CHAPTER

10

Haloalkanes and Haloarenes

CASE STUDY / PASSAGE BASED QUESTIONS

1

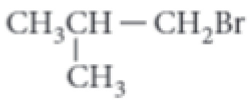
Read the passage given below and answer the following questions :

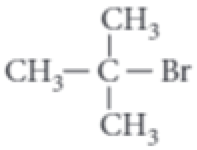
A primary alkyl halide (*A*) C_4H_9Br reacted with alcoholic KOH to give compound (*B*). Compound (*B*) is reacted with HBr to give compound (*C*) which is an isomer of (*A*). When (*A*) reacted with sodium metal, it gave a compound (*D*) C_8H_{18} that is different than the compound obtained when *n*-butyl bromide reacted with sodium metal.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Compound (*A*) is

(a) $CH_3CH_2CH_2CH_2Br$

(b) 
$CH_3\underset{\underset{CH_3}{|}}{CH}-CH_2Br$

(c) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$

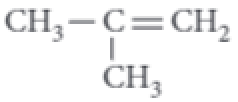
(d) $CH_3CH_2CH_2Br$

(ii) Which type of isomerism is present in compound (*A*) and (*C*)?

(a) Positional (b) Functional (c) Chain (d) Both (a) and (c)

OR

Identify compound (*B*).

(a) 
$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$

(b) $CH_3-CH=CH-CH_3$

(c) $CH_3-CH_2-CH=CH_2$

(d) None of these

(iii) IUPAC name of compound (*D*) is

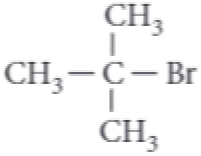
(a) *n*-octane

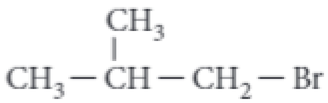
(b) 2,5-dimethylhexane

(c) 2-methylheptane

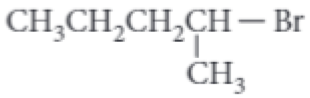
(d) 3,4-dimethyl hexane.

(iv) When compoound (*C*) is treated with alc. KOH and then treated with HBr in presence of peroxide, the compound obtained is

(a) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$

(b) 
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-Br$

(c) $CH_3CH_2CH_2CH_2Br$

(d) 
$CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{CH}-Br$

Syllabus

Haloalkanes : Nomenclature, nature of C–*X* bond, physical and chemical properties, optical rotation, mechanism of substitution reactions.

Haloarenes : Nature of C–*X* bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only).

2

Read the passage given below and answer the following questions :

Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular (S_N2) and substitution nucleophilic unimolecular (S_N1) depending on molecules taking part in determining the rate of reaction. Reactivity of alkyl halide towards S_N1 and S_N2 reactions depends on various factors such as steric hindrance, stability of intermediate or transition state and polarity of solvent. S_N2 reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in case of S_N1 reactions.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following is most reactive towards nucleophilic substitution reaction?
(a) C_6H_5Cl (b) $CH_2=CHCl$ (c) $ClCH_2CH=CH_2$ (d) $CH_3CH=CHCl$

(ii) Isopropyl chloride undergoes hydrolysis by
(a) S_N1 mechanism (b) S_N2 mechanism
(c) S_N1 and S_N2 mechanism (d) neither S_N1 nor S_N2 mechanism.

(iii) The most reactive nucleophile among the following is
(a) CH_3O^- (b) $C_6H_5O^-$ (c) $(CH_3)_2CHO^-$ (d) $(CH_3)_3CO^-$

(iv) Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of
(a) insolubility (b) instability
(c) inductive effect (d) stearic hindrance.

OR

Which of the following is the correct order of decreasing S_N2 reactivity?
(a) $RCH_2X > R_2CHX > R_3CX$ (b) $R_3CX > R_2CHX > RCH_2X$
(c) $R_2CHX > R_3CX > RCH_2X$ (d) $RCH_2X > R_3CX > R_2CHX$

3

Read the passage given below and answer the following questions :

A chlorocompound (*A*) on reduction with Zn-Cu and ethanol gives the hydrocarbon (*B*) with five carbon atoms. When (*A*) is dissolved in dry ether and treated with sodium metal it gave 2,2,5,5-tetramethylhexane. The treatment of (*A*) with alcoholic KCN gives compound (*C*).

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The compound (*A*) is
(a) 1-chloro-2, 2-dimethylpropane (b) 1-chloro-2, 2-dimethyl butane
(c) 1-chloro-2-methyl butane (d) 2-chloro-2-methyl butane.

(ii) The reaction of (*C*) with Na, C_2H_5OH gives
(a) $(CH_3)_3C\,CH_2CONH_2$ (b) $(CH_3)_3C\,NH_2$
(c) $(CH_3)_3C\,CH_2CH_2NH_2$ (d) $(CH_3)_2CHCH_2NH_2$

(iii) The reaction of (*C*) with Na, C_2H_5OH is called
(a) Gilman reaction (b) Mendius reaction
(c) Grooves process (d) Swart's reaction.

OR

The reaction of (*A*) with aq. KOH will preferably favour

(a) S_N1 mechanism (b) S_N2 mechanism (c) E_1 mechanism (d) E_2 mechanism.

