CHAPTER 10

Hydrocarbons

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. .... is most acidic.
(Ethane, Ethene, Ethyne) *(1981 - 1 Mark)*
2. Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess methyl iodide. The final product is .... *(1983 - 1 Mark)*
3. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with .... *(1983 - 1 Mark)*
4. Kolbe electrolysis of potassium succinate gives CO_2 and .... *(1993 - 1 Mark)*
5. Addition of water to acetylenic compounds is catalyzed by.........and............ *(1993 - 1 Mark)*
6. The bond dissociation energy needed to form the benzyl radical from toluene is........than the formation of the methyl radical from methane. *(1994 - 1 Mark)*
7. 1, 3-Butadiene with bromine in molar ratio generates predominantly .... *(1997 - 1 Mark)*

B True / False

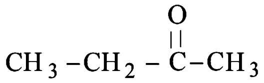
1. Moist ethylene can be dried by passing it through concentrated sulphuric acid. *(1982 - 1 Mark)*
2. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio of 9: 1. *(1993 - 1 Mark)*

C MCQs with One Correct Answer

1. Marsh gas mainly contains *(1980)*
(a) C_2H_2 (b) CH_4
(c) H_2S (d) CO
2. Which of the following decolourises alkaline $KMnO_4$ solution *(1980)*
(a) C_3H_8 (b) C_2H_4
(c) CH_4 (d) CCl_4
3. The compound with the highest boiling point is *(1982 - 1 Mark)*
(a) *n*-hexane (b) *n*-pentane
(c) 2, 2-dimethylpropane (d) 2-methylbutane
4. The maximum number of isomers for an alkene with the molecular formula C_4H_8 is *(1982 - 1 Mark)*
(a) 2 (b) 3
(c) 4 (d) 5
5. When propyne is treated with aqueous H_2SO_4 in presence of $HgSO_4$ the major product is *(1983 - 1 Mark)*
(a) propanal
(b) propyl hydrogensulphate
(c) acetone
(d) propanol
6. Which of the following compounds does not dissolve in conc. H_2SO_4 even on warming? *(1983 - 1 Mark)*
(a) ethylene (b) benzene
(c) hexane (d) aniline
7. Baeyer's reagent is : *(1984 - 1 Mark)*
(a) alkaline permanganate solution
(b) acidified permanganate solution
(c) neutral permanganate solution
(d) aqueous bromine solution
8. Acidic hydrogen is present in : *(1985 - 1 Mark)*
(a) ethyne (b) ethene
(c) benzene (d) ethane
9. *Anti*-Markovnikoff addition of HBr is not observed in : *(1985 - 1 Mark)*
(a) propene (b) 1-butene
(c) but-2-ene (d) pent-2-ene
10. The highest boiling point is expected for : *(1986 - 1 Mark)*
(a) iso-octane
(b) *n*-octane
(c) 2, 2, 3, 3-tetramethylbutane
(d) *n*-butane
11. Which of the following will have least hindered rotation about carbon-carbon bond? *(1987 - 1 Mark)*
(a) Ethane (b) Ethylene
(c) Acetylene (d) Hexachloroethane

12. When cyclohexane is poured on water, it floats, because:
(a) cyclohexane is in 'boat' form ***(1997 - 1 Mark)***
(b) cyclohexane is in 'chair' form
(c) cyclohexane is in 'crown' form
(d) cyclohexane is less dense than water.

13. The product(s) obtained via oxymercuration ($HgSO_4 + H_2SO_4$) of 1- butyne would be ***(1999 - 2 Marks)***

(a) 
$CH_3-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$

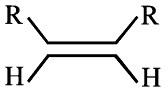
(b) $CH_3-CH_2-CH_2-CHO$

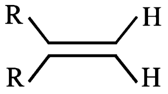
(c) $CH_3-CH_2-CHO+HCHO$

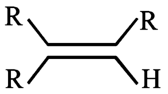
(d) $CH_3\,CH_2\,COOH+HCOOH$

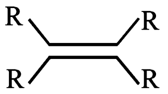
14. Propyne and propene can be distinguished by ***(2000S)***
(a) conc. H_2SO_4 (b) Br_2 in CCl_4
(c) dil. $KMnO_4$ (d) $AgNO_3$ in ammonia

15. Which one of the following will react fastest with H_2 under catalytic hydrogenation condition ? ***(2000S)***

(a) 

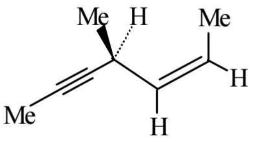
(b) 

(c) 

(d) 

16. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give *anti*-Markovnikov addition to alkenes because ***(2001S)***
(a) both are highly ionic
(b) one is oxidizing and the other is reducing
(c) one of the steps is endothermic in both the cases
(d) all the steps are exothermic in both the cases

17.

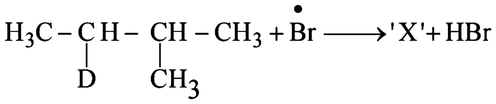


Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives ***(2001S)***
(a) an optically active compound
(b) an optically inactive compound
(c) a racemic mixture
(d) a diastereomeric mixture

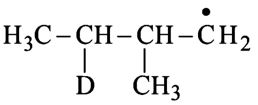
18. The reaction of propene with HOCl proceeds via the addition of ***(2001S)***
(a) H^+ in the first step
(b) Cl^+ in the first step
(c) OH^- in the first step
(d) Cl^+ and OH^- in a single step

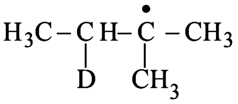
19. The nodal plane in the π-bond of ethene is located in
(a) the molecular plane ***(2002S)***
(b) a plane parallel to the molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon - carbon σ -bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon - carbon σ -bond.

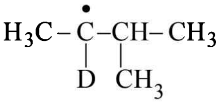
20. Consider the following reaction ***(2002S)***

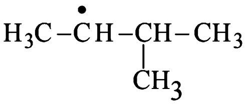

$H_3C-\underset{D}{C}H-\underset{CH_3}{C}H-CH_3+\overset{\bullet}{Br}\longrightarrow 'X'+HBr$

Identify the structure of the major product 'X'

(a) 
$H_3C-\underset{D}{C}H-\underset{CH_3}{C}H-\overset{\bullet}{C}H_2$

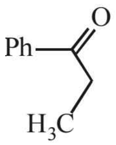
(b) 
$H_3C-\underset{D}{C}H-\underset{CH_3}{\overset{\bullet}{C}}-CH_3$

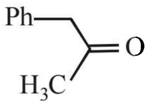
(c) 
$H_3C-\underset{D}{\overset{\bullet}{C}}-\underset{CH_3}{C}H-CH_3$

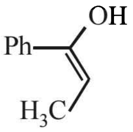
(d) 
$H_3C-\overset{\bullet}{C}H-\underset{CH_3}{C}H-CH_3$

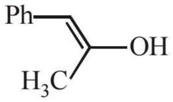
21. Identify the reagent from the following list which can easily distinguish between 1-butyne and 2-butyne ***(2002S)***
(a) bromine, CCl_4
(b) H_2, Lindlar catalyst
(c) dilute H_2SO_4, $HgSO_4$
(d) ammonical Cu_2Cl_2 solution

22. $Ph—C\equiv C—CH_3 \xrightarrow{Hg^{2+}/H^+} A$. A is: ***(2003S)***

(a) 

(b) 

(c) 

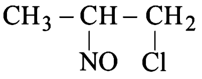
(d) 

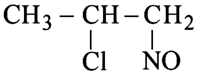
23. Which of the following is used for the conversion of 2-hexyne into *trans*-2-hexene ? ***(2004S)***
(a) $H_2/Pd/BaSO_4$ (b) H_2, PtO_2
(c) $NaBH_4$ (d) Li-NH_3/C_2H_5OH

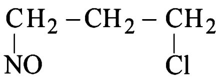
24. On monochlorination of 2-methylbutane, the total number of chiral compounds formed is ***(2004S)***
(a) 2 (b) 4
(c) 6 (d) 8

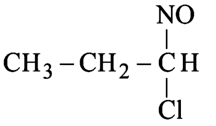
25. Identify the product, P in the following reaction :

$CH_3-CH=CH_2+NOCl\longrightarrow P$ ***(2006 - 3M, –1)***

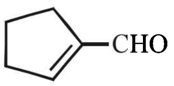
(a) 
$CH_3-\underset{NO}{C}H-\underset{Cl}{C}H_2$

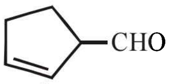
(b) 
$CH_3-\underset{Cl}{C}H-\underset{NO}{C}H_2$

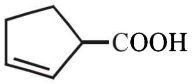
(c) 
$\underset{NO}{C}H_2-CH_2-\underset{Cl}{C}H_2$

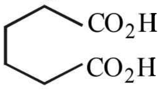
(d) 
$CH_3-CH_2-\overset{\overset{\displaystyle NO}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}H$

26. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound **E**. Compound **E** on further treatment with aqueous KOH yields compound **F**. Compound **F** is *(2007)*

(a) 

(b) 

(c) 

(d) 

27. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are *(2010)*

(a) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$
(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C\equiv CH$
(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C\equiv CH$
(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$

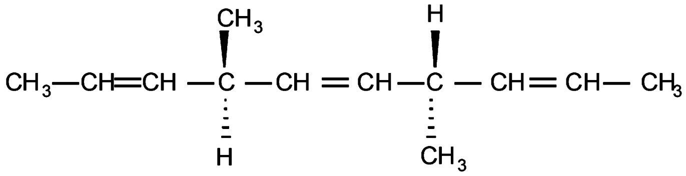
28. The bond energy (in **kcal mol^{-1}**) of a C–C single bond is approximately *(2010)*

(a) 1 (b) 10
(c) 100 (d) 1000

29. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are) : *(2012)*

(a) *sp* and sp^3 (b) *sp* and sp^2
(c) only sp^3 (d) sp^2 and sp^3

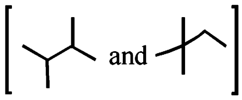
30. The number of optically active products obtained from the **complete** ozonolysis of the given compound is : *(2012)*



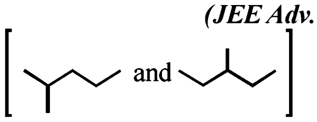
$$CH_3-CH=CH-\underset{H}{\overset{CH_3}{C}}-CH=CH-\underset{CH_3}{\overset{H}{C}}-CH=CH-CH_3$$

(a) 0 (b) 1
(c) 2 (d) 4

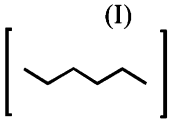
31. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. *(JEE Adv. 2014)*



(I)



(II)



(III)

The correct order of their boiling point is

(a) I > II > III (b) III > II > I
(c) II > III > I (d) III > I > II

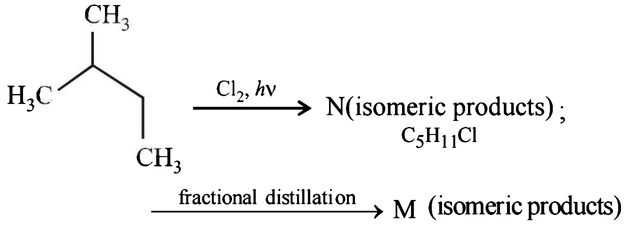
D MCQs with One or More Than One Correct

1. Which one of the following has the smallest heat of hydrogenation per mole? *(1993 - 1 Mark)*

(a) 1-butene (b) *trans*-2-butene
(c) *cis* -2-butene (d) 1,3-butadiene

2. Toluene, when treated with Br_2/Fe, gives p-bromotoluene as the major product because CH_3 group *(1999 - 3 Marks)*

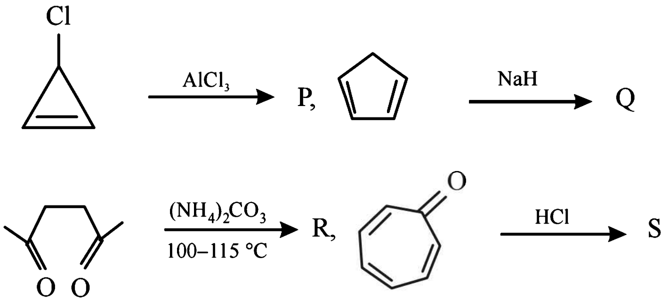
(a) is para directing
(b) is meta directing
(c) activates the ring by hyperconjugation
(d) deactivates the ring

3. 

