STRUCTURAL ISOMERISM, STRUCTURAL IDENTIFICATION & POC

CONTENTS

JEE (Advanced) Syllabus

Concepts : Structural identification

Catalytic hydrogenation, Monochlorination & ozonolysis reactions.

Detection of elements (N, S, halogens); Detection and identification of the following functional groups: hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl, amino and nitro.

JEE (Main) Syllabus

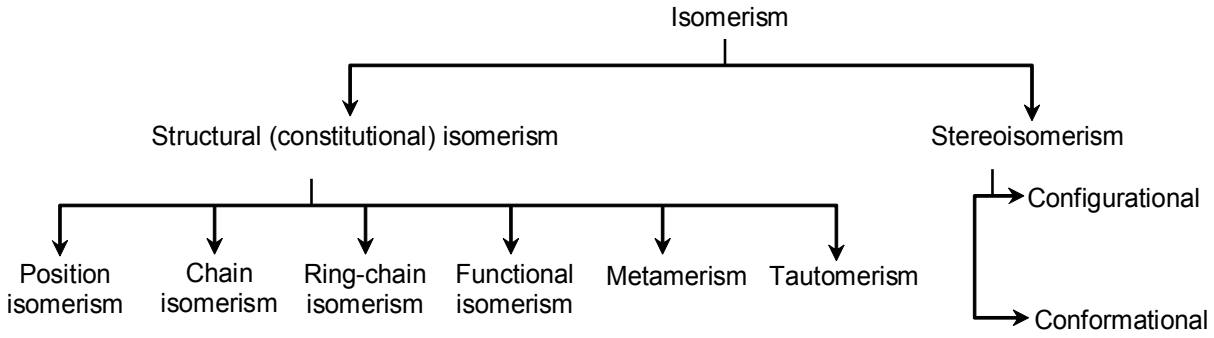
General introduction, qualitative analysis of organic compounds & Lab test of functional groups.

1. Structural Isomerism

Isomerism

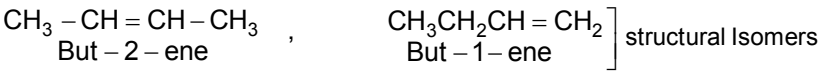
The phenomenon of existence of two or more compounds possessing the same molecular formula but different physical or chemical or both properties is known as isomerism. Such compounds are known as isomers.

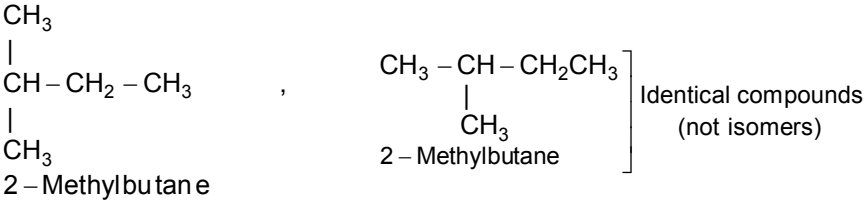
Classification of isomerism



1 Structural isomerism

When two or more organic compounds have same molecular formula but different structural formula, (i.e., they differ in connectivity of atoms) they are called **structural isomers** and the phenomenon is called structural isomerism.





1.1 Chain isomerism

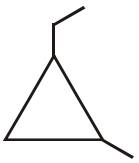
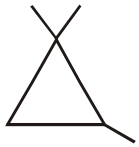
Compounds having same molecular formula but different carbon skeletons (either difference in main chain or side chain) are known as chain isomers & phenomenon is known as chain isomerism.

Condition : They should have same nature of locants.

(i) $CH_3–CH_2–CH_2–CH_2–CH_3$ $\quad$ $CH_3–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_2–CH_3$ $\quad$ $CH_3–\underset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}–CH_3$

Pentane	Isopentane	Neopentane
(Main chain of 5C)	(Main chain of 4 C)	(Main chain of 3C)

All the above are chain isomers.

(ii)  

Size of main chain = 3 Size of main chain = 3
Size of longest Side chain = 2 Size of longest side chain = 1
Both are chain isomers due to difference in number of carbon atoms in side chain.

(iii) $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H(\overset{1}{C}N)-CH_2-CH_3$ & $\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H(\overset{1}{C}N)-CH_3$

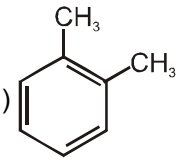
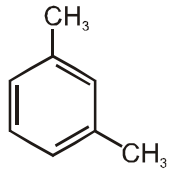
2-Ethylbutanenitrile 2-Methylpentanenitrile
Both are chain isomers due to difference in number of carbon atoms in parent chain.

1.2 Position isomerism

Compounds having same carbon skeleton along with same nature of locants but having different position of locants are known as position isomers & phenomenon is position isomerism.

(i) $CH_3CH_2CH_2OH$ & $CH_3-\underset{OH}{CH}-CH_3$

Propan-1-ol Propan-2-ol
Difference only in position of –OH group so these are positional isomers.

(ii)  ,  & 

o-Xylene m-Xylene p-Xylene
Difference only in position of $-CH_3$ group so these are positional isomers.

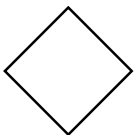
1.3 Functional isomerism

Compounds having same molecular formula but different functional groups are known as functional isomers & phenomenon is functional isomerism.

(i) $CH_3CH_2-NH_2$ & $CH_3-NH-CH_3$ (ii) $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$ & $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

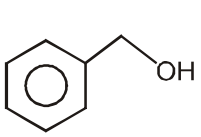
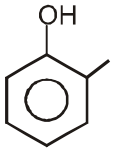
Ethanamine Dimethylamine Propanal Propanone

1.4 Ring-chain isomerism

$CH_3-CH=CH-CH_3$ (But-2-ene) &  Cyclobutane

Sometimes it is also known as **functional isomerism**.

Note : (1) 1º, 2º, 3º amines are functional isomers.
(2) 1º, 2º, 3º amides are functional isomers.
(3) Alcohol attached to sp^2 C is chemically different from alcohol attached to sp^3 C.
(4) Alchol and enol are functional isomers.



are functional isomers.

(5) Following compounds do not exist at room temperature therefore should not be considered as structural isomers.

(i) –C=C–OH (enol) (ii) –C≡C–OH (ynol) (iii) –C(OH)– OH (gemdiol)

(iv) –C(OR)–OH (hemiacetal) (v) –C(OH)–O–C=C– (vi) –O–O– (peroxy compound)

1.5 Metamerism

It arises due to different alkyl chains on either side of the functional group.
(Polyvalent hetro atomic functional group must be present in the compounds).

(i) $CH_3–CH_2–O–CH_2–CH_2$ & $CH_3–O–CH_2–CH_2–CH_3$

Ethoxy ethane — Methoxy propane

[Ethyl groups on either sides of O.] [Methyl & propyl groups on either sides of O.]

(ii) $CH_3–C(=O)–O–CH_2–CH_3$ & $CH_3–CH_2–C(=O)–OCH_3$ & $H–C(=O)–O–CH_2–CH_2–CH_3$ are metamers.

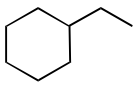
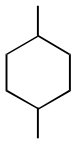
$CH_3–CH_2–N(CH_3)–CH_2–CH_2–CH_3$ & $CH_3–CH_2–N(CH_2–CH_3)–CH_2–CH_3$ are metamers.

Que. Identify relationship between the given pair of compounds.

(1) (i) $CH_3 – CH_2CH_2 – CH_3$ (ii) $CH_3 – CH(CH_3) – CH_3$

(i)	(ii)
Butane	2–Methylpropane
Size of main chain = 4	Size of main chain = 3
Size of side chain = 0	Size of side chain = 1

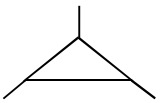
Structure (i) & (ii) are chain isomers.

(2) (i)  (ii) 

(i)	(ii)
1–Ethylcyclohexane	1,4–Dimethylcyclohexane
Size of main chain = 6	Size of main chain = 6
Size of side chain = 2	Size of side chain 1 = 1
	Size of side chain 2 = 1

Structure (i) & (ii) are chain isomers.

(3) (i) 
Cyclohexane

(ii) 
1,2,3–Trimethylcyclopropane

Size of main chain = 6
Size of side chain = 0

Size of main chain = 3
Size of side chain 1 = 1
Size of side chain 2 = 1
Size of side chain 3 = 1

Structure (i) & (ii) are chain isomers.

(4) $H_3C-CH_2-CH=CH_2$ (but – 1 – ene)
$H_3C-CH=CH-CH_2$ (but – 2 – ene)
] position isomers

(5) $HC\equiv C-CH_2-CH_2-CH_3$ (pent – 1 – yne)
$H_3C-C\equiv C-CH_2-CH_3$ (pent – 2 – yne)
] position isomers

(6) (i) CH_3-CH_2OH
Ethanol
Functional group – OH

(ii) CH_3-O-CH_3
Methoxymethane
Functional group – O – (Ether)

Structure (i) & (ii) are functional isomers.

(7) (i) $CH_3-\overset{\overset{O}{\|}}{C}-OH$
Ethanoic acid

(ii) $H-\overset{\overset{O}{\|}}{C}-OCH_3$
Methyl methanoate

Functional groups – COOH

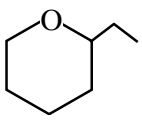
Functional groups $-\overset{\overset{O}{\|}}{C}-O-$ (Ester)

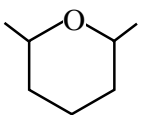
Structure (i) & (ii) are functional isomers.

(8) (i) $C_2H_5-O-C_2H_5$
Diethyl ether
Alkyl groups $-C_2H_5$ & $-C_2H_5$

(ii) $C_3H_7-O-CH_3$
Methyl propyl ether
Alkyl groups $-C_3H_7$ & $-CH_3$

Structure (i) & (ii) are metamers.

(9) (i) 

(ii) 

Struture (i) and (ii) have different alkyl groups but same functional groups, so these are metamers.

(10) (i) $CH_3-O-CH_2-CH_2-CH=O$
Functional groups-ether and aldehyde

(ii) $CH_3-CH_2-CH_2-O-CH=O$
Functional group-Ester

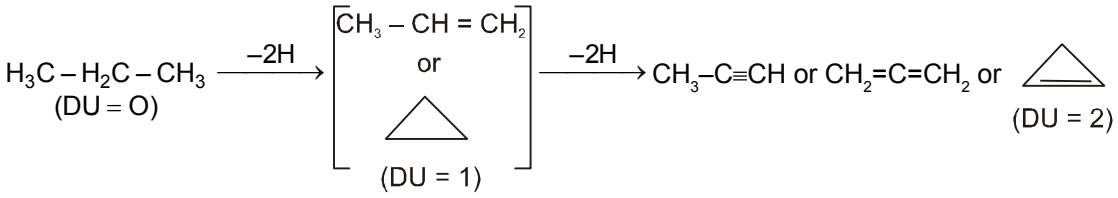
Struture (i) and (ii) have different functional groups, so these are functional isomers.

1.6. Degree of unsaturation (DU)

The presence of double bonds or rings within a molecule is indicated by a quantity called degree of unsaturation.

Applications : To identify the no. of π bonds or rings and also helpful in determining the structure of the molecule.

Definition : Deficiency of 2H atoms with respect to fully saturated acyclic hydrocarbon is equivalent to one DU. It is also known as Index of Hydrogen Deficiency (IHD) or Double Bond Equivalence (DBE)



$$\text{Degree of unsaturation (D.U.)} = \frac{(2n+2)-(\text{No. of H atoms}+\text{No. of X atoms}-\text{No. of N atoms})}{2}$$

Where n = number of carbon atoms in the molecule

Note : Total no. of cyclic rings + double bonds will give us degree of unsaturation.

One double bond = one DU

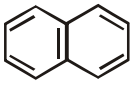
One ring = one DU

One triple bond = two DU

(i) $CH_2=CH_2$ DU= $\frac{(2\times2+2)-4}{2}$ =1

(ii)  DU = 2

(iii)  DU = 4

(iv)  DU = 7

(v) $C_2FClBrI$ DU= $\frac{(2\times2+2)-4}{2}$ = 1

(vi) $C_{15}H_{28}O_2N_2$ DU= $\frac{(2\times15+2)-(28-2)}{2}$ =3

2. Structural identification

Introduction

The main objective of an organic chemist is the determination of the structure of a new organic compound which has been obtained in pure state either from a natural source or synthesised in the laboratory.

In order to establish the correct structure of an organic compound, it is necessary to detect skeleton of compound, elements and functional groups present in the organic compound.