(iv) Compound (*B*) is

(a) *n*-pentane (b) 2, 2-dimethylpropane

(c) 2-methylbutane (d) none of these.

4

Read the passage given below and answer the following questions :

When haloalkanes with β-hydrogen atom are boiled with alcoholic solution of KOH, they undergo elimination of hydrogen halide resulting in the formation of alkenes. These reactions are called β-elimination reactions or dehydrohalogenation reactions. These reactions follow Saytzeff's rule. Substitution and elimination reactions often compete with each other. Mostly bases behave as nucleophiles and therefore can engage in substitution or elimination reactions depending upon the alkyl halide and the reaction conditions.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Among the following the most reactive towards alcoholic KOH is

(a) $CH_2{=}CHBr$ (b) $CH_3COCH_2CH_2Br$

(c) CH_3CH_2Br (d) $CH_3CH_2CH_2Br$

(ii) The general reaction, $R{-}X \xrightarrow{\text{aq. OH}^-} ROH + X^-$, is expected to follow decreasing order of reactivity as in

(a) *t*-BuI > *t*-BuBr > *t*-BuCl > *t*-BuF (b) *t*-BuF > *t*-BuCl > *t*-BuBr > *t*-BuI

(c) *t*-BuBr > *t*-BuCl > *t*-BuI > *t*-BuF (d) *t*-BuF > *t*-BuCl > t-BuI > *t*-BuBr

(*t*-Bu = tertiary Butyl group)

(iii) Reaction of *t*-butyl bromide with sodium methoxide produces

(a) sodium *t*-butoxide (b) *t*-butyl methyl ether

(c) *iso*-butane (d) *iso*-butylene.

(iv) In the elimination reactions, the reactivity of alkyl halides follows the sequence

(a) $R-F > R-Cl > R-Br > R-I$ (b) $R-I > R-Br > R-Cl > R-F$

(c) $R-I > R-F > R-Br > R-Cl$ (d) $R-F > R-I > R-Br > R-Cl$

OR

The ease of dehydrohalogenation of alkyl halide with alcoholic KOH is

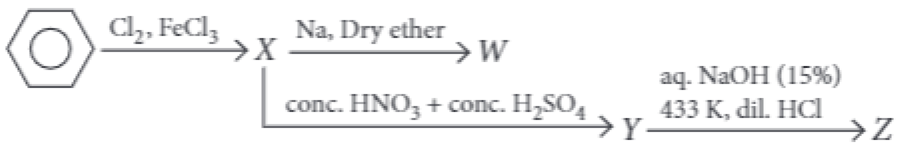
(a) 3° < 2° < 1° (b) 3° > 2° > 1°

(c) 3° < 2° > 1° (d) 3° > 2° < 1°

5

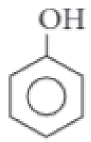
Read the passage given below and answer the following questions :

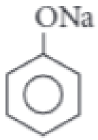
Consider the given sequence of reactions :

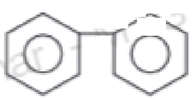


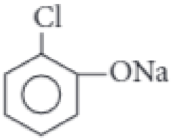
The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Identify *W*.

(a) 

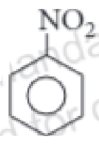
(b) 

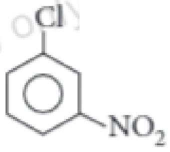
(c) 

(d) 

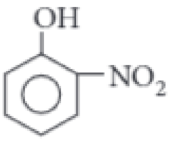
OR

Compound *Y* is

(a) 

(b) 

(c) 

(d) 

(ii) When *X* reacts with CH_3COCl in presence of anhy. $AlCl_3$, the reaction is known as

(a) Fittig reaction
(b) Ullmann reaction
(c) Wurtz-Fittig reaction
(d) Friedel–Crafts acylation reaction.

(iii) When *X* is treated Ni-Al/NaOH the product obtained is

(a) benzene
(b) phenol
(c) *p*-chlorophenol
(d) triphenyl.

(iv) Compound *Z* is

(a) phenol
(b) *p*-chlorophenol
(c) *p*-nitrophenol
(d) nitrobenzene.

6

Read the passage given below and answer the following questions :

Haloarenes are less reactive than haloalkanes. The low reactivity of haloarenes can be attributed to

- resonance effect
- *sp*^{2} hybridisation of C — *X* bond
- polarity of C — *X* bond
- instability of phenyl cation (formed by self-ionisation of haloarene)
- repulsion between the electron rich attacking nucleophiles and electron rich arenes.

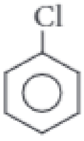
Reactivity of haloarenes can be increased or decreased by the presence of certain groups at certain positions for example, nitro ($-NO_2$) group at *o*/*p* positions increases the reactivity of haloarenes towards nucleophilc substitution reactions.

