10

Hydrocarbons

Section-A : JEE Advanced/ IIT-JEE

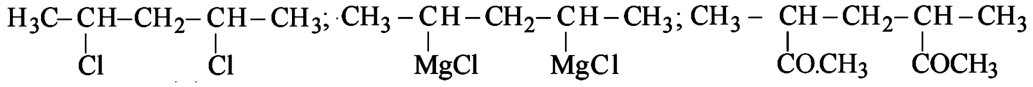
A 1. ethyne 2. 2-butyne 3. C_2H_2
4. ethylene 5. H_2SO_4, $HgSO_4$ 6. less
7. 3, 4-dibromo-1-butene-1 (at low temperature) or 1, 4-dibromo-2-butene (at high temperature)

B 1. F 2. F

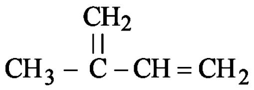
C 1. (b) 2. (b) 3. (a) 4. (c) 5. (c) 6. (c) 7. (a)
8. (a) 9. (c) 10. (b) 11. (a) 12. (d) 13. (a) 14. (d)
15. (a) 16. (c) 17. (b) 18. (b) 19. (a) 20. (b) 21. (d)
22. (a) 23. (d) 24. (b) 25. (b) 26. (a) 27. (d) 28. (c)
29. (b) 30. (a) 31. (b)

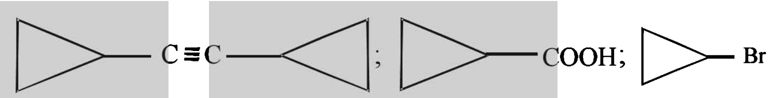
D 1. (b) 2. (a, c) 3. (a) 4. (a, b, c, d) 5. (d) 6. (b, d) 7. (b, c, d)

E 8. C_6H_{12}
10. 55.55 *l* 11. Butene-2 12. 3-methylpentene-1

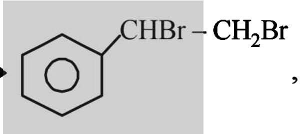
14.

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

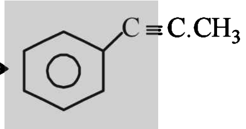
[X] [Y] [Z]

15.

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

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 : $C_6H_5C_2H_5$
cis – and *trans* –

23. $R_3Al+TiCl$

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**

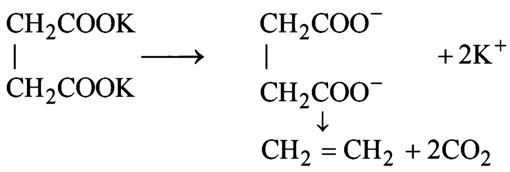
$$CH \equiv CH + Na \xrightarrow[NH_3]{Na,Liq} CH \equiv CNa \xrightarrow{NaNH_2} NaC \equiv CNa$$

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

3. C_2H_2

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

4. **ethylene**



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

5. H_2SO_4, $HgSO_4$

6. **less;**

NOTE:

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

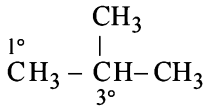
Benzyl ($C_6H_5\dot{C}H_2$) free radical is more stable than methyl ($\dot{C}H_3$) free radical because of hyperconjugation (no bond resonance).

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.



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

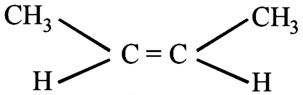
C. MCQs with One Correct Answer

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.

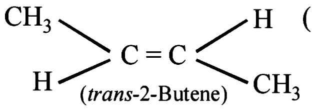
4. **(c)** Four isomers

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



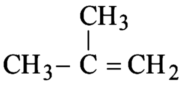
(*cis*-2-Butene)

(iii)



(*trans*-2-Butene)

(iv)



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

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

$$[CH_3\,CH(OH) = CH_2] \rightarrow \underset{\text{acetone}}{CH_3COCH_3}$$

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*.

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

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

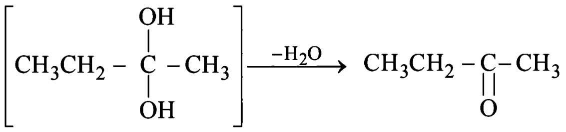
10. **(b)** For isomeric alkanes, th one having longest straight chain has highest b.p. because of larger surface area.

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

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



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

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.

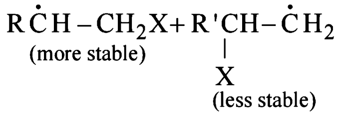
16. **(c)** **TIPS/Formulae :**

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)

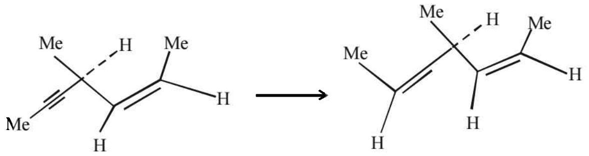
$R'-\dot{C}H-CH_2X+HX \longrightarrow R'-CH_2-CH_2X+X\cdot$

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.

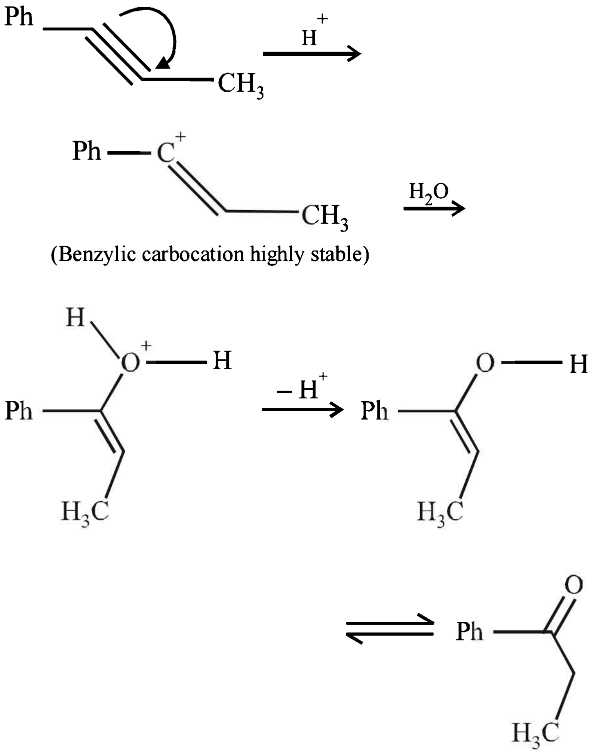
The molecular plane does not have any π electron density as the *p*-orbitals are perpendicular to the plane containing the ethene molecule. The nodal plane in the π-bond of ethene is located in the molecular plane.