2.1. Catalytic hydrogenation

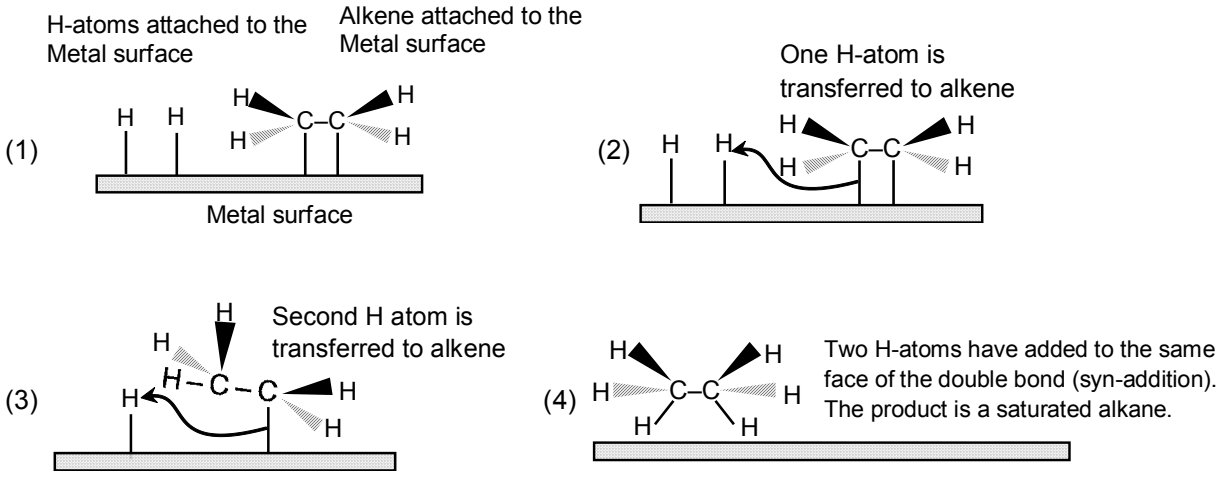
Alkenes, Alkynes, polyenes or polyynes can be hydrogenated by using catalysts Ni/Pt/Pd at room temperature. All Carbon–Carbon π bonds(C=C, C≡C) get hydrogenate. The reaction can't be stopped at any intermediate stage.

Steps in the hydrogenation of a C=C double bond at a catalyst surface (for example Ni or Pt)

(1) The reactants are adsorbed on the catalyst surface and H_2 dissociates.

(2) A H atom bonds to one C atom. The other C atom is still attached to the surface.

(3) A second C atom bonds to a H atom. The molecule leaves the surface.



Note : **(1)** Aromatic π bonds are stable at room temperature but can be hydrogenate at high temperature.

(2) It can be concluded that the hydrogenation product of an alkene or alkyne or any unsaturated compound is always a saturated compound.

(3) The no. of moles of H_2 consumed by 1 mole of compound is equal to the no. of π bonds.

(4) During catalytic hydrogenation ***carbon skeleton*** does not change.

Application : This reaction gives an information about molecule that the molecule, is saturated or unsaturated.

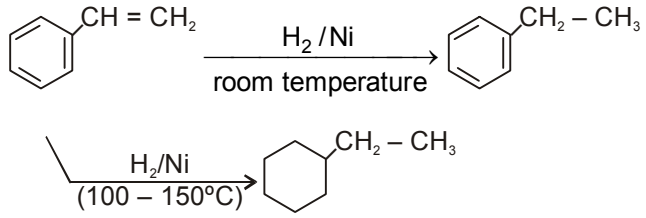
(i) $R–CH=CH–R + H_2 \xrightarrow{Ni} R–CH_2–CH_2–R$

(ii) $R–C\equiv C–R + 2H_2 \xrightarrow{Ni/Pt/Pd} R–CH_2–CH_2–R$

$\downarrow H_2$

$R-CH=CH-R \xrightarrow{H_2} R-CH_2-CH_2-R$
(Not isolated)

(iii) $CH_2=CH–CH=CH_2 \xrightarrow{2H_2/Ni} CH_3–CH_2–CH_2–CH_3$

(iv) 

2.2. Monohalogenation

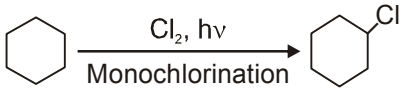
When an alkane or a cycloalkane is treated with halogen a photochemical reaction takes place, in which a C–H bond cleaves and a C–X bond is formed. In such reactions if one H-atom is substituted by one halogen atom, then this is known as monohalogenation reaction.

Application : If a molecule has more than one type of H-atoms, then on monochlorination, it forms a mixture of monochloroisomers. **All these products (structures) are position isomers.**

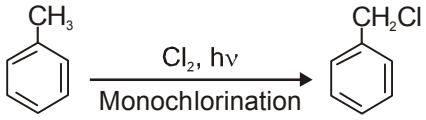
Conclusion : Hence, it can be concluded that the total no. of position isomers (structural) of monochloro compounds is equal to the number of different types of H-atoms present in the reactant. The different type of H-atoms are also known as non-identical hydrogens or non-equivalent hydrogens or chemically different hydrogens.

Note : In aromatic hydrocarbons, the hydrogen atoms of the side-chain are chlorinated, but H-atoms of benzene ring are stable.

(i) $CH_4 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu} CH_3Cl + HCl$ (1–Monochloroproduct)

(ii) 

(1–Monochloroproduct)

(iii) 

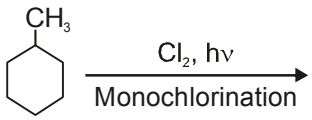
(1–Monochloroproduct)

Note : Only one monochloro product is formed because aromatic H atoms are inert towards this reaction.

(iv) $CH_3–CH_2–CH_2–CH_3 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu}$ 2 Products (structural isomers)

(v) $CH_3–CH_2–CH_2–CH_2–CH_3 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu}$ 3 Products (structural isomers)

(vi) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu}$ 4 Products (structural isomers)

(vii) 

5 Products (structural isomers)

2.3. Ozonolysis

Ozonolysis reaction is used to determine the position of C=C, C≡C in a molecule. In this reaction alkene, alkyne and polyalkene on ozonolysis undergo oxidative cleavage. It is of two types.

(i) Reductive ozonolysis

Reagents are : (1) O_3 (ozone) (2) Zn or $(CH_3)_2S$ and H_2O or CH_3COOH

The products are carbonyl compounds (aldehydes, ketones).

(ii) Oxidative ozonolysis

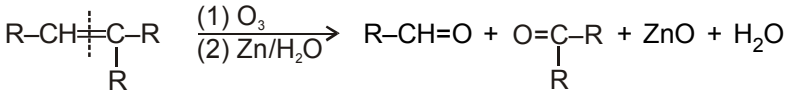
Reagents are : (1) O_3 (ozone) (2) H_2O_2 or H_2O

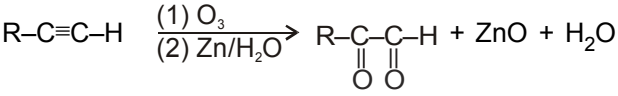
The products are ketones and/or acids.

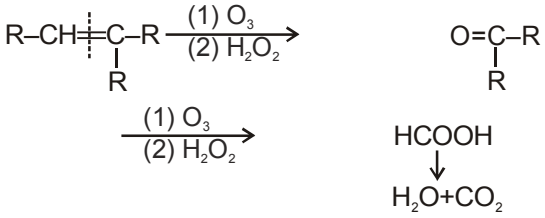
Note : (i) Ozonolysis does not interfere with other functional groups.

(ii) At higher temperature, the aromatic double bonds can also undergo ozonolysis reaction.

(a) Reductive ozonolysis





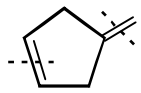


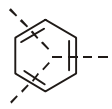
Ex. (i) $CH_2=CH_2 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_2=O + CH_2=O$

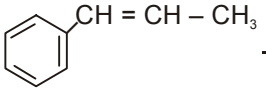
(ii) $CH_3–CH_2–CH=CH_2 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_3–CH_2–CH=O + O=CH_2$

(iii) $CH_2=CH–CH_2–CH=CH–CH_3 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_2=O + O=CH–CH_2–CH=O + O=CH–CH_3$

(iv)  $\xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3}$ 2 OHC–CH_2–CHO (Propanedial)

(v)  $\xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3}$ O=CH–CH_2–C(=O)–CH_2–CH=O + O=CH_2

(vi)  $\xrightarrow[Zn,H_2O]{O_3(\Delta)}$ 3 O = C(H) – C(H) = O (Ethanedial) or (glyoxal)

(vii) 

3. Practical Organic Chemistry (POC)

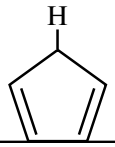
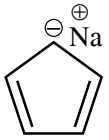
While looking for the information regarding the functional nature of the compound, we go for the following lab tests.

3.1. Test for acidic/active hydrogen

When any compound release H_2 gas after reaction with sodium or potassium or alkali metals or sodamide then this reflects the presence of acidic hydrogen.

Active H : The H atoms which are attached with more electronegative atoms like O,N,S,X, C_{sp}.

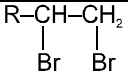
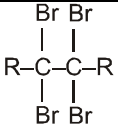
General reaction : $Z - \textcircled{H} + Na \rightarrow \overset{-}{Z}\overset{+}{Na} + \frac{1}{2}H_2\uparrow$

S.No	Reactant	Reagent (Na metal)	Product
1	$R-NH_2$	$\xrightarrow{Na}$	$R-NHNa+\frac{1}{2}H_2\uparrow$
2	$R-SH$	$\xrightarrow{Na}$	$RSNa+\frac{1}{2}H_2\uparrow$
3	$R-COOH$	$\xrightarrow{Na}$	$R-COONa+\frac{1}{2}H_2\uparrow$
4	$PhOH$	$\xrightarrow{Na}$	$PhONa+\frac{1}{2}H_2\uparrow$
5	R—OH	$\xrightarrow{Na}$	$R-O^-Na^+ + \frac{1}{2}H_2\uparrow$
6	$R—SO_3H$	$\xrightarrow{Na}$	$R—SO_3^-Na^+ + \frac{1}{2}H_2\uparrow$
7	R—C≡CH	$\xrightarrow{Na}$	$R—C\equiv C^-Na^+ + \frac{1}{2}H_2\uparrow$
8	$R — CH = CH_2$	$\xrightarrow{Na}$	No reaction.
9	$R — CH_2—O —CH_3$	$\xrightarrow{Na}$	No reaction.
10	HCl	$\xrightarrow{Na}$	$NaCl+\frac{1}{2}H_2\uparrow$
11		$\xrightarrow{Na}$	 $+\frac{1}{2}H_2$

3.2 Test for unsaturation

(a) Bromine water test ($Br_2 + H_2O$, Red-brown solution)

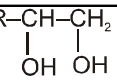
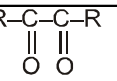
This is used to distinguish between saturated (alkane) and unsaturated (alkene/alkyne) hydrocabon.

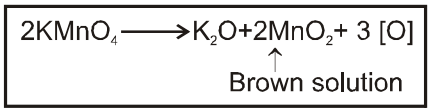
S.No	Reactant	Reagent	Product	Observation
1	$R–CH_2–CH_3$	Bromine water ($Br_2 + H_2O$)	–	No reaction
2	$R–CH=CH_2$	Bromine water ($Br_2 + H_2O$)		Red-brown colour disappears
3	R–C≡CR	Bromine water ($Br_2 + H_2O$)		Red-brown colour disappears

Note : Benzene does not give this test, whereas phenol and aniline give this test.

(b) Baeyer reagent (Cold dil. alkaline $KMnO_4$ Pink/purple solution)

This is also used to distinguish between saturated (alkane) and unsaturated (alkene/alkyne) compounds.

S.No	Reactant	Reagent	Product	Observation
1	$R–CH_2–CH_3$	Cold dil. alkaline $KMnO_4$	–	No reaction
2	$R–CH=CH_2$	Cold dil. alkaline $KMnO_4$		Purple colour disappears
3	R–C≡CR	Cold dil. alkaline $KMnO_4$		Purple colour disappears



3.3 Test for terminal alkyne

S.No	Reactant	Reagent	Product	Observation
1	RC≡CH	Tollen's Reagent [$AgNO_3$ + NH_4OH or $\{Ag(NH_3)_2\}^+ OH^-$]	R–C≡CAg + NH_4NO_3	White precipitate
2	RC≡CH	Ammonical cuprous chloride (Cu_2Cl_2 + NH_4OH)	R–C ≡ CCu ↓ + $2NH_4Cl$	Red precipitate

3.4. Test for alcohols

(a) Lucas reagent test (Conc. HCl + anhydrous $ZnCl_2$)

* It gives white turbidity or cloudiness with alcohols (OH groups attached with sp^3 hybridised carbon).

* Lucas reagent is also used to distinguish between 1°, 2°, 3° alcohol because 1°, 2°, 3° alcohols react with different rates.

(i) 1° alcohol $R–CH_2–OH \xrightarrow{\text{Conc. HCl + anhydrous } ZnCl_2} R–CH_2–Cl$

(does not give appreciable reaction or gives white turbidity in 30 min.)

(ii) 2° alcohol $R_2CH–OH \xrightarrow{\text{Conc. HCl + anhydrous } ZnCl_2} R_2CH–Cl$ (gives white turbidity in 5 min.)