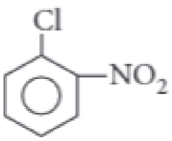
The following questions are multiple choice questions. Choose the most appropriate answer :

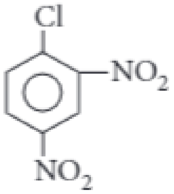
(i) Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to

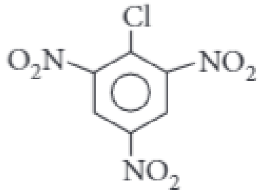
(a) the formation of less stable carbonium ion
(b) resonance stabilisation
(c) larger carbon-halogen bond
(d) inductive effect.

(ii) Which of the following aryl halides is the most reactive towards nucleophilic substitution?

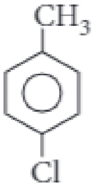
(a) 

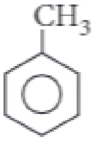
(b) 

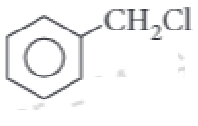
(c) 

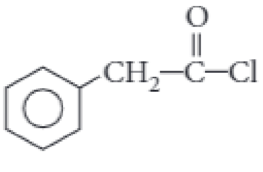
(d) 

(iii) Which one of the following will react fastest with aqueous NaOH?

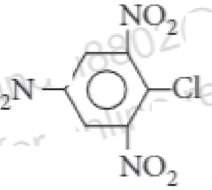
(a) 

(b) 

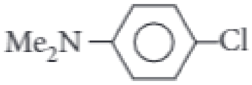
(c) 

(d) 

(iv) Which chloro derivative of benzene among the followings would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?

(a) 

(b) 

(c) 

(d) C_6H_5Cl

OR

The reactivity of the compounds (i) MeBr, (ii) $PhCH_2Br$, (iii) MeCl, (iv) *p*-$MeOC_6H_4Br$ decreases as

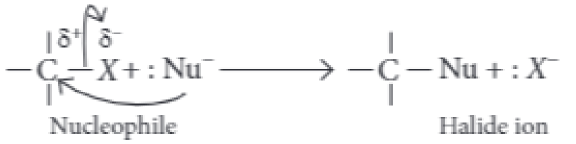
(a) (i) > (ii) >(iii) > (iv) (b) (iv) > (ii) >(i) > (iii)

(c) (iv) > (iii) >(i) > (ii) (d) (ii) > (i) >(iii) > (iv)

7

Read the passage given below and answer the following questions :

In haloalkanes, when a nucleophile stronger than the halide ion approaches the positively charged carbon atom of an alkyl halide, the halogen atom along with its bonding electron pair gets displaced and a new bond with the carbon and the nucleophile is formed. These reactions are called nucleophilic substitution reactions.



$$-\overset{|}{\underset{|}{C}}{}^{\delta+}-X^{\delta-} + \underset{\text{Nucleophile}}{:Nu^-} \longrightarrow -\overset{|}{\underset{|}{C}}-Nu + \underset{\text{Halide ion}}{:X^-}$$

$$CH_3CH_2Br + \underset{\text{Nucleophile}}{OH^-} \longrightarrow CH_3CH_2OH + :Br^-$$

In these reactions the atom or group of atoms which loses its bond from carbon and takes on an additional pair of electrons is called leaving group. Halide ions are good leaving groups. Some important nucleophilic substitution reactions of haloalkanes with common nucleophiles are given in the table below.

	Reagent	Nucleophile (Nu^-)	Substitution product R — Nu	Class of main product
1.	NaOH or KOH or moist Ag_2O	^-OH	ROH	Alcohol
2.	H_2O	H_2O	ROH	Alcohol
3.	NaI	I^-	R — I	Alkyl iodide
4.	$R'NH_2$	$R'\ddot{N}H_2$	RNHR′	Sec. amine
5.	KCN	$\bar{C}\equiv N:$	RCN	Nitrile (cyanide)
6.	KNO_2	$O=N-O^-$	R—O—N=O	Alkyl nitrite

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Alkyl halides are hydrolysed to alcohols by moist silver oxide.
Reason : *R*Cl is hydrolysed to *R*OH easily but reactions slow down on addition of KI.

(ii) **Assertion :**Alkyl halides form alkenes when heated above 300°C.
Reason : CH_3CH_2I reacts slowly with strong base as compared to CD_3CH_2I.

(iii) **Assertion :***R*Br reacts with $AgNO_2$ to give nitroalkane.
Reason : Silver nitrite ($AgNO_2$) is an ionic compound, therefore the negative charge on nitrogen is the attacking site.

(iv) **Assertion :** The nucleophilic substitution of vinyl chloride is difficult than ethyl chloride.
Reason : Vinyl group is electron donating group.