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

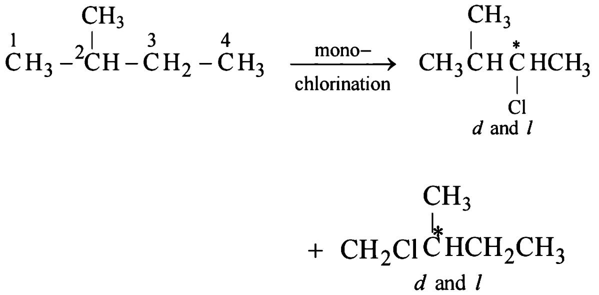
22. **(a)**



(Benzylic carbocation highly stable)

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)**



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

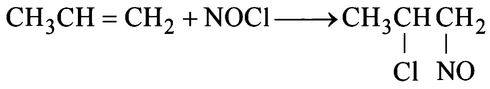
$+ CH_2Cl\overset{*}{C}H(CH_3)CH_2CH_3$ (*d* and *l*)

(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).

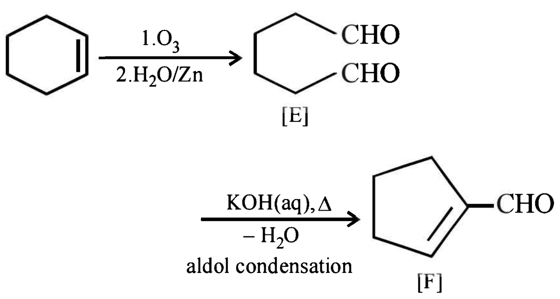
(iii) Chlorination at C-1 also produces a chiral carbon marked with star (*d* and *l* form).

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

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

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

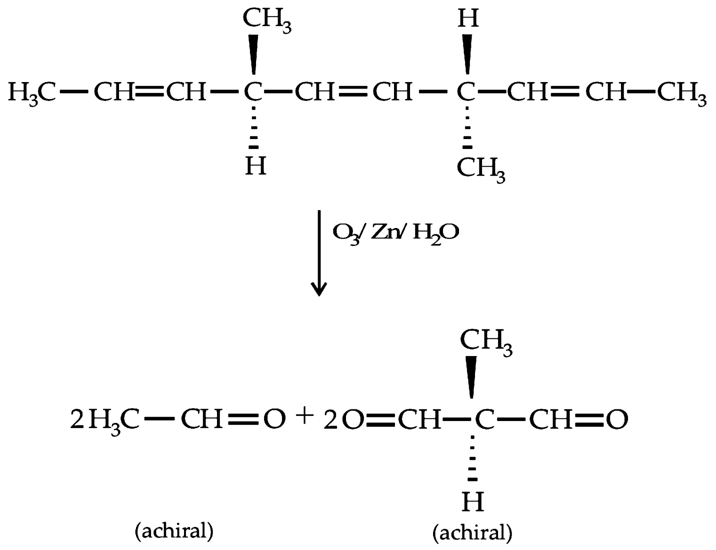
$$CH_3CH_2C\equiv CCH_2CH_2CH_2CH_3 + NaBr$$

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

$= 82.85$ kcal/mol ≈ 100 kcal/mol.

29. **(b)** **Allene (C_3H_4) is** $\overset{sp^2}{H_2C} = \overset{sp}{C} = \overset{sp^2}{CH_2}$

30. **(a)**



(achiral) (achiral)

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

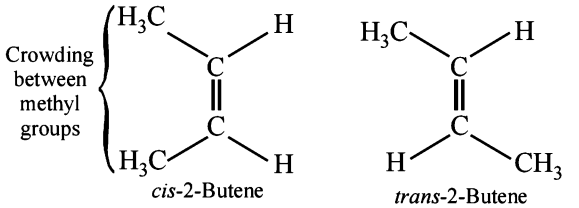
$$\underset{\substack{\text{tetrasubstituted}\\\text{(most stable due to}\\\text{hyper conjugative}\\\text{sturctures)}}}{R_2C=CR_2} > R_2C=CHR > RCH=CHR$$

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

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.

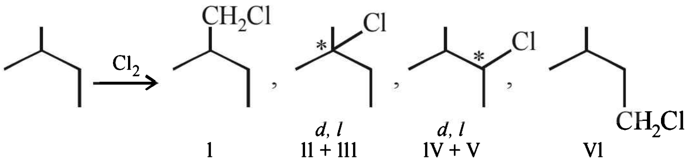


cis-2-Butene

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)**

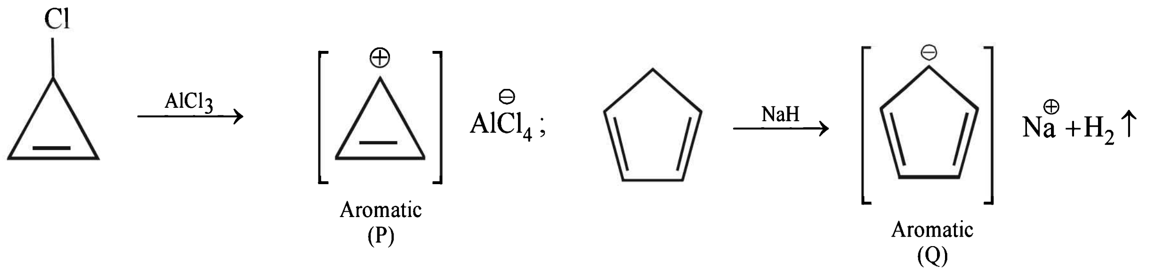


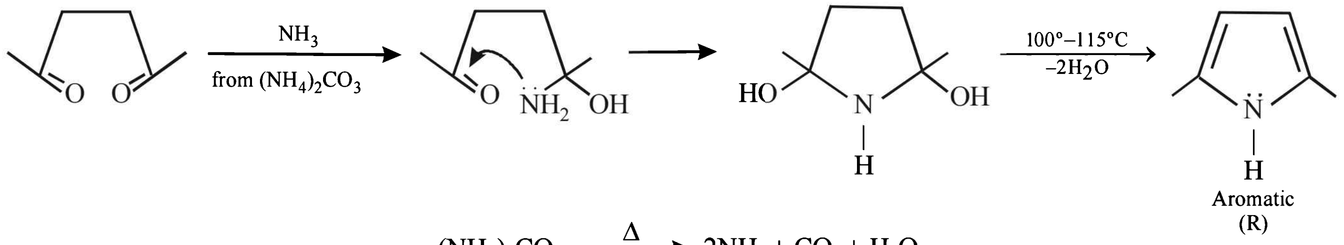
So, the value of N will be $1 + 2 + 2 + 1 = 6$.

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

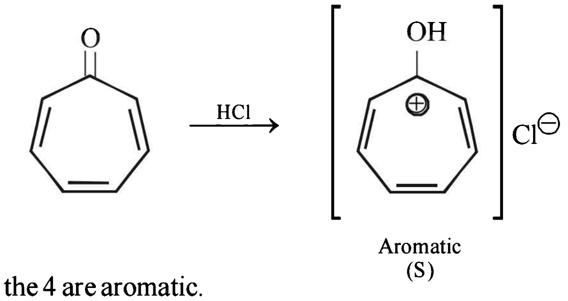
$1 + 1 + 1 + 1 = 4$.