(iii) 3° alcohol $R_3C–OH \xrightarrow{\text{Conc. HCl + anhydrous } ZnCl_2} R_3C–Cl$ (gives white turbidity immediately)

*** Phenols and enols do not give Lucas test.**

(b) Victor Mayer test

1° Alcohol : $RCH_2–OH \xrightarrow{P+I_2} RCH_2–I \xrightarrow{AgNO_2} RCH_2–NO_2 \xrightarrow{HNO_2} R–\overset{\overset{NO_2}{|}}{C}=N–OH \xrightarrow{base}$ Blood Red colour

2° Alcohol : $R_2CH–OH \xrightarrow{P+I_2} R_2CH–I \xrightarrow{AgNO_2} R_2CH–NO_2 \xrightarrow{HNO_2} R_2\overset{\overset{N=O}{|}}{C}–NO_2 \xrightarrow{base}$ Blue colour

3° Alcohol : $R_3C–OH \xrightarrow{P+I_2} R_3C–I \xrightarrow{AgNO_2} R_3C–NO_2 \xrightarrow{HNO_2}$ no reaction $\xrightarrow{base}$ no colour

(c) Cerric Ammonium Nitrate test

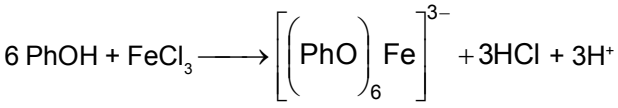
Alcohols(1°,2°,3°) give characteristic red colour with cerric ammonium nitrate $[(NH_4)_2Ce(NO_3)_6]$ solution.

It is group reagent for alcohols.

3.5. Test for phenol or enol

Neutral $FeCl_3$ test :

It forms violet purple complex with phenol or enol (OH groups attached with sp^2 carbon).



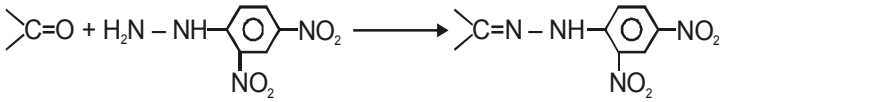
(Coloured complex)

*** It does not give positive test with alcohols.**

3.6. Test for carbonyl compounds

2, 4-DNP (2,4-Dinitrophenyl hydrazine) Test :

Carbonyl compounds (all aldehydes and ketones) give yellow–orange precipitate with 2,4–DNP. It is also known as **Brady's reagent**.

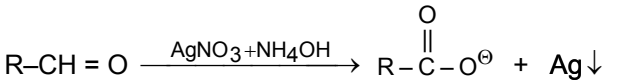


2, 4-DNP (yellow–orange precipitate of Hydrazone)

3.7. Test for aldehydes

(a) Tollen's reagent [$AgNO_3 + NH_4OH$ or $\{Ag(NH_3)_2\}^+ OH^\ominus$] :

Tollen's reagent gives silver mirror or Black precipitate with aldehydes.

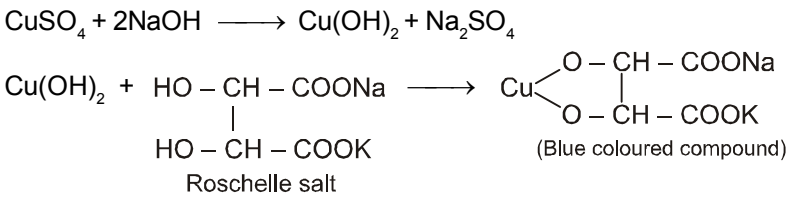


silver mirror

Note : HCOOH also gives this test.

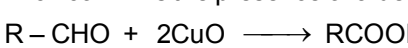
(b) Fehling's solution

It is an alkaline solution of cupric ion complexed with sodium potassium tartrate.
There are two solutions in Fehling solution
Solution (A) : $CuSO_4$ solution
Solution (B) : Alkaline solution of sodium potassiumtartrate.
When these two solutions are mixed we get deep blue coloured solution.

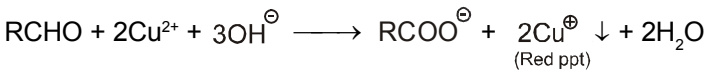


Roschelle salt (Blue coloured compound)

Equal volume of both the solutions are heated with aldehyde to give red brown precipitate of cuprous oxide (Cu_2O) which confirms the presence of aldehyde.



Blue



(Red ppt)

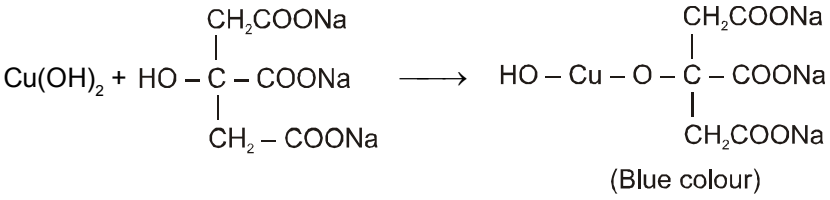
(c) Benedict solution

It also consists of two solutions.

Solution (A) : $CuSO_4$ solution

Solution (B) : Alkaline solution of sodium citrate.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$



(Blue colour)

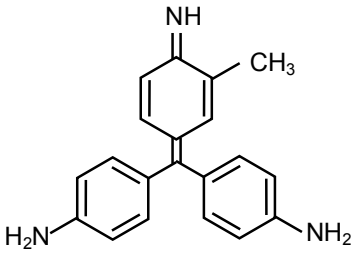
Aldehyde gives positive test with Benedict solution.

$$RCH = O + \underset{\text{(blue)}}{2Cu^{2+}} + 3OH^{\ominus} \longrightarrow RCOO^{\ominus} + \underset{\text{(Red ppt.)}}{2Cu^{\oplus}} + 2H_2O$$

(d) Schiff's reagent

It is dilute solution of rosaniline hydrochloride whose pink colour has been discharged by passing SO_2. Aldehyde restores pink colour when treated with Schiff's reagent (Magenta solution in H_2SO_3).

*** Aromatic aldehydes (**Benzaldehyde**) do not give** Fehling and Benedict **tests.**

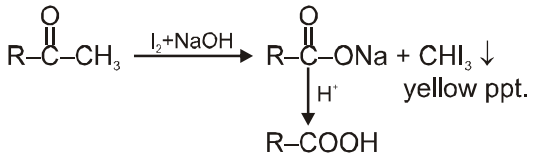


Schiff reagent

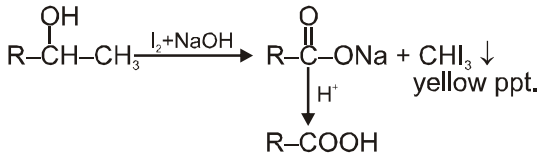
3.8. Iodoform Test

Reagents : I_2 + NaOH or NaOI (Where R = H, alkyl, aryl group)

Acetaldehyde, all methyl ketones & ethyl alcohol give Iodoform test.



(Acid of 1 carbon less)

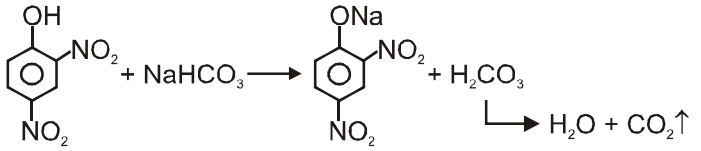


3.9. Test for acids/esters/amides

(a) Sodium bicarbonate test ($NaHCO_3$)

All the acids which are stronger than H_2CO_3 give CO_2 gas with $NaHCO_3$.

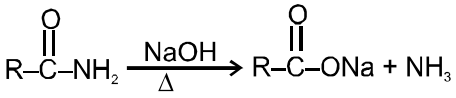
$$HCl + NaHCO_3 \longrightarrow NaCl + H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$$
$$RCOOH + NaHCO_3 \longrightarrow RCO_2Na + H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$$
$$RSO_3H + NaHCO_3 \longrightarrow RSO_3Na + H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$$



Note : If electron withdrawing group (NO_2) is present at ortho or para position of phenol then it gives positive test with sodium bicarbonate.

(b) Litmus test : Acid converts blue litmus into red litmus while base converts red litmus into blue.

(c) Acid amide gives smell of ammonia when heated with alkali.



(d) Esters are sweet (fruity) smelling liquids.
Esters when react with NaOH & phenolphthalein, pink colour disappears on heating.

RCOOR' + NaOH + Phenolphthalein (Pink) $\xrightarrow{\Delta}$ R COOH + R' OH (Colourless solution)

3.10. Test for amines

(i) $NaNO_2$ + aqueous HCl test : it is used to distinguish between 1°, 2° and 3° amines and also distinguish between aliphatic and aromatic primary amines.

1° Aliphatic amine : $R–CH_2–NH_2 \xrightarrow{NaNO_2 + aq.\ HCl} R–CH_2–OH + N_2\uparrow$

1° Aromatic amine : $Ph–NH_2 \xrightarrow[(0–5°C)]{NaNO_2 + aq.\ HCl} Ph–\overset{+}{N_2}\overset{\ominus}{Cl}$ (diazonium salt)

2° Amine : $R – NH – R \xrightarrow{NaNO_2 + aq.\ HCl} R–\underset{\displaystyle N=O}{\overset{|}{N}}–R$ (N -Nitroso amine) yellow oily liquid

3° Amine : $R_3N \xrightarrow{NaNO_2 + aq.\ HCl}$ unstable nitrite

(ii) Carbyl amine test ($CHCl_3$ + KOH)

1° Amine (Aliphatic and Aromatic)

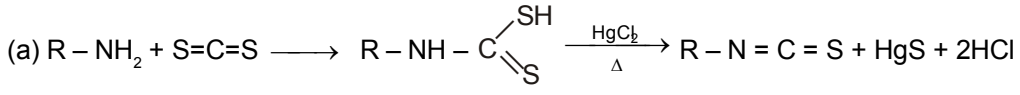
$$R–CH_2–NH_2 \xrightarrow{CHCl_3 + KOH} R–CH_2–N \equiv C + 3KCl + 3H_2O$$
(unpleasent smell of isocyanide)

$$Ph – NH_2 \xrightarrow{CHCl_3 + KOH} Ph – N \equiv C$$

*** 2° Amines and 3° Amines do not give this test.**

(iii) Hofmann mustard oil test

It is a test for 1° amine and aniline. Primary amine reacts with carbon disulphide to form dithioalkyl carbamic acids which decompose on heating with mercuric chloride ($HgCl_2$) to give alkyl isothiocyanate having smell like mustard oil.



Dithioethylcarbamic acid Alkylisothiocyanate

(b) $CH_3CH_2NH_2 + S=C=S \xrightarrow{\Delta} CH_3CH_2NH-\underset{\underset{S}{\|}}{C}-SH \xrightarrow[\Delta]{HgCl_2} CH_3CH_2-N=C=S + HgS + 2HCl$

(1° amine) Ethyl isothiocyanate

Similarly aniline gives phenlyisothiocyanate.

(c) $C_6H_5NH_2 \xrightarrow[(ii)\ HgCl_2/]{(i)\ S=C=S} C_6H_5N=C=S$

Phenylisothiocyanate

*** 2° Amines and 3° Amines do not give this test.**

(iv) Hinsberg reagent ($C_6H_5SO_2Cl$)

This is used to distinguish between 1°,2° & 3° amines.

1° Amine : $R-NH_2 + PhSO_2Cl \xrightarrow{Pyridine} R-NH-SO_2-Ph \xrightarrow{Base}$ Compound is **soluble** in base.

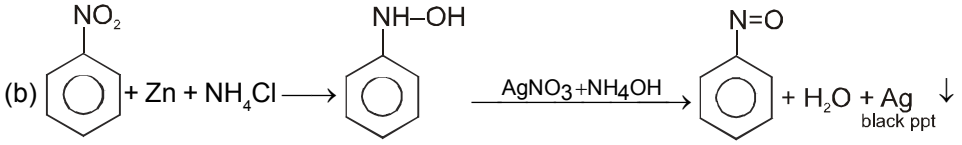
2° Amine : $R_2NH + PhSO_2Cl \xrightarrow{Pyridine} R_2N-SO_2-Ph \xrightarrow{Base}$ Compound is **insoluble** in base.

3° Amine : $R_3N + PhSO_2Cl \xrightarrow{Pyridine}$ No reaction.

3.11. Test of nitro group (Mulliken- Barker Test)

Nitroalkane & nitrobenzene gives black ppt on reduction with Zn and ammonium chloride followed by treating with Tollen's reagent. **This is also called Mulliken's test.**

(a) $R-NO_2 \xrightarrow[\Delta]{Zn-NH_4Cl} R-NHOH \xrightarrow[T.R.]{AgNO_3 + NH_4OH} Ag(\text{black ppt})\downarrow$

(b) 

4. Elements detection

4.1. Detection of carbon and hydrogen

Carbon and hydrogen are detected by heating the compound with copper(II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

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

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

$CO_2 + Ca(OH)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O$

$5H_2O + CuSO_4 \xrightarrow{\Delta} CuSO_4.5H_2O$

White Blue

4.2. Detection of other elements

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "Lassaigne's test". The elements present in the compound are converted from their covalent form to their ionic form by fusing the organic compound with sodium metal.

