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.

1. Monohalogenation :

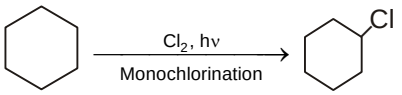
When an alkane or a cycloalkane is treated with halogen (Cl_2, Br_2, F_2, I_2), a photochemical reaction takes place, in which a C–H bond cleaves and a C–X bond is formed. In such reactions if one H-atom is substituted by one halogen atom, then this is known as monohalogenation reaction.

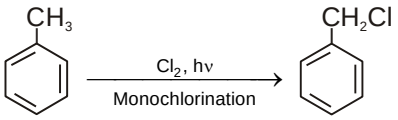
Applications : If a molecule has more than one type of H-atoms, then on monochlorination, it forms a mixture of monochloroisomers. **All these products (structures) are position isomers.**

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.

Ex. (i) $CH_4 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu} CH_3Cl + HCl$ ¼1–Monochloroproduct½

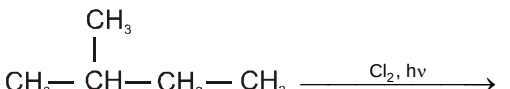
(ii)  ¼1–Monochloroproduct½

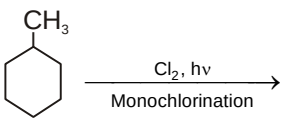
(iii) 

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 (structure isomers)

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

(vi) 

(vii) 

2. 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.

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

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

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

(iv) During catalytic hydrogenation *carbon skelton* does not change.

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

General reaction :

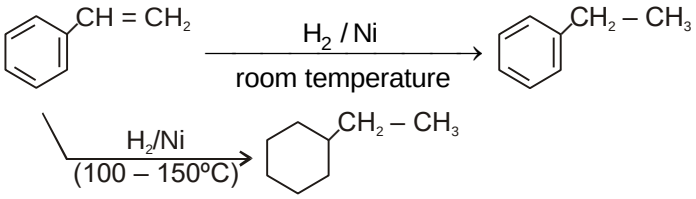
(a) $R–CH=CH–R + H_2 \xrightarrow{Ni} R–CH_2–CH_2–R$

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

$\downarrow H_2$

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

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

(d) 

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 or ketones).

(ii) Oxidative ozonolysis:

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

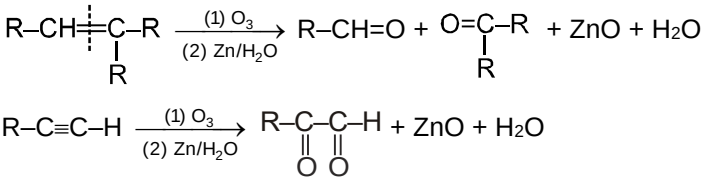
The products are ketones and/or acids.

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

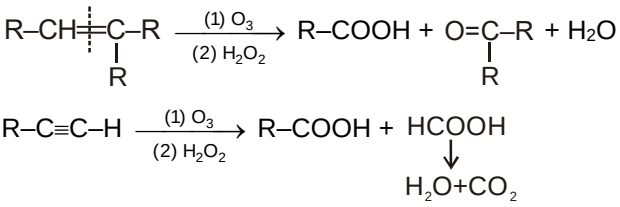
(ii) At higher temperature, the aromatic double bonds can also undergo ozonolysis reaction.

General reaction :

(i) Reductive ozonolysis



(ii) Oxidative ozonolysis

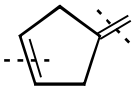


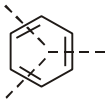
Ex. (a) $CH_2=CH_2 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_2=O + CH_2=O$

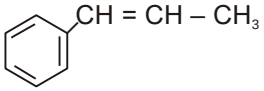
(b) $CH_3–CH_2–CH=CH_2 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_3–CH_2–CH=O + O=CH_2$

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

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

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

(f)  $\xrightarrow[(2)\ H_2O_2]{(1)\ O_3(\Delta)}$ 3 O = C(H) – C(H) = O (Ethanedial) or (glyoxal)

(g) 

Exercise

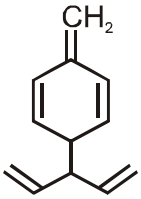
✍ **Marked questions are recommended for Revision.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1. The degree of unsaturation of following compound $C_8H_{12}O$, C_3H_5N, C_4H_8O are respectively :
(A) 4, 3, 2 (B) 3, 2, 1 (C) 2, 1, 3 (D) 2, 2, 3

2.✍ Which of the following hydrocarbons give same product on hydrogenation.
(A) 2-Methyl hex-1-ene & 3-Methyl hex-3-ene
(B) 3-Ethyl hex-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

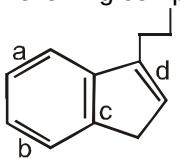
3. Number of moles of hydrogen will required for complete hydrogenation of one mole of following compound :



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

4. How many alkenes on catalytic hydrogenation give isopentane as a product (consider only structural isomers)?
(A) 2 (B) 3 (C) 4 (D) 5