Identify N and M *(2006 - 5M, –1)*

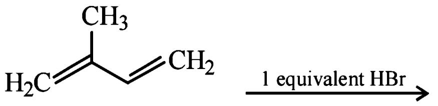
(a) 6, 4 (b) 6, 6
(c) 4, 4 (d) 3, 3

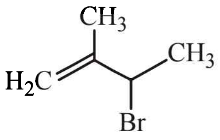
4. Among P, Q, R and S, the aromatic compound(s) is/are *(JEE Advanced 2013-I)*

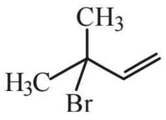


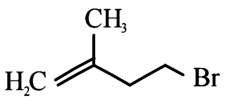
(a) P (b) R
(c) Q (d) S

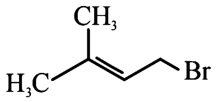
5. In the following reaction, the major product is *(JEE Adv. 2015)*



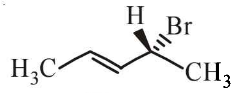
(a) 

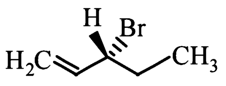
(b) 

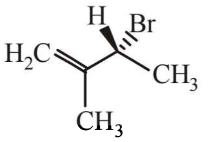
(c) 

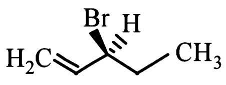
(d) 

6. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are) *(JEE Adv. 2015)*

(a) 

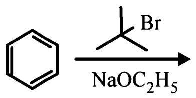
(b) 

(c) 

(d) 

7. Among the following, reaction(s) which gives(give) tert-butyl benzene as the major product is(are) *(JEE Adv. 2016)*

(a)



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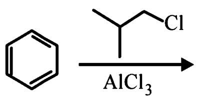

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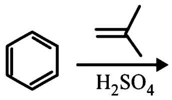

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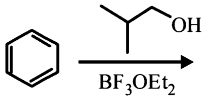


E Subjective Problems

1. Give one characteristic test which would distinguish. CH_4 from C_2H_2 *(1979)*
2. Write the structural formula of the major product in each of the following cases :
   (*i*) the compound obtained by the hydration of ethyne is treated with dilute alkali *(1981 - ½ Mark)*
   (*ii*) ethene mixed with air is passed under pressure over a silver catalyst at 250°C. *(1981 - ½ Mark)*

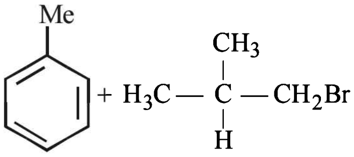
   (*iii*)

$+ (CH_3)_2CHCH_2Cl \xrightarrow{AlCl_3}$ *(1992 - 1 Mark)*

   (*iv*) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$ *(1994 - 1 Mark)*

   (*v*) $C_6H_5C_2H_5 \xrightarrow[2.\ NaCN]{1. Br_2,\ Heat, Light}$ *(1994 - 1 Mark)*

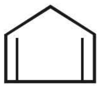
   (*vi*)



$+ H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2Br$

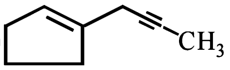
$+ \text{Anhyd. } AlCl_3 \longrightarrow$ --- *(1997 - 1 Mark)*

   (*vii*)



$+ CHBr_3 + t-BuOK \longrightarrow$ ---- *(1997 - 1 Mark)*

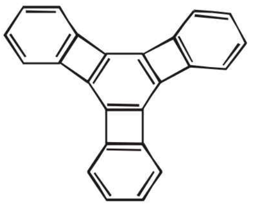
   (*viii*)



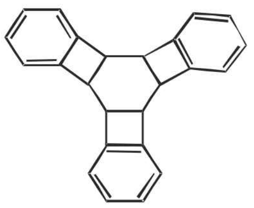
$\xrightarrow[\text{Lindlar catalyst}]{H_2}$ *(2000 - 1 Mark)*

3. Outline the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two). *(1981 - 1 Mark)*
4. State with balanced equations, what happens when propene is bubbled through a hot aqueous solution of potassium permanganate. *(1982 - 1 Mark)*
5. Give reasons for the following :
   (*i*) Methane does not react with chlorine in the dark. *(1983 - 1 Mark)*
   (*ii*) Propene reacts with HBr to give isopropyl bromide but does not give n-propyl bromide. *(1983 - 1 Mark)*
   (*iii*) Although benzene is highly unsaturated, normally it does not undergo addition reaction. *(1983 - 1 Mark)*
   (*iv*) Toluene reacts with bromine in the presence of light to give benzyl bromide while in presence of $FeBr_3$ it gives *p*-bromotoluene. Give explanation for the above observations. *(1996 - 2 Marks)*
   (*v*) The central carbon-carbon bond in 1, 3 – butadiene is shorter than that in n-butane. *(1998 - 2 Marks)*
   (*vi*) *tert*-Butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$. *(2000 - 1 Mark)*

   (*vii*)

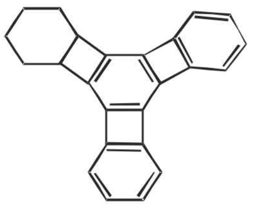


$\xrightarrow{3H_2/Pd}$ *(2005 - 1 Mark)*



but not

(A)



(B)

6. (*i*) 2-Methylpropene can be converted into isobutyl bromide by hydrogen bromide, is true under what conditions? *(1984 - 1 Mark)*
   (*ii*) 'Ethyne and its derivatives will give white precipitate with ammonical silver nitrate solution', is true under what conditions. *(1984 - 1 Mark)*
7. Write down the reactions involved in the preparation of the following, using the reagents indicated against it in parenthesis.

   Ethylbenzene from benzene [C_2H_5OH, PCl_5, anhydrous $AlCl_3$]. *(1984 - 2 Marks)*
8. A certain hydrocarbon A was found to contain 85.7 percent carbon and 14.3 per cent hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon B. 1.00 g of hydrocarbon A just decolourized 38.05 g of a 5 per cent solution (by weight) of Br_2 in CCl_4. Compound A, on oxidation with concentrated $KMnO_4$, gave compound C (molecular formula C_4H_8O) and acetic acid. Compound C could easily be prepared by the action of acidic aqueous mercuric sulphate on 2- butyne. Determine the molecular formula of A and deduce the structure of A, B and C. *(1984 - 6 Marks)*
9. How would you distinguish between
   (i) 2-butyne and 1-butyne. *(1985 - 1 Mark)*
   (ii) cyclohexane and cyclohexene. *(1988 - 1 Mark)*

10. *n*-Butane is produced by the monobromination of ethane followed by the Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g *n*-butane, if the bromination takes place with 90 per cent yield and the Wurtz reaction with 85 per cent yield. ***(1989 - 3 Marks)***

11. Identify, **B**(C_4H_8) which adds on HBr in the presence and in the absence of peroxide to give the same product, C_4H_9Br. ***(1993 - 1 Mark)***

12. Identify, **D**(C_6H_{12}), an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound, C_6H_{14}. ***(1993 - 1 Mark)***

13. Draw the stereochemical structures of the products in the following reactions : ***(1994 - 4 Marks)***

$$R-C\equiv C-R \xrightarrow[\text{Lindlar catalyst}]{H_2}$$

14. 1, 4–Pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound X which upon reaction with excess of Mg in dry ether forms Y. Compound Y on treatment with ethyl acetate followed by dilute acid yields Z. Identify the structures of compounds X, Y and Z. ***(1995 - 4 Marks)***

15. An organic compound **E**(C_5H_8) on hydrogenation gives compound **F**(C_5H_{12}). Compound **E** on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound **E**. ***(1995 - 2 Marks)***

16. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. ***(1995 - 2 Marks)***

17. A hydrocarbon A, of the formula C_8H_{10}, on ozonolysis gives compound B($C_4H_6O_2$) only. The compound B can also be obtained from the alkyl bromide, C(C_3H_5Br) upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify A, B and C and also give equations for the reactions. ***(1996 - 3 Marks)***

18. Give the structures of the major organic products from 3-ethyl-2-pentene under each of the following reaction conditions. ***(1996 - 3 Marks)***
- (a) HBr in the presence of peroxide
- (b) Br_2/H_2O
- (c) $Hg(OAc)_2/H_2O$; $NaBH_4$

19. The hydrocarbon A, adds one mole of hydrogen in the presence of a platinum catalyst to form n-hexane. When A is oxidized vigorously with $KMnO_4$, a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of A and explain. ***(1997 - 2 Marks)***

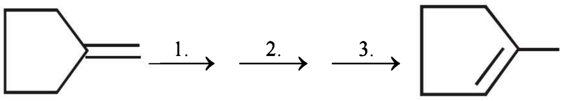
20. Show the steps to carry out the following transformations.
- (i) Ethylbenzene → benzene ***(1998 - 2 Marks)***
- (ii) Ethylbenzene → 2- phenylpropionic acid. ***(1998 - 3 Marks)***

21. Complete the following reactions with appropriate structures of products/reagents.

(i) $C_6H_5CH=CH_2 \xrightarrow{Br_2} [A]$

$$\xrightarrow[\text{(ii) } CH_3I]{\text{(i) } NaNH_2 \text{ (3.0 equiv.)}} [B\}$$ ***(1998 - 2 + 2 Marks)***

(ii)



(1999 - 3 Marks)

22. An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only one product (B) C_8H_8O. Compund (B) on reaction with NaOH/I_2 yields sodium benzoate. Compound (B) reacts with KOH/NH_2NH_2 yielding a hydrocarbon (C) C_8H_{10}. Write the structures of compounds (B) and (C). Based on this information, two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation (H_2/Pd – C) gives a racemic mixture. ***(2001 - 5 Marks)***

23. Write down the heterogeneous catalyst involved in the polymerisation of ethylene. ***(2003 - 2 Marks)***

24. $A(C_6H_{12}) \xrightarrow{HCl} \underset{(C_6H_{13}Cl)}{B + C}$ ***(2003 - 4 Marks)***

$B \xrightarrow{\text{alc. KOH}} D$ (isomer of A)

$D \xrightarrow{\text{ozonolysis}} E$ (it gives negative test with Fehling solution but responds to iodoform test).

$A \xrightarrow{\text{Ozonolysis}} F + G$ (both gives positive Tollen's test but do not give iodoform test).

$F + G \xrightarrow{\text{conc. NaOH}} HCOONa + A$ primary alochol.

Identify from A to G.

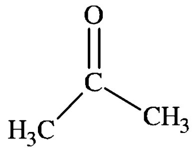
25. Draw Newmann projection of relatively less stable staggered form of *n*-butane. The reason of low stability of this form is van der Waal's repulsion, torsional strain, or both. ***(2004 - 2 Marks)***

G Comprehension Based Questions

PASSAGE-I

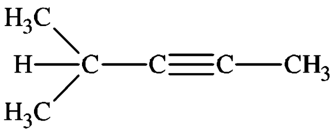
An acyclic hydrocarbon **P**, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in which **Q** is an intermediate organic compound.

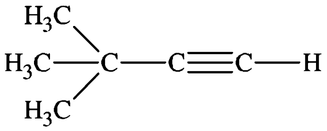
$$\underset{(C_6H_{10})}{P} \xrightarrow[\substack{\text{(ii) } NaBH_4/\text{ethanol} \\ \text{(iii) dil. acid}}]{\text{(i) dil. } H_2SO_4/HgSO_4} Q \xrightarrow[\substack{\text{(ii) } O_3 \\ \text{(iii) } Zn/H_2O}]{\substack{\text{(i) conc. } H_2SO_4 \\ \text{(catalytic amount)} \\ (-H_2O)}} 2$$



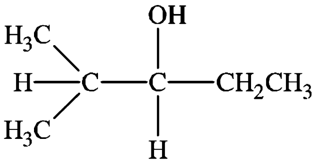
(2011 - I)

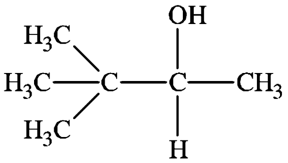
1. The structure of compound **P** is
- (a) $CH_3CH_2CH_2CH_2C\equiv CH$
- (b) $CH_3CH_2C\equiv CCH_2CH_3$

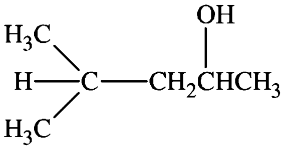
(c) 

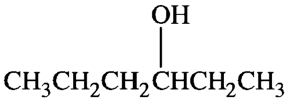
(d) 

2. The structure of the compound **Q** is

(a) 

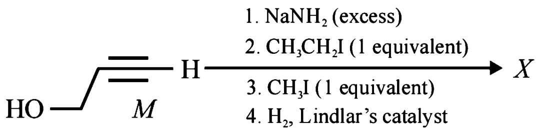
(b) 

(c) 

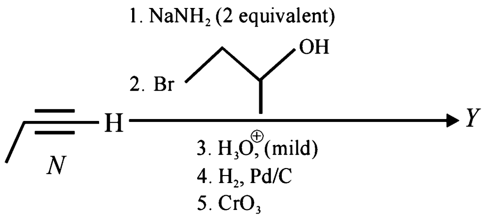
(d) 
$CH_3CH_2CH_2\overset{\displaystyle OH}{C}HCH_2CH_3$

PASSAGE - II

Schemes 1 and 2 describe sequential transformation of alkynes *M* and *N*. Consider only the major products formed in each step for both the schemes.

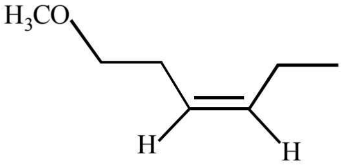


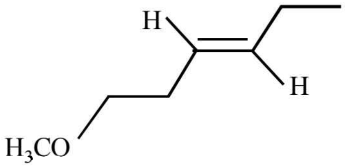
Scheme-1

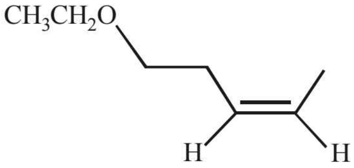


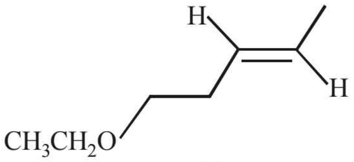
Scheme-2

3. The product *X* is ***(JEE Adv. 2014)***

(a) 

(b) 

(c) 

(d) 

4. The correct statement with respect to product *Y* is ***(JEE Adv. 2014)***

(a) It gives a positive Tollen's test and is a functional isomer of *X*

(b) It gives a positive Tollen's test and is a geometrical isomer of *X*

(c) It gives a positive iodoform test and is a functional isomer of *X*

(d) It gives a positive iodoform test and is a geometrical isomer of *X*

H Assertion & Reason Type Questions

Read the following statement (Assertion) and explanation (Reason) and answer each question as per the options given below :

(a) If both *assertion* and *reason* are correct, and *reason* is the correct explanation of the *assertion*.

(b) If both *assertion* and *reason* are correct, but *reason* is not the correct explanation of the *assertion*.

(c) If *assertion* is correct but *reason* is incorrect.

(d) If *assertion* is incorrect but *reason* is correct.

1. **Assertion :** Addition of Br_2 to 1-butene gives two optical isomers.

Reason : The product contains one asymmetric carbon. ***(1998 - 2 Marks)***

2. **Assertion :** 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.

Reason : It involves the formation of a primary radical. ***(2000S)***

3. **Assertion :** Addition of bromine to *trans*–2–butene yields *meso*–2,3–dibromobutane.