Following reactions take place: C, N, S and X come from organic compound.
Cyanide, sulphide and halide of sodium formed by sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract or Lassaigne solution.

$Na + C + N \xrightarrow{\Delta} NaCN$; $2Na + S \xrightarrow{\Delta} Na_2S$

$Na + X \xrightarrow{\Delta} NaX$; $Na + C + N + S \xrightarrow{\Delta} NaSCN$

(i) Test for nitrogen

The sodium fusion extract is boiled with iron(II) sulphate and then acidified with dilute sulphuric acid. The formation of Prussian blue or green colour confirms the presence of nitrogen. Alternatively $FeCl_3$ and dil. HCl may be added.

$$6NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6]$$

$$Na_4[Fe(CN)_6] + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3 . xH_2O$$

Ferric ferrocyanide (Prussian blue)

(ii) Test for sulphur

(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow PbS \text{ (Black)}$$

(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour indicates the presence of sulphur.

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5\,NO]} \longrightarrow \underset{\text{Sodium thionitroprusside (Violet/Purple)}}{Na_4[Fe(CN)_5NOS]}$$

(c) In case, nitrogen and sulphur both are present in an organic compound, then sodium thiocyanate is formed. It gives blood red colour with neutral $FeCl_3$.

$Na + C + N + S \longrightarrow NaSCN$; Neutral $FeCl_3 + NaSCN \longrightarrow Fe(SCN)_3$(Blood red)

(iii) Test for halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

Note The sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

$$NaX + AgNO_3 \longrightarrow AgX \downarrow$$

(iv) Test for phosphorus

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$\underset{\substack{\text{Ammonium}\\\text{molybdate}}}{H_3PO_4 + 12(NH_4)_2MoO_4} + 21\,HNO_3 \longrightarrow \underset{\substack{\text{Ammonium}\\\text{Phosphomolybdate}}}{(NH_4)_3PO_4 . 12\,MoO_3} + 21\,NH_4NO_3 + 12H_2O$$

Exercise # 1

PART - I : NUMERICAL TYPE QUESTIONS

Section (A) : Structural isomerism

A-1. How many number of all structurally isomeric dienes with molecular formula C_5H_8 are possible ?

A-2. How many cyclic structurally isomeric amines of molecular formula C_3H_7N are possible?

A-3. How many structurally isomeric ethers with molecular formula $C_5H_{12}O$ are possible?

A-4. How many structurally isomeric esters with molecular formula $C_5H_{10}O_2$ are possible?

A-5. How many structurally isomeric ketones with molecular formula $C_6H_{12}O$ are possible?

A-6. How many number of all aldehydes (structurally isomeric) with molecular formula $C_5H_{10}O$ are possible?

A-7. How many benzenoid structural isomers are possible for C_7H_8O ?

A-8. Total number of benzenoid isomers of molecular formula C_9H_{12} would be-

A-9. How many structural alkenes of formula $C_2FClBrI$ are possible ?

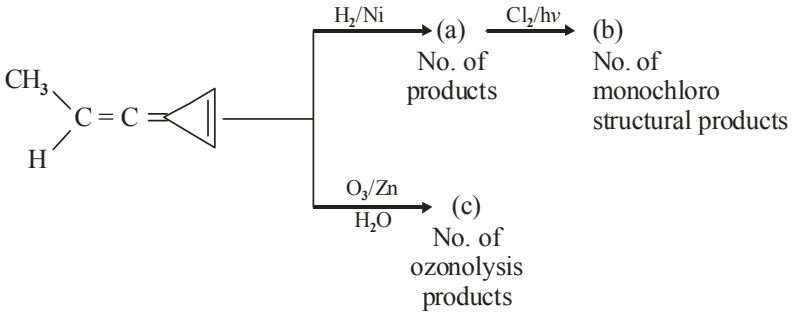
A-10. How many structural isomers can be obtained by the replacement of one hydrogen atom of propene with chlorine ?

Section (B) : Structural Identification

B-1. How many alkenes, alkynes and alkadienes can be hydrogenate to form Isopentane (Including all structural isomers)?

B-2. Find the number of structural isomers of fully saturated cycloalkane of molecular formula C_6H_{12} which give two monochloro structural products.

B-3.

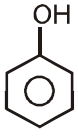


Calculate sum of number of products formed in the reaction a, b and c.

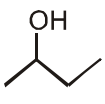
Section (C) : POC (Lab tests and Element detection)

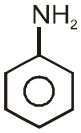
C-1. How many of the following compounds decolorise Br_2 water solution ?

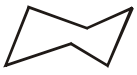
(I) 

(II) 

(III) Me – C ≡ C – Me

(IV) 

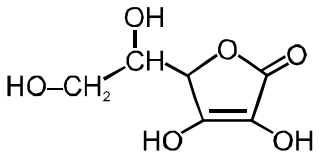
(V) 

(VII) 

(VIII) Me – CH = CH – Et

(IX) 

C-2. Structure of Ascorbic acid is represented as follows.

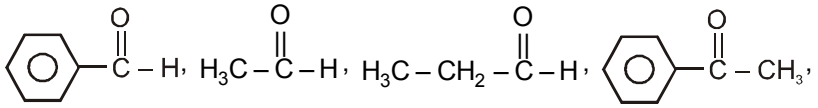


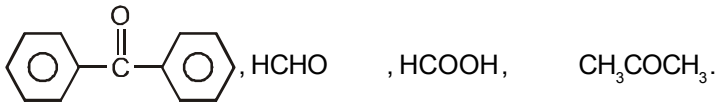
(Ascorbic acid)

How many of the following reagents can give positive test with ascorbic acid?

$Cu_2Cl_2 + NH_4OH$	2,4-DNP	Na Metal	$HCl + ZnCl_2$	$FeCl_3$
(I)	(II)	(III)	(IV)	(V)
$NaOH +$ Phenolthalein	dil.$KMnO_4$	Br_2/H_2O	$AgNO_3 + NH_4OH$	I_2 + NaOH
(VI)	(VII)	(VIII)	(XI)	(X)

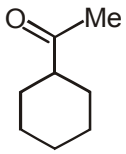
C-3. Among the following the number of compounds which react with Fehling's solution is :



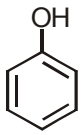


, HCHO , HCOOH, CH_3COCH_3.

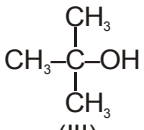
C-4. Observe the the following compounds.



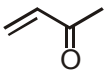
(I)



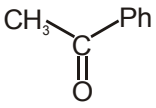
(II)



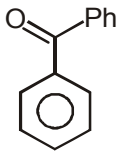
(III)



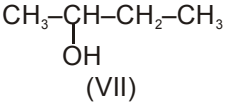
(IV)



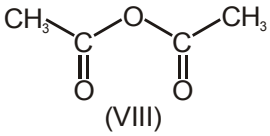
(V)



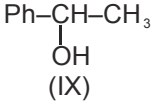
(VI)



(VII)



(VIII)



(IX)

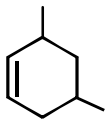
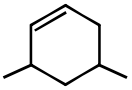
Number of compounds which can give positive haloform test = (x)
Number of compounds which can give positive Lucas reagent test = (y)
Report your answer (x + y)

-5. In the Lassaigne's test, one of the organic compound X gives blood red colour with $FeCl_3$. Compound X, when fused with sodium metal forms compound Y. Molecular mass of compound Y is

-6. How many oxygen atoms are present in 1 molecule of ammonium phosphomolybdate ?

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Structural isomerism

A-1. Relation between compounds  &  is:

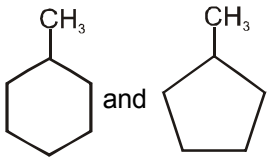
(A) Position isomers (B) Chain isomers (C) Identical (D) Functional isomers

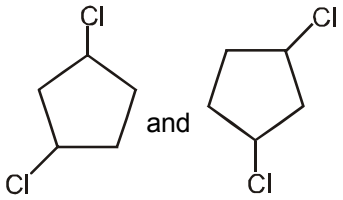
A-2. Which type of isomerism is observed between I and II ?

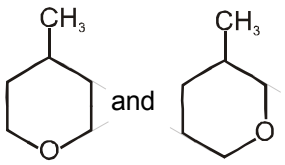
(I) $CH_3 - CH_2 - \underset{\underset{O}{\|}}{C} - OCH_3$, (II) $CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - O - CH_3$

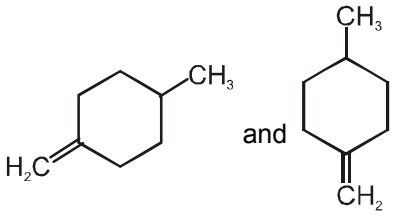
(A) Functional isomerism (B) Metamerism
(C) Position isomerism (D) Stereoisomerism

A-3. Which of the following is a pair of structural isomers?

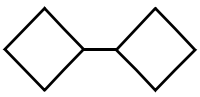
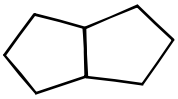
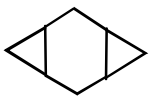
(A)  and

(C)  and

(C)  and

(D)  and

A-4. Which one of the following compound is not isomer of others?

(A)  (B)  (C)  (D) 

A-5. What is the relation between 3-Ethylpentane and 3-Methylhexane ?

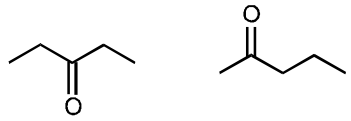
(A) Chain isomers (B) Position isomers
(C) Functional isomers (D) No relation

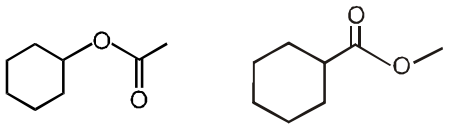
A-6. Which type of isomerism is observed between I and II?

(I) $CH_3 - CH_2 - NH - CHO$ (II) $CH_3 - \underset{\underset{NH_2}{|}}{CH} - CHO$

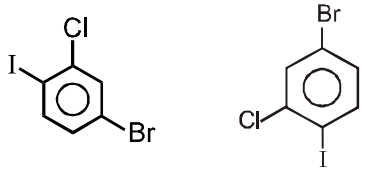
(A) Chain isomers (B) Position isomers
(C) Functional isomers (D) Metamers

A-7. Which of the following pair is identical ?

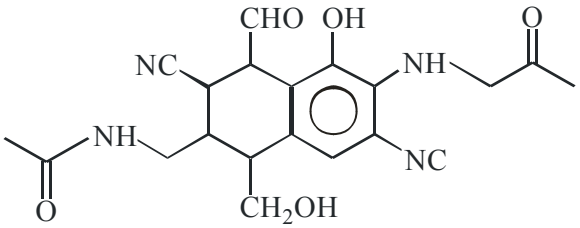
(A) 

(B) 

(C) 

(D) 

A-8. Degree of unsaturation (DU) & total number of different functional groups in given compound are?



(A) 8, 7 (B) 9, 8 (C) 12, 8 (D) 12, 7

A-9. How many positional isomers are possible for dimethylcyclohexane?
(A) 3 (B) 4 (C) 5 (D) 6

A-10. How many aromatic isomers are possible for trichlorobenzene ($C_6H_3Cl_3$) ?
(A) 2 (B) 3 (C) 4 (D) 5

A-11. The number of ether isomers represented by formula $C_4H_{10}O$ is (only structural)?
(A) 4 (B) 3 (C) 2 (D) 1

A-12. Total number of 2° amine isomers of $C_4H_{11}N$ would be (only structural)?
(A) 4 (B) 3 (C) 5 (D) 2

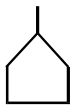
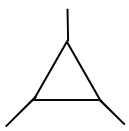
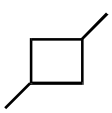
A-13. Find the total number of structurally isomeric 1° amides with molecular formula $C_5H_{11}NO$?
(A) 1 (B) 3 (C) 2 (D) 4

A-14. How many structural isomers of all the tertiary alcohols with molecular formula $C_6H_{14}O$ are ?
(A) 2 (B) 3 (C) 4 (D) 5

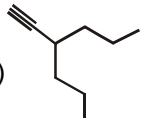
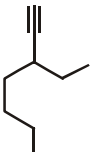
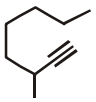
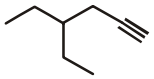
A-15. Total number of structural isomers for C_5H_{10} would be?
(A) 8 (B) 6 (C) 9 (D) 10

Section (B) : Structural Identification

B-1. Compound A (C_6H_{12}) does not absorb H_2 in presence of Ni. It forms two monochloro structural isomers on photochemical chlorination. Its structure can be :

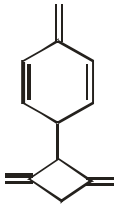
(A)  (B)  (C)  (D) 

B-2. Which alkyne will give 3-Ethylheptane on catalytic hydrogenation?