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



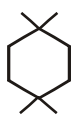
Which double bond will be hydrogenated ?
(A) c (B) b (C) a (D) d

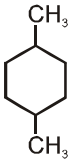
6. Only two isomeric monochloro derivatives are possible for :-
(A) n-Pentane (B) 2,4-Dimethyl pentane
(C) Toluene (D) 2,3-Dimethyl butane

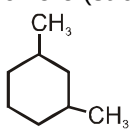
7. The number of possible monochloro derivatives of 2, 2, 3, 3-Tetramethylbutane is -
(A) 2 (B) 3 (C) 4 (D) 1

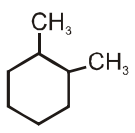
8.✍ Which of the following alkene gives four monochloro (structural isomer) products after hydrogenation ?
(A) Pent-2-ene (B) 2-Methylbut-2-ene
(C) 3-Methylhex-2-ene (D) 2, 3-Dimethylbut-2-ene

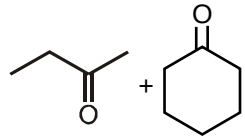
9. Which of the following compound will give four monochloro (structural) product on monochlorination.

(A) 

(B) 

(C) 

(D) 

10. X $\xrightarrow{O_3/Zn}$  +

$\xrightarrow{H_2/Ni}$ Y

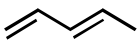
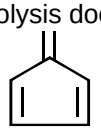
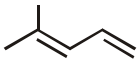
The IUPAC name of compound Y is :

(A) 2-Cyclohexylbutane
(B) 1-Methylpropylcyclohexane
(C) Butylcyclohexane
(D) 1-Cyclohexylbutane

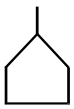
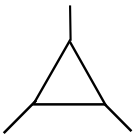
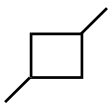
11. An alkene give two moles of HCHO, one mole of CO_2 and one mole of $CH_3-\underset{\underset{O}{\|}}{C}-CHO$ on ozonolysis. What is its structure?

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

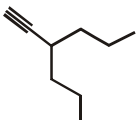
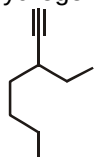
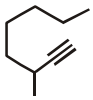
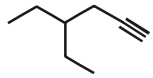
12. Which of the following compound on reductive ozonolysis does not give glyoxal as one of the product.

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

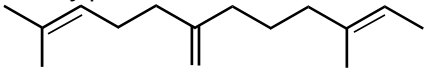
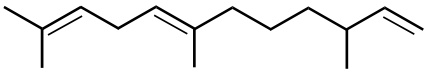
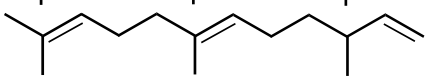
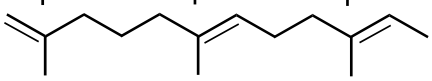
13. Compound A (C_6H_{12}) does not absorb H_2 in presence of Ni. It forms two monochloro isomers on photochemical chlorination. Its structure can be :

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

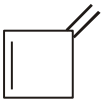
14. Which alkyne will give 3-Ethyl heptane on catalytic hydrogenation.

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

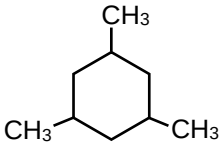
15. Farnesene is a compound found in the waxy coating of apples. On hydrogenation it gives 2,6, 10-Trimethyl dodecane. On ozonolysis it gives one mole acetone, one mole of formaldehyde, one mole of 2-Methylpentanedial and one mole of 4-Oxopentanal. The structure proposed for Farnesene may be

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

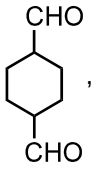
16. A compound P(C_5H_6) on hydrogenation form a hydrocarbon B(C_5H_{10}) which gives only one monochloro product. The compound 'P" is:

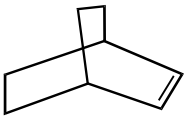
(A)  (B)  (C)  (D) $CH\equiv C-CH_2-CH=CH_2$

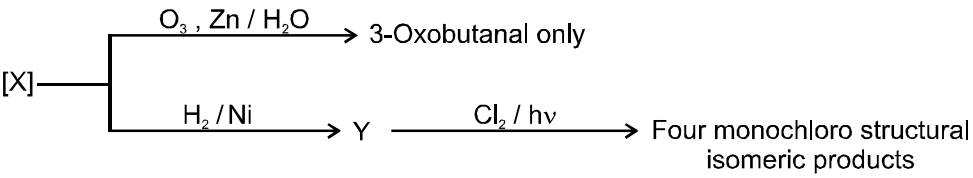
17. How many products (structural isomers only) are formed by monochlorination of given compound.



(A) 4 (B) 3 (C) 5 (D) 6

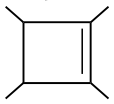
18. An alkene (A) $\xrightarrow{\text{Ozonolysis}}$  , A is :

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

19. 