4. (a, b, c, d)



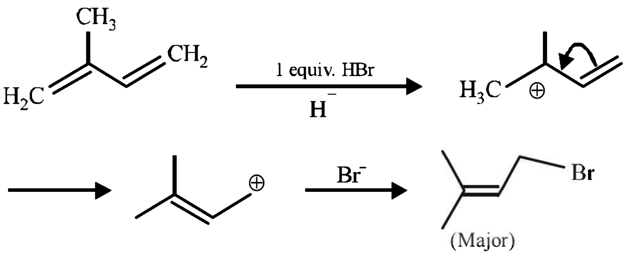


$$(NH_4)_2CO_3 \xrightarrow{\Delta} 2NH_3 + CO_2 + H_2O$$



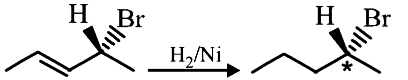
Note : P has 2 π electrons, while Q, R & S have 6 π electrons each. Hence all the 4 are aromatic.

5. (d)



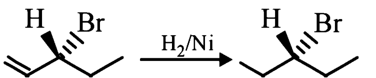
6. (b, d)

(A)



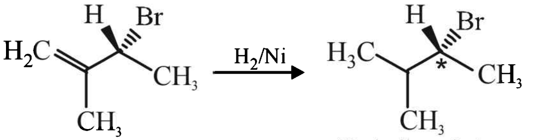
(Optically active)

(B)



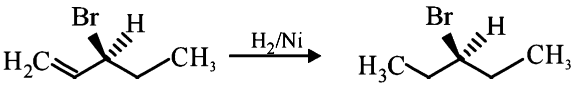
(Optically inactive)

(C)



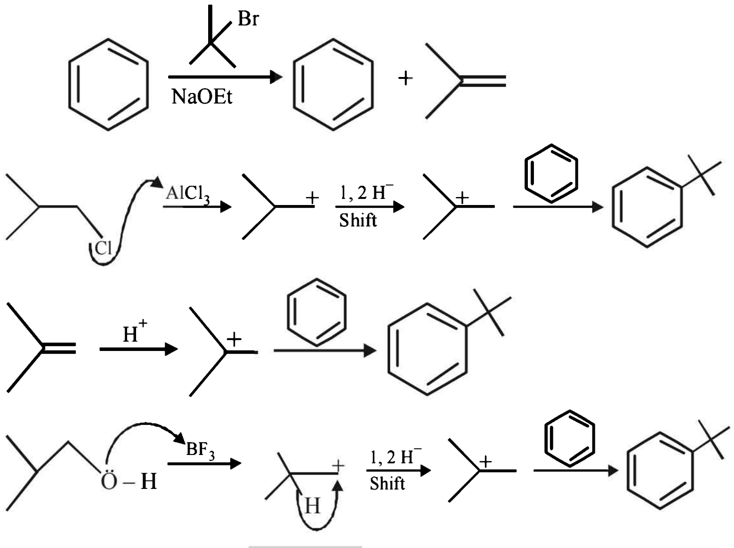
(Optically active)

(D)



(Optically inactive)

7. (b, c, d)

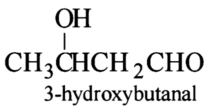


E. Subjective Problems

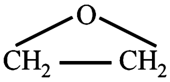
1. Bromine water test : C_2H_2 decolourises bromine water while CH_4 does not decolourises bromine water.

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

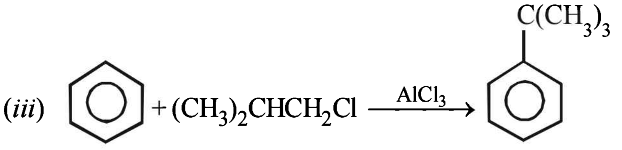
ethyne



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

(*ii*) 

Ethylene oxide

(*iii*) 

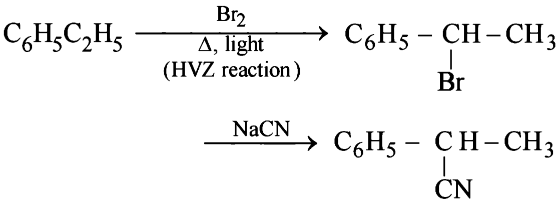
NOTE : that the 1° carbocation, $(CH_3)_2CH\overset{+}{C}H_2$ formed during reaction rearranges to the more stable, 3° carbocation, $(CH_3)_3\overset{+}{C}$ and hence the above product is formed.] (see also *ix* part)

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

Explanation :

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

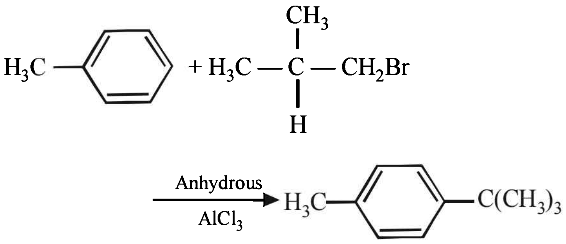
$$\xrightarrow[\text{to}]{\text{rearranges}} \underset{3^\circ\ \text{carbocation}}{(CH_3)_3C^+} \xrightarrow{C_6H_6} C_6H_5C(CH_3)_3$$

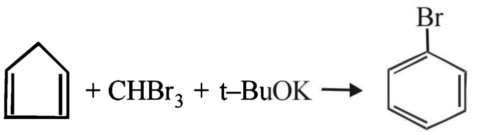
(*v*) 

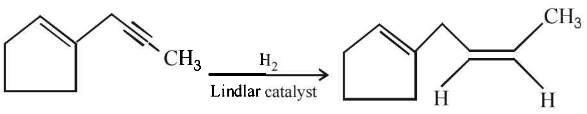
$$C_6H_5C_2H_5 \xrightarrow[\substack{\Delta,\ \text{light}\\ \text{(HVZ reaction)}}]{Br_2} C_6H_5-\underset{\underset{Br}{|}}{C}H-CH_3$$

$$\xrightarrow{NaCN} C_6H_5-\underset{\underset{CN}{|}}{C}H-CH_3$$

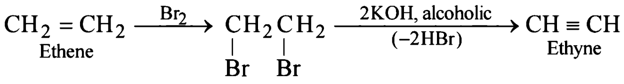
2-phenylpropanenitrile

(*vi*) 

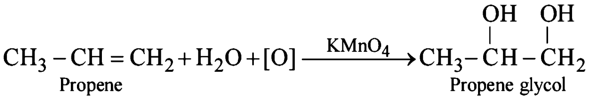
(*vii*) 

(*viii*) 

(Partial reduction of triple bond in syn-manner)

3. 

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

4. 

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

[**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.