(A)  (B)  (C)  (D) 

B-3. Which of the following hydrocarbons give same product on hydrogenation?
(A) 2-Methylhex-1-ene & 3-Methylhex-3-ene
(B) 3-Ethylhex-1-en-4-yne & 2-Methylhept-2-en-4-yne
(C) 3-Ethylcycloprop-1-ene & 1,2-Dimethylcycloprop-1-ene
(D) 2-Methylbut-2-ene & 3-Methylbut-1-ene

B-4. How many number of moles of hydrogen will be required for complete hydrogenation of one mole of the following compound ?



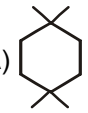
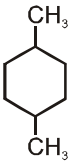
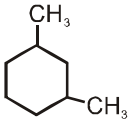
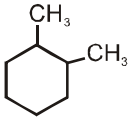
(A) 6 (B) 7 (C) 5 (D) 3

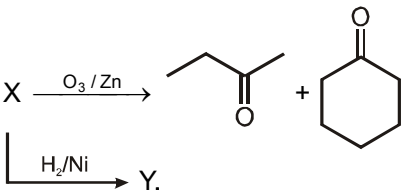
B-5. Only two structural isomeric monochloro derivatives are possible for :-
(A) n-Pentane (B) 2,4-Dimethyl pentane
(C) Toluene (D) 2,3-Dimethyl butane

B-6. The number of possible monochloro derivatives of 2,2,3,3-Tetramethylbutane is -
(A) 2 (B) 3 (C) 4 (D) 1

B-7. Which of the following alkene gives four monochloro (structural isomer) products after hydrogenation ?
(A) Pent-2-ene (B) 2-Methylbut-2-ene (C) 3-Methylhex-2-ene (D) 2, 3-Dimethylbut-2-ene

B-8. Which of the following compounds will give four monochloro (structural) product on monochlorination?

(A)  (B)  (C)  (D) 

B-9. 

The IUPAC name of compound Y is :
(A) 2-Cyclohexylbutane (B) 1-Methylpropylcyclohexane
(C) Butylcyclohexane (D)1-Cyclohexylbutane

B-10. An alkene give two moles of HCHO, one mole of CO_2 and one mole of $CH_3-\underset{\underset{O}{\|}}{C}-CHO$ on ozonolysis.

What is its structure?

(A) $CH_2=CH-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$ (B) $CH_2=C=CH-\underset{\underset{CH_2}{\|}}{C}-CH_3$

(C) $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH=CH_2$ (D) $CH_2=C=CH-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$

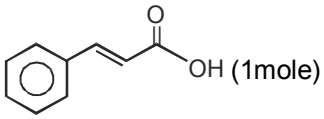
B-11. An unknown compound on ozonolysis gives acid $C_3H_6O_2$ and a ketone C_4H_8O. From this information, identifiy structure of unknown compound.

(A) $(CH_3)_2C=CHCH_2-CH_2CH_3$ (B) $CH_3CH_2-\underset{\underset{CH_3}{|}}{C}=CHCH_2CH_3$

(C) $(CH_3)_2CHCH=CHCH_2CH_3$ (D) $CH_3CH_2CH_2CH=CHCH_2CH_3$

Section (C) : POC (Lab tests and Element detection)

C-1. When one mole of the given compound reacts with sodium metal then how many moles of H_2 gas will be released?



(A) 1 mole (B) 1.5 mole (C) 2 mole (D) 0.5 mole

C-2. C_6H_{10} (X) $\xrightarrow{Br_2/H_2O}$ + ve

$\xrightarrow{O_3/H_2O_2}$ CH_3CH_2COOH

Identify X :

(A) $CH_3-CH_2-C\equiv C-CH_2-CH_3$ (B) $CH_3-C\equiv C-CH_2-CH_2-CH_3$

(C)  (D) 

C-3. Compound 'A' gives red precipitate with Cu_2Cl_2 / NH_4OH solution and decolourises bromine water. The compound 'A' can be :

(A) $CH_2=CH-\underset{\underset{O}{\|}}{C}-CH_3$ (B) $CH_2=CH-\underset{\underset{O}{\|}}{C}-H$ (C) $CH_3-C\equiv CH$ (D) PhCHO

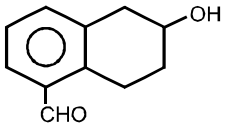
C-4. An organic compound does not react appreciably with Lucas reagent but gives white precipitate with Tollen's reagent. What is the possible structure of compound ?

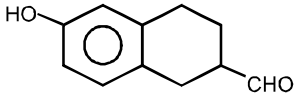
(A) $CH_3-\underset{\underset{OH}{|}}{CH}-C\equiv CH$ (B) $CH_3-C\equiv C-CH_2-CH_2-OH$

(C) $HC\equiv C-CH_2-CH_2-OH$ (D) $CH_2=C=CH-CH_2-OH$

C-5. The group reagent for the test of alcohols is :
(A) Cerric ammonium nitrate (B) Schiff's reagent
(C) Molisch's reagent (D) Bromine water

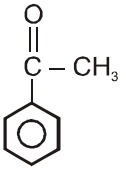
C-6. The following two compounds I and II can be distinguished by using reagent.

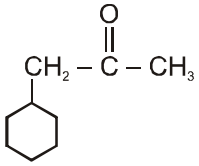
(I) 

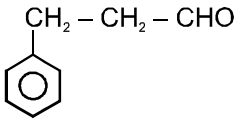
(II) 

(a) aq. $NaHCO_3$ (b) Neutral $FeCl_3$ (c) Fehling solution (d) Na metal
(A) a or c (B) b or c (C) c or d (D) b or d

C-7. Which of the following compounds will not react with I_2/OH^-?

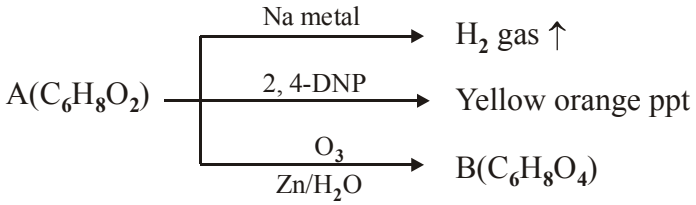
(A) 

(B) 

(C) 

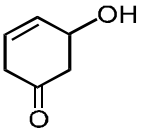
(D) $CH_3 - CHO$

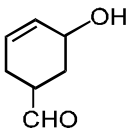
C-8. The compound A gives following reactions.



Its structure can be

(A) $CH_2 = CH - (CH_2)_2 - \underset{\underset{O}{\|}}{C} - CH_2OH$ (B) $OHC - (CH_2)_2 - CH = CH - COOH$

(C) 

(D) 

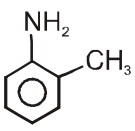
C-9. An organic compound X ($C_4H_8O_2$) gives positive test with NaOH and phenolphthalein. Structure of X will be :

(A) $CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - OH$ (B) $CH_3 - \underset{\underset{O}{\|}}{C} - \underset{\underset{O}{\|}}{C} - CH_3$

(C) $CH_3 - \underset{\underset{O}{\|}}{C} - O - C_2H_5$ (D) $CH_3 - \underset{\underset{O}{\|}}{C} - OCH_3$

C-10. Which of the following compound will give smell of NH_3 with conc. NaOH ?

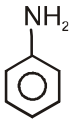
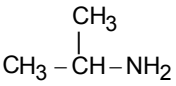
(A) $CH_3 - CH_2 - \underset{\underset{O}{\|}}{C} - NH_2$ (B) $CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - NH_2$

(C) 

(D) $CH_3 - CH_2 - \underset{\underset{O}{\|}}{C} - OH$

C-11. Which of the following will not give positive test with $CHCl_3$ / KOH ?

(A) $CH_3–CH_2–NH–CH_3$ (B) $CH_3–CH_2–CH_2–NH_2$

(C)  (D) 

C-12. A positive carbylamine test is given by :

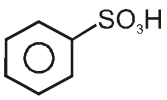
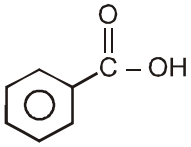
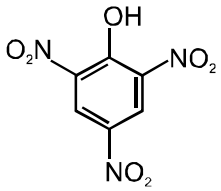
(A) N,N–dimethylaniline (B) 2, 4-dimethylaniline

(C) N-methyl-o-methylaniline (D) N-methylaniline

C-13. A research scholar get a mixture of three product during an experiment with ammonia. In product I only one H of ammonia is replaced by ethyl group and in II two H atoms of ammonia are replaced by ethyl groups and in III all the H-atoms are replaced by ethyl groups . Which test he should use to distinguish or separate the products ?

(A) Carbyl amine test (B) Iodoform test (C) Fehling solution test (D) Hinsberg test

C-14._ Which of the following would produce effervescence with sodium bicarbonate?

(A)  (B)  (C)  (D) All of these

C-15. A compound is heated with zinc dust and ammonium chloride followed by addition of the Tollen's reagent. Formation of silver mirror indicates the presence of following group

(A) –CHO (B)  (C) $–NO_2$ (D) $–NH_2$

C-16. In the Lassaigne's test, one of the organic compound gives red colour with $FeCl_3$. Compound can be :

(A) Na_2S (B) NH_2CSNH_2 (C) C_6H_5Cl (D) NaCN

C-17. Lassaigne's test is used in qualitative analysis to detect

(A) Nitrogen (B) Sulphur (C) Chlorine (D) All of these

C-18. The compound that does not give a blue colour in Lassaigne's test is

(A) $C_6H_5–NH_2$ (B) CH_3CONH_2 (C) $NH_2–NH_2$ (D) $C_6H_5–NO_2$

C-19. Nitrogen containing organic compound when fused with sodium metal then it forms:

(A) $NaNO_2$ (B) NaCN (C) $NaNH_2$ (D) NaN_3

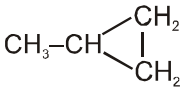
C-20. The sodium extract of an organic compound on acidification with acetic acid and addition of lead acetate solution gives a black precipitate. The organic compound contains

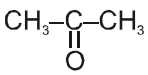
(A) Nitrogen (B) Halogen (C) Sulphur (D) Phosphorus

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

Section (A) : Structural isomerism

A-1. Which of the following pairs of structures represent the constitutional isomers ?

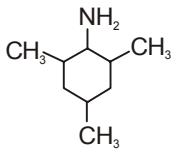
(A) $CH_2=CHCH_2CH_3$ and 

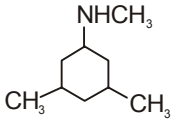
(B) $CH_3OCH_2CH_3$ and 

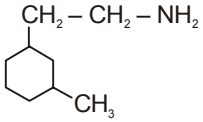
(C) $(CH_3)_3CCH_2CH_2CH_2OH$ and $(CH_3)_2CHCH_2OCH_2CH_2CH_3$

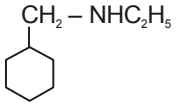
(D) $CH_2ClCHClCH_2CHO$ and $CHCl_2CH=CH–CH_2–OH$

A-2. Which of the following is/are the correct relationship ?


I


II

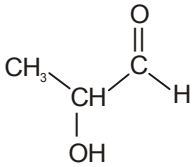

III

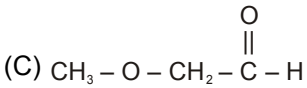

IV

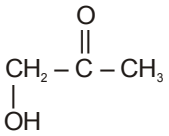
(A) I & II are functional isomers.
(B) II & IV are metamers.
(C) I & IV are position isomers.
(D) I & III are chain isomers.

A-3. Which of the following are functional isomers of methyl ethanoate ?

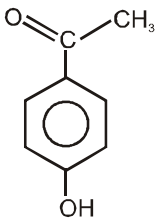
(A) $CH_3 – CH_2 – COOH$

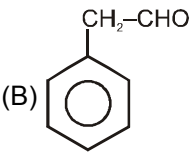
(B) 

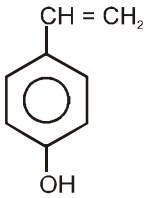
(C) 

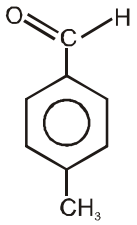
(D) 

A-4. Which of the following can be the isomer(s) of C_8H_8O ?

(A) 

(B) 

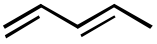
(C) 

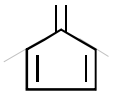
(D) 

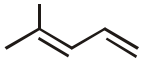
Section (B) : Structural Identification

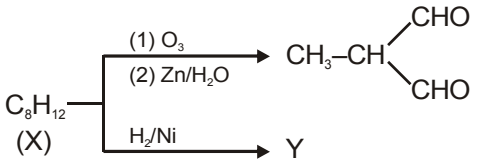
B-1. Which of the following compound on reductive ozonolysis give glyoxal as one of the product?

(A) 

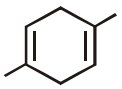
(B) 

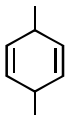
(C) 

(D) 

B-2. 

