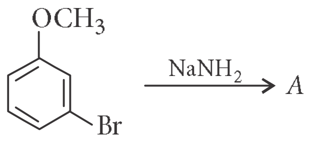
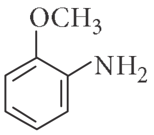
Chapter 24. Haloalkanes and Haloarenes

1. Identify *A* and predict the type of reaction.

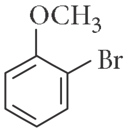


(a)



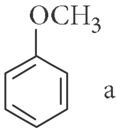
and elimination addition reaction

(b)



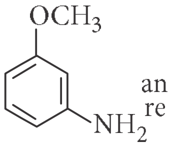
and cine substitution reaction

(c)



and cine substitution

(d)



and substitution reaction

(NEET 2017)

2. Consider the reaction,

$CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$

This reaction will be the fastest in

(a) ethanol (b) methanol

(c) *N, N′*-dimethylformamide (DMF)

(d) water. *(NEET-II 2016)*

3. Two possible stereo-structures of $CH_3CHOHCOOH$, which are optically active, are called

(a) atropisomers (b) enantiomers

(c) mesomers (d) diastereomers. *(2015)*

4. In an S_N1 reaction on chiral centres, there is

(a) inversion more than retention leading to partial racemisation

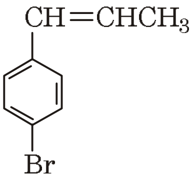
(b) 100% retention (c) 100% inversion

(d) 100% racemisation. *(2015)*

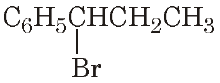
5. The reaction of $C_6H_5CH{=}CHCH_3$ with HBr produces

(a) $C_6H_5CH_2CH_2CH_2Br$

(b)

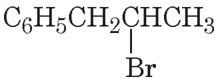


(c)



$C_6H_5\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$

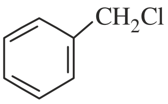
(d)



$C_6H_5CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$ *(2015, Cancelled)*

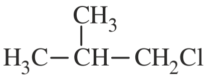
6. Which of the following compounds will undergo racemisation when solution of KOH hydrolyses?

(i)



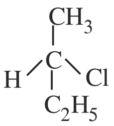
(ii) $CH_3CH_2CH_2Cl$

(iii)



$H_3C-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_2Cl$

(iv)

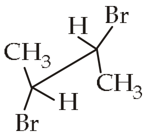


(a) (i) and (ii) (b) (ii) and (iv)

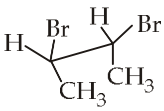
(c) (iii) and (iv) (d) (i) and (iv)

(2014)

7. Given:



and



I II

I and II are

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(a) identical
(b) a pair of conformers
(c) a pair of geometrical isomers
(d) a pair of optical isomers
(Karnataka NEET 2013)

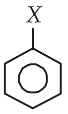
8. In the replacement reaction

The reaction will be most favourable if M happens to be
(a) Na (b) K
(c) Rb (d) Li *(Mains 2012)*

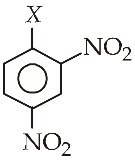
9. Consider the reactions.
(i) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH-CH_2OC_2H_5 + HBr$
(ii) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH-CH_2OC_2H_5 + Br^-$
The mechanisms of reactions (i) and (ii) are respectively
(a) S_N1 and S_N2 (b) S_N1 and S_N1
(c) S_N2 and S_N2 (d) S_N2 and S_N1
(Mains 2011)

10. Which one is most reactive towards S_N1 reaction?
(a) $C_6H_5CH(C_6H_5)Br$
(b) $C_6H_5CH(CH_3)Br$
(c) $C_6H_5C(CH_3)(C_6H_5)Br$
(d) $C_6H_5CH_2Br$ *(2010)*

11. The correct order of increasing reactivity of



I



II

$(CH_3)_3C-X$ III

$(CH_3)_2CH-X$ IV

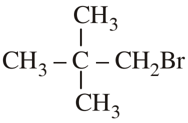
C—X bond towards nucleophile in the following compounds is
(a) I < II < IV < III (b) II < III < I < IV
(c) IV < III < I < II (d) III < II < I < IV
(2010)

12. In the following reaction
$C_6H_5CH_2Br \xrightarrow[2.\ H_3O^+]{1.\ Mg,\ Ether} X$, the product '$X$' is
(a) $C_6H_5CH_2OCH_2C_6H_5$ (b) $C_6H_5CH_2OH$
(c) $C_6H_5CH_3$
(d) $C_6H_5CH_2CH_2C_6H_5$ *(Mains 2010)*