Reason : Bromine addition to an alkene is an electrophilic addition. ***(2001S)***

Section-B JEE Main / AIEEE

1. Which of these will not react with acetylene? **[2002]**
(a) NaOH (b) ammonical $AgNO_3$
(c) Na (d) HCl.

2. What is the product when acetylene reacts with hypochlorous acid? **[2002]**
(a) CH_3COCl (b) $ClCH_2CHO$
(c) Cl_2CHCHO (d) ClCHCOOH.

3. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be **[2003]**
(a) pentane (b) isopentane
(c) neopentane (d) propane

4. 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly **[2005]**
(a) 1-bromo-3-methylbutane
(b) 2-bromo-3-methylbutane
(c) 2-bromo-2-methylbutane
(d) 1-bromo-2-methylbutane

5. Butene-1 may be converted to butane by reaction with
(a) $Sn-HCl$ (b) $Zn-Hg$ **[2003]**
(c) Pd/H_2 (d) $Zn-HCl$

6. Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at 40°C gives predominantly **[2005]**
(a) 1-bromo-2-butene under kinetically controlled conditions
(b) 3-bromobutene under thermodynamically controlled conditions
(c) 1-bromo-2-butene under thermodynamically controlled conditions
(d) 3-bromobutene under kinetically controlled conditions

7. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is **[2005]**
(a) 2-methylpentane (b) 2, 2-dimethylbutane
(c) 2, 3-dimethylbutane (d) n-hexane

8. Acid catalyzed hydration of alkenes except ethene leads to the formation of
(a) mixture of secondary and tertiary alcohols
(b) mixture of primary and secondary alcohols
(c) secondary or tertiary alcohol
(d) primary alcohol

9. Which types of isomerism is shown by 2, 3-dichlorobutane? **[2005]**
(a) Structural (b) Geometric
(c) Optical (d) Diastereo

10. The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is **[2007]**
(a) benzyl alcohol (b) benzophenone
(c) acetophenone (d) benzoic acid.

11. Which of the following reactions will yield 2, 2-dibromopropane? **[2007]**
(a) $CH_3-CH=CH_2+HBr \rightarrow$
(b) $CH_3-C\equiv CH+2HBr \rightarrow$
(c) $CH_3CH=CHBr+HBr \rightarrow$
(d) $CH\equiv CH+2HBr \rightarrow$

12. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives predominantly **[2007]**
(a) m-chlorobenzene
(b) benzoyl chloride
(c) benzyl chloride
(d) o- and p-chlorotoluene.

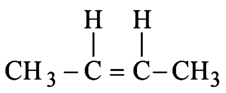
13. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated wth cuprous bromide. The reaction mixture so formed contans **[2008]**
(a) mixture of *o*- and *p*-bromotoluenes
(b) mixture of *o*- and *p*-dibromobenzenes
(c) mixture of *o*- and *p*-bromoanilines
(d) mixture of *o*- and *m*-bromotoluenes

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

$$CH_3-CH=CH-CH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B.$$

The compound B is **[2008]**
(a) CH_3CH_2CHO (b) CH_3COCH_3
(c) $CH_3CH_2COCH_3$ (d) CH_3CHO

15. The hydrocarbon which can react with sodium in liquid ammonia is **[2008]**
(a) $CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3$
(b) $CH_3CH_2C\equiv CH$
(c) $CH_3CH=CHCH_3$
(d) $CH_3CH_2C\equiv CCH_2CH_3$

16. The treatment of CH_3MgX with $CH_3C\equiv C-H$ produces
(a) $CH_3-CH=CH_2$ **[2008]**
(b) $CH_3C\equiv C-CH_3$
(c) 
$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-CH_3$
(d) CH_4

17. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is **[2010]**
(a) propene (b) 1-butene
(c) 2-butene (d) ethene

18. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of : **[2011]**

(a) two ethylenic double bonds
(b) a vinyl group
(c) an isopropyl group
(d) an acetylenic triple bond

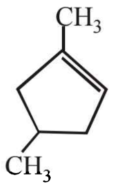
19. Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide ? **[2012]**

(a) Tertiary butyl chloride (b) Neopentane
(c) Isohexane (d) Neohexane

20. 2-Hexyne gives *trans*-2-Hexene on treatment with : **[2012]**

(a) Pt/H_2 (b) Li/NH_3
(c) $Pd/BaSO_4$ (d) $LiAlH_4$

21. Which compound would give 5 - keto - 2 - methylhexanal upon ozonolysis ? **[JEE M 2015]**

(a)


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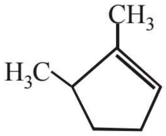

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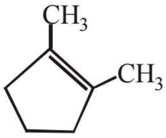

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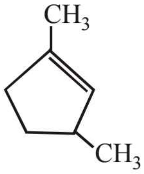
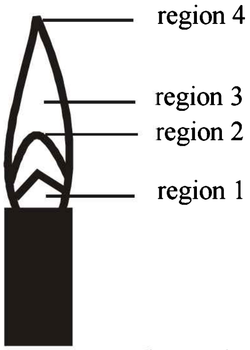


22. The hottest region of Bunsen flame shown in the figure below is : **[JEE M 2016]**



(a) region 3 (b) region 4
(c) region 1 (d) region 2

23. At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20% O_2 by volume for complete combustion. After combustion the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is: **[JEE M 2016]**

(a) C_4H_8 (b) C_4H_{10}
(c) C_3H_6 (d) C_3H_8

24. The reaction of propene with HOCl ($Cl_2 + H_2O$) proceeds through the intermediate: **[JEE M 2016]**

(a) $CH_3-CH(OH)-CH_2^+$

(b) $CH_3-CHCl-CH_2^+$

(c) $CH_3-CH^+-CH_2-OH$

(d) $CH_3-CH^+-CH_2-Cl$

10

Hydrocarbons

Section-A : JEE Advanced/ IIT-JEE

A **1.** ethyne **2.** 2-butyne **3.** C_2H_2

4. ethylene **5.** H_2SO_4, $HgSO_4$ **6.** less

7. 3, 4-dibromo-1-butene-1 (at low temperature) or 1, 4-dibromo-2-butene (at high temperature)

B **1.** F **2.** F

C

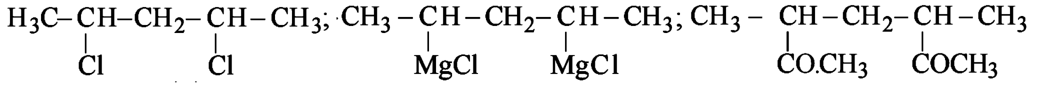
1. (b)	**2.** (b)	**3.** (a)	**4.** (c)	**5.** (c)	**6.** (c)	**7.** (a)
8. (a)	**9.** (c)	**10.** (b)	**11.** (a)	**12.** (d)	**13.** (a)	**14.** (d)
15. (a)	**16.** (c)	**17.** (b)	**18.** (b)	**19.** (a)	**20.** (b)	**21.** (d)
22. (a)	**23.** (d)	**24.** (b)	**25.** (b)	**26.** (a)	**27.** (d)	**28.** (c)
29. (b)	**30.** (a)	**31.** (b)				

D **1.** (b) **2.** (a, c) **3.** (a) **4.** (a, b, c, d) **5.** (d) **6.** (b, d) **7.** (b, c, d)

E **8.** C_6H_{12}

10. 55.55 *l* **11.** Butene-2 **12.** 3-methylpentene-1

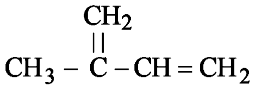
14.



$H_3C-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_3$; $CH_3-\underset{MgCl}{CH}-CH_2-\underset{MgCl}{CH}-CH_3$; $CH_3-\underset{CO.CH_3}{CH}-CH_2-\underset{COCH_3}{CH}-CH_3$

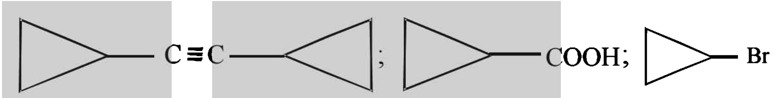
[X] [Y] [Z]

15.



$CH_3-\overset{CH_2}{\overset{||}{C}}-CH=CH_2$

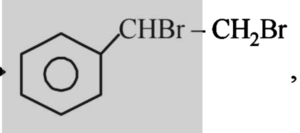
17.



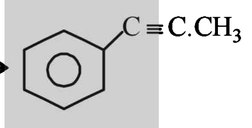
[A] [B] [C]

19. $CH_3CH_2CH=CHCH_2CH_3$

21. [A] →



, [B] →



22. A : $C_6H_5(CH_3)C=C(CH_3)C_6H_5$ B : $C_6H_5COCH_3$; C : $C_6H_5C_2H_5$ **23.** $R_3Al + TiCl$

cis – and *trans* –

G **1.** (d) **2.** (b) **3.** (a) **4.** (c)

H **1.** (a) **2.** (c) **3.** (b)

Section-B : JEE Main/ AIEEE

1. (a)	**2.** (c)	**3.** (c)	**4.** (c)	**5.** (c)	**6.** (c)	**7.** (c)
8. (a)	**9.** (c)	**10.** (d)	**11.** (b)	**12.** (d)	**13.** (a)	**14.** (d)
15. (b)	**16.** (d)	**17.** (c)	**18.** (b)	**19.** (b)	**20.** (b)	**21.** (d)
22. (d)	**23.** (d)	**24.** (d)				

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **Ethyne,** because of the high *s* character of the $-C\equiv H$ bond in ethyne (*sp* hybridisation).

2. **2-butyne**

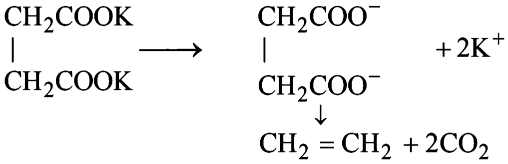
$$CH\equiv CH+Na\xrightarrow[NH_3]{Na,Liq}CH\equiv CNa\xrightarrow{NaNH_2}NaC\equiv CNa$$

$$NaC\equiv CNa+2CH_3I\rightarrow \underset{\text{2-Butyne}}{CH_3C\equiv C\,CH_3}$$

3. C_2H_2

$$CH\equiv CH+HCl\longrightarrow CH_2=CHCl\longrightarrow PVC$$

4. **ethylene**



$$\begin{matrix}CH_2COOK\\ |\\ CH_2COOK\end{matrix}\longrightarrow\begin{matrix}CH_2COO^-\\ |\\ CH_2COO^-\\ \downarrow\\ CH_2=CH_2\ +2CO_2\end{matrix}\quad +2K^+$$

5. H_2SO_4, $HgSO_4$

6. **less;**

NOTE:

$$\text{Stability of free radical}\propto\frac{1}{\text{Bond dissociation energy}}$$

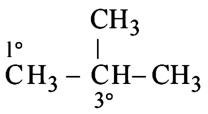
Benzyl ($C_6H_5\dot{C}H_2$) free radical is more stable than methyl ($\dot{C}H_3$) free radical because of hyperconjugation (no bond resonance).

7. **3, 4-dibromo-1-butene** (at low temperature) or **1, 4- dibromo-2-butene** (at high temperature)

B. True/False

1. **False :** Ethylene reacts with sulphuric acid to form ethyl hydrogen sulphate. It can be dried by passing it through phosphorus pentoxide.

2. **False :** Bromine is less reactive, hence it is more selective and thus 3° hydrogen will be removed more easily than the 1° hydrogen leading to 2-bromo-2-methylpropane as the main product.



$$\overset{1^\circ}{CH_3}-\underset{3^\circ}{\overset{\overset{CH_3}{|}}{C}H}-CH_3$$

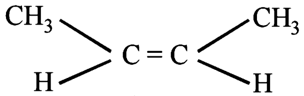
C. MCQs with One Correct Answer

2. **(b)** Unsaturated hydrocarbons decolourise alk. $KMnO_4$ solution; C_2H_4 ($H_2C=CH_2$) is an alkene.

3. **(a)** In a homologous series, higher the number of C-atoms, higher is the b.p.

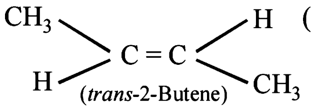
4. **(c)** Four isomers

(i) $\underset{\text{(1–butene)}}{CH_3CH_2CH=CH_2}$ (ii)



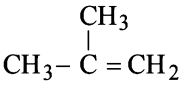
(*cis*-2-Butene)

(iii)



(*trans*-2-Butene)

(iv)



$$\underset{\text{(2–Methylpropene)}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2}$$

5. **(c)** $CH_3C\equiv CH+H_2O\xrightarrow[HgSO_4]{H_2SO_4}$

$$[CH_3CH(OH)=CH_2]\rightarrow\underset{\text{acetone}}{CH_3COCH_3}$$

6. **(c)** $CH_2=CH_2+H_2SO_4\rightarrow CH_3CH_2OSO_3H$

$C_6H_6+H_2SO_4\rightarrow C_6H_5SO_3H+H_2O$

$C_6H_{14}+H_2SO_4\rightarrow$ No reaction

$C_6H_5NH_2+H_2SO_4\rightarrow C_6H_5\overset{+}{N}H_3HSO_4^-$

Only hexane does not dissolve in conc. H_2SO_4 even on warming.

8. **(a)** Acidic hydrogen is present in alkynes, attached to the triply bonded C-atoms. They can be easily removed by means of a strong base.

9. **(c)** **TIPS/Formulae :**

Anti-Markovnikoff's addition of HBr is observed only with unsymmetrical alkenes, *a*, *b*, and *d*.

$\underset{(a)}{CH_3CH=CH_2}$ $\underset{(b)}{CH_2=CHCH_2CH_3}$

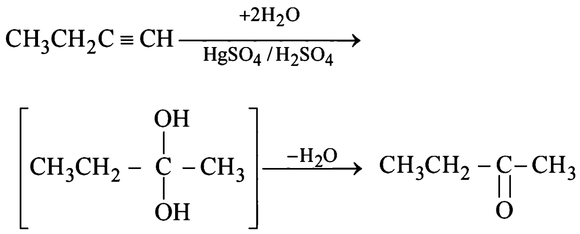
$\underset{(c)}{CH_3CH=CHCH_3}$ $\underset{(d)}{CH_3CH=CHCH_2CH_3}$

10. **(b)** For isomeric alkanes, th one having longest straight chain has highest b.p. because of larger surface area.