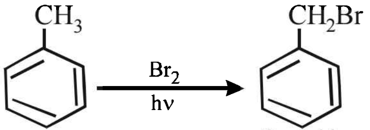
(*ii*) **TIPS/Formulae :**

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

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

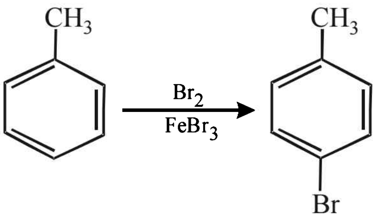
(*iii*) Unlike olefins, π-electrons of benzene are delocalised (resonance) and hence these are unreactive towards addition reactions. Moreover, addition reaction leads to destruction of the benzenoid ring.

(*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.

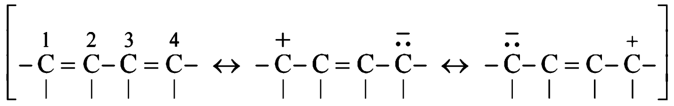


p-bromotoluene

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

(v) **TIPS/Formulae :**

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



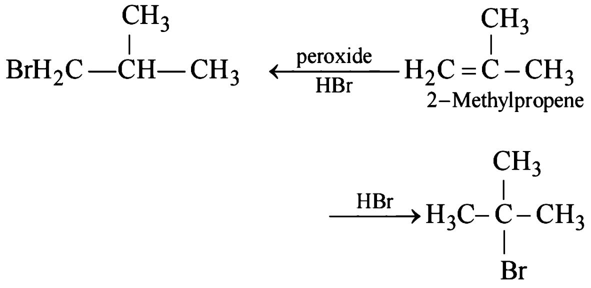
$$\left[-\underset{|}{\overset{1}{C}}=\underset{|}{\overset{2}{C}}-\underset{|}{\overset{3}{C}}=\underset{|}{\overset{4}{C}}- \leftrightarrow -\underset{|}{\overset{+}{C}}-\underset{|}{C}=\underset{|}{C}-\underset{|}{\overset{\overline{..}}{C}}- \leftrightarrow -\underset{|}{\overset{\overline{..}}{C}}-\underset{|}{C}=\underset{|}{C}-\underset{|}{\overset{+}{C}}-\right]$$

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.

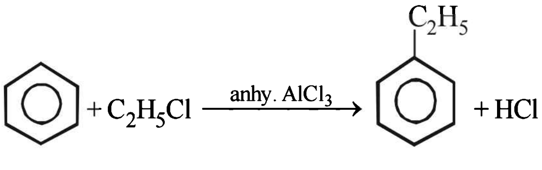


$$\mathrm{BrH_2C-\overset{\overset{CH_3}{|}}{C}H-CH_3 \xleftarrow[HBr]{peroxide} \underset{2\text{-}Methylpropene}{H_2C=\overset{\overset{CH_3}{|}}{C}-CH_3}}$$

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

(*ii*) Ethyne (HC ≡ CH) and only those derivatives which have at least one acetylenic hydrogen atom ($\equiv C-H$) 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**

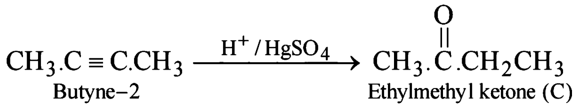
$$\text{Hence, } n = \frac{84}{12+2} = 6$$

∴ 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.

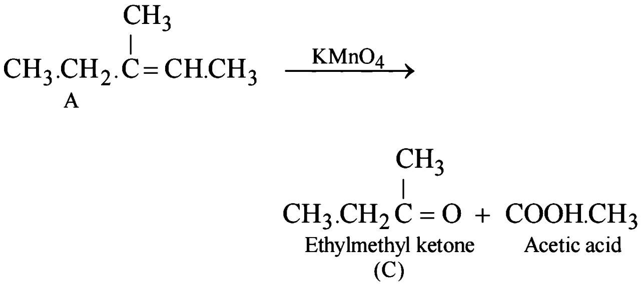
$$\underset{A}{C_4H_8=CHCH_3} \xrightarrow{KMnO_4} \underset{C}{C_4H_8O} + \underset{\text{Acetic acid}}{CH_3COOH}$$

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.



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

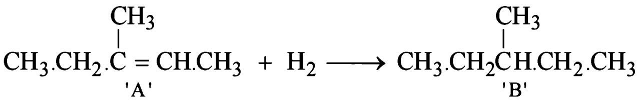
The formation of ketone 'C' from C_4H_8 fragment of 'A' can be explained by the following structure of A.



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

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

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



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

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

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

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)

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

$\therefore$ Required volume of ethane at NTP

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

11. **TIPS/Formulae :**

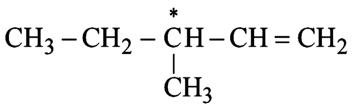
A symmetric alkene does not follow Markovnikoff and *anti*-Markovnikoff's rule (Peroxide effect).

B has to be a symmetric alkene (**butene-2**)

$CH_3CH = CHCH_3$ as it will give the same product

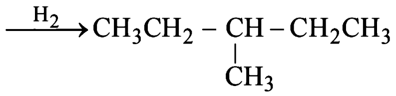
$CH_3 - CH(Br) - CH_2 - CH_3$ in presence /absence of peroxide.

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**,



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

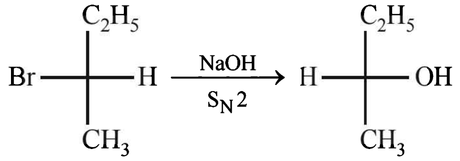
(D) Optically active(C_6H_{12})

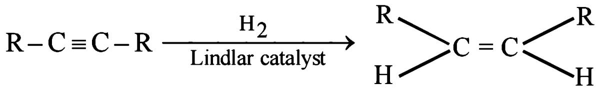


$$\xrightarrow{H_2} CH_3CH_2 - CH(CH_3) - CH_2CH_3$$

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 :**

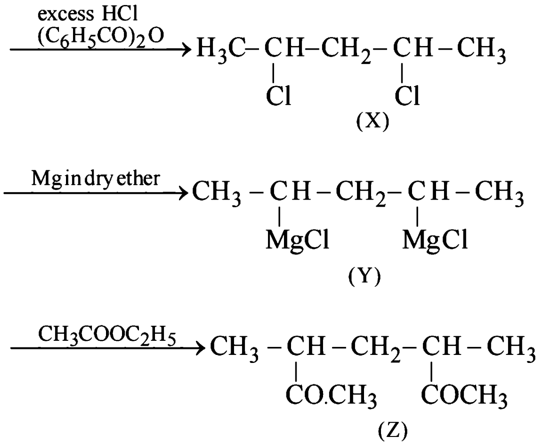
(i) 1, 4-Pentadiene reacts with HCl in presence of benzoyl peroxide in Markownikoff's way.

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.