True statements is/are

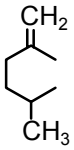
(A) Structure of X is 

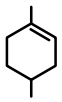
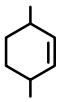
(B) Structure of X is 

(C) Y on monochlorination produce 3 monochloro structural products.

(D) Oxidative ozonolysis product of X is $CH_3–CH$(COOH)(COOH)

B-3. Which of the following compounds give 1,4-Dimethyl cyclohexane when undergo catalytic hydrogenation?

(A) 

(B) 
(C) 
(D) 

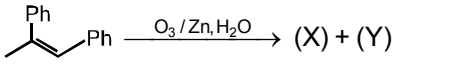
Section (C) : POC (Lab tests and Element detection)

C-1. Which of the following compounds on reaction with Na metal, liberate hydrogen gas ?

(A) $CH_3–OH$ (B) $CH_3–C\equiv CH$ (C) Ph–OH (D) 

C-2. Which of the following will perform iodoform reaction with I_2/OH^-?

(A) $CH_3COCH_2CH_3$ (B) CH_3CONH_2 (C) $C_6H_5COCH_3$ (D) CH_3CHO

C-3. 

Compound (X) and (Y) can be distinguish by

(A) Tollen's reagent (B) Fehling solution (C) Haloform test (D) 2,4-DNP Test

C-4. Formic acid and acetaldehyde can be distinguish by-

(A) I_2 + NaOH (B) Tollen's reagent (C) Fehling solution (D) 2,4-DNP test

C-5. An organic compound having molecular formula C_3H_4, reacts with sodium metal to give a colourless and odourless gas. Select the correct statements about this organic compound.

(A) It gives bromine water test

(B) It reacts with Bayer's reagent

(C) It reacts with Tollen's reagent

(D) It reacts with ammonical cuprous chloride.

C-6. Compound P Liberates H_2 gas with Na metal. P gives white precipitate with Tollen's reagent, there is no response towards Lucas reagent and compound Q gives instant turbidity with anhydrous $ZnCl_2$ / HCl, and with sodium metal 1 mole of compound Q liberates 11.2 litre H_2 gas at STP. Find the structural formula of compound P and Q.

(A) P is $CH_2=CH-\overset{\overset{O}{\|}}{C}-H$

(B) Q is $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-O-CH_3$

(C) P is $CH_3-O-C\equiv C-H$

(D) Q is $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH\ OH}{|\quad|}}{C}}-CH-CH_3$

C-7. Phenol can be distinguished from ethanol by

(A) Cerric ammonium nitrate (B) Neutral $FeCl_3$

(C) Br_2, H_2O (D) Blue litmus

Exercise # 2

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

*** Marked Questions may have more than one correct option.**

1. Four isomeric para-disubstituted aromatic compounds A to D with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations, give structures of the compounds. **[JEE 2002, 5/60]**

(i) Both A and B form a silver mirror with Tollen's reagent; also B gives a positive test with $FeCl_3$ solution.

(ii) C gives positive iodoform test.

(iii) D is readily extracted in aqueous $NaHCO_3$ solution.

2. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne ? **[IIT-JEE-2002(S), 3/90]**

(A) bromine, CCl_4 (B) H_2, Lindlar catalyst

(C) dilute H_2SO_4, $HgSO_4$ (D) Ammonical Cu_2Cl_2 solution

3. In conversion of 2-butanone to propanoic acid which reagent is used ? **[JEE 2005, 3/84]**

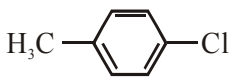
(A) NaOH, NaI / $H^{\oplus}$ (B) Fehling solution (C) NaOH, I_2 / $H^{\oplus}$ (D) Tollen's reagent

4. The total number of cyclic isomers possible for a hydrocarbon molecular formula C_4H_6 is / are : **[IIT-JEE 2010]**

5. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are) : **[IIT-JEE 2012]**

(A) sp and sp^3 (B) sp and sp^2 (C) only sp^3 (D) sp^2 and sp^3

6. The IUPAC name(s) of the following compound is(are) : **[JEE. Adv 2017]**



(A) 4-methylchlorobenzene (B) 4-chlorotoluene

(C) 1-chloro-4-methylbenzene (D) 1-methyl-4-chlorobenzene

PART - II : JEE(MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. The general formula $C_nH_{2n}O_2$ could be for open chain **[AIEEE- 2003]**

(1) diketones (2) carboxylic acids (3) diols (4) dialdehydes.

2. Which of the following reagents may be used to distinguish between phenol and benzoic acid ?

[AIEEE 2011, 4/120]

(1) Aqueous NaOH (2) Tollen's reagent (3) Molisch reagent (4) Neutral $FeCl_3$

3.* Silver mirror test is given by which one of the following compounds? **[AIEEE 2011, 4/120]**

(1) Acetaldehyde (2) Acetone (3) Formaldehyde (4) Benzophenone

4. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds : **[AIEEE 2011, 4/120]**

(1) 1-Pentene (2) 2-Pentene

(3) 2-Methyl-2-pentene (4) 2-Methyl-1-pentene

5. Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide ? **[AIEEE 2012, 4/120]**

(1) Tertiary butyl chloride (2) Neopentane

(3) Isohexane (4) Neohexane

6. Iodoform can be prepared from all except : **[AIEEE 2012, 4/120]**

(1) Ethyl methyl ketone (2) Isopropyl alcohol

(3) 3–Methyl–2–butanone (4) Isobutyl alcohol

7. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is : **[JEE MAINS -2014, 4/120]**

(1) an alkanol (2) an alkanediol (3) an alkyl cyanide (4) an alkyl isocyanide

8. In the Victor-Meyer's test, the colour given by 1°, 2° and 3° alcohols are respectively :

[JEE (Main) 2014 Online (20-04-14), 4/120]

(1) Red, colourless, blue (2) Red, blue, colourless

(3) Colourless, red, blue (4) Red, blue, violet

9. Match the organic compounds in column-I with lassaigne's test results in column-II appropriately :

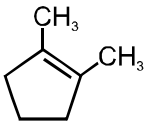
[JEE(Main) 2015 Online (11-04-15), 4/120]

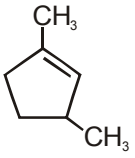
	Column-I		**Column-II**
(A)	Aniline	(i)	Red colour with $FeCl_3$
(B)	Benzene sulfonic acid	(ii)	Violet colour with sodium nitroprusside
(C)	Thiourea	(iii)	Blue colour with hot and acidic solution of $FeSO_4$

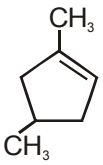
(1) (A)-(ii); (B)-(iii); (C)-(i) (2) (A)-(iii); (B)-(i); (C)-(ii)

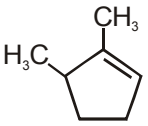
(3) (A)-(iii); (B)-(ii); (C)-(i) (4) (A)-(ii); (B)-(i); (C)-(iii)

10. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis ? **[JEE Main 2015, 4/120]**

(1) 

(2) 

(3) 

(4) 

11. The test to distinguish primary, secondary and tertiary amine is :

[JEE (Main) 2016 Online (09-04-16), 4/120]

(1) Mustard oil test

(2) $C_6H_5SO_2Cl$

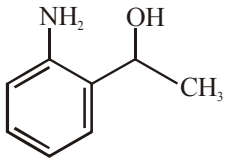
(3) Sandmeyer's reaction

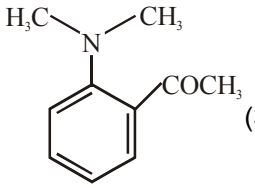
(4) Carbylamine reaction

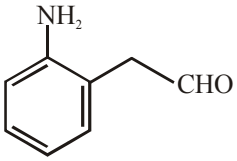
12. The tests performed on compound X and their inferences are: **[JEE Main 2019, Online]**

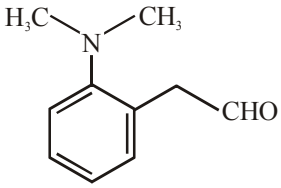
Test	Inference
(a) 2,4 - DNP test	Coloured precipitate
(b) Iodoform test	Yellow precipitate
(c) Azo-dye test	No dye formation

Compound 'X' is:

(1) 

(2) 

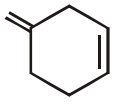
(3) 

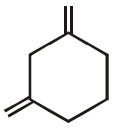
(4) 

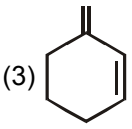
13. An unsaturated hydrocarbon X absorbs two hydrogen molecules on catalytic hydrogenation, and also gives following reaction : **[JEE Main 2020, Online]**

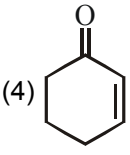
$$X \xrightarrow[Zn/H_2O]{O_3} A \xrightarrow{[Ag(NH_3)_2]^+} B(3\text{-oxo-hexanedicarboxylic acid})$$

X will be :-

(1) 

(2) 

(3) 

(4) 

Answers

EXERCISE # 1

PART - I

A-1.	6	**A-2.**	4	**A-3.**	6	**A-4.**	9	**A-5.**	6
A-6.	4	**A-7.**	5	**A-8.**	8	**A-9.**	3	**A-10.**	3
B-1.	6	**B-2.**	1	**B-3.**	9	**C-1.**	5	**C-2.**	6
C-3.	4	**C-4.**	8	**C-5.**	81	**C-6.**	40		

PART - II

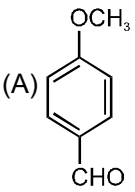
A-1.	(C)	**A-2.**	(A)	**A-3.**	(C)	**A-4.**	(D)	**A-5.**	(A)
A-6.	(C)	**A-7.**	(D)	**A-8.**	(C)	**A-9.**	(B)	**A-10.**	(B)
A-11.	(B)	**A-12.**	(B)	**A-13.**	(D)	**A-14.**	(B)	**A-15.**	(D)
B-1.	(C)	**B-2.**	(B)	**B-3.**	(D)	**B-4.**	(C)	**B-5.**	(D)
B-6.	(D)	**B-7.**	(B)	**B-8.**	(D)	**B-9.**	(B)	**B-10.**	(B)
B-11.	(B)	**C-1.**	(D)	**C-2.**	(A)	**C-3.**	(C)	**C-4.**	(C)
C-5.	(A)	**C-6.**	(B)	**C-7.**	(C)	**C-8.**	(C)	**C-9.**	(C)
C-10.	(A)	**C-11.**	(A)	**C-12.**	(B)	**C-13.**	(D)	**C-14.**	(D)
C-15.	(C)	**C-16.**	(B)	**C-17.**	(D)	**C-18.**	(C)	**C-19.**	(B)
C-20.	(C)								

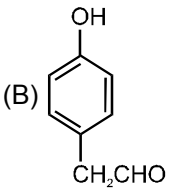
PART - III

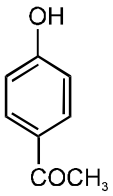
A-1.	(ACD)	**A-2.**	(ABD)	**A-3.**	(ABCD)	**A-4.**	(BCD)	**B-1.**	(BCD)
B-2.	(BCD)	**B-3.**	(ABC)	**C-1.**	(ABC)	**C-2.**	(ACD)	**C-3.**	(AC)
C-4.	(AD)	**C-5.**	(ABCD)	**C-6.**	(BC)	**C-7.**	(ABCD)		

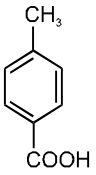
EXERCISE # 2

PART - I

1. (A) 

(B) 

(C) 

(D) 

2.	(D)	**3.**	(C)	**4.**	5	**5.**	(B)	**6.**	(BC)

PART - II

1.	(2)	**2.**	(4)	**3.**	(1,3)	**4.**	(3)	**5.**	(2)
6.	(4)	**7.**	(4)	**8.**	(2)	**9.**	(3)	**10.**	(2)
11.	(2)	**12.**	(2)	**13.**	(1)				

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Reliable students.

Self Assessment Test

PART- 1 : PAPER JEE (MAIN) PATTERN

SECTION–I : (Maximum Marks : 80)

- This section contains **TWENTY** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :
  Full Marks : +4If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

1. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane, this alkane could be :
(A) propane (B) pentane (C) isopentane (D) neopentane.

2. The prussian blue colour obtained during the test of nitrogen by Lassaigne's test is due to the formation of :
(A) $Fe_4[Fe(CN)_6]_3$ (B) $Na_3[Fe(CN)_6]$ (C) $Fe(CN)_3$ (D) $Na_4(Fe(CN)_5NOS]$

3. Of the five isomeric hexanes,the isomer which can give two monochlorinated compounds is ?
(A) n–Hexane (B) 2,3-Dimethylbutane (C) 2,2-Dimethylbutane (D) 2-Methylpentane

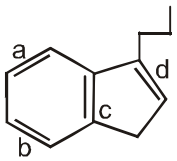
4. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is ?
(A) $CH_3CH_2CH(OH)CH_2CH_3$ (B) $C_6H_5CH_2CH_2OH$
(C) $CH_3-\underset{\displaystyle CH_2-OH}{\underset{|}{CH}}-CH_3$ (D) $PhCHOHCH_3$

5. In the following sequence of reactions, the alkene affords the compound 'B'

$$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B, \text{ compound B is}$$

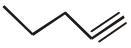
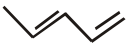
(A) CH_3CH_3CHO (B) CH_3COCH_3 (C) $CH_3CH_2COCH_3$ (D) CH_3CHO

6. If 1 mole H_2 is reacted with 1 mole of the following compound.



Which double bond will be hydrogenated ?
(A) c (B) b (C) a (D) d

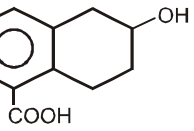
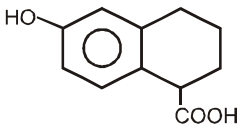
7. Identify the hydrocarbon having molecular formula C_5H_6 which gives white ppt with ammonical $AgNO_3$?