11. **(a)** Ethylene has restricted rotation [due to C = C], acetylene no rotation [due to C ≡ C], hexachloroethane has more rotation than ethylene but less than ethane because of greater size of the substituent (chlorine) than in ethane (substituent is hydrogen).

13. **(a)** **TIPS/Formulae :**

Hydration of alkynes via mercuration takes place in accordance with Markovnikov's manner rule



$$CH_3CH_2C\equiv CH\xrightarrow[HgSO_4/H_2SO_4]{+2H_2O}$$

$$\left[CH_3CH_2-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3\right]\xrightarrow{-H_2O}CH_3CH_2-\underset{\underset{O}{||}}{C}-CH_3$$

14. **(d)** In propyne ($CH_3C\equiv CH$), the terminal hydrogen is acidic and reacts with ammonical $AgNO_3$.

15. **(a)** **TIPS/Formulae :**

The relative rates of hydrogenation decreases with increase of steric hinderance.

$R_2C=CH_2 > RCH=CHR > R_2C=CHR > R_2C=CR_2$

Among the four olefins, (a) and (b) are less stable (Saytzeff rule). Further in (a), the bulky alkyl groups are on same side (*cis*-isomer), hence it is less stable.

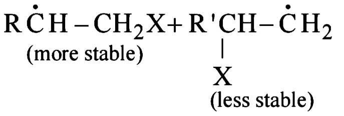
16. **(c)** **TIPS/Formulae :**

Peroxide effect is effective only in case of HBr and not in case of HCl and HI.

Step: I (a) $R-O-O-R \xrightarrow{\Delta} 2RO\cdot$;

Step: I (b) $RO\cdot + H-X \longrightarrow RO-H + X\cdot$

Step II: $R'CH=CH_2 + X^{\bullet} \longrightarrow$



$$R\dot{C}H-CH_2X + R'\underset{\underset{X}{|}}{C}H-\dot{C}H_2$$

(more stable) (less stable)

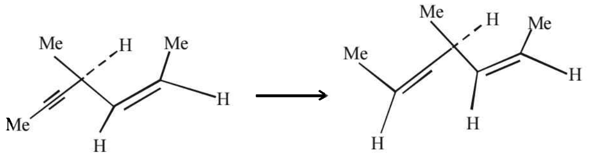
$R'-\dot{C}H-CH_2X + HX \longrightarrow R'-CH_2-CH_2X + X\cdot$

For HCl, Step–I (b) is endothermic while step–II is exothermic but for HI, Step–I(b) is exothermic while Step–II is endothermic.

17. **(b)** **TIPS/Formulae :**

Addition on triple bond takes place by the *syn*-addition of hydrogen.

Since the configuration of the double bond already present is *cis*, the compound formed will have a plane of symmetry and hence optically inactive.



18. **(b)** **TIPS/Formulae :**

Alkenes undergo electrophilic addition reactions.

HOCl undergoes self–ionization

$(HOCl + HOCl \longrightarrow H_2O + OCl^- + Cl^+)$

to give $H_2O^+ + OCl^- + Cl^+$.

So, it is the Cl^+ that attacks in the first step.

19. **(a)** **TIPS/Formulae :**

The π bond is formed by the sideways overlapping of two *p*-orbitals of the two carbon atoms.

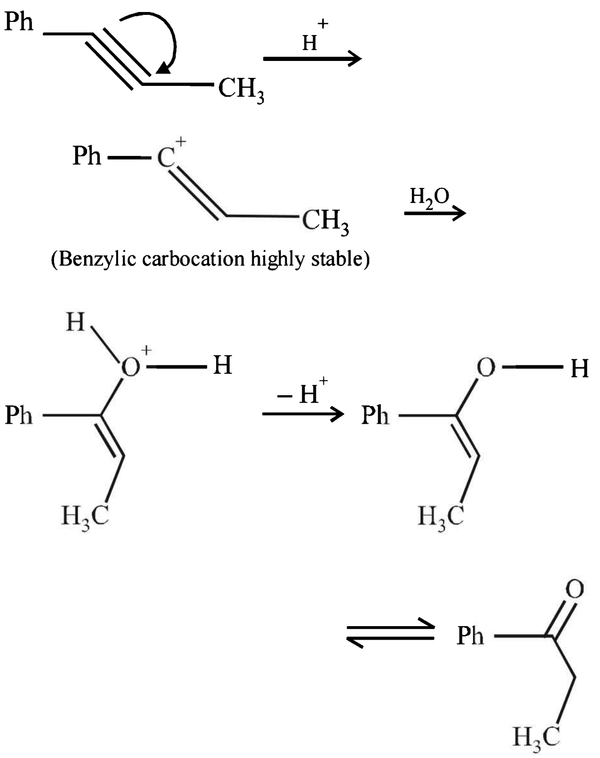
The molecular plane does not have any π electron density as the *p*-orbitals are perpendicular to the plane containing the ethene molecule. The nodal plane in the π-bond of ethene is located in the molecular plane.

20. **(b)** $Br^{\bullet}$ is less reactive and more selective and so the most stable free radical (3°) will be the major product.

21. **(d)** **TIPS/Formulae :**

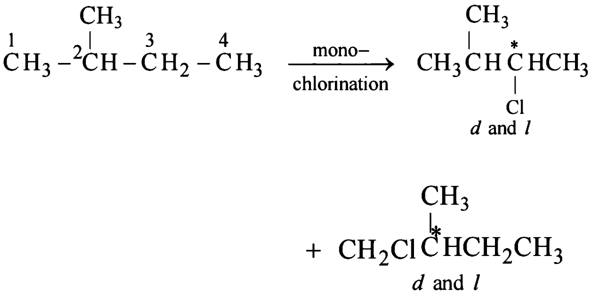
In 1-butyne terminal hydrogen is acidic where as in 2-butyne there is no terminal hydrogen. Thus 2-butyne will not react with ammonical Cu_2Cl_2. While 1-butyne, being terminal alkyne, will give red ppt. with ammonical cuprous chloride

22. **(a)**



23. **(d)** $H_2/Pd/BaSO_4$ reduces an alkyne to *cis*-alkene, H_2/Pt reduces it to alkane, $NaBH_4$ does not reduce an alkyne. Reduction of an alkyne by active metal in liq. NH_3 gives *trans*-alkene.

24. **(b)**



$$\overset{1}{C}H_3-\overset{2}{\underset{}{\overset{CH_3}{\overset{|}{C}}}}H-\overset{3}{C}H_2-\overset{4}{C}H_3 \xrightarrow[\text{chlorination}]{\text{mono–}} CH_3\overset{\overset{CH_3}{|}}{C}H\overset{*}{\underset{\underset{Cl}{|}}{C}}HCH_3 \quad (d \text{ and } l)$$

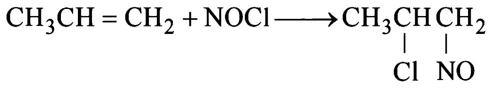
$$+\ CH_2Cl\overset{\overset{CH_3}{|}}{\overset{*}{C}}HCH_2CH_3 \quad (d \text{ and } l)$$

(i) Chlorination at C-2 and C-4 produces no chiral compounds

(ii) Chlorination at C-3 produces a chiral carbon marked with star (*d* and *l* form).

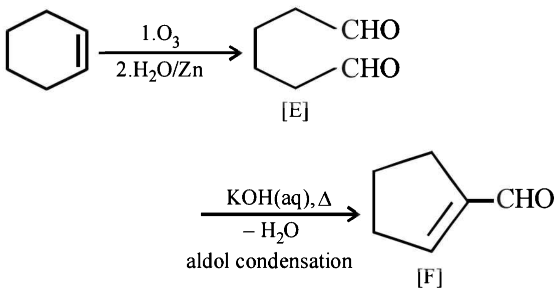
(iii) Chlorination at C-1 also produces a chiral carbon marked with star (*d* and *l* form).

25. **(b)** Nitrosyl chloride adds on olefins according to Markovnikof's rule, where NO^+ constitutes the positive part of the addendum.



$$CH_3CH=CH_2 + NOCl \longrightarrow CH_3\underset{\underset{Cl}{|}}{C}H\underset{\underset{NO}{|}}{C}H_2$$

26. **(a)**



27. **(d)** Only (d) can form 3-Octyne

$$CH_3CH_2C \equiv CH \xrightarrow[-NH_3]{NaNH_2} CH_3CH_2C \equiv C^-Na^+$$

$$\xrightarrow[(S_N2)]{CH_3CH_2CH_2CH_2Br}$$

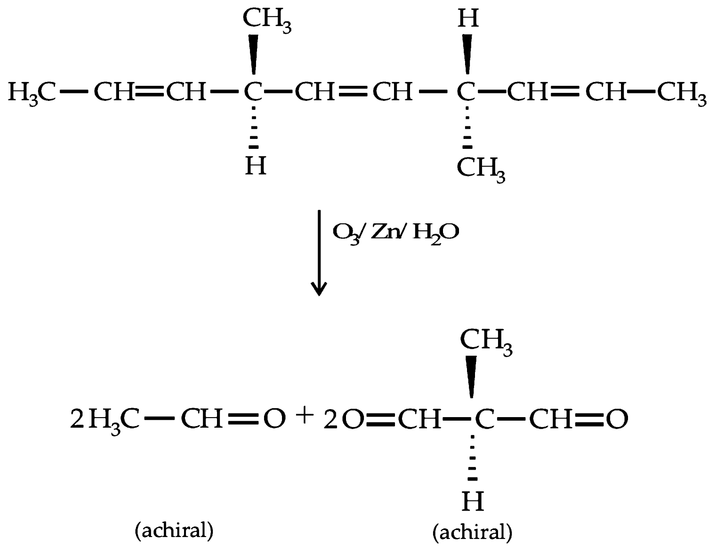
$$CH_3CH_2C \equiv CCH_2CH_2CH_2CH_3 + NaBr$$

28. **(c)** $C-C$ bond energy $= 348$ kJ/mol $= \frac{348}{4.2}$ kcal/mol

$= 82.85$ kcal/mol $\approx$ 100 kcal/mol.

29. **(b)** **Allene (C_3H_4) is** $H_2\overset{sp^2}{C} = \overset{sp}{C} = \overset{sp^2}{C}H_2$

30. **(a)**



31. **(b)** Greater the extent of branching, lesser is the boiling point of the hydrocarbon, so order of b.p is III > II > I.

D. MCQs with One or More Than One Correct

1. **(b)** **TIPS/Formulae :**

Heat of hydrogenation is related to stability of molecules; higher the stability, lower is the heat of hydrogenation.

Butadiene, $CH_2=CHCH=CH_2$ has two double bonds so its heat of hydrogenation will be more than the other three.

Alkenes follow the following order of stability

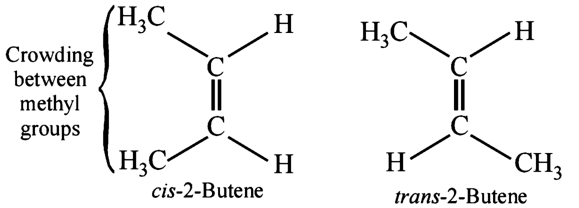
$$\underset{\substack{\text{tetrasubstituted}\\ \text{(most stable due to}\\ \text{hyper conjugative}\\ \text{sturctures)}}}{R_2C = CR_2} > R_2C = CHR > RCH = CHR$$

$$> RCH = CH_2 > \underset{\substack{\text{Unsubstituted}\\ \text{(least stable due to}\\ \text{no hyperconjugation)}}}{CH_2 = CH_2}$$

Thus here stability order of the given monoalkenes is

$$\underset{\substack{\text{Butene-2}\\ (\textit{trans-} \text{ and } \textit{cis-})}}{CH_3CH = CHCH_3} > \underset{\text{Butene-1}}{CH_3CH_2CH = CH_2}$$

NOTE : The *trans*-2-butene is more stable than the *cis*-because in the *cis*-isomer the two bulky groups are crowded together with the result it has more van der Waal's strain than the *trans*-isomer.

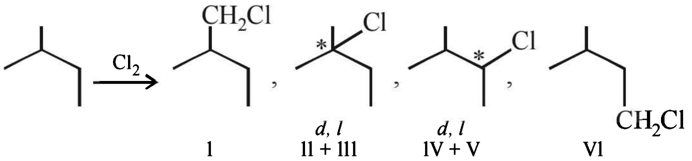


cis-2-Butene

trans-2-Butene
(Less van der Waal's strain hence more stable)

2. **(a, c)** Hyperconjugation in toluene activates the benzene ring for electrophilic substitution.

3. **(a)**

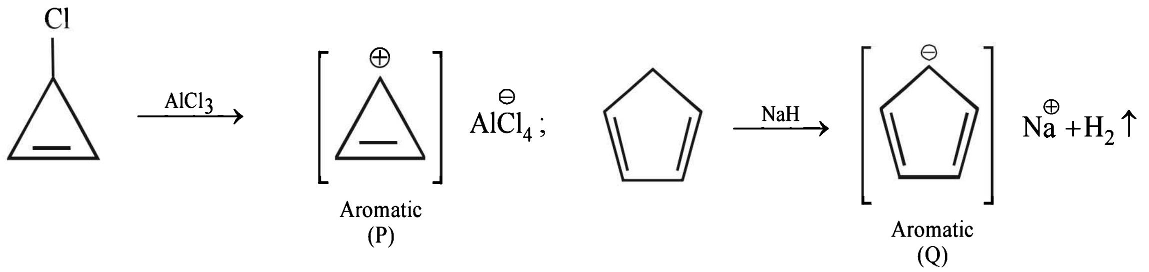


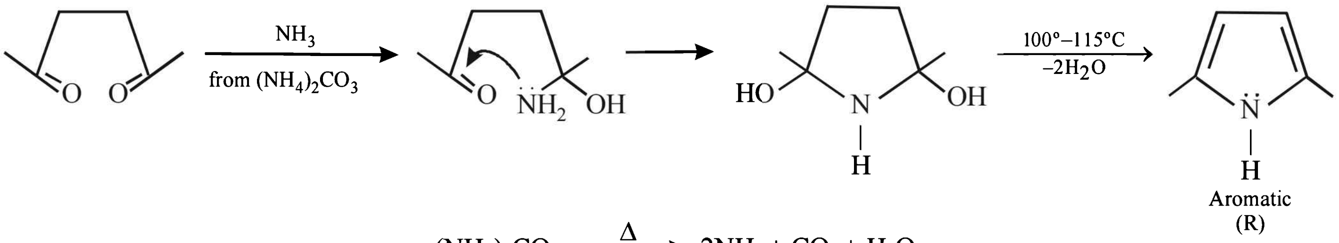
So, the value of N will be $1+2+2+1=6$.

