Chapter-24 : Haloalkanes and Haloarenes

1. **(b)** $CS_2 + 3Cl_2 \xrightarrow{\text{Iodine}} CCl_4 + S_2Cl_2$

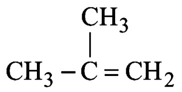
   $2S_2Cl_2 + CS_2 \longrightarrow CCl_4 + 6S$

2. **(a)** Since $CHCl_3$ is a covalent compound it does not produce Cl^- ion in H_2O, hence no white ppt is formed during reaction with $AgNO_3$.

3. **(b)** C_4H_7Cl is a monochloro derivative of C_4H_8 which itself exists in three acyclic isomeric forms.

   $CH_3CH_2CH = CH_2$ I (Its four C's are different)

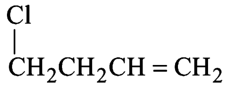
   $CH_3CH = CHCH_3$ II (It has 2 types of carbon)



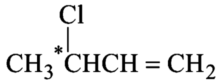
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2$$

III (It has 2 types of carbon)

Four monochloro derivatives of I respectively are

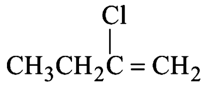


$$\overset{\displaystyle Cl}{\overset{|}{C}}H_2CH_2CH = CH_2$$



$$CH_3\overset{*}{}\overset{\displaystyle Cl}{\overset{|}{C}}HCH = CH_2$$

(optically active) *d* and *l* isomers

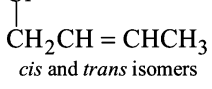


$$CH_3CH_2\overset{\displaystyle Cl}{\overset{|}{C}} = CH_2$$

$CH_3CH_2CH = CHCl$ *cis* and *trans* isomers

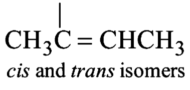
Hence total isomers from I = 6

Two monochloro derivatives of II respectively are



$$\overset{\displaystyle Cl}{\overset{|}{C}}H_2CH = CHCH_3$$

cis and *trans* isomers

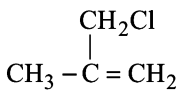


$$CH_3\overset{\displaystyle Cl}{\overset{|}{C}} = CHCH_3$$

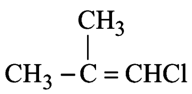
cis and *trans* isomers

Hence total isomers from II = 4

Two monochloro derivatives from III respectively are



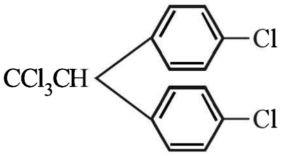
$$CH_3-\overset{\displaystyle CH_2Cl}{\overset{|}{C}}=CH_2$$



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CHCl$$

Grand total of acyclic isomers = 6 + 4 + 2 = 12

4. **(d)** $C_2H_5Br + \text{alc. } AgNO_2 \longrightarrow \underset{\text{nitroethane}}{C_2H_5NO_2}$

5. (a) 

(DDT)

6. (b) $$CHCl_3 + \frac{1}{2}O_2 \xrightarrow{\text{Light}} \underset{\text{unstable}}{CCl(OH)_3} \rightarrow COCl_2 + HCl$$

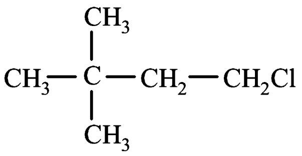
7. (b) Gem-dihalides are those in which two halogen atoms are attached on the same carbon atom.

8. (b) $$\underset{\text{iodoform}}{CHI_3} + 3KOH \longrightarrow CH(OH)_3 + 3KI$$
$$\downarrow$$
$$HCOOH + H_2O$$

9. (b) In Corey House synthesis of alkanes alkyl halide react with lithium dialkyl cuprate

$$R'X + R_2CuLi \longrightarrow R' - R + RCu + LiX$$

10. (d) Neo-hexyl chloride is a primary halide as in it Cl-atom is attached to a primary carbon.



$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - CH_2 - CH_2Cl$$

11. (d) $$CH \equiv CH \xleftarrow{-HCl} CH_2 = CHCl \xrightarrow{H_2} CH_3CH_2Cl$$

12. (d) Freons are chlorofluorocarbons.

$\therefore$ $CClF_3$, $CFCl_3$ and CCl_2F_2, all are freons.

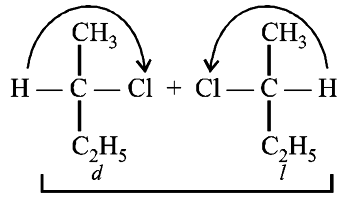
13. (b) $$\underset{n\text{-Propyl bromide}}{CH_3 - CH_2 - CH_2Br} \xrightarrow[-HBr]{\text{ethanolic KOH}} \underset{\text{Propene}}{CH_3 - CH = CH_2}$$

Further, dehydrohalogenation of propane can be occurred in the presence of strong base like $NaNH_2$.