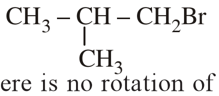
13. Which of the following reactions is an example of nucleophilic substitution reaction?
(a) $2RX + 2Na \rightarrow R-R + 2NaX$
(b) $RX + H_2 \rightarrow RH + HX$
(c) $RX + Mg \rightarrow RMgX$
(d) $RX + KOH \rightarrow ROH + KX$ *(2009)*

14. How many stereoisomers does this molecule have?
$CH_3CH{=}CHCH_2CHBrCH_3$
(a) 8 (b) 2
(c) 4 (d) 6 *(2008)*

15. In a S_N2 substitution reaction of the type
$R\text{—}Br + Cl^- \xrightarrow{DMF} R\text{—}Cl + Br^-$
which one of the following has the highest relative rate?

(a) 
$CH_3-C(CH_3)_2-CH_2Br$
(b) CH_3CH_2Br

(c) $CH_3CH_2CH_2Br$

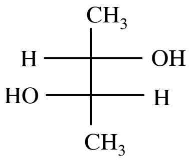
(d) 
$CH_3-CH(CH_3)-CH_2Br$
(2008)

16. If there is no rotation of plane polarised light by a compound in a specific solvent, though to be chiral, it may mean that
(a) the compound is certainly meso
(b) there is no compound in the solvent
(c) the compound may be a racemic mixture
(d) the compound is certainly a chiral.
(2007)

17. Which of the following is not chiral?
(a) 2-Hydroxypropanoic acid
(b) 2-Butanol
(c) 2,3-Dibromopentane
(d) 3-Bromopentane *(2006)*

18. Which of the following is least reactive in a nucleophilic substitution reaction?
(a) $(CH_3)_3C-Cl$ (b) $CH_2{=}CHCl$
(c) CH_3CH_2Cl
(d) $CH_2{=}CHCH_2Cl$ *(2004)*

19. Which of the following pairs of compounds are enantiomers?

(a) 

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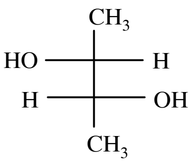

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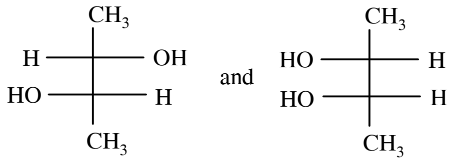
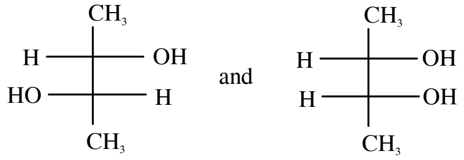
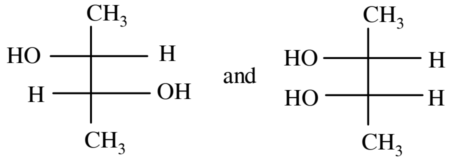
(b) 

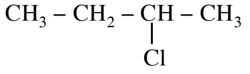
(c) 

(d) 

(2003)

20. Reactivity order of halides for dehydrohalogenation is
(a) $R-F > R-Cl > R-Br > R-I$
(b) $R-I > R-Br > R-Cl > R-F$
(c) $R-I > R-Cl > R-Br > R-F$
(d) $R-F > R-I > R-Br > R-Cl$ *(2002)*

21. $CH_3CH_2Cl \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} Y \xrightarrow{\text{acetic anhydride}} Z$
Z in the above reaction sequence is
(a) $CH_3CH_2CH_2NHCOCH_3$
(b) $CH_3CH_2CH_2NH_2$
(c) $CH_3CH_2CH_2CONHCH_3$
(d) $CH_3CH_2CH_2CONHCOCH_3$ *(2002)*

22. 
$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$ obtained by chlorination of n-butane will be
(a) meso form (b) racemic mixture
(c) d-form (d) l-form. *(2001)*

23. An organic compound A (C_4H_9Cl) on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative then, A is
(a) t-butyl chloride (b) s-butyl chloride
(c) *iso*-butyl chloride (d) n-butyl chloride.
(2001)

24. A compound of molecular formula C_7H_{16} shows optical isomerism, compound will be
(a) 2,3-dimethylpentane
(b) 2,2-dimethylbutane (c) 2-methylhexane
(d) none of these. *(2001)*

