nitrogen = $\frac{14}{1000} \times \frac{20}{0.5} \times 100$ = **56.0%**.

Alternatively, % of N can be determined by applying the following equation,

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

Substituting the values of all the items in the above equation, we have

$$\%\ N = \frac{1.4 \times 1 \times 2 \times 10}{0.5} = \mathbf{56.0\%}.$$

S21.

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

Substituting the values of % of C and mass of the substance taken, we have,

$$69 = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{0.2\ g} \times 100$$

or Mass of CO_2 formed = $\frac{69 \times 44 \times 0.2}{12 \times 100}$ = **0.506 g**

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

Substituting the values of % of H and mass of the substance taken, we have

$$4.8 = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{0.2} \times 100$$

or Mass of H_2O formed = $\frac{4.8 \times 18 \times 0.2}{2 \times 100}$ = **0.0864 g**.

S22. Mass of the compound taken = 0.25 g

Mass of water produced (increase in the mass of calcium chloride tube)

= 0.15 g

Mass of caron dioxide produced (increase in the mass of potash bulbs)

= 0.1837 g

Percentage of hydrogen = $\frac{2}{18} \times 0.15 \times \frac{100}{0.25}$ = **6.66%**

$$\text{Percentage of carbon} = \frac{12}{44} \times 0.1837 \times \frac{100}{0.25} = \mathbf{20.04\%}$$

$$\text{Percentage of oxygen} = 100 - (6.66 + 20.04) = \mathbf{73.30\%}.$$

S23. The mass of substance taken = 0.3780 g.

Mass of AgCl formed = 0.5740 g

1 mole of AgCl = 1 g atom of Cl

or (108 + 35.5) = 143.5 g of AgCl = 35.5 g of Cl

Applying the relation,

$$\text{Percentage of chlorine} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of subs tan ce taken}} \times 100$$

$$= \frac{35.5}{143.5} \times \frac{0.5740}{0.3780} \times 100 = \mathbf{37.566\ g}.$$

S24. Two compounds with different solubilities in a solvent S can be separated by fractional crystallisation. When a hot saturated solution of these two compounds is allowed to cool, the less soluble compound crystallises out first while the more soluble remains in the solution. The crystals are separated from the mother liquor and the mother liquor is again concentrated and the hot solution again allowed to cool when the crystals of the second (*i.e.*, moe soluble) compound ar obtained. These are again filtered and dried.

S25. For testing sulphur, the sodium extract is acidified with acetic acid because lead acetate is soluble and does not interfere with the test. If H_2SO_4 were used, lead acetate itself with react with H_2SO_4 to form white ppt. of lead sulphate which will interfere with the test.

$$\underset{\text{Lead acetate}}{Pb(OCOCH_3)_2} + H_2SO_4 \longrightarrow \underset{\text{(White ppt.)}}{PbSO_4\downarrow} + 2CH_3COOH$$

S26. CO_2 is acidic in nature, therefore, it reacts with the strong base KOH to form K_2CO_3.

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

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 cargon in the organic compound can be estimated by using the equation,

$$\%\,C = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of subs tan ce taken}} \times 100\,.$$

S27. In steam distillation, the mixture consists of the organic liquid and water boils at a temperature when the sum of the vapour pressure of the liquid (p_1) and that of water (p_2) becomes equal to the atmospheric pressure (p), *i.e.*, $p = p_1 + p_2$.

Since the vapour pressure of water around the boiling point of the mixture is quite high and that of liquid is quite low (10 – 15 mm), therefore, the organic liquid distils at a pressure much lower thant the atmospheric pressure. In other words, the organic liquid vapourises at a temperature much lower than its normal boiling point.

S28. The organic compound is fused with sodium method to convert these elements (which are present in the covalent form) to ionic form. For example, sulphur is changed to Na_2S, nitrogen to NaCN and phosphorus to Na_3PO_4. The presence of sulphide ions, cyanide ions and phosphte ions can thus be confirmed by suing suitable reagents.

S29. A mixture of $CaSO_4$ and camphor can be separated by the following two methods:

(a) Camphor is sublimable but $CaSO_4$ is not, therefore, sublimation of the mixture gives camphor on the sides of funnel while $CaSO_4$ is left in the china dish.