14. (c) $$C_6H_5Cl + NH_3 \xrightarrow[\text{Pressure}]{CuCl_2,\ 573\text{ K}} C_6H_5NH_2 + HCl$$

15. (a) $C_6H_5N_2^+Cl^- \xrightarrow{CuCl} C_6H_5Cl$ (Sandmeyer reaction)

16. (d) $$CH_3 — CH_2 — CH_2 — CH_3 \xrightarrow{Cl_2/hv}$$



Racemic mixture
50% *d* form + 50% *l* form

$Cl^\bullet$ may attack on either side and gives a racemic mixture of 2-chloro butane which contain 50% *d* form and 50% *l*-form.

17. (a) Peroxide effect is observed only in case of HBr. Therefore, addition of HCl to propene even in the presence of benzoyl peroxide occurs according to Markonikov's rule :

$$CH_3 - CH = CH_2 \xrightarrow[\text{Benzoyl peroxide}]{HCl} CH_3 - CHCl - CH_3$$

18. (b) The decreasing order of atomic size of halogens is $I > Br > Cl > F$. On moving down in a group atomic size increases. Further the bond length of C-X bond decreases in the order

$C - I > C - Br > C - Cl > C - F$

and hence the bond dissociation energy decreases in the order

$R - F > R - Cl > R - Br > R - I$

Therefore, $R - I$ being a weakest bond break most easily. hence $R - I$ is most reactive.

19. (b) At high temp. *i.e.*, 400°C substitution occurs in preference to addition.

$$CH_3CH = CH_2 \xrightarrow{Cl_2,\ 400\ °C} ClCH_2CH = CH_2$$

20. (a) Due to steric hindrance tertiary alkyl halide do not react by S_N2 mechanism rather they react by S_N1 mechanism. S_N2 mechanisam is followed in case of primary and secondary alkyl halides. The order is

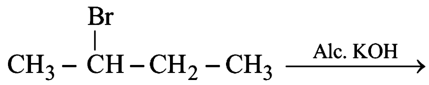
$$CH_3 - X > CH_3 - CH_2X > (CH_3)_2 - CH.X > (CH_3)_3 - C–X$$

21. (c) Potassium ethoxide is a strong base, and 2-bromopentane is a 2° bromide, so elimination reaction predominates.

$$CH_3CH(Br)CH_2CH_2CH_3 \xrightarrow{OC_2H_5^-}$$
$$\underset{\text{Pentene - 2(major) } trans}{CH_3CH = CHCH_2CH_3} + \underset{\text{Pentene–1(min) } cis}{CH_2 = CHCH_2CH_2CH_3}$$

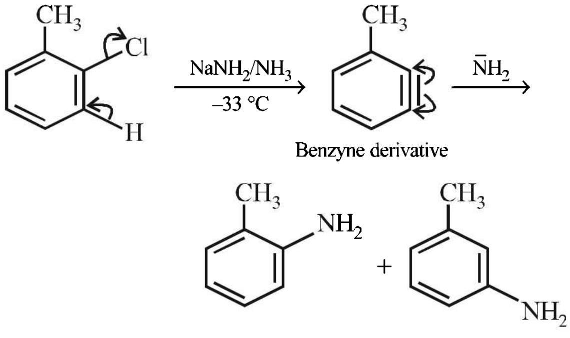
Since *trans*- alkene is more stable than *cis* thus *trans*-pentene -2 is the main product.

22. (b) $$CH_3CH_2CH_2Br \xrightarrow{\text{aq. NaOH}} CH_3CH_2CH_2OH$$
$$\xrightarrow[\text{heat}]{Al_2O_3} CH_3CH = CH_2$$
$$\xrightarrow{Cl_2/H_2O} CH_3.CHOH.CH_2Cl$$

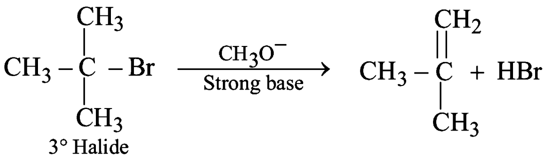
23. (c) 

$$CH_3 - \overset{\overset{Br}{|}}{C}H - CH_2 - CH_3 \xrightarrow{\text{Alc. KOH}}$$
$$CH_3 - CH = CH - CH_3 + HBr$$

The formation of 2-butene is in accordance to **Saytzeff's rule**. The more substituted alkene is formed in major quantity.