(A)  (B)  (C)  (D) 

8. Which of the following compounds will give a positive iodoform test ?

(A) Methanol (B) 2,2-Dimethylpropanol
(C) Ethanol (D) Methanal

9. The following two compounds I and II can be distinguished by using reagent

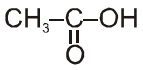
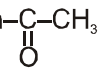
(I)  (II) 

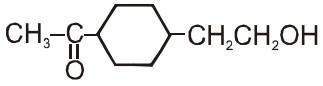
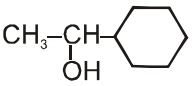
(I) (II)

(a) aq. $NaHCO_3$ (b) Neutral $FeCl_3$
(c) Blue litmus solution (d) Na metal (e) $HCl/ZnCl_2$ anhydrous

(A) a or c (B) b or e (C) d or e (D) c or d

10. Which of the following compound cannot give Iodoform when react with IO^-(hypoiodite)?

(A)  (B) 

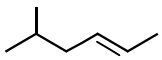
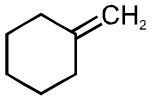
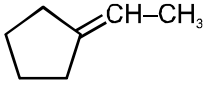
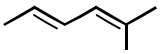
(C)  (D) 

11. Which of the following statement is incorrect ?

(A) Phenol gives positive bromine water test.
(B) Aniline gives foul smelling compound on reaction with $CHCl_3$ + KOH.
(C) Formic acid gives positive Tollen's test.
(D) Nitrobenzene gives positive Tollen's test.

12. (x) $C_7H_{12} \xrightarrow[Me_2S]{O_3} P + Q$

Compound P responds to Tollen's test and iodoform test but Q does not respond with both the reagents. Structure of compound (x) is :

(A)  (B)  (C)  (D) 

13. Yellow precipitate obtained during the test of halogen by lassaigne's test is due to the formation of

(A) AgF (B) AgCl (C) AgBr (D) None of these

14. The Hinsberg's method is used for :

(A) preparation of primary amines (B) preparation of secondary amines
(C) preparation of tertiary amines (D) separation of amine mixtures

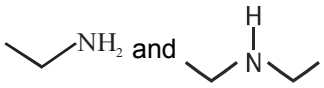
15. Which is incorrect match with respect to the reagent used for lab test ?

(A) Carbonyl → 2,4–DNP
(B) Nitro ethane → Zn, NH_4Cl and $AgNO_3$ (Mulliken Barker test)
(C) Phenol → Anhydrous $ZnCl_2$ + Conc. HCl (Lucas Reagent)
(D) Benzoic acid → $NaHCO_3$

16. On oxidative ozonolysis of 3-Methylhex-3-ene, two products A & B are formed. A gives CO_2 gas with sodium bicarbonate, but B does not. The structures of A & B are respectively :

(A) $CH_3–CH_2–\underset{\underset{O}{\|}}{C}–CH_3$ & $CH_3–CH_2–COOH$ (B) $CH_3–CH_2–COOH$ & $CH_3–CH_2–CH=O$

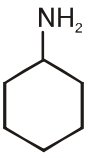
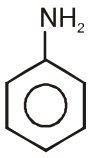
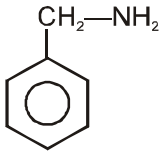
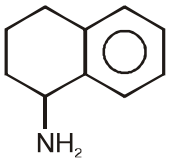
(C) $CH_3–CH_2–COOH$ & $CH_3–CH_2–\underset{\underset{O}{\|}}{C}–CH_3$ (D) $CH_3–CH_2–CH_2–COOH$ & $CH_3–\underset{\underset{O}{\|}}{C}–CH_3$

17.  and can be differentiated by :

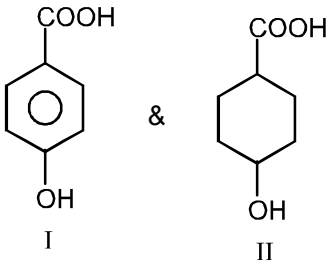
(A) Carbylamine reaction (B) Iodoform test

(C) Cold $KMnO_4$ (D) $Br_2–H_2O$

18. Which of the following compound gives azo dye test ?

(A)  (B)  (C)  (D) 

19. Which of the following reagent can be used to distinguish the given compounds I & II ?



I II

(A) Na metal (B) $NaHCO_3$ (C) Lucas Reagent (D) 2, 4-D.N.P

20. A compound (P) on reaction with "Q" in basic medium (KOH) gives a bad smelling compound (CH_3CH_2NC). Compound Q can be prepare by reaction of acetone with calciumhypochlorite ($Ca(OCl)_2$]. P and Q can be

(A) $CH_3–CH_2–NH_2$ & $CHCl_3$ (B) $CH_3–CH_2–NO_2$ & CH_3Cl

(C) $CH_3–CH_2–NH–CH_3$ & $COCl_2$ (D) $(CH_3–CH_2)_3N$ & Cl_2

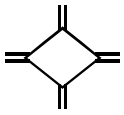
SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 If ONLY the correct numerical value is entered as answer.

21. How many structural isomeric ketones having molecular formula ($C_5H_{10}O$) give iodoform test ?

22.  $\xrightarrow{H_2/Ni}$ P $\xrightarrow{Cl_2/h\nu}$ Q (Total number of monochloro structural products).

23. How many alcohols give immediate turbidity with Lucas reagent having molecular formula ($C_5H_{12}O$)?

24. How many hydrocarbons having molecular mass 68 can give white precipitate with Tollen's reagent ?

25. How many isomeric structural alkene on catalytic hydrogenation gives 2-Methylhexane?

PART 2 : PAPER JEE (ADVANCED) PATTERN

SECTION-I : (Maximum Marks : 12)

- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks	:	+3	If only the bubble corresponding to the correct option is darkened.
Zero Marks	:	0	If none of the bubbles is darkened.
Negative Marks	:	–1	In all other cases

1. An organic compound "A" of molecular weight 120, gives Tollen's reagent test and 2,4-DNP test but no Iodoform with $I_2/OH^{\ominus}$. The compound "A" may be –

(A) Benzoic acid (B) Phenyl methyl ketone

(C) 2-Phenyl ethanal (D) 1-Phenyl ethanol

2. 'X' compound (C_4H_8O) decolorises bromine water & gives instant turbidity with lucas reagent. When 'X' react with I_2 & NaOH it give yellow ppt Identify 'X'.

(A) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$ (B) $CH_3-\underset{\underset{OH}{|}}{CH}-CH=CH_2$ (C) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$ (D) $CH_3-HC=CH-\underset{\underset{OH}{|}}{CH_2}$

3. Compounds I and II can be distinguished by using reagent.

(I) 4–Hydroxy–4–methylpent–2–enoic acid

(II) 5–Hydroxypent–2–ynoic acid

(A) $NaHCO_3$

(B) Br_2 / H_2O

(C) $HCl / ZnCl_2$ (anhydrous)

(D) Cu_2Cl_2 / NH_4OH

4. Test to differentiate between ethanol (CH_3CH_2OH) and phenol (Ph–OH) is/are :
(A) $NaHCO_3$ test (B) Neutral $FeCl_3$ (C) Sodium metal test (D) All of these

SECTION-II : (Maximum Marks: 32)

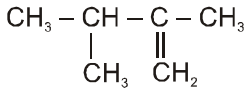
- This section contains **EIGHT** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

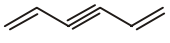
Full Marks	:	+4	If only (all) the correct option(s) is (are) chosen.
Partial Marks	:	+3	If all the four options are correct but ONLY three options are chosen.
Partial Marks	:	+2	If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks	:	+1	If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks	:	0	If none of the options is chosen (i.e. the question is unanswered).
Negative Marks	:	–1	In all other cases.

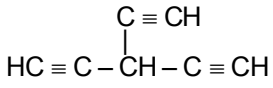
- **For Example :** If first, third and fourth are the **ONLY** three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in –1 marks.

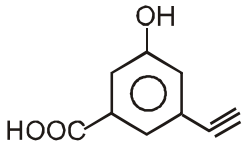
5. Which of the following compounds after complete hydrogenation will form three monochloro structural isomeric products ?

(A) 

(B) 

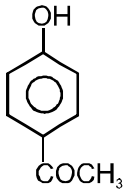
(C) 

(D) 

6. Correct statment(s) about  is /are :

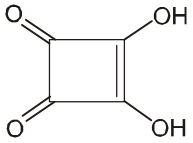
(A) librate $\frac{3}{2}$ mole of H_2 on treatment with Na. (B) Positive test with $FeCl_3$

(C) Positive test with $NaHCO_3$ (D) Positive test with Tollen's reagent

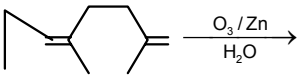
7. Correct statement(s) about  is/are

(A) It gives coloured solution with neutral $FeCl_3$ solution.
(B) It liberates H_2 gas with Na metal.
(C) It gives positive Iodoform test.
(D) It forms sweet smelling compound with alcohols.

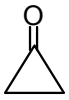
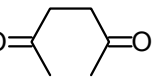
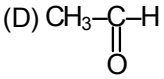
8. Which of the following lab tests are given by Ph–CH=CH–COOH (cinnamic acid) ?
(A) Br_2 water test (B) Neutral $FeCl_3$ (C) $NaHCO_3$ test (D) Tollen's test

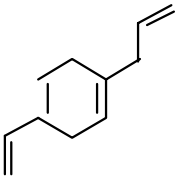
9. Which of the following tests will be given by  (Squaric acid)?

(A) Br_2 water test (B) 2, 4-DNP test (C) Neutral $FeCl_3$ (D) Tollen's test

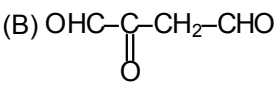
10.  Products

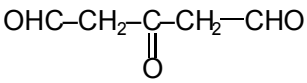
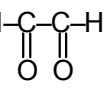
Which of the following product(s) is/are formed in above reaction?

(A)  (B)  (C)  (D) 

11.  Products

Which of the following product(s) is/are formed in above reaction ?

(A)  (B) 

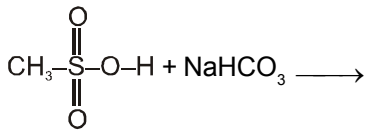
(C)  (D) 

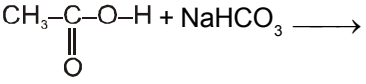
12. Acetaldehyde and propyne can be distinguish by :
(A) Tollen's reagent (B) I_2/NaOH (C) 2,4-DNP test (D) neutral $FeCl_3$

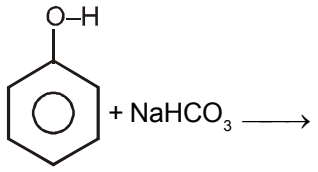
SECTION-III : (Maximum Marks: 18)

- This section contains **SIX** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.
  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:
  Full Marks : +3 If ONLY the correct numerical value is entered as answer.
  Zero Marks : 0 In all other cases.

13. In how many reactions CO_2 gas is released after reaction ?

(1) 

(2) 

(3) 

(4) $CH_3–CH_2–OH + NaHCO_3 \longrightarrow$

(5) $CH_3–C \equiv C–H + NaHCO_3 \longrightarrow$

(6) $HCOOC_2H_5 + NaHCO_3 \longrightarrow$

14. How many alkadienes form Isopentane after hydrogenation reaction (Including all structural isomers)?

15. How many acyclic structural isomeric compounds having molecular formula $C_6H_{12}O$ can give haloform test and 2,4-DNP test?

16. If sodium fusion extract of halogen is acidified with nitric acid followed by addition of $AgNO_3$. Find out the correct statements.

(a) A white precipitate soluble in ammonium hydroxide confirm the presence of chloride ion.

(b) A yellow precipitate soluble in ammonium hydroxide confirm the presence of bromide ion.

(c) A yelllow precipitate insoluble in ammonium hydroxide confirm the presence of iodine ion.

(d) This sodium fusion extract of halogen is first boiled with conc. HNO_3 to decompose cyanide or sulphide ions formed during lassaigne's test, that interfere with $AgNO_3$ test for halogens.

17. How many no. of active hydrogen atoms are present in a compound (mol.mass 90) 0.45 g of which when treated with Na metal liberates 112 ml of the H_2 gas at STP ?