Since enantiomers have nearly same physical properties, II and III as well as IV and V can't be separated, hence the number of isomers (M) will be

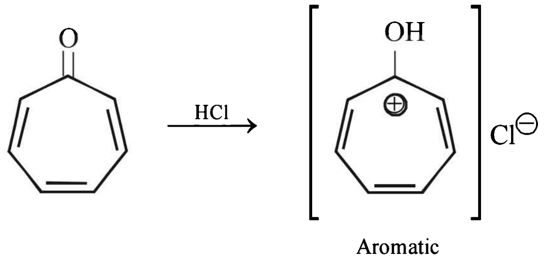
$1+1+1+1=4$.

4. (a, b, c, d)



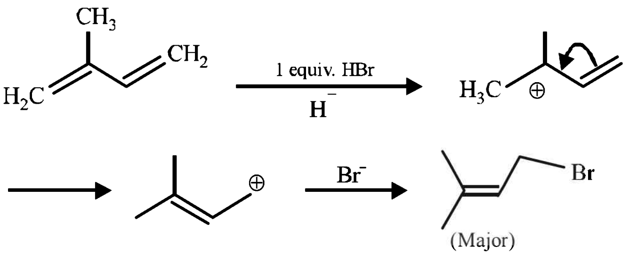


$(NH_4)_2CO_3 \xrightarrow{\Delta} 2NH_3 + CO_2 + H_2O$

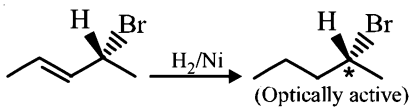


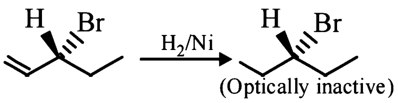
Note : P has 2 π electrons, while Q, R & S have 6 π electrons each. Hence all the 4 are aromatic.

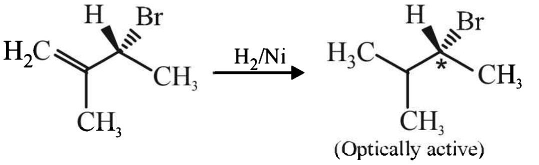
5. (d)

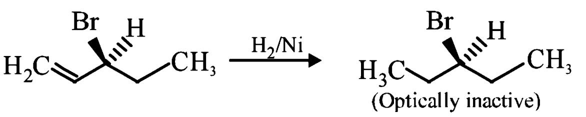


6. (b, d)

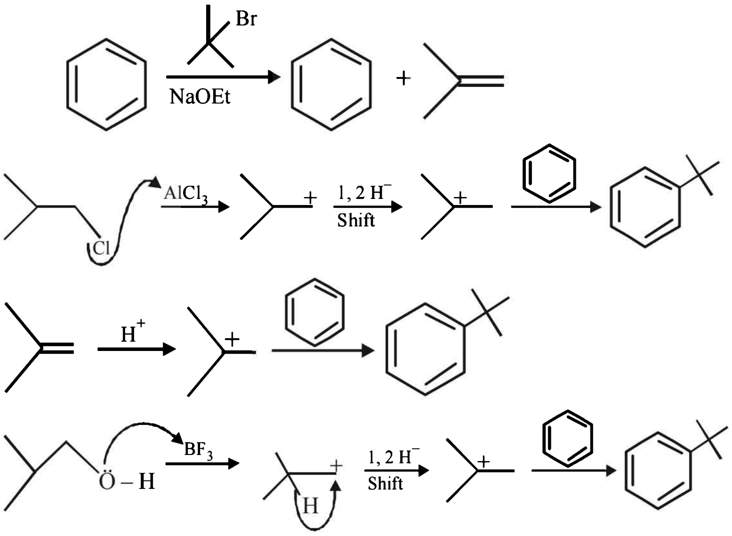
(A)


(B)


(C)


(D)


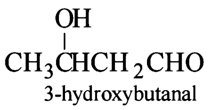
7. (b, c, d)



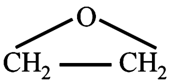
E. Subjective Problems

1. Bromine water test : C_2H_2 decolourises bromine water while CH_4 does not decolourises bromine water.

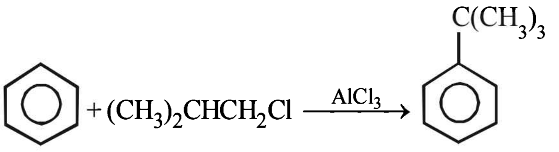
2. (*i*) $\underset{\text{ethyne}}{CH \equiv CH} \xrightarrow{\text{hydration}} CH_3CHO \xrightarrow[\text{aldol cond.}]{OH^-}$



$\underset{\text{3-hydroxybutanal}}{CH_3\overset{OH}{C}HCH_2CHO} \xrightarrow{-H_2O} CH_3 = CHCHO$

(*ii*)


Ethylene oxide

(*iii*)


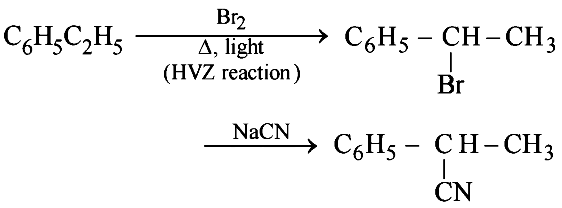
NOTE : that the 1° carbocation, $(CH_3)_2CH\overset{+}{C}H_2$ formed during reaction rearranges to the more stable, 3° carbocation, $(CH_3)_3\overset{+}{C}$ and hence the above product is formed.] (see also *ix* part)

(*iv*) $C_6H_6+(CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4} C_6H_5(CH_3)_3$ *tert*–Butylbenzene

Explanation :

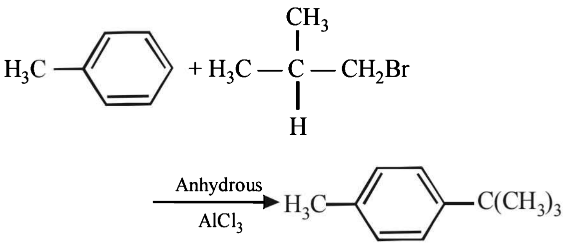
$$(CH_3)_2CHCH_2OH \xrightarrow{H^+} \underset{1^\circ\text{ carbocation}}{(CH_3)_2CH\overset{+}{C}H_2}$$

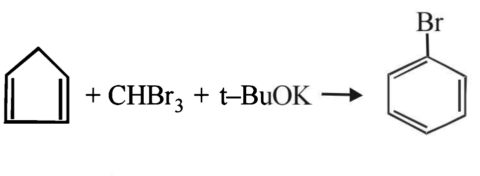
$$\xrightarrow[\text{to}]{\text{rearranges}} \underset{3^\circ\text{ carbocation}}{(CH_3)_3C^+} \xrightarrow{C_6H_6} C_6H_5C(CH_3)_3$$

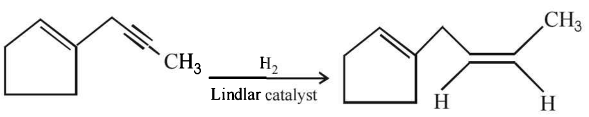
(*v*)


$$C_6H_5C_2H_5 \xrightarrow[\substack{\Delta,\text{ light}\\ \text{(HVZ reaction)}}]{Br_2} C_6H_5-\underset{\substack{|\\Br}}{CH}-CH_3 \xrightarrow{NaCN} C_6H_5-\underset{\substack{|\\CN}}{CH}-CH_3$$

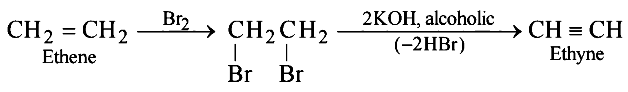
2–phenylpropanenitrile

(*vi*)


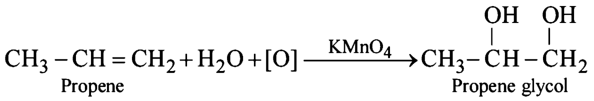
(*vii*)


(*viii*)


(Partial reduction of triple bond in syn-manner)

3.


$$\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{Br_2} \underset{\substack{|\quad|\\Br\ \ Br}}{CH_2CH_2} \xrightarrow[(-2HBr)]{\text{2KOH, alcoholic}} \underset{\text{Ethyne}}{CH\equiv CH}$$

4.


$$\underset{\text{Propene}}{CH_3-CH=CH_2+H_2O+[O]} \xrightarrow{KMnO_4} \underset{\text{Propene glycol}}{CH_3-\underset{}{\overset{\substack{OH\\|}}{C}H}-\overset{\substack{OH\\|}}{C}H_2}$$

[**NOTE :** Colour of $KMnO_4$ is discharged]

5. (*i*) **TIPS/Formulae :**

Chlorination of methane is a free radical substitution reaction.

In dark, chlorine is unable to be converted into free radicals, hence the reaction does not occur.

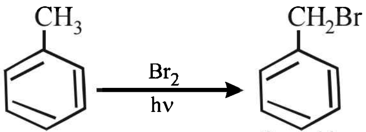
(*ii*) **TIPS/Formulae :**

Addition of unsymmetrical addendum (HBr in present case) to unsymmetrical olefin ($CH_3CH=CH_2$, in present case) takes place according to Markownikoff rule.

$$\underset{\text{Propene}}{CH_3CH=CH_2}+HBr \rightarrow \underset{\textit{iso}\text{-Propyl bromide}}{CH_3.CHBr.CH_3}$$

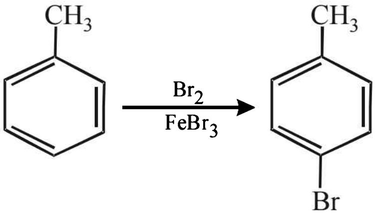
(*iii*) Unlike olefins, π-electrons of benzene are delocalised (resonance) and hence these are unreactive towards addition reactions. Moreover, addition reaction leads to destruction of the benzenoid ring.

(*iv*) In presence of light, toluene undergoes *side chain bromination* through a free radical mechanism.



Benzyl bromide

In presence of $FeBr_3$, toluene undergoes *electrophilic substitution* in the benzene ring.

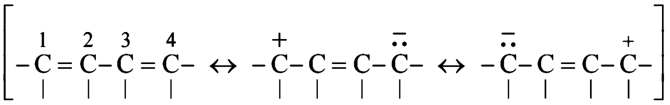


p-bromotoluene

[**NOTE :**–CH_3 is *o*-, *p*-directing]

(v) **TIPS/Formulae :**

1, 3 - Butadiene is a conjugated diene and is a reasonance hybrid:



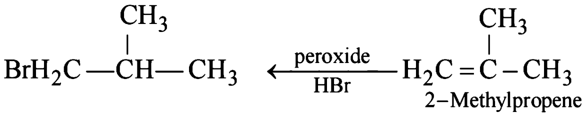
$$\left[\overset{1}{-C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C}- \leftrightarrow -\overset{+}{C}-C=C-\overset{\cdot\cdot}{\bar{C}}- \leftrightarrow -\overset{\cdot\cdot}{\bar{C}}-C=C-\overset{+}{C}-\right]$$

Thus resonance induces some double bond character in the central C-C bond leading to the shortening of this bond. **Alternatively**, all the four C atoms of 1, 3–butadiene are sp^2 hybridised and thus their C – C bond length will be lower than that of n- butane in which all the four C atoms are sp^3 hybridised.

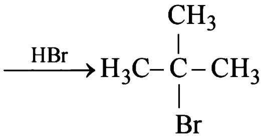
(*vi*) *tert*-Butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$ because it does not contain any hydrogen atom on the key carbon atom.

(*vii*) Reduction of cental ring to form A involves reduction of all the three cyclobutadiene rings (which are antiaromatic as they have 4π electrons each), i.e. antiaromatic rings are converted into nonaromatic rings. On the other hand, reduction of the terminal ring to form B involves reduction of only one antiaromatic ring. *Remember that antiaromatic rings impart unstability.*

6. (*i*) **NOTE :** Under normal conditions, *ter*-butyl bromide is formed, isobutyl bromide is formed in presence of peroxide.



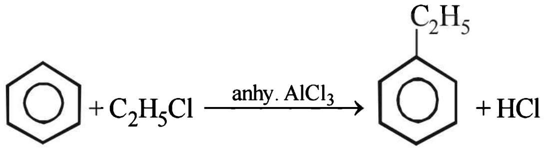
$$BrH_2C-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xleftarrow[HBr]{peroxide} \underset{\text{2-Methylpropene}}{H_2C=\overset{\overset{CH_3}{|}}{C}-CH_3}$$



$$\xrightarrow{HBr} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3$$

(*ii*) Ethyne (HC ≡ CH) and only those derivatives which have at least one acetylenic hydrogen atom (≡ C – H) i.e. terminal alkynes will give white precipitate with ammonical silver nitrate solution.