25. Ethyl chloride is converted into diethyl ether by
(a) Perkins reaction
(b) Grignard reaction
(c) Wurtz synthesis
(d) Williamson's synthesis *(1999)*

26. Which of the following compounds is not chiral?
(a) CH_3CHDCH_2Cl (b) CH_3CH_2CHDCl
(c) $DCH_2CH_2CH_2Cl$ (d) $CH_3CHClCH_2D$
(1998)

27. Replacement of Cl of chlorobenzene to give phenol requires drastic conditions. But chlorine of 2,4-dinitrochlorobenzene is readily replaced because
(a) NO_2 donates e^- at *meta* position
(b) NO_2 withdraws e^- from *ortho*/*para* positions
(c) NO_2 make ring electron rich at *ortho* and *para*
(d) NO_2 withdraws e^- from *meta* position.
(1997)

28. The alkyl halide is converted into an alcohol by
(a) elimination
(b) dehydrohalogenation
(c) addition
(d) substitution. *(1997)*

29. Reaction of t-butyl bromide with sodium methoxide produces
(a) sodium t-butoxide
(b) t-butyl methyl ether
(c) isobutane (d) isobutylene.
(1994)

30. Grignard reagent is prepared by the reaction between
(a) magnesium and alkane
(b) magnesium and aromatic hydrocarbon
(c) zinc and alkyl halide
(d) magnesium and alkyl halide. *(1994)*

31. Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ to give
(a) 3-propyl-1-chlorobenzene
(b) n-propylbenzene
(c) no reaction
(d) isopropylbenzene. *(1993)*

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32. Industrial preparation of chloroform employs acetone and

(a) phosgene
(b) calcium hypochlorite
(c) chlorine gas
(d) sodium chloride. *(1993)*

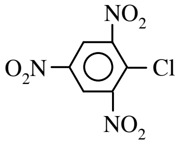
33. Chlorobenzene reacts with Mg in dry ether to give a compound (*A*) which further reacts with ethanol to yield

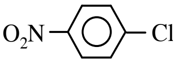
(a) phenol
(b) benzene
(c) ethyl benzene
(d) phenyl ether. *(1993)*

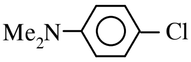
34. When chlorine is passed through propene at 400°C, which of the following is formed?

(a) PVC
(b) Allyl chloride
(c) Propyl chloride
(d) 1, 2-Dichloroethane *(1993)*

35. Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?

(a) 

(b) 

(c) 

(d) C_6H_5Cl *(1989)*

36. Which of the following is an optically active compound?

(a) 1-Butanol (b) 1-Propanol
(c) 2-Chlorobutane
(d) 4-Hydroxyheptane *(1989)*

37. Phosgene is a common name for

(a) phosphoryl chloride
(b) thionyl chloride
(c) carbon dioxide and phosphine
(d) carbonyl chloride. *(1988)*

38. Which one is formed when sodium phenoxide is heated with ethyl iodide?

(a) Phenetole
(b) Ethyl phenyl alcohol
(c) Phenol
(d) None of these *(1988)*

Answer Key

1.	(d)	**2.**	(c)	**3.**	(b)	**4.**	(a)	**5.**	(c)	**6.**	(None)			**7.**	(b)	**8.**	(c)	**9.**	(c)
10.	(c)	**11.**	(a)	**12.**	(c)	**13.**	(d)	**14.**	(c)	**15.**	(b)	**16.**	(a)	**17.**	(d)	**18.**	(b)	**19.**	(a)
20.	(b)	**21.**	(a)	**22.**	(b)	**23.**	(a)	**24.**	(a)	**25.**	(d)	**26.**	(c)	**27.**	(b)	**28.**	(d)	**29.**	(d)
30.	(d)	**31.**	(d)	**32.**	(b)	**33.**	(b)	**34.**	(b)	**35.**	(a)	**36.**	(c)	**37.**	(d)	**38.**	(a)		

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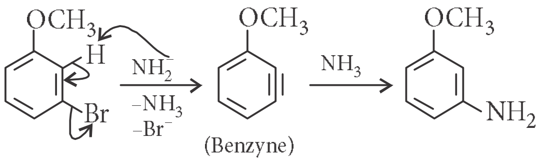
EXPLANATIONS

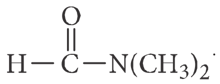
1. **(d) :** *m*-Bromoanisole gives only the respective *meta* substituted aniline. This is a substitution reaction which goes by an elimination-addition pathway.