18. 'n' number of alkenes yield 2,2,3,4,4-pentamethyl-pentane on catalytic hydrogenation and 'm' number of monochloro structural isomers are possible for this compound.
Report your answer as (n + m).

Answers

PART - 1

1.	(D)	**2.**	(A)	**3.**	(B)	**4.**	(D)	**5.**	(D)
6.	(D)	**7.**	(A)	**8.**	(C)	**9.**	(B)	**10.**	(A)
11.	(D)	**12.**	(C)	**13.**	(C)	**14.**	(D)	**15.**	(C)
16.	(C)	**17.**	(A)	**18.**	(B)	**19.**	(C)	**20.**	(A)
21.	2	**22.**	2	**23.**	1	**24.**	2	**25.**	5

PART - 2

1.	(C)	**2.**	(B)	**3.**	(C)	**4.**	(B)	**5.**	(CD)
6.	(ABCD)	**7.**	(ABC)	**8.**	(AC)	**9.**	(ABC)	**10.**	(ABC)
11.	(ABC)	**12.**	(ABC)	**13.**	2	**14.**	2	**15.**	4
16.	4	**17.**	2	**18.**	4				

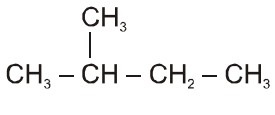
Solution

PART - 1

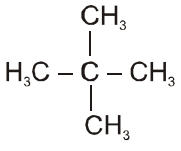
1. The number of monohalogenation products obtained from any alkane depends upon the number of different types of hydrogen it contains. Compound containing only one type of hydrogen gives only one monohalogenation product.

$CH_3CH_2CH_3$ — two types of hydrogen
propane (two monohalogenation structural products)

$CH_3CH_2CH_2CH_2CH_3$ — three types of hydrogen
pentane (three monohalogenation structural products)



isopentane — four types of hydrogen (four monohalogenation structural products)



neopentane — one types of hydrogen (one monohalogenation structural product)

Thus the given alkane should be neopentane.

2. $6NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6]$

$$Na_4[Fe(CN)_6] + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3 . xH_2O$$

Ferric ferrocyanide (Prussian blue)

3. 2,3-Dimethylbutane has two chemically different hydrogen atoms so it can give two monochlorinated structural compounds.

4. For positive iodoform test, alcohol molecules must have $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-$ group

$$Ph-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow{I_2+NaOH} CHI_3 + Ph-COO^- .$$

5. $CH_3CH = CHCH_3 \xrightarrow[H_2O]{O_3 / Zn} 2CH_3CHO.$

6. Aromatic π bonds are stable and cannot hydrogenate at room temperature.

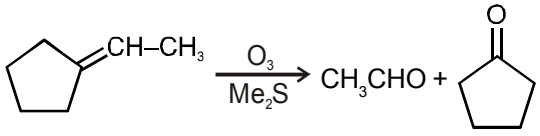
7. Terminal alkyne can react with ammonical $AgNO_3$ and compound have 3 DU.

8. $\left(CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-\right)$, $\left(CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\right)$ groups give positive iodoform test.

9. (a) Both give the test with aq. $NaHCO_3$ because both have –COOH group and acidic hydrogen.
(b) II give + ve test with neutral $FeCl_3$ due to presence of phenolic –OH group, but (I) does not.
(c) In (I) and (II) acidic hydrogen atom is present so both give + ve test with blue litmus paper.
(d) In (I) and (II) acidic hydrogen atom is present so both give + ve test with Na metal.
(e) (I) give + ve test with $HCl/ZnCl_2$ due to presence of aliphatic alcoholic group, but (II) does not.

10. $\left(CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-\right)$, $\left(CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\right)$ groups give positive iodoform test.

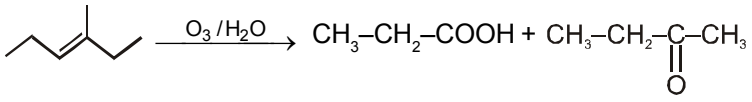
11. Nitrobenzene does not give positive Tollen's test.

12. 

13. $NaBr + AgNO_3 \longrightarrow AgBr$ (yellow)

14. Hinsberg's reagent is used to separation of amines mixtures.

15. Phenol does not gives Lucas reagent test.

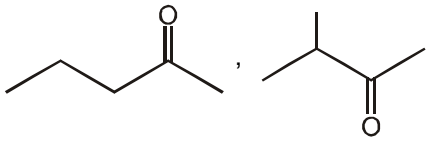
16. 

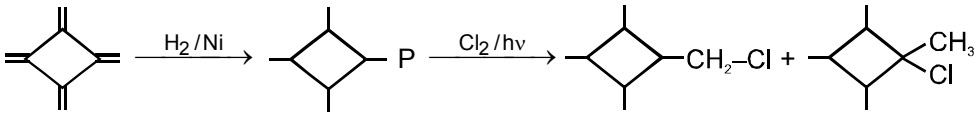
17. 1º and 2º amine can be differentiated by Carbylamine test.

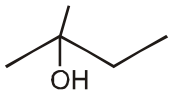
18. Aromatic 1º amine gives positive azo dye test.

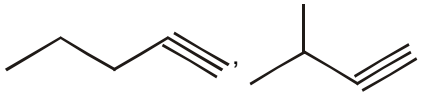
19. Lucas reagent is used to distinguish between alcohol and phenol.

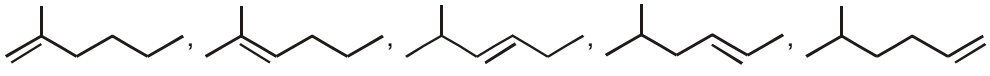
20. $CH_3–CH_2–NH_2 + CHCl_3 + KOH \longrightarrow CH_3CH_2NC$
$CH_3–CO–CH_3 + Ca(OCl)_2 \longrightarrow CHCl_3 + (CH_3COO)_2Ca$

21. 

22. 

23. 

24. C_5H_8  (Molecular Mass = 68)

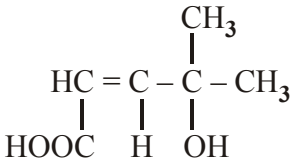
25. 

PART - 2

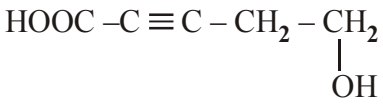
1. The compound gives Tollen's reagent and 2,4-DNP test i.e. the compound is aldehyde. Further it gives no Iodoform test. Expected molecular formula is C_8H_8O. Therefore the correct answer is (C).

2. $CH_3–\underset{\underset{OH}{|}}{CH}–CH=CH_2$ gives bromine water test, lucas reagent test and haloform test.

3.



(I)

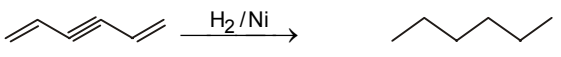


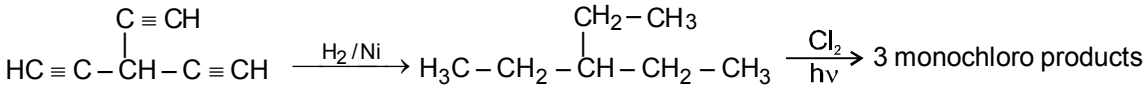
(II)

(I) gives immediate turbidit with by Lucas reagent and (II) does not give turbidity appreciably.

4. Ethanol can not give neutral $FeCl_3$ test but phenol gives this test.

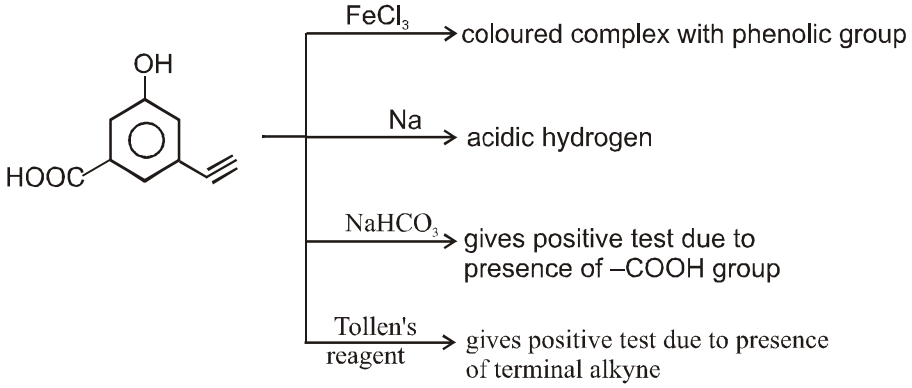
5.



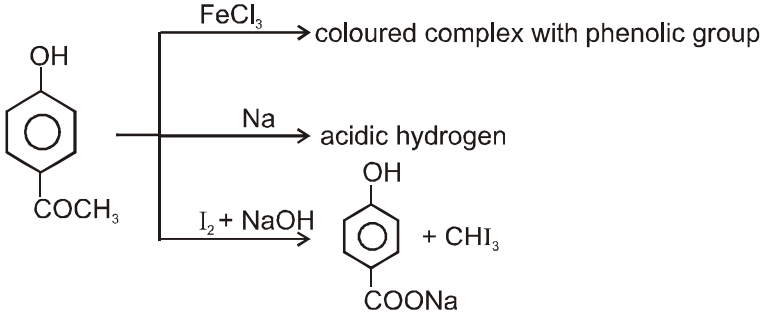


Both structures give three monochloro structural isomeric products.

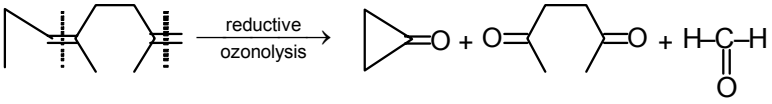
6.

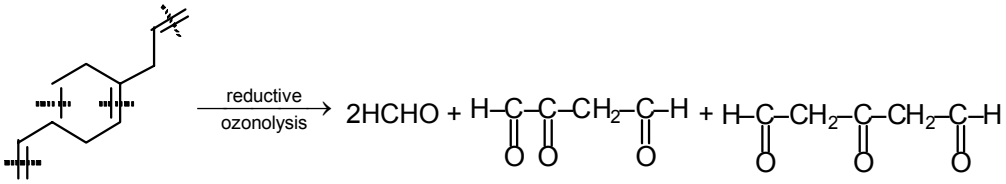


7.



9. Generally terminal alkyne and –CH=O group gives positive test with tollens reagent.

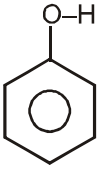
10. 

11. 

12. Acetaldehyde and propyne can be distinguish by Tollen's reagent and Iodoform test.

13. (1) $CH_3–\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}–O–H + NaHCO_3 \longrightarrow CH_3–\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}–\overset{\ominus}{O}\,Na^{\oplus} + H_2O + CO_2\uparrow$

(2) $CH_3–\underset{\underset{O}{\|}}{C}–O–H + NaHCO_3 \longrightarrow CH_3–\underset{\underset{O}{\|}}{C}–\overset{\ominus}{O}–\overset{\oplus}{Na} + H_2O + CO_2\uparrow$

(3)  $+ NaHCO_3 \longrightarrow$ No reaction

(4) $CH_3–CH_2–OH + NaHCO_3 \longrightarrow$ No reaction

(5) $CH_3–C\equiv C–H + NaHCO_3 \longrightarrow$ No reaction

(6) $HCOOC_2H_5 + NaHCO_3 \longrightarrow$ No reaction

14. $H_2C=\underset{\underset{CH_3}{|}}{C}–C=CH_2$ $\qquad$ $CH_3–\underset{\underset{CH_3}{|}}{C}=C=CH_2$

15. $CH_3–\underset{\underset{O}{\|}}{C}–CH_2–CH_2–CH_2–CH_3$ $\qquad$ $CH_3–\underset{\underset{O}{\|}}{C}–\underset{\underset{CH_3}{|}}{CH}–CH_2–CH_3$

$CH_3–\underset{\underset{O}{\|}}{C}–CH_2–\underset{\underset{CH_3}{|}}{CH}–CH_3$ $\qquad$ $CH_3–\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}}–\underset{\underset{CH_3}{|}}{C}–CH_3$

17. 122 ml of H_2 is obtained from 0.45 g

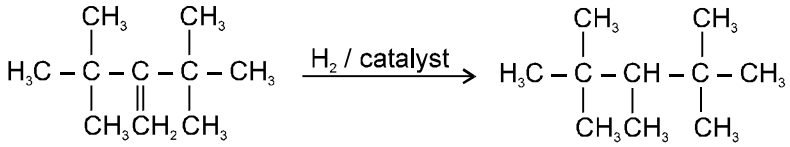
22400 ml of H_2 is obtained from $\frac{0.45 \times 22400}{112} = 90$ g

90 g compound gives one mole H_2 gas

i.e. 2H obtained from 1 mole of compound.

Ans. No. of active H = 2

18. Only one alkene



Three monochloro isomers are possible as it has three different types of 'H' atoms.