$H_2C = CH - CH_2 - CH = CH_2$

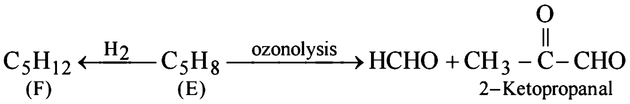


$$\xrightarrow[(C_6H_5CO)_2O]{\text{excess HCl}} H_3C-CH(Cl)-CH_2-CH(Cl)-CH_3 \ (X)$$

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

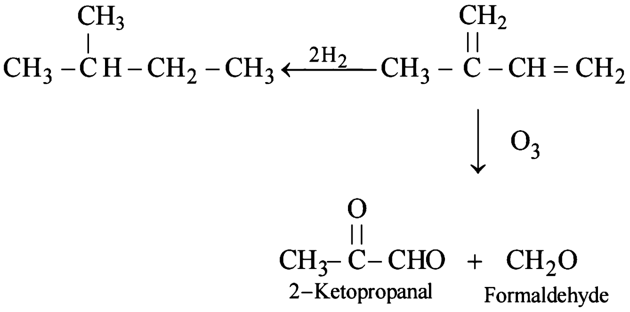
$$\xrightarrow{CH_3COOC_2H_5} CH_3-CH(CO.CH_3)-CH_2-CH(COCH_3)-CH_3 \ (Z)$$

15. Summary of the given reactions



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

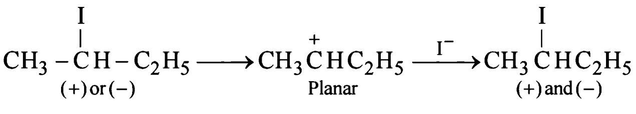
Since hydrogenation of (E) to (F) takes up two molecules of hydrogen, it indicates the presence of two double bonds in E which is further supported by its ozonolysis to form two products having three carbonyl groups. Further structure of ozonolysis product leads to following structure to compound (E).



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

16. **TIPS/Formulae :**

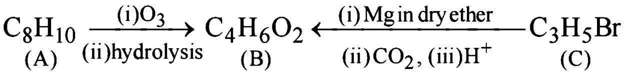
In S_N1 reaction racemization as well as inversion is observed. Reaction of optically active 2-iodobutane with NaI in acetone is an S_N1 reaction which involves formation of carbocation as intermediate.



$$\underset{(+)\text{or}(-)}{CH_3 - CH(I) - C_2H_5} \longrightarrow \underset{\text{Planar}}{CH_3\overset{+}{C}HC_2H_5} \xrightarrow{I^-} \underset{(+)\text{and}(-)}{CH_3CH(I)C_2H_5}$$

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

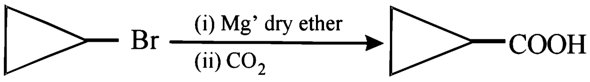
17. Summary of the given facts



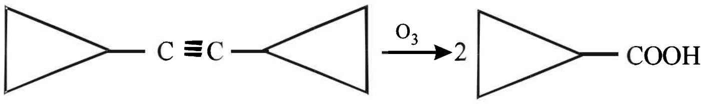
$$\underset{(A)}{C_8H_{10}} \xrightarrow[\text{(ii)hydrolysis}]{(i)O_3} \underset{(B)}{C_4H_6O_2} \xleftarrow[(ii)CO_2,\ (iii)H^+]{\text{(i)Mg in dry ether}} \underset{(C)}{C_3H_5Br}$$

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.

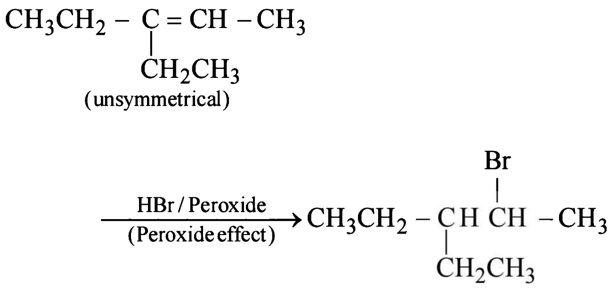


(C) C_3H_5Br (B) $C_4H_6O_2$



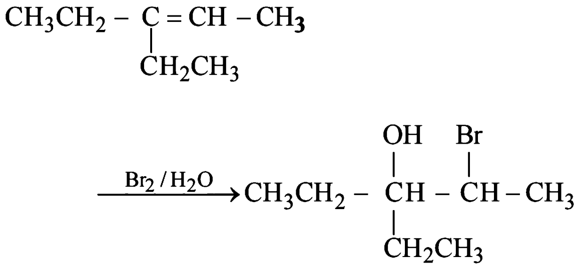
(A) C_8H_{10} (B) $C_4H_6O_2$

18. (a)



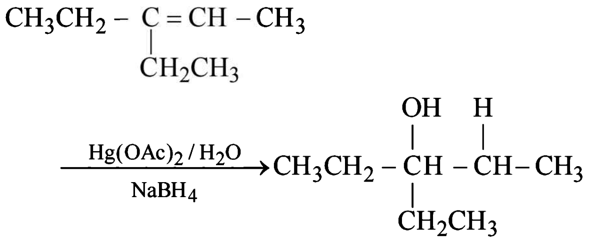
$$CH_3CH_2-\underset{\underset{\text{(unsymmetrical)}}{CH_2CH_3}}{C}=CH-CH_3 \xrightarrow[\text{(Peroxide effect)}]{\text{HBr / Peroxide}} CH_3CH_2-\underset{CH_2CH_3}{CH}-\overset{Br}{CH}-CH_3$$

(b)



$$CH_3CH_2-\underset{CH_2CH_3}{C}=CH-CH_3 \xrightarrow{Br_2/H_2O} CH_3CH_2-\underset{CH_2CH_3}{\overset{OH}{CH}}-\overset{Br}{CH}-CH_3$$

(c)



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

19. TIPS/Formulae :

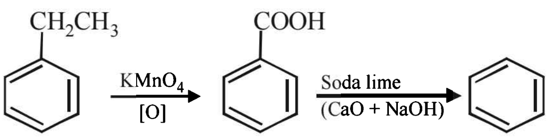
(i) It should be an alkene as it adds one mole of H_2.

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

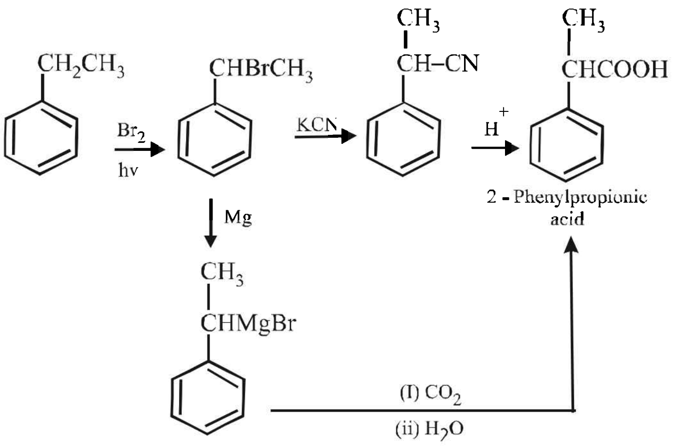
$$\underset{n\text{–Hexane}}{CH_3(CH_2)_4CH_3} \xleftarrow{H_2} \underset{\text{(A)}}{CH_3CH_2CH=CHCH_2CH_3}$$