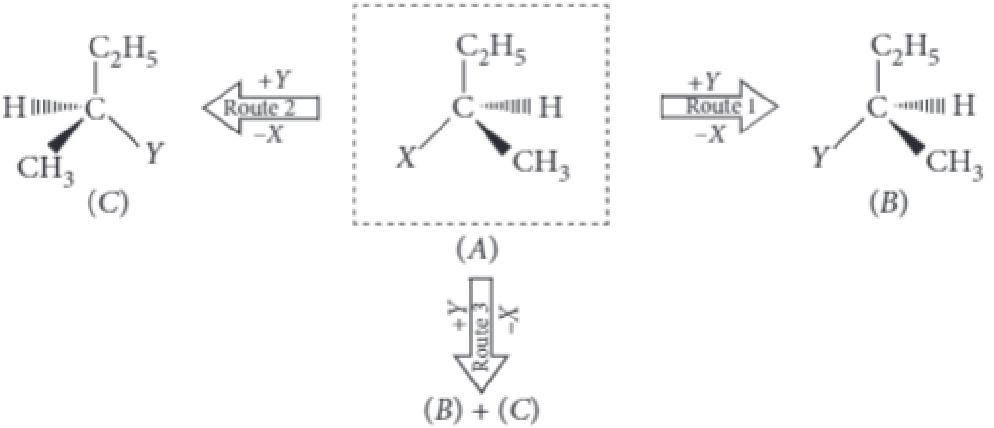
OR

Assertion : 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 1-butene as the major product.
Reason : 1-Butene is less stable than 2-butene.

8

Read the passage given below and answer the following questions :

When a chemical reaction involves bond cleavage or bond formation at an asymmetric carbon atom, three different products may be formed. For example, during the substitution of a group *X* by *Y* in the following reaction, the three possible products may be shown below :



(i) If *B* is the only product, the process is called retention of configuration because *B* has the same configuration as the starting reactant (*A*).
(ii) If *C* is the only product, the process is called inversion of configuration because *C* has the configuration opposite to the starting reactant (*A*).
(iii) If an equimolar mixture of *B* and *C* (*i.e.*, a 50 : 50 mixture) is formed, then the process is called racemisation and the product is optically inactive because one isomer will rotate the light in the direction opposite to another.

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(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** A reaction is said to be stereospecific if a particular stereoisomer of the reactant produces a specific stereoisomer of the product.
Reason : Bromination of *cis*-2-butene gives *meso*-2, 3-dibromobutane which is stereospecific.

(ii) **Assertion :** Addition of Br_2 to *cis*-but-2-ene is stereoselective.
Reason : S_N2 reactions are stereospecific as well as stereoselective.

(iii) **Assertion :** Optically active 2-iodobutane on treatment with NaI in acetone undergoes recemization.
Reason : Repeated Walden inversions on the reactant and its product eventually gives a racemic mixture.

(iv) **Assertion :** S_N2 reaction of an optically active alkyl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.
Reason : S_N2 reactions always proceed with inversion of configuration.

OR

Assertion : Nucleophilic substitution reaction of an optically active alkyl halide gives a mixture of enantiomers.
Reason : The reaction occurs by S_N1 mechanism.

9

Read the passage given below and answer the following questions :

The order of reactivity towards S_N1 reaction depends upon the stability of carbocation in the first step. Greater the stability of the carbocation, greater will be its ease of formation from alkyl halide and hence faster will be the rate of the reaction. As we know, 3° carbocation is most stable, therefore, the *tert*-alkyl that halides will undergo S_N1 reaction very fast. For example, it has been observed that the reaction $(CH_3)_3CBr$ with OH^- ion to give 2-methyl-2-propanol is about 1 million times as fast as the corresponding reaction of the methyl bromide to give methanol.

The primary alkyl halides always react predominantly by S_N2 mechanism. On the other hand, the tertiary alkyl halides react predominantly by S_N1 mechanism. Secondary alkyl halides may react by either mechanism or by both the mechanisms without much preference depending upon the nature of the nucleophile and solvent.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

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(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Low concentration of nucleophile favours S_N1 mechanism.
Reason : 2° alkyl halides are less reactive than 1° towards S_N1 reactions.

(ii) **Assertion :** Polar solvent slows down S_N2 reactions.
Reason : CH_3-Br is less reactive than CH_3Cl.

(iii) **Assertion :** Benzyl bromide when kept in acetone- water it produces benzyl alcohol.
Reason : The reaction follows S_N2 mechanism.

(iv) **Assertion :** Rate of hydrolysis of methyl chloride to methanol is higher in DMF than in water.
Reason : Hydrolysis of methyl chloride follows second order kinetics.

OR

Assertion : S_N1 reaction is carried out in the presence of a polar protic solvent.
Reason : A polar protic solvent increases the stability of carbocation due to solvation.

10

Read the passage given below and answer the following questions :

The aryl halides are relatively less reactive towards nucleophilic substitution reactions as compared to alkyl halides. This low reactivity can be attributed to the following factors :

- The C — *X* bond in halobenzene has a partial double bond character due to involvement of halogen electrons in resonance with benzene ring.
- The C — *X* bond in aryl halides is less polar as compared to that in alkyl halides as sp^2 hyridised carbon is more electronegative than sp^3 hybridised carbon.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

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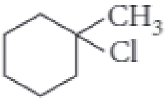
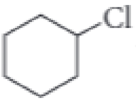
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Primary benzylic halides are more reactive than primary alkyl halides towards S_N1 reactions.
Reason : Reactivity depends upon the nature of the nucleophile and the solvent.

(ii) **Assertion :** 

is more reactive than 

towards nucleophilic substitution reactions.

Reason : Tertiary alkyl halides react predominantly by S_N1 mechanism.

(iii) **Assertion :** Chlorobenzene is more reactive than *p*-chloroanisole to nucleophilic substitution reactions.
Reason : Greater the stability of carbanion, greater is its ease of formation and hence, more reactive is the aryl halide.