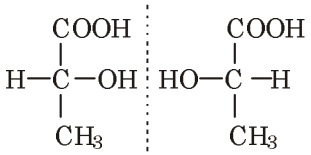
2. **(c) :** The reaction,

$$CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$$

follows S_N2 mechanism which is favoured by polar aprotic solvent *i.e.*, *N*, *N′*–dimethylformamide (DMF),


$$H-\overset{\overset{O}{\|}}{C}-N(CH_3)_2.$$

3. **(b) :**

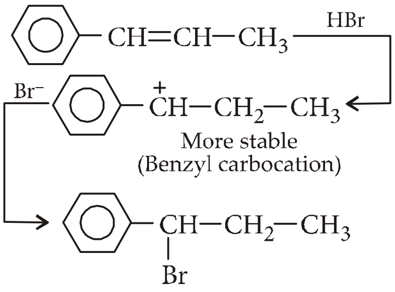


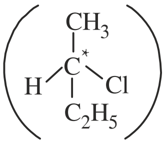
Enantiomers

4. **(a) :** In case of optically active alkyl halides, S_N1 reaction is accompanied by racemisation. The carbocation formed in the slow step being sp^2 hybridised is planar and attack of nucleophile may take place from either side resulting in a mixture of products, one having the same configuration and other having inverted configuration.

The isomer corresponding to inversion is present in slight excess because S_N1 also depends upon the degree of shielding of the front side of the reacting carbon.

5. **(c) :**



6. **(None) :** Due to chirality , only compound (iv) will undergo racemisation. Hence, all the given options are incorrect.

7. **(b) :** I and II are staggered and eclipsed conformers.

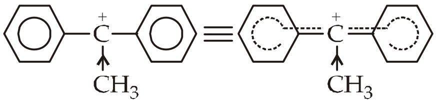
8. **(c) :** Tertiary halide shows S_N1 mechanism *i.e.*, ionic mechanism. In the given reaction negative ion will attack on carbocation. Thus greater the tendency of ionisation (greater ionic character in $M-F$ bond) more favourable will be reaction. The most ionic bond is Rb – F in the given examples thus most favourable reaction will be with Rb–F.

9. **(c) :** If reaction is S_N1, there will be the formation of carbocation and the rearrangement takes place. In these reactions there is no rearrangement hence both are S_N2 mechanism.

10. **(c) :** S_N1 reactions proceed *via* the formation of a carbocation intermediate.

More stable is the carbocation more reactive is the alkyl/aryl halide towards S_N1.

In $C_6H_5C^+(CH_3)(C_6H_5)$ carbocation, the two phenyl rings by their –*R* effect and —CH_3 by its +*I* effect diminish the positive charge and make it stable.



11. **(a) :** I < II < IV < III

The order of reactivity is dependent on the stability of the intermediate carbocation formed by cleavage of C—*X* bond. The 3° carbocation (formed from III) will be more stable than its 2° counter part (formed from IV) which in turn will be more stable than the arenium ion (formed from I). Also, the aryl halide has a double bond character in the C—*X* bond which makes the cleavage more difficult. However, inspite of all the stated factors, II will be more reactive than I due to the presence of the electron withdrawing –NO_2 group. C—*X* bond becomes weak and undergoes nucleophilic substitution reaction.

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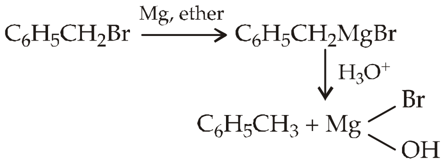
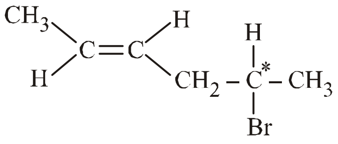
12. (c) : 

$$C_6H_5CH_2Br \xrightarrow{\text{Mg, ether}} C_6H_5CH_2MgBr \xrightarrow{H_3O^+} C_6H_5CH_3 + Mg\begin{matrix}Br\\OH\end{matrix}$$

13. (d)

14. (c) : The given compound may be written as



Both geometrical isomerism (*cis-trans* form) and optical isomerism is possible in the given compound.