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

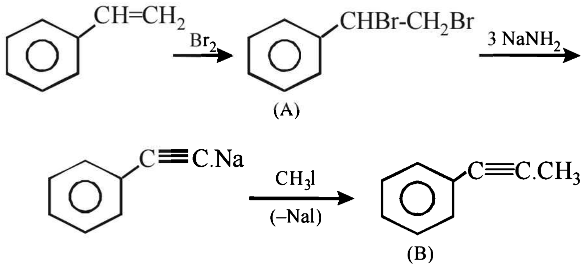
20. (i)



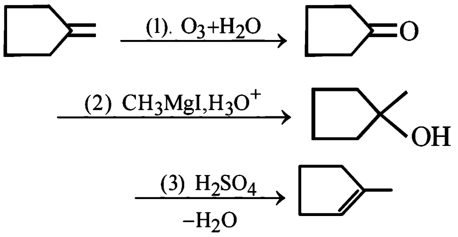
(ii)



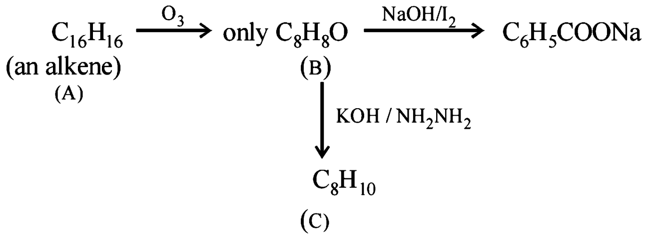
21. (i)



(ii)

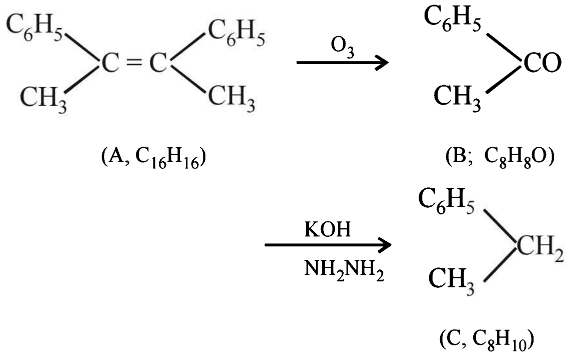


22.



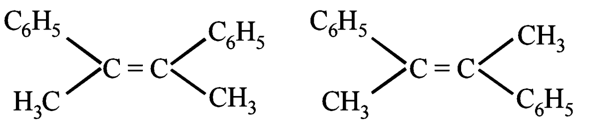
(i) Conversion of (B) to (C) involves iodoform reaction, hence (B) must contain – $COCH_3$ group leading to $C_6H_5COCH_3$ (C_8H_8O) as its molecular formula.

(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



(C, C_8H_{10})

Isomeric structures of A



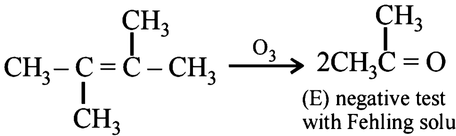
cis *trans*

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

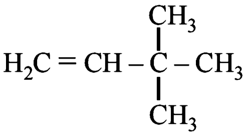


$$CH_3-\underset{CH_3}{C}=\overset{CH_3}{C}-CH_3 \xrightarrow{O_3} 2CH_3\overset{CH_3}{C}=O$$

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

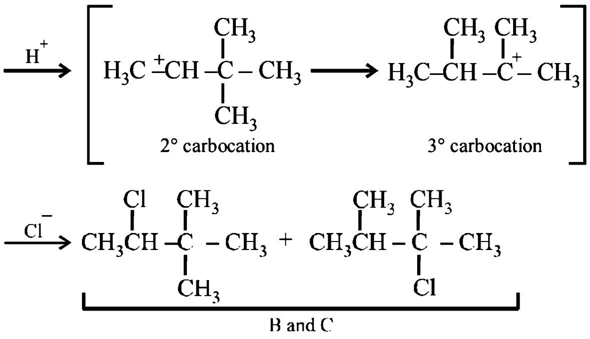
NOTE : Fehling's test is given by aldehydes and not ketones.

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



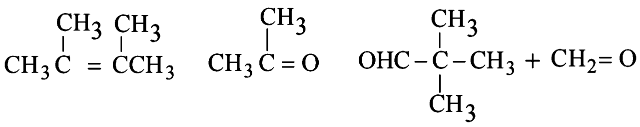
$$H_2C=CH-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

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



$$\xrightarrow{H^+}\left[H_3C\overset{+}{C}H-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow H_3C-\overset{CH_3}{CH}-\overset{CH_3}{\overset{+}{C}}-CH_3\right]$$

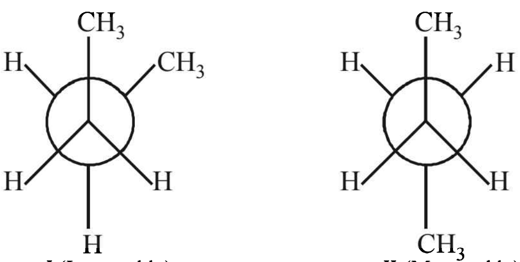
$$\xrightarrow{Cl^-} \underbrace{CH_3\overset{Cl}{CH}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + CH_3\overset{CH_3}{CH}-\underset{Cl}{\overset{CH_3}{C}}-CH_3}_{B\ and\ C}$$



$$CH_3\overset{CH_3}{C}=\overset{CH_3}{C}CH_3 \quad CH_3\overset{CH_3}{C}=O \quad OHC-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + CH_2=O$$

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

25.



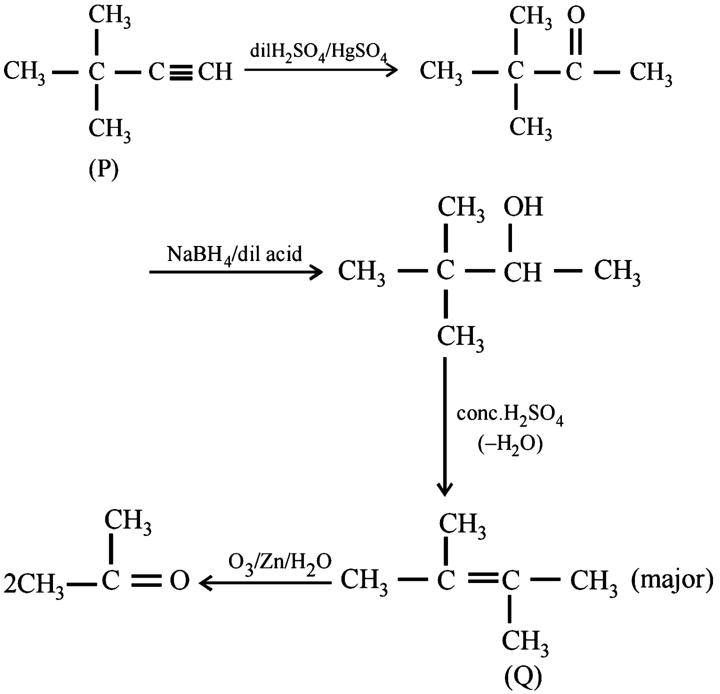
I (Less stable) II (Most stable)