(b) Camphor is soluble in organic solvents like $CHCl_3$, CCl_4 etc., while $CaSO_4$ is not. Therefore, when the mixture is shaken with the solvent, camphor goes into solution while $CaSO_4$ remains as residue. It is filtered and evaporation of solvent gives camphor.

S30. The mass of substance taken = 0.468 g.

Mass of $BaSO_4$ formed = 0.668 g

1 mole of $BaSO_4$ = 1 g atom of S

or $(137 + 32 + 4 \times 16) = 233$ g of $BaSO_4$ = 32 g of S

$$\text{Percentage of sulphur} = \frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{32}{233} \times \frac{0.668}{0.468} \times 100 = \mathbf{19.60\ g.}$$

S31. Lassaigne's test: Lassaigne's extract is prepared as described in the case of nitrogen. The extract contains sodium sulphide formed by the reaction between sulphur (present in the compound) and sodium.

$$2Na + S \longrightarrow Na_2S$$

The Lassaigne's extract is divided into two parts and following tests are performed

(a) **Lead acetate test:** One part of the extract is acidified with acetic acid and then lead acetate solution is added. Formation of a black precipitate confirms the presence of sulphur in the organic compound.

$$Na_2S + Pb(CH_3COO)_2 \longrightarrow \underset{\text{Black ppt.}}{PbS\downarrow} + 2CH_3COONa$$

(b) **Sodium nitroprusside test:** A few drops of sodium nitroprusside solution are added to another part of the Lassaigne's extract. The appearance of purple colouration confirms the presence of sulphur:

$$\underset{\text{Sodium extract}}{Na_2S} + \underset{\text{Sosium nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Purple colouration}}{Na_4[Fe(CN)_5NO\ .\ S]}$$

S32. (a) **Dumas method:** In Dumas method, a known mass of the organic compound is heated with excess of CuO in an atmosphere of CO_2, when nitrogen of the organic compound is converted into N_2 gas. The dinitrogen gas is collected over water. The volume of N_2 thus obtained is converted into S.T.P. and the percentage of nitrogen determined by applying the equation,

$$\% N = \frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ at S.T.P.}}{\text{Mass of subs tan ce taken}} \times 100$$

(b) **Kjeldahl's method:** In Kjeldahl's method, a known mass of the organic substance is digested (heated) with conc. H_2SO_4 in presence of K_2SO_4 and little $CuSO_4$ or Hg (catalyst) in a long necked flask called Kjelhahl's flask when nitrogen present in the organic compound is quantitatively converted into $(NH_4)_2SO_4$. 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 unused is found by titration against a standard alkali solution. From the volume of the acid used, the percentage of nitrogen is determined by aplying the equation,

$$\% N = \frac{1.4 \times \text{Molarity of the acid} \times \text{Basicity of the acid} \times \text{Vol. of the acid used}}{\text{Mass of suvs tan ce taken}}$$

S33. **Distillation** involves conversion of a liquid into vapours followed by condensation of the vapours thus produced by cooling to get the pure liquid while the non-volatile impurities remain in the flask. *This method is commonly used for those liquids which are sufficiently stable at their boiling points and contain non-volatile impurities*.

Distillation under reduced pressure also involves conversion of a liquid into vapours by heating followed by condensation of the vapours thus produced by cooling but the pressure acting on the system is not atmospheric but is reduced by using a vacuum pump. Since the boiling point of a liquid decreases as the pressure acting on it is reduced, therefore, this method is used to purify such liquids which have high boiling liquids or liquids which decompose below their boiling points.

Steam distillation *is comparable to distillation under reduced pressure* (*vacuum distillation*) *even though there is no reduction in the total pressure acting on the solution*. Here, the mixture of organic liquid and water boils at a temperature when the sum of the vapour pressures of the orgnic liquid (p_1) and that of water (p_2) becomes equal to the atmospheric pressure (p), *i.e.*, $p = p_1 + p_2$.

Since the vapour pressure of water around its boiling point is quite high and that of the liquid is quite low, therefore, the organic liquid will boil at a temperature much lower than its normal boiling point and hene its decomposition is avoided. Steam distillation is used to purify *such liquids which are volattile in steam, insoluble in water, possess a vapour pressure of about 10-5 mm of Hg and contain non-volatile impurities*.