24. (b) 

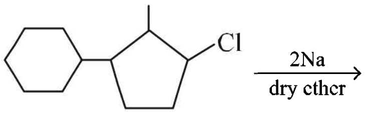
25. **(b)** 3° halide on reaction with strong base (CH_3O^-) undergo elimination reaction and forms alkene as major product.



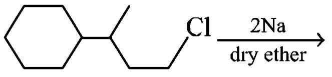
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br \xrightarrow[\text{Strong base}]{CH_3O^-} CH_3-\overset{CH_2}{\underset{CH_3}{\overset{\|}{C}}} + HBr$$

3° Halide

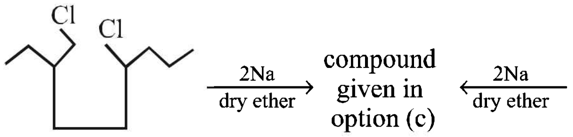
26. **(d)**

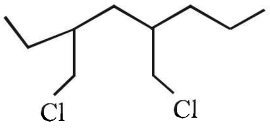


compound given in option (a)



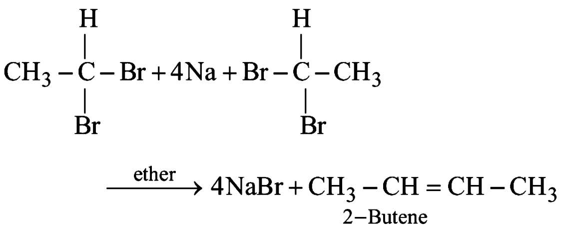
compound given in option (b)





Only the compound given in option (d) is assymetric as well as acyclic. So it cannot be synthesized by Wurtz reaction using one type of halide only.

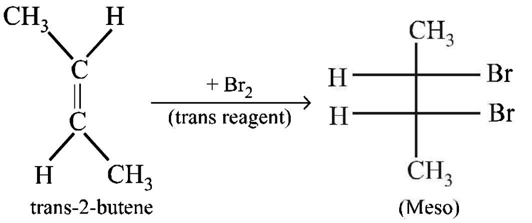
27. **(c)**



$$CH_3-\overset{H}{\underset{Br}{C}}-Br+4Na+Br-\overset{H}{\underset{Br}{C}}-CH_3 \xrightarrow{\text{ether}} 4NaBr+CH_3-CH=CH-CH_3$$

2–Butene

28. **(d)**



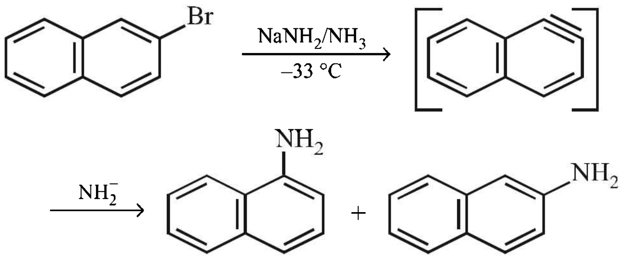
trans-2-butene

(Meso)

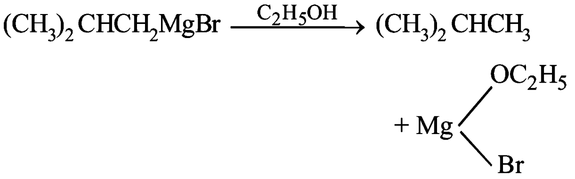
29. **(a)** $(CH_3)_3C-MgCl+D_2O\longrightarrow$

$(CH_3)_3C-D+Mg(OD)Cl$

30. **(a)**

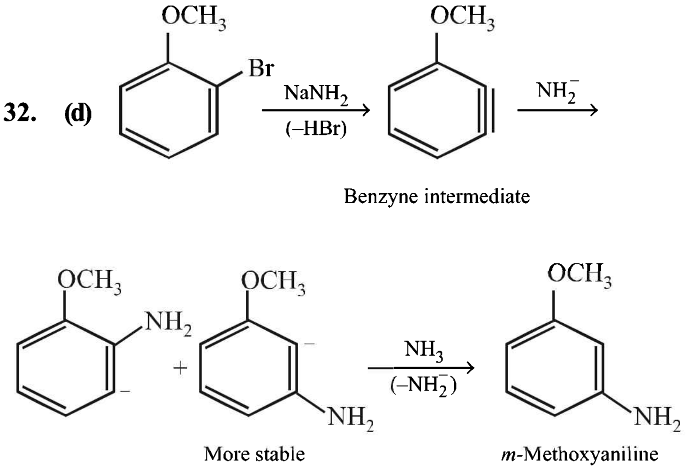


31. **(b)**



$$(CH_3)_2CHCH_2MgBr \xrightarrow{C_2H_5OH} (CH_3)_2CHCH_3 + Mg\begin{matrix}OC_2H_5\\Br\end{matrix}$$