OR

Assertion : 4-Nitrochlorobenzene undergoes nucleophilic substitution more readily than chlorobenzene.
Reason : Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism while 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.

(iv) **Assertion :** Chlorobenzene is less reactive than benzene towards the electrophilic substitution reaction.
Reason : Resonance destabilises the carbocation.

ASSERTION & REASON

In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

11. **Assertion :** Boiling point of alkyl halides increases with increase in molecular weight.
Reason : Boiling point of alkyl halides is in the order $RI > RBr > RCl > RF$.

12. **Assertion :** The presence of nitro group facilitates nucleophilic substitution reactions in aryl halides.
Reason : The intermediate carbanion is stabilised due to the presence of nitro group.

13. **Assertion :** Boiling point of RCl is greater than RF.
Reason : R–Cl is more stable than R–F.

14. **Assertion :** Bromobenzene upon reaction with Br_2/Fe gives 1, 4-dibromobenzene as the major product.
Reason : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

15. **Assertion :** *n*-Butyl bromide has higher boiling point than isobutyl bromide.
Reason : The branching of the chain makes the molecule more compact and therefore decreases the surface area.

16 **Assertion :** Carbon-halogen bond in aryl halide has partial double bond character.
Reason : Aryl halides undergo nucleophilic substitution easily.

17. **Assertion :** *p*-Dichlorobenzene has higher melting point than *o*-dichlorobenzene.
Reason : Stronger the van der Waals' forces of attraction, higher is the melting point.

18. **Assertion :** Haloalkanes show H-bonding.
Reason : Haloalkanes are insoluble in water.

19. **Assertion :** Vinyl chloride is less reactive than alkyl chloride.
Reason : Stability of alkyl halide decreases as the strength of C–X bond decreases.

20. **Assertion :** Aryl halide gives a mixture of *o*-and *p*-products.
Reason : Aryl halides undergo electrophilic substitutions more readily than benzene.

21. **Assertion :** Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.
Reason : The reaction occurs by S_N2 mechanism.

22. **Assertion :** Electron withdrawing groups in aryl halides decrease the reactivity towards nucleophilic substitution.
Reason : 2,4-Dinitrochlorobenzene is more reactive than chlorobenzene.

23. **Assertion :** *p*-Dichlorobenzene is less soluble in organic solvents than the corresponding *o*-isomer.
Reason : *o*-Dichlorobenzene is polar while *p*-dichlorobenzene is not.

24. **Assertion :** S_N1 mechanism is facilitated by polar protic solvents like water, alcohol, etc.
Reason : $C_6H_5CH(C_6H_5)Br$ is less reactive than $C_6H_5CH(CH_3)Br$ in S_N1 reactions.

25. **Assertion :** Tertiary haloalkanes are more reactive than primary haloalkanes towards elimination reactions.
Reason : The $+I$-effect of the alkyl groups weakens the $C - X$ bond.

26. **Assertion :** Vinylic halides are highly reactive towards nucleophilic substitution reactions.
Reason : Reactivity is due to the polarity of carbon-halogen bond.

27. **Assertion :** Benzyl chloride is more reactive than *p*-chlorotoluene towards aqueous NaOH.
Reason : The C – Cl bond in benzyl chloride is more polar than C – Cl bond in *p*-chlorotoluene.

28. **Assertion :** 2-Chloro-3-methylbutane on treatment with alcoholic potash gives 2-methylbut-2-ene as major product.
Reason : The reaction occurs according to Saytzeff rule.

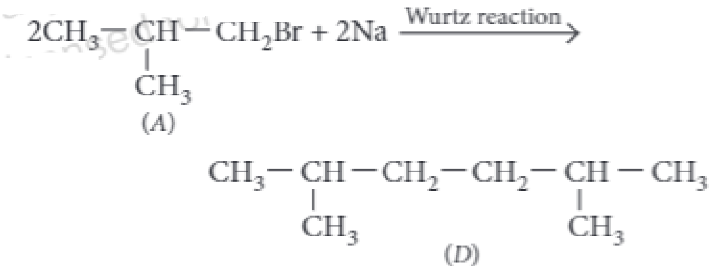
29. **Assertion :** Lower members of alkyl halides are colourless gases.
Reason : Alkyl iodides in general turn black on exposure to air and light.

30. **Assertion :** Isopropyl chloride is less reactive than CH_3Br in S_N2 reactions.
Reason : S_N2 reactions are always accompanied by inversion of configuration.