7. $[C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl]$



Benzene Ethylbenzene

8. **Calculation of molecular formula of A.**

Element	Percentage	Relative No. of atoms	Simplest whole ratio
C	85.7	85.7/12=7.14	7.14/7.14=1
H	14.3	14.3/1=14.3	14.3/7.14=2

∴ Empirical formula of A = CH_2

Determination of molecular weight of A

1 g of A consumes = 38.05 g of 5% Br_2 (in CCl_4)

$$= \frac{38.05 \times 5}{100} \text{ g of } 100\% \ Br_2$$

$$= 1.90 \text{ g of } 100\% \ Br_2.$$

Now since 1.90 g of Br_2 is consumed by 1 g of compound A

∴ 160 g (1 mole) of Br_2 will be consumed by

$$= \frac{1}{1.90} \times 160 = 84.2 \text{ g of A} = 84.0 \text{ (app.)g of A}$$

∴ Molecular weight of A = **84**

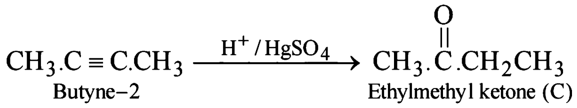
$$\text{Hence, } n = \frac{84}{12+2} = 6$$

∴ Molecular formula of A = $(CH_2)_6 = \mathbf{C_6H_{12}}$

Since the hydrocarbon A consumes 1 molar equivlaent of hydrogen, it must contain one double bond. Oxidation of compound A with $KMnO_4$ to form compound C (C_4H_8O) and acetic acid indicates $=CH.CH_3$ fragment in A, i.e.

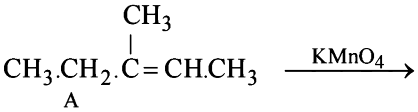
$$\underset{A}{C_4H_8=CHCH_3} \xrightarrow{KMnO_4} \underset{C}{C_4H_8O} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Now the fragment C_4H_8 of A on oxidation forms the compound 'C' (C_4H_8O) which may be easily obtained from butyne-2 and acidic aq. $HgSO_4$, the compound 'C' must be ethylmethyl ketone.

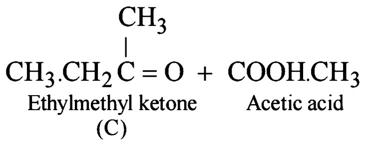


$$\underset{\text{Butyne-2}}{CH_3.C\equiv C.CH_3} \xrightarrow{H^+/HgSO_4} \underset{\text{Ethylmethyl ketone (C)}}{CH_3.\overset{\overset{O}{||}}{C}.CH_2CH_3}$$

The formation of ketone 'C' from C_4H_8 fragment of 'A' can be explained by the following structure of A.

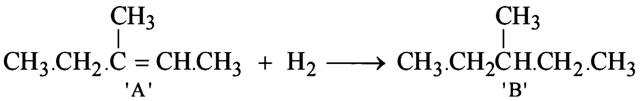


$$\underset{A}{CH_3.CH_2.\overset{\overset{CH_3}{|}}{C}=CH.CH_3} \xrightarrow{KMnO_4}$$



$$\underset{\text{Ethylmethyl ketone (C)}}{CH_3.CH_2\overset{\overset{CH_3}{|}}{C}=O} + \underset{\text{Acetic acid}}{COOH.CH_3}$$

Hence formation of 'B' can be represented as below.



$$\underset{'A'}{CH_3.CH_2.\overset{\overset{CH_3}{|}}{C}=CH.CH_3} + H_2 \longrightarrow \underset{'B'}{CH_3.CH_2\overset{\overset{CH_3}{|}}{CH}.CH_2.CH_3}$$

9. (i) By amm. $AgNO_3$ or by acidic-H tests : Terminal alkynes give white precipitate with amm. $AgNO_3$ or red ppt. with amm. Cu_2Cl_2 (H atom attached on *sp* hybridized carbon is acidic).

$2CH_3CH_2C\equiv CH + Ag_2O \rightarrow 2CH_3CH_2C\equiv CAg + H_2O$

$CH_3-C\equiv C-CH_3 + Ag_2O \rightarrow$ No reaction

NOTE : Only terminal alkynes respond to these reactions.

(ii) Cyclohexene gives positive response to *bromine water test* and *Baeyer's test* while cyclohexane does not respond to these reagents.

10. $2C_2H_6 \xrightarrow{\text{monobromination}} 2C_2H_5Br$ (yield 90%) (given)

$2C_2H_5Br \xrightarrow[\text{reaction}]{\text{Wurtz}} C_4H_{10} + 2HBr$ (yield 85%) (given)

Moles of *n*-butane to be produced

$$= \frac{55 \text{ g}}{58 \text{ g mol}^{-1}} = 0.948 \text{ mol} \ (\because \text{molecular mass of } C_4H_{10} = 58)$$

Amount of C_2H_5Br required to obtain 0.948 mol. of C_4H_{10} $= 2 \times 0.948$ mol.

Hence, the amount of C_2H_5Br required

$$= \frac{2 \times 0.948 \times 100}{85} \text{ mol.} \quad ...(1) \quad [\because \text{ yield is 85\% only}]$$

Further 1 mole of C_2H_6 gives one mole of C_2H_5Br, hence number of moles of C_2H_6 reqd. for C_2H_5Br in (1)

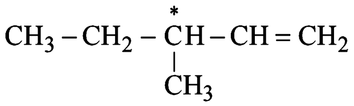
$$= \frac{2 \times 0.948 \times 100 \times 100}{85 \times 90} \text{ mol.} = 2.48 \text{ mol} \quad [\because \text{ yield is 90\%}]$$

∴ Required volume of ethane at NTP

$= 22400 \times 2.48 = 55552$ ml. = **55.55 litres**

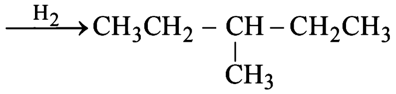
11. **TIPS/Formulae :**
A symmetric alkene does not follow Markovnikoff and *anti*-Markovnikoff's rule (Peroxide effect).
B has to be a symmetric alkene (**butene-2**)
$CH_3CH=CHCH_3$ as it will give the same product
$CH_3-CH(Br)-CH_2-CH_3$ in presence /absence of peroxide.

12. An optically active hydrocarbon will have an asymmetric C-atom. This means D(C_6H_{12}) should have an asymmetric C-atom & C_6H_{14} will have **no** asymmetric C-atom, hence D would be **3-methylpentene-1**,



$CH_3-CH_2-\overset{*}{C}H(CH_3)-CH=CH_2$

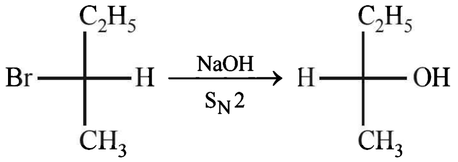
(D) Optically active (C_6H_{12})



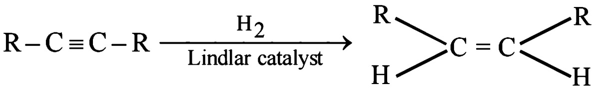
$\xrightarrow{H_2} CH_3CH_2-CH(CH_3)-CH_2CH_3$

Optically inactive (C_6H_{14})

13. (i) S_N2 reaction leads to inversion in configuration.



(ii) $R-C\equiv C-R \xrightarrow[\text{Lindlar catalyst}]{H_2}$

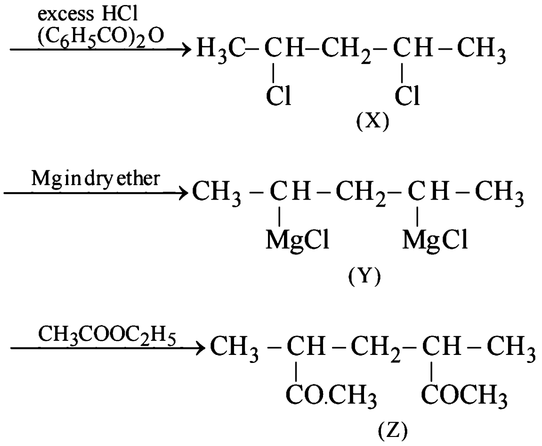


(*cis*-alkene)

NOTE :
(i) **Lindlar's catalyst** is Pd supported over $CaCO_3$ which is partially poisoned by $(CH_3COO)_2Pb$. It can restrict the hydrogenation of alkyne to alkene stage. It yields a *cis*-alkene.
(ii) Reduction of alkynes to alkene stage can also be carried out with sodium or lithium in liquid NH_3. Here *trans*-alkene is major product.

14. **TIPS/Formulae :**
(i) 1, 4-Pentadiene reacts with HCl in presence of benzoyl peroxide in Markownikoff's way.
NOTE : : Peroxide effect applies to HBr only.
(ii) Grignard reagent reacts with ethyl acetate to form ketones, or *ter*-alcohol if Grignard reagent is taken in excess.
Thus the given reactions can be written as below.

$H_2C=CH-CH_2-CH=CH_2$

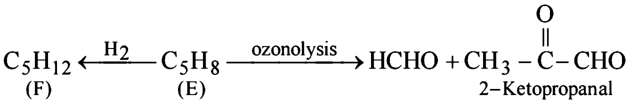


$\xrightarrow[(C_6H_5CO)_2O]{\text{excess HCl}} H_3C-CH(Cl)-CH_2-CH(Cl)-CH_3$ (X)

$\xrightarrow{\text{Mg in dry ether}} CH_3-CH(MgCl)-CH_2-CH(MgCl)-CH_3$ (Y)

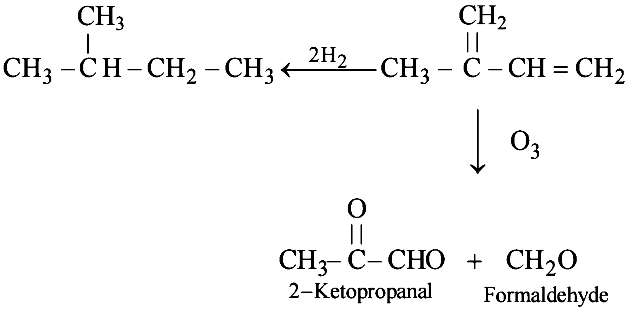
$\xrightarrow{CH_3COOC_2H_5} CH_3-CH(CO.CH_3)-CH_2-CH(COCH_3)-CH_3$ (Z)

15. Summary of the given reactions



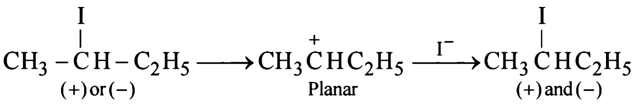
$\underset{(F)}{C_5H_{12}} \xleftarrow{H_2} \underset{(E)}{C_5H_8} \xrightarrow{\text{ozonolysis}} HCHO + \underset{\text{2-Ketopropanal}}{CH_3-\overset{O}{\overset{\|}{C}}-CHO}$

Since hydrogenation of (E) to (F) takes up two molecules of hydrogen, it indicates the presence of two double bonds in E which is further supported by its ozonolysis to form two products having three carbonyl groups. Further structure of ozonolysis product leads to following structure to compound (E).



$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_3 \xleftarrow{2H_2} CH_3-\overset{CH_2}{\overset{\|}{C}}-CH=CH_2 \xrightarrow{O_3} \underset{\text{2-Ketopropanal}}{CH_3-\overset{O}{\overset{\|}{C}}-CHO} + \underset{\text{Formaldehyde}}{CH_2O}$

16. **TIPS/Formulae :**
In S_N1 reaction racemization as well as inversion is observed. Reaction of optically active 2-iodobutane with NaI in acetone is an S_N1 reaction which involves formation of carbocation as intermediate.



$\underset{(+)\text{or}(-)}{CH_3-\overset{I}{\overset{|}{C}}H-C_2H_5} \longrightarrow \underset{\text{Planar}}{CH_3\overset{+}{C}HC_2H_5} \xrightarrow{I^-} \underset{(+)\text{and}(-)}{CH_3\overset{I}{\overset{|}{C}}HC_2H_5}$

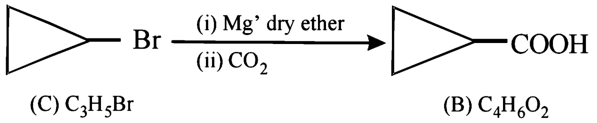
Thus the product, being a racemic mixture will be optically inactive.

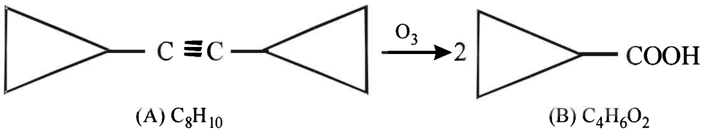
17. Summary of the given facts

$$\underset{(A)}{C_8H_{10}} \xrightarrow[\text{(ii)hydrolysis}]{\text{(i)}O_3} \underset{(B)}{C_4H_6O_2} \xleftarrow[\text{(ii)}CO_2,\ \text{(iii)}H^+]{\text{(i)Mg in dry ether}} \underset{(C)}{C_3H_5Br}$$

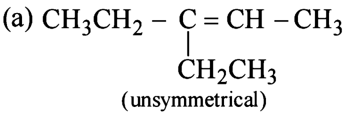
Since compound (B) is obtained from compound (C) C_3H_5Br through reaction with Mg and CO_2, it seems that compound

(B) is a carboxylic acid formed via the formation of Grignard reagent. Hence compound (C) should be an alkyl halide having three carbon atoms. The alkyl halide (C) is unsaturated (indicated by number of hydrogen atoms) which is present in the form of ring and thus (C) should be bromocyclopropane.