32. **(d)**



Benzyne intermediate

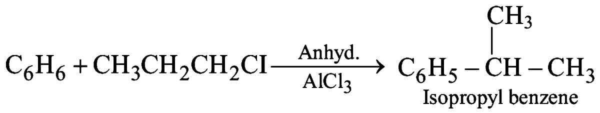
More stable

m-Methoxyaniline

33. **(d)** Debromination is a *trans*-elimination reaction. *meso*- 2, 3-Dibromobutane on debromination gives *trans*-2-butene.

34. **(a)** When *tert* -alkyl halides are used in Williamson synthesis elimination occurs rather than substitution resulting into formation of alkene. Here alkoxide ion abstract one of the β-hydrogen atom along with acting as a nucleophile.

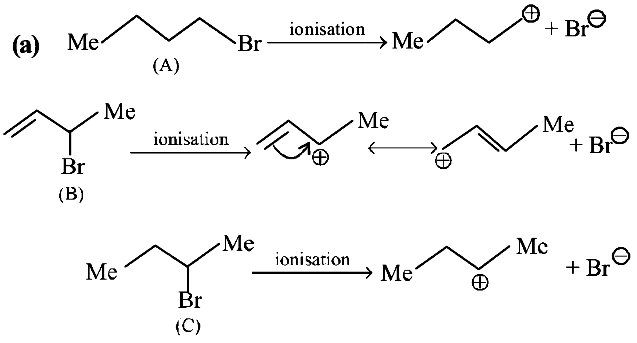
35. **(c)**



$$C_6H_6+CH_3CH_2CH_2Cl \xrightarrow[AlCl_3]{\text{Anhyd.}} C_6H_5-\overset{CH_3}{CH}-CH_3$$

Isopropyl benzene

36. **(a)**



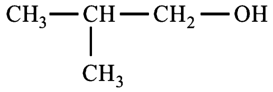
Since S_N1 reactions involve the formation of carbocation as intermediate in the rate determining step, more is the stability of carbocation higher will be the reactivity of alkyl halides towards S_N1 route. Now we know that stability of carbocations follows the order : 3° > 2° > 1°, so S_N1 reactivity should also follow the same order.

3° > 2° > 1° > Methyl **(S_N1 reactivity)**

37. (b) $C_6H_5Br \xrightarrow{Mg} C_6H_5MgBr$

$\xrightarrow{CH_3CH_2OH} C_6H_6 + CH_3CH_2OMgBr$

38. (d) Iodoform test is given by methyl ketones, acetaldehyde and methyl secondary alcohols.



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$$

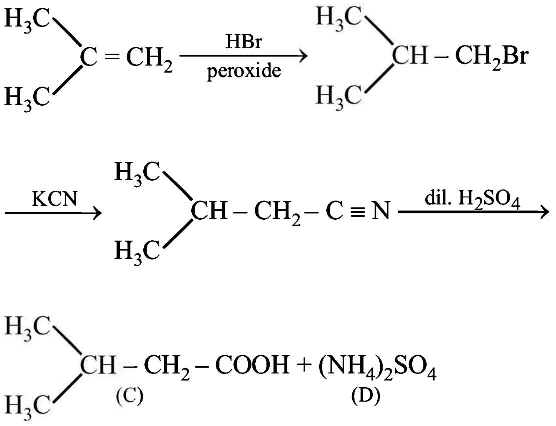
Isobutyl alcohol is a primary alcohol hence doesn't give positive iodoform test.

39. (d) $C_6H_5COOAg + Br_2 \xrightarrow{\text{Hunsdiecker reaction}} C_6H_5Br + CO_2 + AgBr$

40. (a) Grignard reagents react with compounds containing active hydrogen to form hydrocarbons corresponding to alkyl (or aryl) part of the Grignard reagent.