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)**



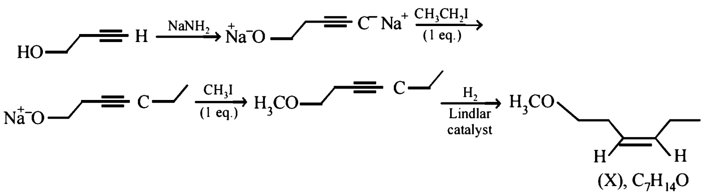
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-C\equiv CH \xrightarrow{dilH_2SO_4/HgSO_4} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

$$\xrightarrow{NaBH_4/dil\ acid} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{OH}{CH}-CH_3$$

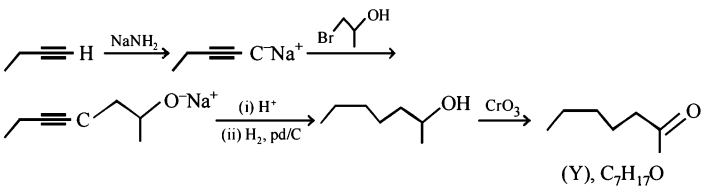
$$\xrightarrow[(-H_2O)]{conc.H_2SO_4} CH_3-\overset{CH_3}{C}=\underset{CH_3}{C}-CH_3\ (major)\ (Q)$$

$$CH_3-\overset{CH_3}{C}=\underset{CH_3}{C}-CH_3 \xrightarrow{O_3/Zn/H_2O} 2CH_3-\overset{CH_3}{C}=O$$

3. (a)

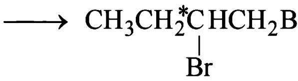


4. (c)



H. Assertion & Reason Type Questions

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

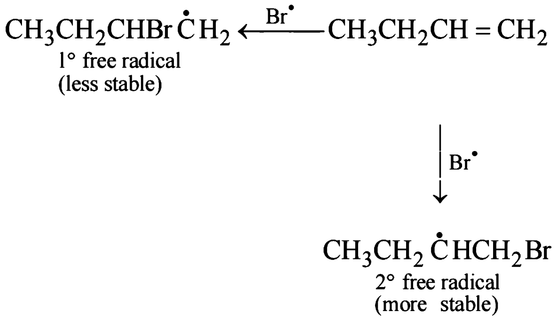


$$\longrightarrow CH_3CH_2\underset{Br}{\overset{*}{C}}HCH_2Br$$

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.*

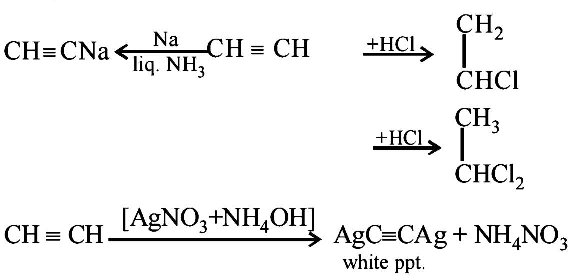


$$CH_3CH_2CHBr\dot{C}H_2 \xleftarrow{Br^\bullet} CH_3CH_2CH=CH_2 \xrightarrow{Br^\bullet} CH_3CH_2\dot{C}HCH_2Br$$

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

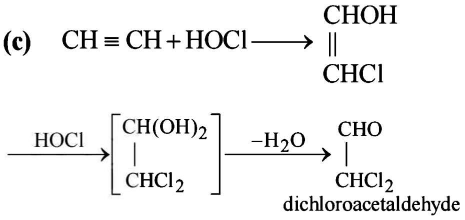
1. **(a)** Acetylene reacts with the other three as:



$$CH\equiv CNa \xleftarrow[\text{liq. }NH_3]{Na} CH\equiv CH \xrightarrow{+HCl} \begin{matrix} CH_2 \\ | \\ CHCl \end{matrix} \xrightarrow{+HCl} \begin{matrix} CH_3 \\ | \\ CHCl_2 \end{matrix}$$

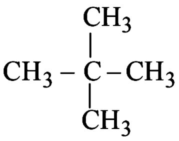
$$CH\equiv CH \xrightarrow{[AgNO_3+NH_4OH]} \underset{\text{white ppt.}}{AgC\equiv CAg} + NH_4NO_3$$

2. **(c)**



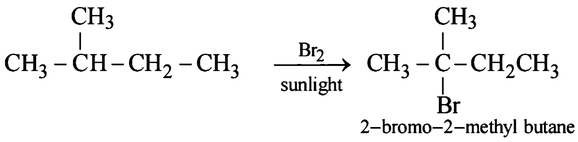
$$CH\equiv CH + HOCl \longrightarrow \begin{matrix} CHOH \\ \| \\ CHCl \end{matrix} \xrightarrow{HOCl} \left[\begin{matrix} CH(OH)_2 \\ | \\ CHCl_2 \end{matrix}\right] \xrightarrow{-H_2O} \underset{\text{dichloroacetaldehyde}}{\begin{matrix} CHO \\ | \\ CHCl_2 \end{matrix}}$$

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



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

4. **(c)**



$$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3 \xrightarrow[\text{sunlight}]{Br_2} CH_3-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2CH_3$$

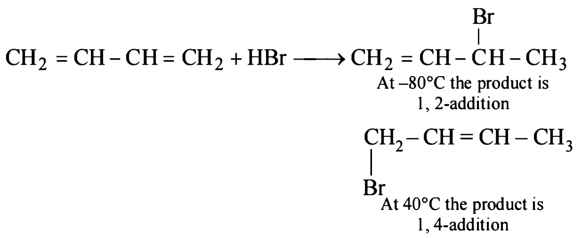
2–bromo–2–methyl butane

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)**



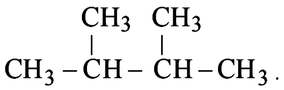
$$CH_2=CH-CH=CH_2+HBr \longrightarrow CH_2=CH-\overset{Br}{\overset{|}{C}H}-CH_3$$

At –80°C the product is 1, 2-addition

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

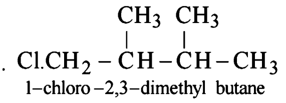
At 40°C the product is 1, 4-addition

7. **(c)**



$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{CH_3}{\overset{|}{C}H}-CH_3$$

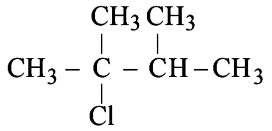
. Since it contains only two types of H-atoms hence it will give only two mono chlorinated compounds viz.