No. of optical isomer = $2^n = 2^1 = 2$

(where n = no. of asymmetric carbon)

Hence total no. of stereoisomers = 2 + 2 = 4

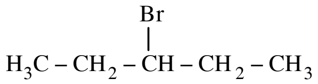
15. (b) : S_N2 mechanism is followed in case of primary and secondary alkyl halides *i.e.* S_N2 reaction is favoured by small groups on the carbon atoms attached to halogen so,

$$CH_3-X > R-CH_2-X > R_2CH-X > R_3C-X.$$

Primary is more reactive than secondary and tertiary alkyl halides.

S_N2 order : Methyl > Ethyl > Isopropyl > Tertiary butyl > Allyl > Benzyl

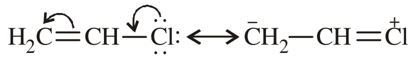
16. (a) : Meso compound does not rotate plane polarised light. Compound which contains tetrahedral atoms with four different groups but the whole molecule is achiral, is known as meso compound. It possesses a plane of symmetry and is optically inactive. One of the asymmetric carbon atoms turns the plane of polarised light to the right and other to the left and to the same extent so that the rotation due to upper half is compensated by the lower half, *i.e.*, internally compensated, and finally there is no rotation of plane polarised light.

17. (d) : 

$$H_3C-CH_2-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_2-CH_3$$

Due to absence of asymmetric carbon atom.

18. (b) : The non-reactivity of the chlorine atom in vinyl chloride may be explained from the molecular orbital point of view as follows. If the chlorine atom has sp^2 hybridisation, the C – Cl bond will be a σ-bond and the two lone pairs of electrons would occupy the other two sp^2 orbitals. This would leave a p orbital containing a lone pair, and this orbital could now conjugate with the π-bond of the ethylenic link. Thus two M.O's will be required to accommodate these four π-electrons. Furthermore, since chlorine is more electronegative than carbon, the electrons will tend to be found in the vicinity of the chlorine atom. Nevertheless, the chlorine atom has now lost full control of the lone pair and so, is less negative than it would have been had there been no conjugation. Since two carbon atoms have acquired a share in the lone pair, each carbon atom acquires a small negative charge. Hence, owing to delocalisation of bonds (through conjugation), the vinyl chloride molecule has an increased stability. Before the chlorine atom can be displaced by some other group, the lone pair must be localised again on the chlorine atom. This requires energy, and so the chlorine is more firmly bound.



19. (a) : These two are non-superimposable mirror images of each other, so they are enantiomers.

20. (b) : I > Br > Cl > F → atomic radii

F, Cl, Br, I belongs to the same group orderly. Atomic radii go on increasing as the nuclear charge increases in preceeding downwards in a group. The decreasing order of bond length C – I > C – Br > C – Cl > C – F. The order of bond dissociation energy $R-F > R-Cl > R-Br > R-I$. During dehydrohalogenation C – I bond breaks more easily than C – F bond. So reactivity order of halides

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

21. (a) : $CH_3CH_2Cl \xrightarrow{NaCN} \underset{(X)}{CH_3CH_2CN} \xrightarrow{Ni/H_2}$

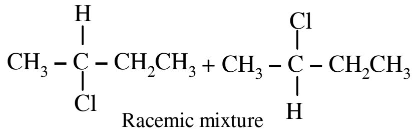
$$\underset{(Y)}{CH_3CH_2CH_2NH_2} \xrightarrow[\text{anhydride}]{\text{acetic}} \underset{(Z)}{CH_3CH_2CH_2NHCOCH_3}$$

22. (b) : Chlorination of n-butane takes place via free radical formation. *i.e.* $Cl_2 \rightarrow {}^{\bullet}Cl + {}^{\bullet}Cl$

$$CH_3CH_2CH_2CH_3 \xrightarrow{{}^{\bullet}Cl} CH_3\dot{C}HCH_2CH_3 + HCl$$

sp^2- hybrid planar shape intermediate and ${}^{\bullet}Cl$ may attack from either side to give

$$CH_3\dot{C}HCH_2CH_3 + \dot{C}l \longrightarrow$$



$$CH_3-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-CH_2CH_3 + CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-CH_2CH_3$$

Racemic mixture

(Mixture of 50% d-form and 50% l-form)

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23. (a) : Wurtz reaction → It involves the reaction of alkyl halides with Na in ethanol solution to form higher alkanes.