HINTS & EXPLANATIONS

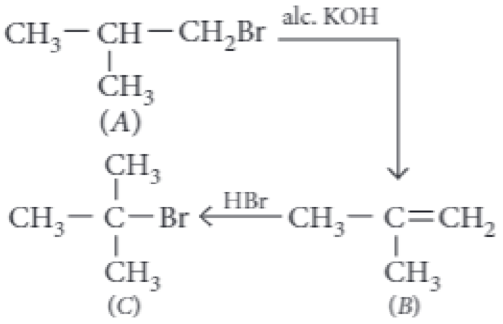
1. **(i) (b):** When compound (*A*) reacted with Na–metal, it gave a compound $D(C_8H_{18})$ which is different from the compound obtained when *n*-butyl bromide reacted with Na metal and hence the compound (*A*) must be isobutyl bromide.

$$2CH_3CH_2CH_2CH_2Br + 2Na \xrightarrow{\text{Wurtz reaction}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$



$$2\underset{(A)}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2Br} + 2Na \xrightarrow{\text{Wurtz reaction}} \underset{(D)}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3}$$

(ii) (d):



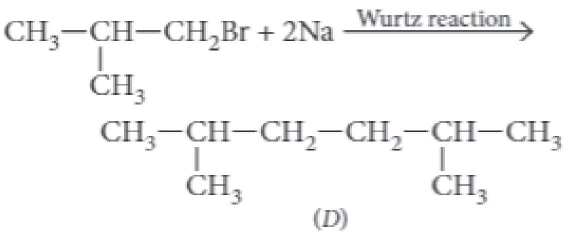
$$\underset{(A)}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2Br} \xrightarrow{\text{alc. KOH}} \underset{(B)}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2}$$

$$\underset{(C)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Br} \xleftarrow{HBr} \underset{(B)}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2}$$

OR

(a)

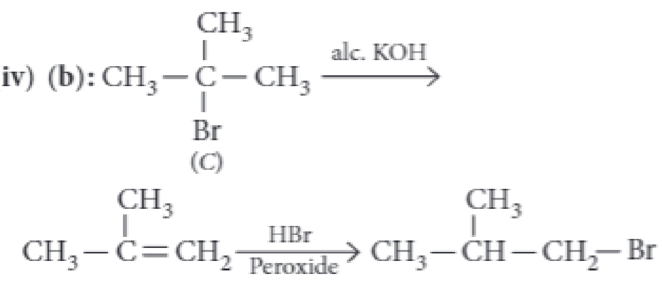
(iii) (b):



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2Br + 2Na \xrightarrow{\text{Wurtz reaction}} \underset{(D)}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3}$$

2,5-Dimethylhexane

(iv) (b):



$$\underset{(C)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3} \xrightarrow{\text{alc. KOH}}$$

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-Br$$

2. **(i) (c) :** Allylic chlorides are most reactive.

(ii) (c) : 2°- alkyl halides undergo hydrolysis by S_N1 or S_N2 mechanism.

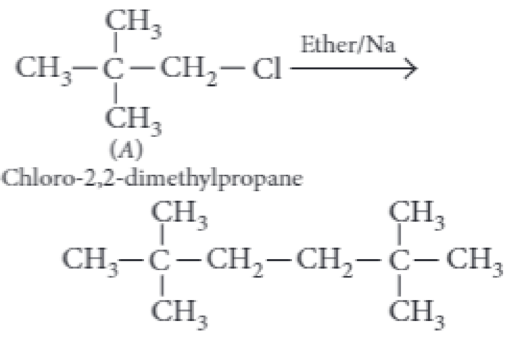
(iii) (a): Smaller the size of the nucleophile (*i.e.*, CH_3O^-), more reactive it is.

(iv) (d): Stearic hindrance due to bulky alkyl groups prevents the attack of the nucleophile in S_N2 mechanism.

OR

(a) : Larger the number of alkyl groups at α-carbon atom, more is the stearic hindrance and hence lesser the reactivity towards S_N2 mechanism.

3. **(i) (a) :**

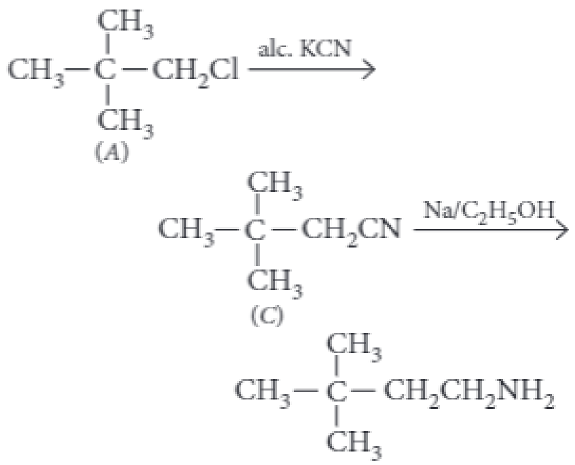


$$\underset{(A)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-Cl} \xrightarrow{\text{Ether/Na}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

1-Chloro-2,2-dimethylpropane

2, 2, 5, 5- Tetramethylhexane

(ii) (c) :



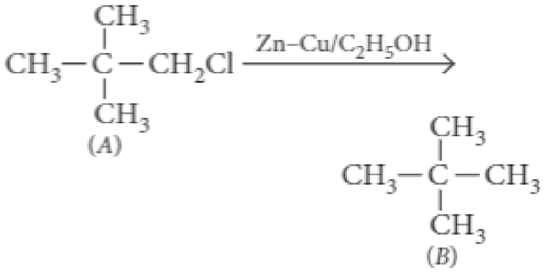
$$\underset{(A)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2Cl} \xrightarrow{\text{alc. KCN}} \underset{(C)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2CN} \xrightarrow{Na/C_2H_5OH} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2CH_2NH_2$$