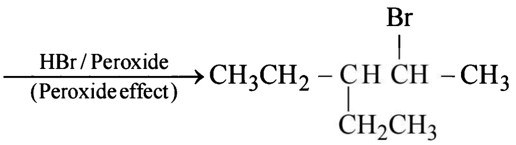




18. (a)

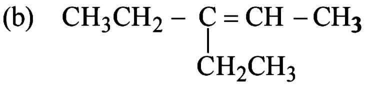


$CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}=CH-CH_3$
(unsymmetrical)

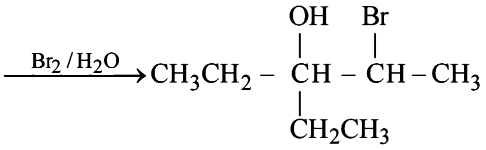


$\xrightarrow[\text{(Peroxide effect)}]{\text{HBr / Peroxide}} CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}H}\ \overset{\displaystyle Br}{\overset{|}{C}H}-CH_3$

(b)

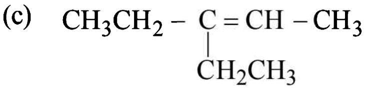


$CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}=CH-CH_3$

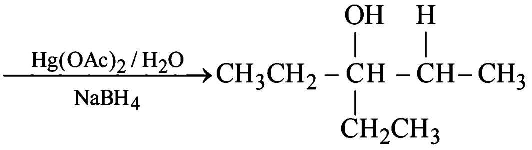


$\xrightarrow{Br_2/H_2O} CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}H}}}-\overset{\displaystyle Br}{\overset{|}{C}H}-CH_3$

(c)



$CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}=CH-CH_3$



$\xrightarrow[NaBH_4]{Hg(OAc)_2/H_2O} CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}H}}}-\overset{\displaystyle H}{\overset{|}{C}H}-CH_3$

19. TIPS/Formulae :

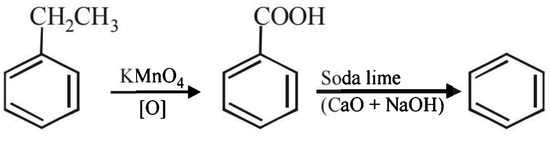
(i) It should be an alkene as it adds one mole of H_2.

(ii) The C_6 alkene should be symmetrical because on oxidation it gives a single carboxylic acid having three carbon atoms.

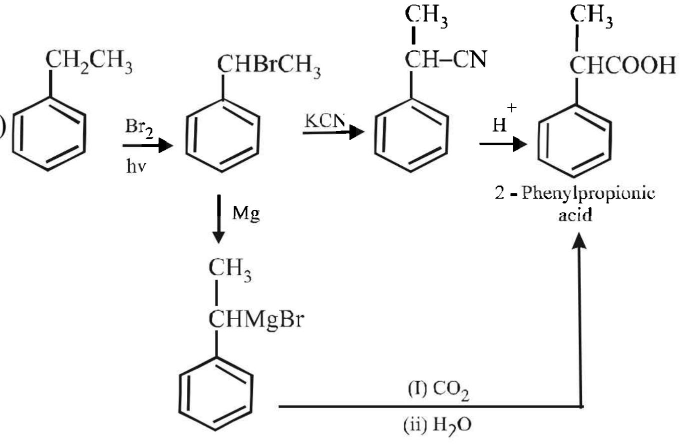
$$\underset{n\text{–Hexane}}{CH_3(CH_2)_4CH_3} \xleftarrow{H_2} \underset{(A)}{CH_3CH_2CH=CHCH_2CH_3}$$

$$\xrightarrow[KMnO_4]{(O)} 2CH_3CH_2COOH$$

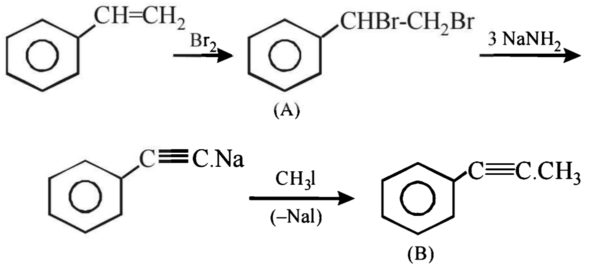
20. (i)



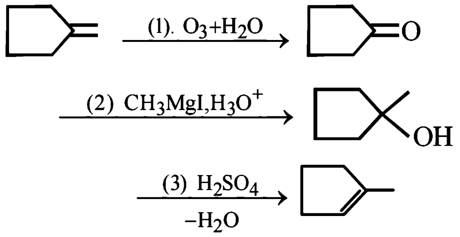
(ii)



21. (i)



(ii)

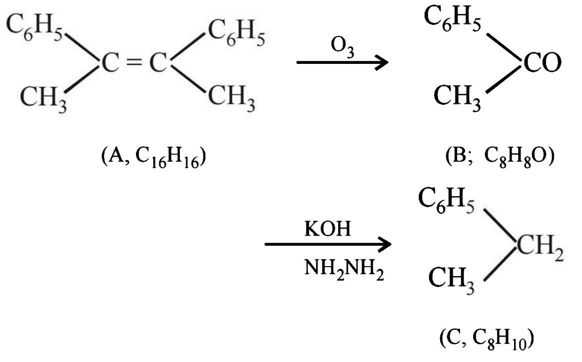


22.

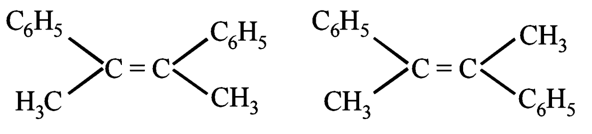
$$\begin{tikzcd} \underset{(A)}{\underset{\text{(an alkene)}}{C_{16}H_{16}}} \arrow[r, "O_3"] & \underset{(B)}{\text{only } C_8H_8O} \arrow[r, "NaOH/I_2"] \arrow[d, "KOH / NH_2NH_2"] & C_6H_5COONa \\ & \underset{(C)}{C_8H_{10}} & \end{tikzcd}$$

(i) Conversion of (B) to (C) involves iodoform reaction, hence (B) must contain – $COCH_3$ group leading to $C_6H_5COCH_3$ (C_8H_8O) as its molecular formula.

(ii) Since the given alkene gives only one product on ozonolysis, so the given alkene must be a symmetrical alkene containing a double bond in centre. Thus the alkene (A) must have following structure



Isomeric structures of A



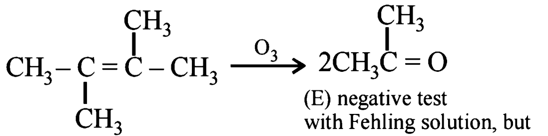
cis *trans*

NOTE : Since catalytic hydrogenation of alkenes takes place in *cis -(syn-)* manner; hence recemic mixture will be formed by the *trans*-isomer.

23. Ziggler – Natta catalyst ($R_3Al + TiCl_4$)

24. (i) Formation of HCOONa and a primary alcohol due to **Cannizzaro reaction** of F and G indicate that either F or G should be HCHO. Thus the alkene A should have $CH_2=$ grouping. The remaining 5 C's of A should have grouping $= HCC_4H_9$.

(ii) Formation of only E by the ozonolysis of D (C_6H_{12}) indicates that D should have following structure



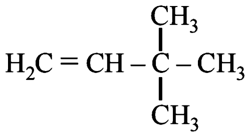
$$CH_3-\underset{CH_3}{C}=\overset{CH_3}{C}-CH_3 \xrightarrow{O_3} 2CH_3\overset{CH_3}{C}=O$$

(D)

(E) negative test with Fehling solution, but responds to iodoform reaction

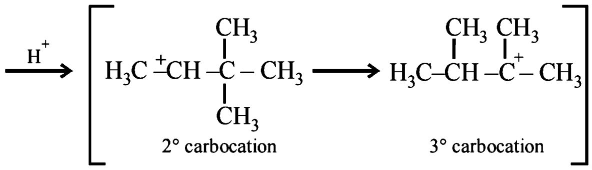
NOTE : Fehling's test is given by aldehydes and not ketones.

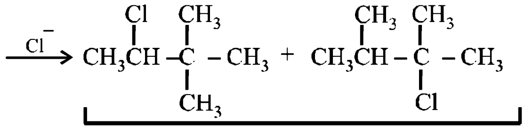
(iii) Since A is isomer of D, former should have following structure.



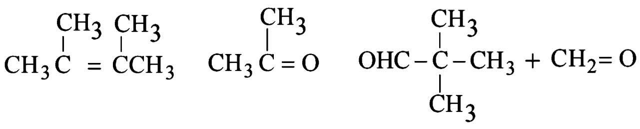
$$H_2C=CH-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

(A) ($C_6 H_{12}$, alkene)



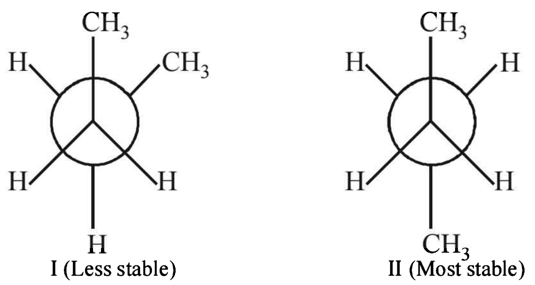


B and C



(D) (E) (F) & (G)

25.



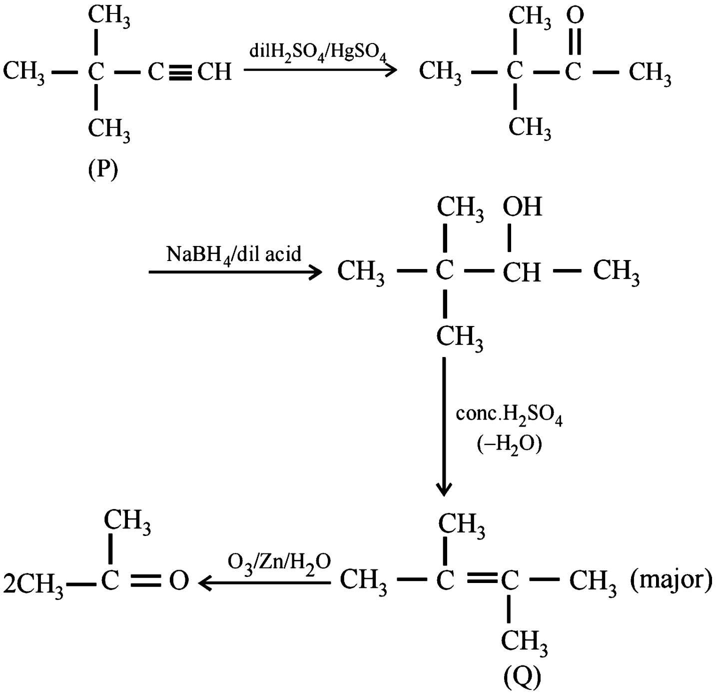
I (Less stable) II (Most stable)

Staggered conformations of n-butane

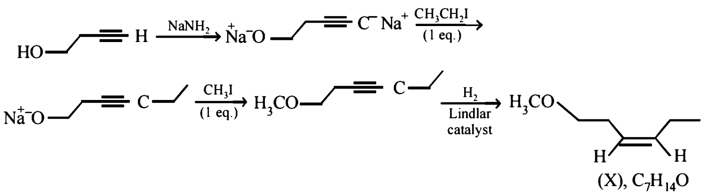
Newmann projection formulae II is the most stable because the bulky groups (CH_3) are at maximum possible distance from each other. Structure I is relatively less stable because the two CH_3 groups are close to each other leading to vander Waal's repulsion between the two methyl groups.

G. Comprehension Based Questions

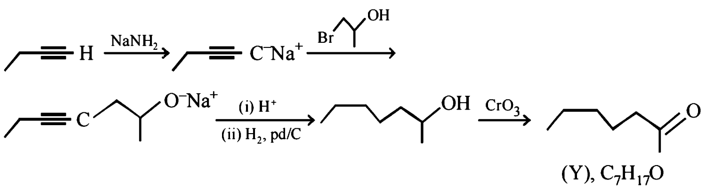
1. **(d)** **2.** **(b)**



3. (a)

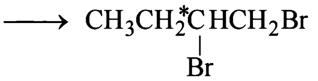


4. (c)



H. Assertion & Reason Type Questions

1. **(a)** $CH_3CH_2-CH=CH_2+Br_2$

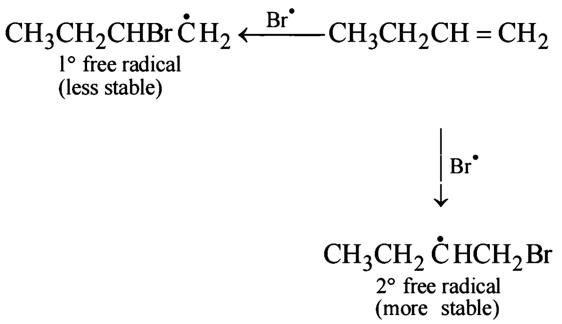


$$\longrightarrow CH_3CH_2\underset{Br}{\overset{*}{C}}HCH_2Br$$

2. **(c)** **TIPS/Formulae :**

In presence of peroxide, addition of HBr on alkenes takes place via free radicals

Here assertion is correct but reasoning is incorrect. Here two free radical are formed, 2° *free radical, being more stable, governs the product.*



$$CH_3CH_2CHBr\dot{C}H_2 \xleftarrow{Br^{\bullet}} CH_3CH_2CH=CH_2 \xrightarrow{Br^{\bullet}} CH_3CH_2\dot{C}HCH_2Br$$

1° free radical (less stable)

2° free radical (more stable)

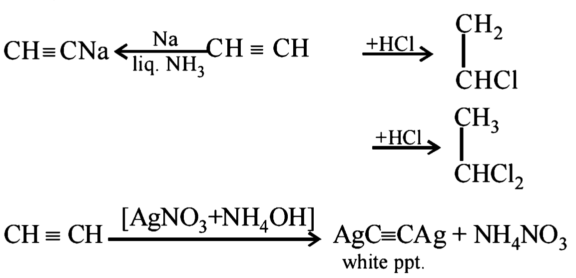
3. **(b)** **TIPS/Formulae :**

With *trans*-2-butene, the product of Br_2 addition is optically inactive.

Even though, both assertion and reason are correct. the correct reason for the formation of *meso*–2,3–dibromobutane from *trans*–2–butene is *anti* addition of Br_2.