$$2R-X+2Na \rightarrow R-R+2NaX$$

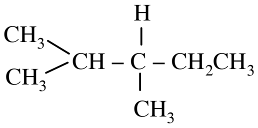
In the given problem,

$$C_4H_9Cl+Na \xrightarrow{\text{ethanol}} C_4H_9\cdot C_4H_9+2NaCl$$

Compound *A* is *t*-butyl chloride in this all – CH_3 groups have primary hydrogen only and able to give only one chloro derivative.

$$(CH_3)_3CC(CH_3)_3 \xrightarrow{Cl_2} CH_2Cl(CH_3)_2C-C(CH_3)_3$$

24. (a) : Organic compounds exhibit the property of enantiomerism (optical isomerism) only when their molecules are chiral. Most chiral compounds have a chiral centre, which is an atom bonded to four different atoms or groups.

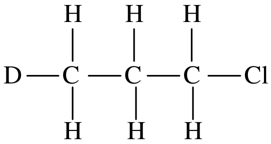


2,3-Dimethylpentane has one chiral C-atom and do not have any symmetric element.

25. (d) : $C_2H_5-Cl+Na-O-C_2H_5 \rightarrow C_2H_5-O-C_2H_5+NaCl$

The above reaction is called as Williamson's synthesis.

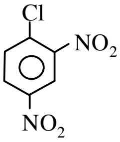
26. (c) :



$$D-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Cl$$

The above compound has no chiral 'C'-atom. All the 'C' atoms are attached to two identical 'H' atoms, so they are not asymmetrical.

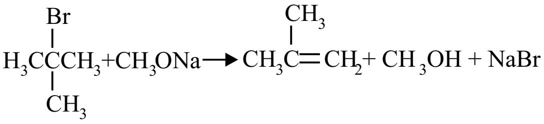
27. (b) :



Withdrawal of electrons by – NO_2 groups from *ortho*/*para* positions cause easier removal of – Cl atom due to the development of positive charge on *o*- and *p*- positions.

28. (d) : $\underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{(aqueous)}}{KOH} \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH}+KBr$

29. (d) : Isobutylene is obtained.



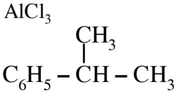
$$H_3C\underset{CH_3}{\overset{Br}{C}}CH_3+CH_3ONa \longrightarrow CH_3\overset{CH_3}{C}=CH_2+CH_3OH+NaBr$$

Thus the reaction produces isobutylene.

30. (d) : Grignard reagent is prepared by heating an alkyl halide with dry magnesium powder in dry ether.

$$R-X+Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R-Mg-X}$$

31. (d) : $C_6H_6+CH_3CH_2CH_2Cl \xrightarrow[\text{AlCl}_3]{\text{Anhy.}}$

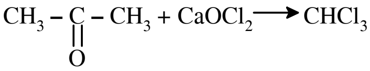


$$C_6H_5-\overset{CH_3}{CH}-CH_3$$

Isopropylbenzene

32. (b) : $CaOCl_2+H_2O \rightarrow Ca(OH)_2+Cl_2$

Cl_2, so obtained acts as a mild oxidising as well as chlorinating agent.



$$CH_3-\underset{O}{\underset{\|}{C}}-CH_3+CaOCl_2 \longrightarrow CHCl_3$$

33. (b) : $C_6H_5Cl \xrightarrow{Mg} \underset{(A)}{C_6H_5MgCl} \xrightarrow{CH_3CH_2OH} C_6H_6+CH_3CH_2OMgCl$

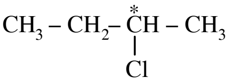
34. (b) :

$$CH_3CH=CH_2 \xrightarrow[-\text{HCl}]{Cl_2,\ 400°C} ClCH_2CH=CH_2$$

At 400°C temperature, substitution occurs instead of addition.

35. (a) : Cl in 2, 4, 6-trinitrochlorobenzene is activated by three $-NO_2$ groups at *o* and *p*-positions and hence undergoes hydrolysis most readily.

36. (c) :



$$CH_3-CH_2-\underset{Cl}{\overset{*}{C}H}-CH_3$$

2-Chlorobutane contains a chiral carbon atom and hence is optically active compound.

37. (d) : Carbonyl chloride ($COCl_2$)

38. (a) : Phenetole is formed when sodium phenoxide is heated with ethyl iodide.

$$C_6H_5ONa+C_2H_5I \xrightarrow{\Delta} \underset{\text{Phenetole}}{C_6H_5OC_2H_5}$$

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