Compound 'X' is :
(A) 1-Methylcyclopropene
(B) 1, 4-Dimethylcyclohexa-1,4-diene
(C) 1, 4-Dimethylcyclohexa-1,3-diene
(D) 1, 2-Dimethylcyclohexa-1,4-diene

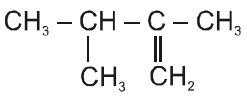
20. The chemical reactions of an unsaturated compound 'M' are given below. Determine the possible structural formula of 'M'

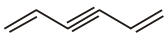
(A)  (B)  (C)  (D) 

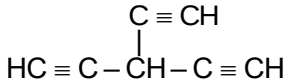
PART - II : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

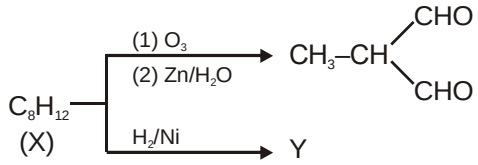
21. Which of the following compounds after complete hydrogenation will form three monochloro structural isomeric products ?

(A) 

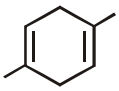
(B) 

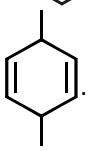
(C) 

(D) 

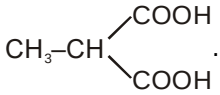
22. 

True statements is/are

(A) Structure of X is  .

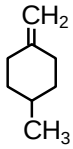
(B) Structure of X is  .

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

(D) Oxidative ozonolysis product of X is 

.

23. Which of the following compound gives 1,4-Dimethyl cyclohexane when undergo catalytic hydrogenation.

(A) 

(B) 

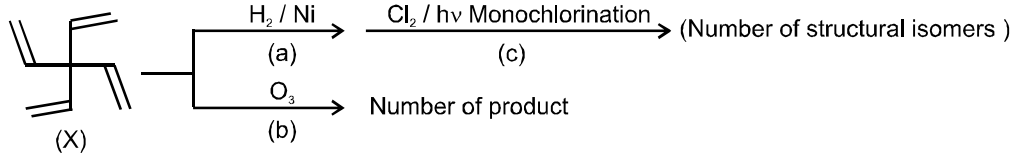
(C) 

(D) 

PART - III : SINGLE AND DOUBLE VALUE INTEGER TYPE

24. How many isomeric alkynes on catalytic hydrogenation gives 3-Ethyl-4-methylheptane ?

25. Find the number of structural isomers of fully saturated cycloalkane of molecular formulae C_6H_{12} which give three monochloro structural products.

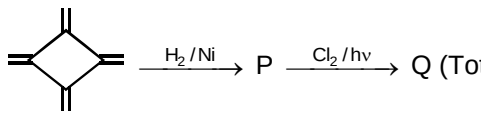
26. 

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

27. How many alkenes, alkynes and alkadienes can be hydrogenated to form Isopentane (Including all structural isomers)

28. '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).

29. How many isomeric structural alkene on catalytic hydrogenation gives 3-Methyl hexane.

30. 

31. How many terminal alkynes having molecular mass 68 is possible ?

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

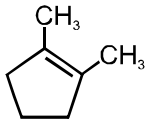
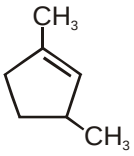
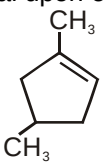
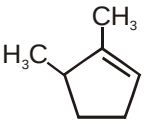
32. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane this alkane could be : **[AIEEE 2003, 3/225]**
(1) propane (2) pentane (3) isopentane (4) neopentane.

33. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is ? **[AIEEE 2005, 3/225]**
(1) n-Hexane (2) 2,3-Dimethylbutane
(3) 2,2-Dimethylbutane (4) 2-Methylpentane

34. In the following sequence of reactions, the alkene affords the compound 'B'
$CH_3CH=CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B$, compound B is **[AIEEE 2008, 3/105]**
(1) CH_3CH_3CHO (2) CH_3COCH_3
(3) $CH_3CH_2COCH_3$ (4) CH_3CHO

35. 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

36. 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

37. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis ? **[JEE(Main)-2015, 4/120]**
(1)  (2)  (3)  (4) 

Answers

EXERCISE

1.	(B)	**2.**	(D)	**3.**	(C)	**4.**	(B)	**5.**	(D)
6.	(D)	**7.**	(D)	**8.**	(B)	**9.**	(D)	**10.**	(B)
11.	(B)	**12.**	(A)	**13.**	(C)	**14.**	(B)	**15.**	(C)
16.	(C)	**17.**	(B)	**18.**	(C)	**19.**	(D)	**20.**	(C)
21.	(CD)	**22.**	(BCD)	**23.**	(ABC)	**24.**	3	**25.**	3
26.	5	**27.**	6	**28.**	4	**29.**	6	**30.**	2
31.	2	**32.**	(4)	**33.**	(2)	**34.**	(4)	**35.**	(3)
36.	(2)	**37.**	(2)						