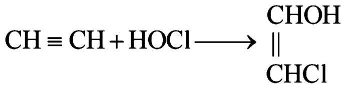
Section-B JEE Main/ AIEEE

1. **(a)** Acetylene reacts with the other three as:

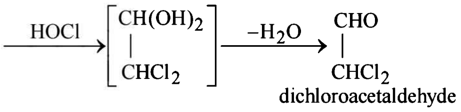


$$CH\equiv CNa \xleftarrow[\text{liq. } NH_3]{Na} CH\equiv CH \xrightarrow{+HCl} \underset{\displaystyle CHCl}{\overset{\displaystyle CH_2}{|}} \xrightarrow{+HCl} \underset{\displaystyle CHCl_2}{\overset{\displaystyle CH_3}{|}}$$

$$CH\equiv CH \xrightarrow{[AgNO_3+NH_4OH]} \underset{\text{white ppt.}}{AgC\equiv CAg} + NH_4NO_3$$



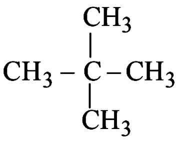
2. **(c)** $$CH\equiv CH + HOCl \longrightarrow \underset{\displaystyle CHCl}{\overset{\displaystyle CHOH}{\|}}$$



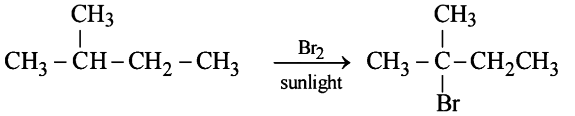
$$\xrightarrow{HOCl} \left[\begin{array}{c} CH(OH)_2 \\ | \\ CHCl_2 \end{array}\right] \xrightarrow{-H_2O} \begin{array}{c} CHO \\ | \\ CHCl_2 \end{array}$$

dichloroacetaldehyde

3. **(c)** In neopentane all the H atoms are same (1°).



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$



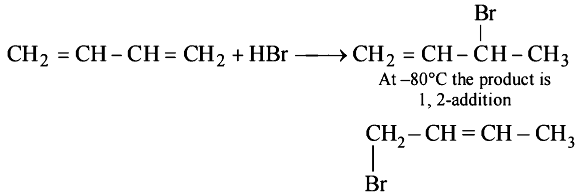
4. **(c)** $$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2-CH_3 \xrightarrow[\text{sunlight}]{Br_2} CH_3-\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2CH_3$$

2–bromo–2–methyl butane

Ease of replacement of H-atom 3° > 2° > 1°.

5. **(c)** Alkenes combine with hydrogen under pressure and in presence of a catalyst (Ni, Pt or Pd) and form alkanes.

$$\text{Butene - 1} \xrightarrow{H_2/Pd} \text{Butane}$$

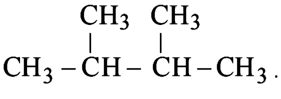


6. **(c)** $$CH_2=CH-CH=CH_2+HBr \longrightarrow CH_2=CH-\overset{\displaystyle Br}{\overset{|}{C}H}-CH_3$$

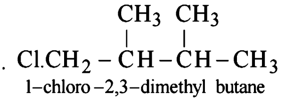
At –80°C the product is 1, 2-addition

$$\underset{\displaystyle Br}{\underset{|}{C}H_2}-CH=CH-CH_3$$

At 40°C the product is 1, 4-addition



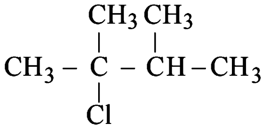
7. **(c)** $$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3$$. Since it contains only two types of H-atoms hence it will give only two mono chlorinated compounds viz.



$$Cl.CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3$$

1–chloro –2,3–dimethyl butane

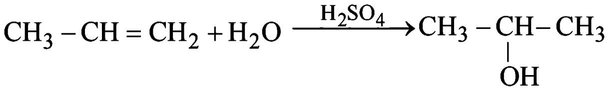
and



$$CH_3-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3$$

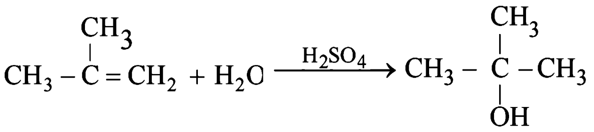
2–chloro–2,3–dimethyl butane

8. **(a)** Water adds directly to the more reactive alkene in presence of a strongly acidic catalyst forming alcohols. Addition occurs according to Markonikov's rule.



$$CH_3-CH=CH_2+H_2O \xrightarrow{H_2SO_4} CH_3-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_3$$

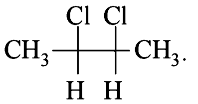
2° alcohol



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2+H_2O \xrightarrow{H_2SO_4} CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$$

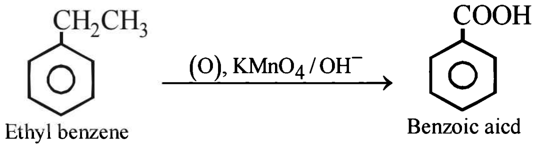
3° alcohol

NOTE : Addition follows Markownikoff's rule.



9. **(c)** $$CH_3-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}}-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}}-CH_3$$. 2, 3-dichloro butane will exhibit optical isomerism due to the presence of two asymmetric carbon atom.

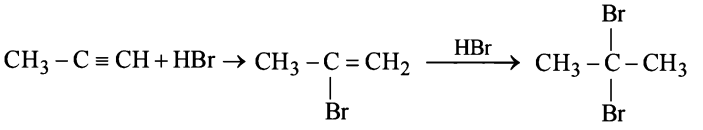
10. **(d)** When alkyl benzene are oxidised with alkaline $KMnO_4$, (strong oxidising agent) the entire alkyl group is oxidised to –COOH group regardless of length of side chain.



Ethyl benzene

Benzoic aicd

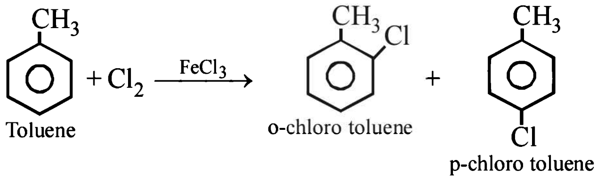
11. (b) The reaction follows Markownikoff rule which states that when unsymmetrical reagent adds across unsymmetrical double or triple bond the negative part adds to carbon atom having lesser number of hydrogen atoms.

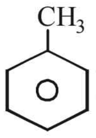


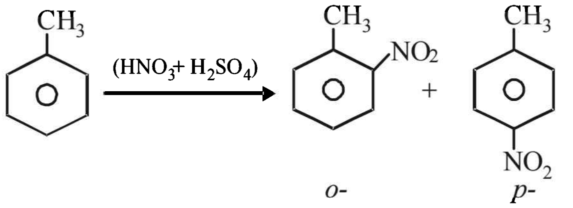
$CH_3-C\equiv CH+HBr \rightarrow CH_3-\underset{Br}{\underset{|}{C}}=CH_2 \xrightarrow{HBr} CH_3-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3$

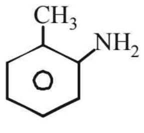
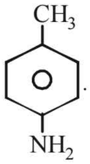
2, 2-dibromo-propane

12. (d) $FeCl_3$ is Lewis acid. In presence of $FeCl_3$ side chain hydrogen atoms of toluene are substituted.



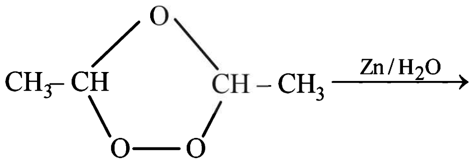
13. (a) **NOTE :** Toluene () contains $-CH_3$ group which is *o-, p-* directing group so on nitration of toluene the $-NO_2$ group will occupy *o-, p-* positions.



on reduction with Sn/HCl they will form corresponding anilines in which $-NO_2$ group changes to $-NH_2$. The mixture now contains  and . These anilines when diazotized and then treated with CuBr forms *o-, p-* bromotoluenes.

14. (d) Completing the sequence of given reactions,

$CH_3-CH=CH-CH_3 \xrightarrow{O_3}$



'A'
(ozonide)

$2CH_3CHO + H_2O + ZnO$
'B'

Thus 'B' is CH_3CHO
Hence (d) is correct answer.

15. (b) Alkynes having terminal $-C\equiv H$ react with Na in liquid ammonia to yield H_2 gas of the given compounds $CH_3CH_2C\equiv CH$ can react with Na in liquid NH_3 so the correct answer is (b).

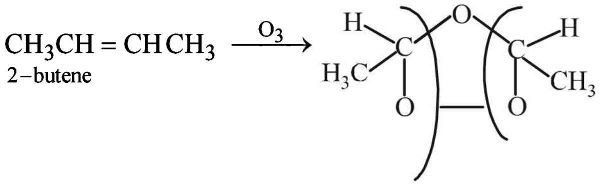
$$CH_3CH_2C\equiv CH \xrightarrow[\text{liquid } NH_3]{\text{Na in}} CH_3CH_2C\equiv C^-Na^+ + \frac{1}{2}H_2(g)$$

16. (d) Writing the reaction we get

$$CH_3MgX + CH_3-C\equiv C-H \longrightarrow CH_3-C\equiv CMgX + CH_4(g)$$

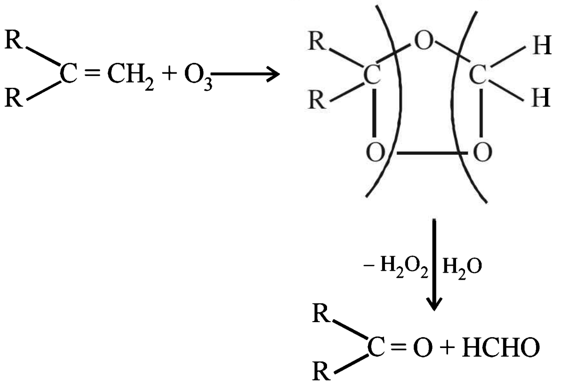
So we find that CH_4 is produced in this reaction.

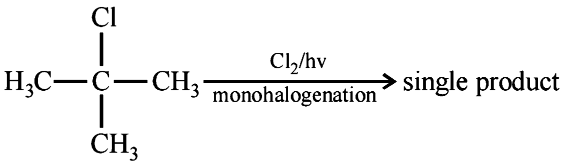
17. (c) The given molecular formula suggests that the aldehyde formed will be acetaldehyde hence the alkene will be



$\xrightarrow{Zn/H_2O} 2CH_3CHO + H_2O_2$

18. (b) Compound must contain a vinyl group $(-\underset{|}{C}=CH_2)$ in order to give formaldehyde as one of the product.



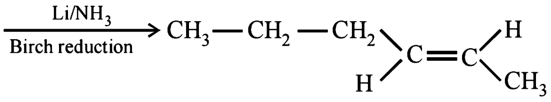
19. (b) 

$H_3C-\underset{CH_3}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-CH_3 \xrightarrow[\text{monohalogenation}]{Cl_2/hv}$ single product

neopentane

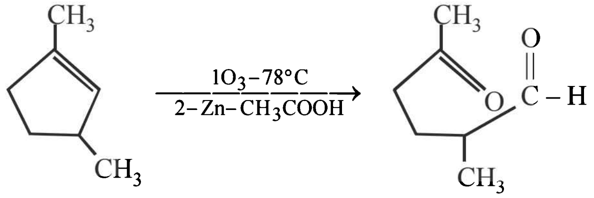
20. (b) Anti addition of hydrogen atoms to the triple bond occurs when alkynes are reduced with sodium (or lithium) metal in ammonia, ethylamine, or alcohol at low temperatures. This reaction called, a dissolving metal reduction, produces an (E)- or *trans*-alkene. Sodium in liq. NH_3 is used as a source of electrons in the reduction of an alkyne to a *trans* alkene.

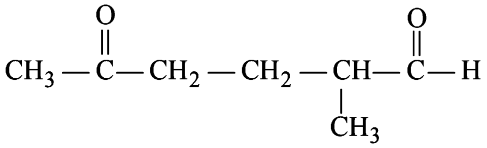
$CH_3-CH_2-CH_2-C\equiv C-CH_3$
2-Hexyne



Trans-2-Hexene

21. **(d)** When 1, 3-dimethylcyclopentene is heated with ozone and then with zinc and acetic acid, oxidative cleavage leads to keto - aldehyde.





$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H$$

5- keto – 2 – methylhexanal

22. **(d)** Region 2 (blue flame) will be the hottest region of Bunsen flame shown in given figure

23. **(d)** $C_xH_{y(g)}+\left(\frac{4x+y}{4}\right)O_{2(g)}\rightarrow xCO_{2(g)}+\frac{y}{2}H_2O(l)$

Volume of O_2 used $=375\times\frac{20}{100}=75$ ml

∴ From the reaction of combustion

1 ml C_xH_y requires $=\frac{4x+y}{4}$ ml O_2

$15\text{ ml}=15\left(\frac{4x+y}{4}\right)=75$

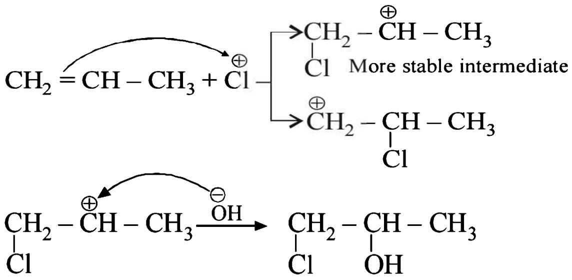
So, $4x+y=20$

$x=3$

$y=8$

$\boxed{C_3H_8}$

24. **(d)**



$$CH_2=CH-CH_3+\overset{\oplus}{Cl}\longrightarrow \begin{cases}\underset{Cl}{\underset{|}{CH_2}}-\overset{\oplus}{CH}-CH_3 & \text{More stable intermediate}\\ \overset{\oplus}{CH_2}-\underset{Cl}{\underset{|}{CH}}-CH_3\end{cases}$$

$$\underset{Cl}{\underset{|}{CH_2}}-\overset{\oplus}{CH}-CH_3\xrightarrow{\overset{\ominus}{OH}}\underset{Cl}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-CH_3$$