$C_6H_5MgBr + Me_3COH \longrightarrow C_6H_6 + Me_3COMgBr$

41. (a)

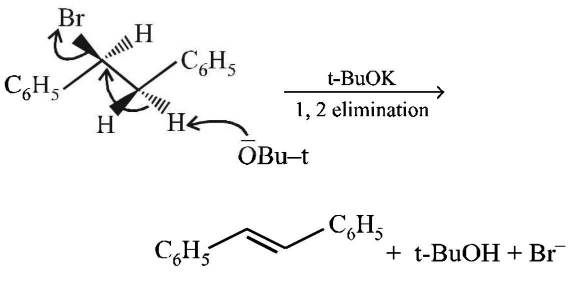


42. (b) Elimination reaction is highly favoured if

(a) Bulkier base is used

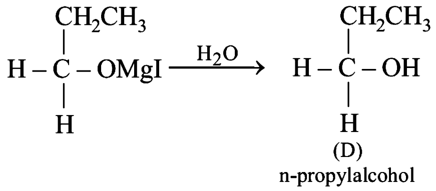
(b) Higher temperature is used

Hence in given reaction biomolecular elimination reaction provides major product.



43. (d) $CH_3CH_2OH \xrightarrow{P+I_2} \underset{(A)}{CH_3CH_2I}$

$\xrightarrow[\text{Ether}]{Mg} \underset{(B)}{CH_3CH_2MgI} \xrightarrow{HCHO}$

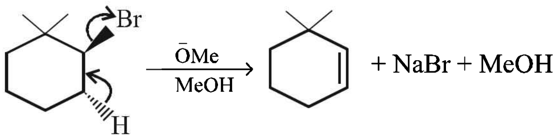


$$H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OMgI \xrightarrow{H_2O} H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

(D)

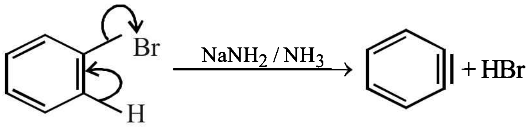
n-propylalcohol

44. (b)



(dehydrohalogenation reaction)

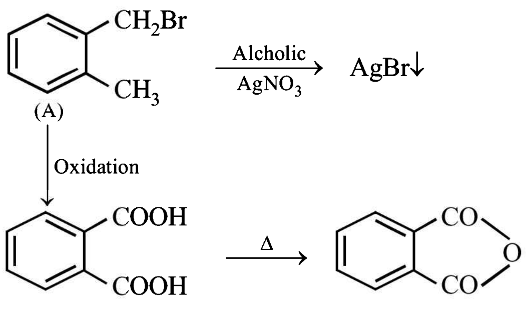
45. (a)



46. (b) $C_2H_5I \xrightarrow{\text{alc. KOH}} CH_2 = CH_2 \xrightarrow{Br_2}$

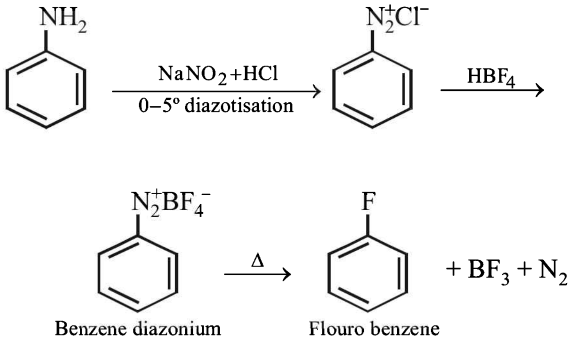
$BrCH_2 - CH_2Br \xrightarrow{KCN} CNCH_2.CH_2CN$

47. (d)



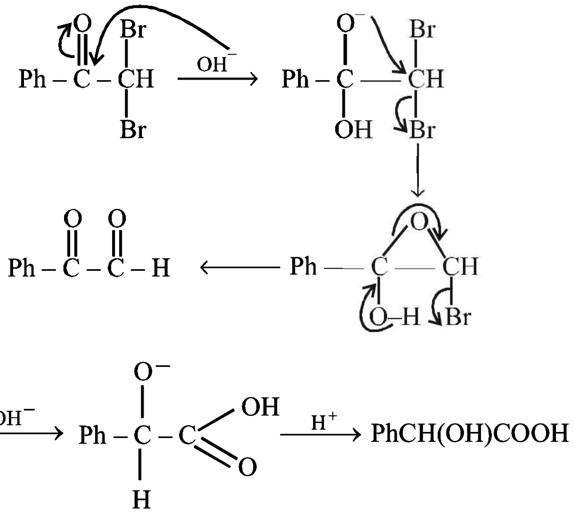
Acid (B) Phthalic Anhydride

48. (d)

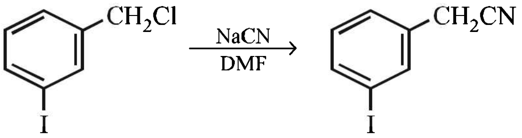


Benzene diazonium tetrafluoroborate Flouro benzene

49. (b)



50. (b)



Nuclear substitution will not take place.