(iii) (b)

OR

(a)

(iv) (b):

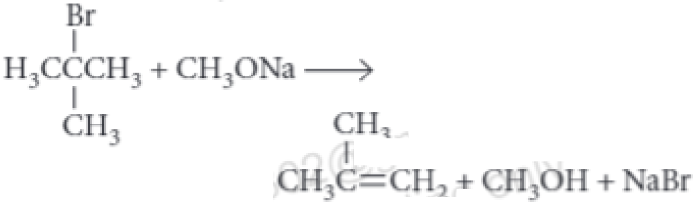


$$\underset{(A)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2Cl} \xrightarrow{Zn-Cu/C_2H_5OH} \underset{(B)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3}$$

4. **(i) (d):** In alkyl halides, polarity of C – Br bond increases with increase in chain length.

(ii) (a) : The order of reactivity of alkyl halides :
iodide > bromide > chloride (nature of the halogen atom)
tertiary > secondary > primary (type of halogen atom).

(iii) (d) : *Iso*-butylene is obtained.



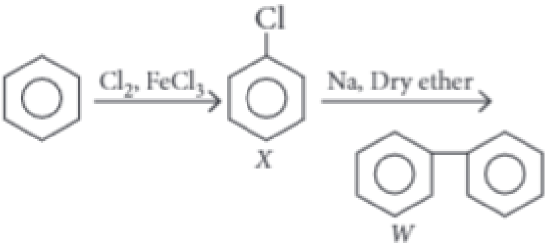
$$H_3C\overset{Br}{\underset{CH_3}{C}}CH_3 + CH_3ONa \longrightarrow CH_3\overset{CH_3}{C}{=}CH_2 + CH_3OH + NaBr$$

(iv) (b): 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
$R - I > R - Br > R - Cl > R - F$.

OR

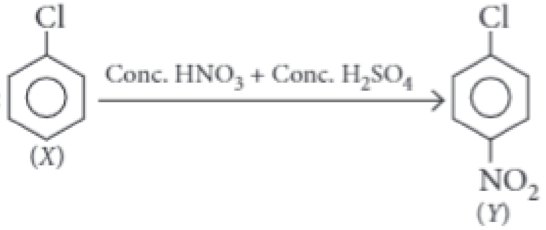
(b) : The ease of dehydrohalogenation of alkyl halide with alcoholic KOH is 3° > 2° > 1°.
This order of alkyl halides can be explained on the basis of the stability of the alkene formed after dehydrohalogenation of haloalkanes. 3° alkyl halides on dehydrohalogenation forms more substituted alkenes, which being more stable and formed at faster rate, while primary alkyl halides yield least substituted alkenes, which being less stable and formed at slower rate.

5. (i) (c) :



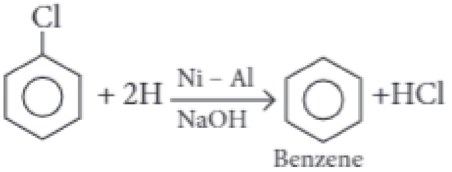
OR

(c) :



(ii) (d)

(iii) (a) :

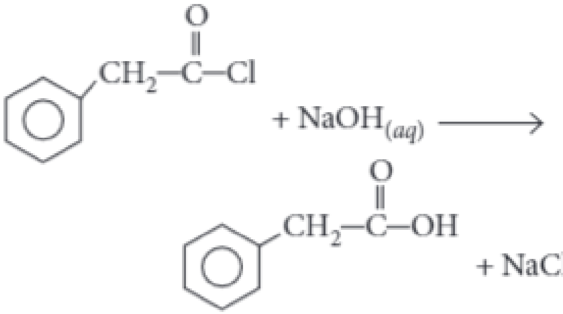


(iv) (c)

6. (i) (b)

(ii) (d): When in aryl halides the electron withdrawing groups are attached at ortho and para positions to the chlorine atom then the removal of chlorine atom as Cl^- ion becomes easy, therefore, 2,4,6-trinitro chlorobenzene is the most reactive among given aryl halides.

(iii) (d):



(iv) (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.

OR

(d) : The order of reactivity follows the sequence:
benzyl halides > alkyl halides > aryl halides.
Out of chlorides and bromides, bromides are more reactive. Therefore, the correct order of reactivity is
$PhCH_2Br$(ii) > MeBr(i) > MeCl(iii) > *p*-$MeOC_6H_4Br$(iv)

7. (i) (c) : KI reacts with *R*Cl to form *R*I. This *R*I molecule now hydrolysed easily to give *R*OH because alkyl iodide are more reactive than alkyl chloride. Thus, reaction becomes faster on addition of KI.

(ii) (c) : CH_3CH_2I reacts more rapidly with strong base in comparison to CD_3CH_2I. The elimination of HI (or DI) in presence of strong base shows E_2 elimination. The rate determining step involves the breaking up of C — H (or C — D) bond. The C — D bond being stronger than C — H bond is difficult to break.

