16. **(i)** $CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2Br$

2-methyl propene — isobutyl bromide

In the absence of peroxide, addition of HBr produce tertiary butyl bromide.

(ii) Tertiary alkynes are slightly acidic, forms silver salt with ammoniacal solution of silver nitrate :

$R-C\equiv C-H + AgNO_3 \xrightarrow{NH_3(aq)} \underset{\text{White ppt.}}{R-C\equiv CAg\downarrow}$

17.(A) Terminal alkynes are slightly acidic, forms salt with Na, $NaNH_2$ etc.

$\underset{\text{ethyne}}{H-C\equiv C-H} + Na \xrightarrow{\Delta} H-C\equiv C^-Na^+ + \frac{1}{2}H_2\uparrow$

18.(sp^3) $\underset{sp^3}{CH_3}-CH=CH-\underset{sp^3}{CH_3}$

19. $H-C\equiv C-H + Na \xrightarrow{\text{heat}} \xrightarrow{CH_3I} CH_3-C\equiv CH \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$

20. 1-butyne (terminal) can be distinguished from 2-butyne (internal) by either Tollen's test or through Fehling's test (reaction with ammoniacal cuprous chloride)

$CH_3-CH_2-C\equiv C-H \xrightarrow[NH_3(aq)]{AgNO_3} \underset{\text{white ppt}}{CH_3-CH_2-C\equiv CAg\downarrow}$

$CH_3-CH_2-C\equiv C-H \xrightarrow[NH_3(aq)]{Cu_2Cl_2} \underset{\text{red ppt}}{CH_3-CH_2-C\equiv CCu\downarrow}$

21.(B) Boiling point of alkane increases with molar mass. Among isomeric alkanes, branching decreases boiling point. Therefore, n-octane has highest boiling point, higher than 2, 2, 3, 3-tetramethyl-butane (an isomer of n-octane).

22. The alkenes are :

$CH_3-CH=O + O=CH-CH(CH_3)_2 \longleftarrow \underset{\text{I (B)}}{CH_3-CH=CH-\overset{\overset{CH_3}{|}}{CH}-CH_3}$

$CH_3CH_2CH=O + O=\overset{\overset{CH_3}{|}}{C}-CH_3 \longleftarrow \underset{\text{II (C)}}{CH_3-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_3}$

Since, both alkenes I and II are obtained by β – elimination of same halides, the halides must be :

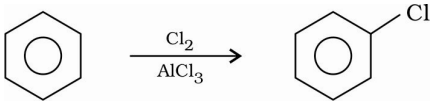
$CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

(A)

23.(AD) **(a)** $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2} H_3C-\underset{Cl}{\underset{|}{CH}}-CH_2-CH_3 + CH_3-CH_2-CH_2CH_2Cl$

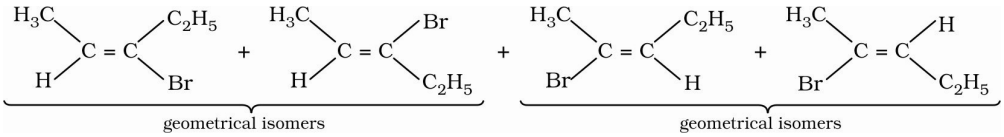
(b) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow{Cl_2} ClCH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

$CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2CH(CH_3)_2 + (CH_3)_2CH-\underset{Cl}{\underset{|}{CH}}-CH(CH_3)_2$

(c) 

(d) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow{Cl_2} ClCH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3 + CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

24.(B) $CH_3-C\equiv C-CH_2CH_3 + HBr \longrightarrow$

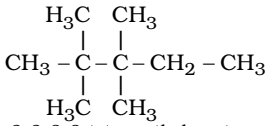


geometrical isomers geometrical isomers

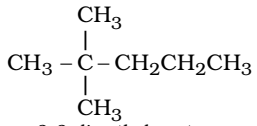
Therefore, two structural and four configurational isomers

25.(C) $C-H$ bond with sp^3-C will be longest in C_2H_6

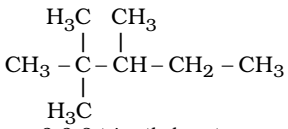
26.(D)



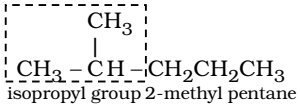
2, 2, 3, 3-tetramethyl pentane
(no isopropyl group)



2, 2-dimethyl pentane
(no isopropyl group)



2, 2, 3-trimethyl pentane
(no isopropyl group)



isopropyl group 2-methyl pentane

27. $3CH_2=CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3HOCH_2CH_2OH + 2KOH + 2MnO_2$

28. Baeyer's reagent (cold, dilute, alkaline permanganate) can be used to distinguish between alkanes and alkenes. Alkenes decolourises purple colour of Baeyer's reagent while alkanes do not.

29.(B) Among alkenes-heat of hydrogenation depends on:

(a) The number of double bonds-greater the number of double bonds, greater the amount of heat evolved in hydrogenation. Hence, 1, 3-butadiene has highest heat of hydrogenation among these.

(b) Relative stability of alkenes-greater the stability, smaller the heat evolved in hydrogenation. 1, 3-Butadiene and trans-2-butene are more stable.

30. H_2SO_4, $HgSO_4$

$H-C\equiv C-H \xrightarrow[HgSO_4]{H_2SO_4} CH_3-CHO$