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

1–chloro –2,3–dimethyl butane

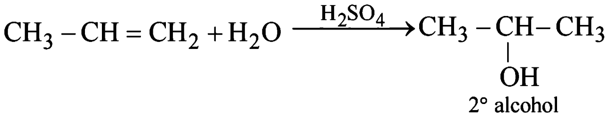
and



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

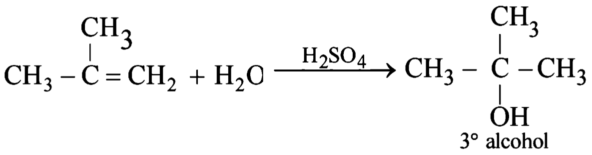
2–chloro–2,3–dimethyl butane

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.



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

2° alcohol

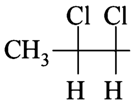


$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2+H_2O \xrightarrow{H_2SO_4} CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

3° alcohol

NOTE : Addition follows Markownikoff's rule.

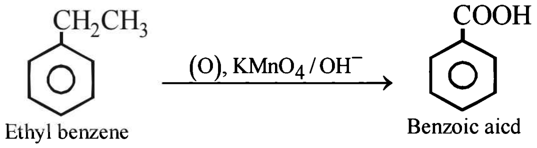
9. **(c)**



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

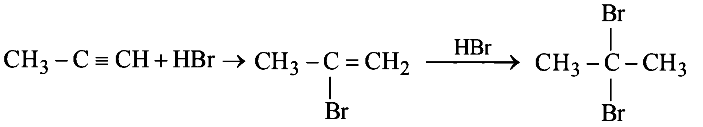
. 2, 3-dichloro butane will exhibit optical isomerism due to the presence of two asymmetric carbon atom.

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

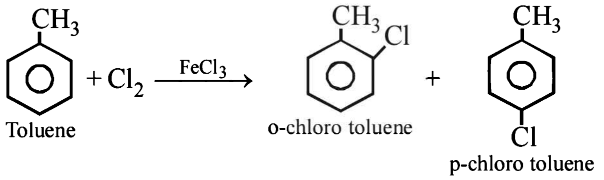
11. (b) The reaction follows Markownikoff rule which states that when unsymmetrical reagent adds across unsymmetrical double or triple bond the negative part adds to carbon atom having lesser number of hydrogen atoms.

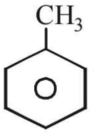


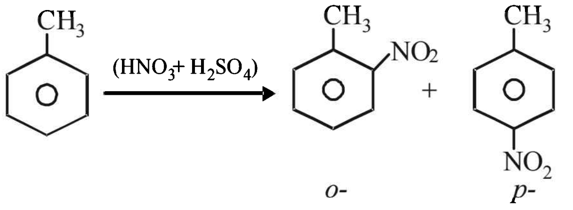
$$CH_3-C\equiv CH+HBr\rightarrow CH_3-\underset{\displaystyle Br}{\underset{|}{C}}=CH_2\xrightarrow{HBr}CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-CH_3$$

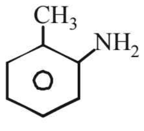
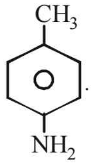
2, 2-dibromo-propane

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



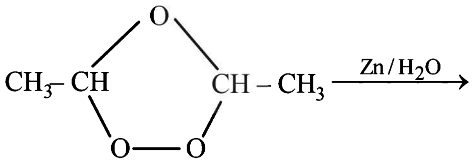
13. (a) **NOTE :** Toluene () contains $-CH_3$ group which is *o-*, *p-* directing group so on nitration of toluene the $-NO_2$ group will occupy *o-*, *p-* positions.



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)

$$\underset{\text{'B'}}{2CH_3CHO}+H_2O+ZnO$$

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).

$$CH_3CH_2C\equiv CH\xrightarrow[\text{liquid }NH_3]{\text{Na in}}$$

$$CH_3CH_2C\equiv C^-Na^++\frac{1}{2}H_2(g)$$

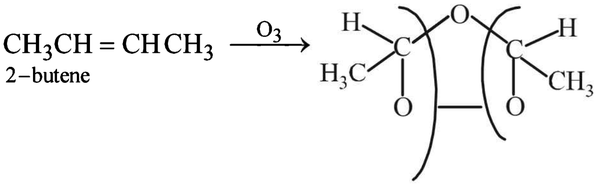
16. (d) Writing the reaction we get

$$CH_3MgX+CH_3-C\equiv C-H\longrightarrow$$

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

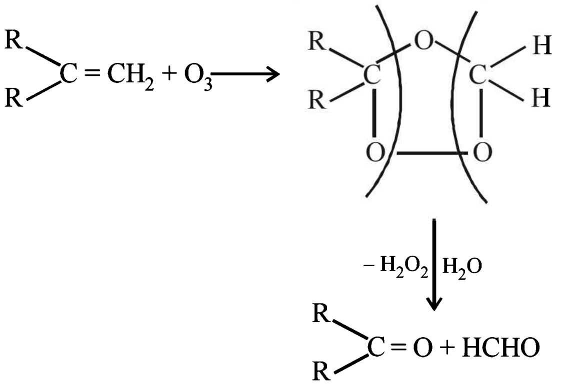
So we find that CH_4 is produced in this reaction.

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

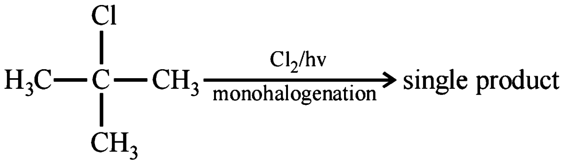


$$\xrightarrow{Zn/H_2O}2CH_3CHO+H_2O_2$$

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



19. (b)



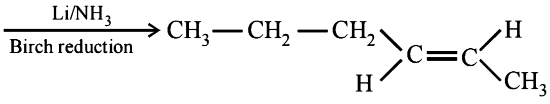
$$H_3C-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3\xrightarrow[\text{monohalogenation}]{Cl_2/hv}\text{single product}$$

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.

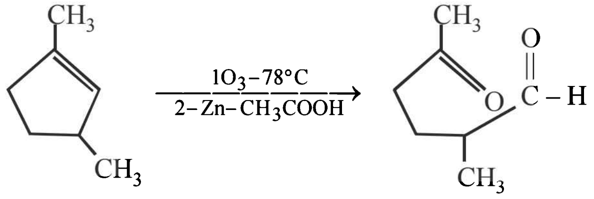
$$CH_3-CH_2-CH_2-C\equiv C-CH_3$$

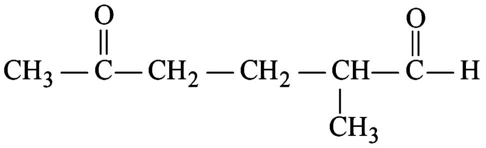
2-Hexyne



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.





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

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

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

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

So, $4x + y = 20$
$x = 3$
$y = 8$

$\boxed{C_3H_8}$

24. (d)