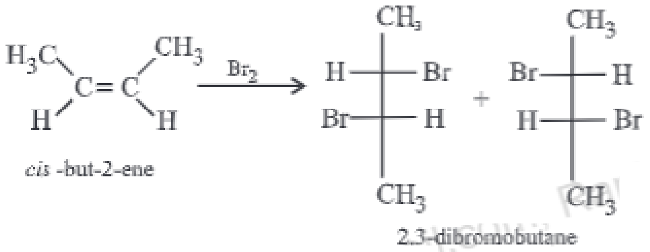
(iii) (c) : Silver nitrite is a covalent compound and the bond between Ag — O is covalent. Therefore, it does not have a negative charge on the oxygen atom. Hence, the nucleophillic attack occurs through the lone pair on nitrogen forming nitroalkanes ($R - NO_2$).

(iv) (c) : The carbon-halogen bond in vinyl halides has some double bond character and hence little difficult to break.

OR

(d) : 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 2-butene as a major product.

8. (i) (c) : Bromination of *cis*-2-butene gives (±) 2,3-dibromobutane.



(ii) (b)

(iii) (a)

(iv) (a)

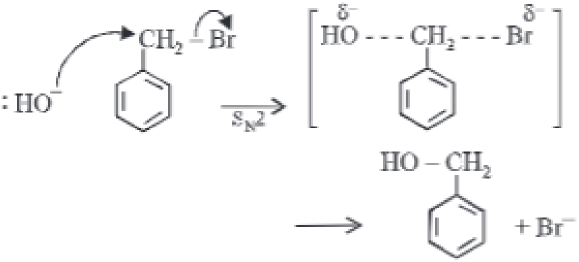
OR

(a) : In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation. The carbocation formed is sp^2 hybridised and planar. The attack of the nucleophile may be accomplished from either side resulting in a mixture of products with opposite configuration *i.e.*, racemic mixture.

9. (i) (c) : Ability to accommodate a positive charge determines the ease of heterolysis leading to S_N1 mechanism. This ability to accommodate positive charge is more in the 2° alkyl halide since it has two alkyl groups as compared to one in 1° alkyl halide.

(ii) (c) : $CH_3—Br$ is more reactive than $CH_3—Cl$. The $C—Br$ has bond dissociation energy of 293 kJ mol^{-1} while $C — Cl$ bond has its dissociation energy of 351 kJ mol^{-1}. As the bond dissociation energy increases, the ease of breaking of $C — X$ bond decreases and hence the reactivity of haloalkanes decreases.

(iii) (a) :



(iv) (a)

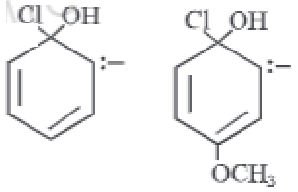
OR

(a)

10. (i) (b) : Primary benzylic halides show higher reactivity in S_N1 reactions than primary alkyl halides. This is due to the greater stabilisation of the benzylic carbocation intermediates by resonance.

(ii) (a)

(iii) (a) : On comparing the relative stabilities of carbanion of chlorobenzene and *p*-chloroanisole,



the electron donating group (OCH_3) in anisole tends to intensify the negative charge relative to carbanion in chlorobenzene. Thus, *p*-chloroanisole is less reactive than chlorobenzene.

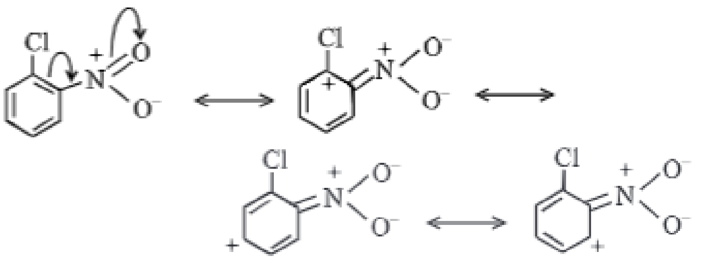
OR

(b) : As compared to chlorobenzene, the intermediate carbanion resulting from 4-nitrochlorobenzene is stabilized by –*R*-effect of the NO_2 group.

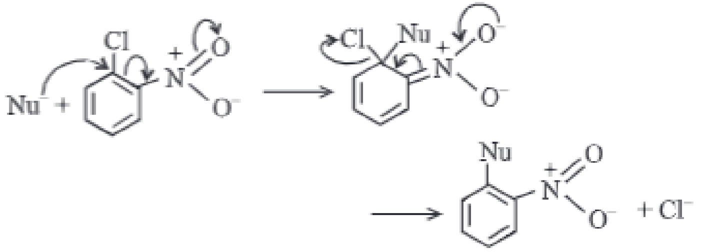
(iv) (c) : Chlorobenzene is less reactive than benzene towards the electrophilic substitution reactions due to –*I* effect.

11. (b) : Greater the molecular mass, stronger the van der Waals' forces of attraction and hence higher is the melting point/boiling point.

12. (a) : The C-atom of C – Cl in chloronitrobenzene carries a small +ve charge.



Because of the positive charge, attack at this carbon atom by the nucleophile is facilitated.



13. (c) : For the same alkyl group, the boiling points are in the order *RI* > *R*Br > *R*Cl > *RF*. This is because with the increase in the size of halogen, the magnitude of van der Waals' force increases and boiling point increases.

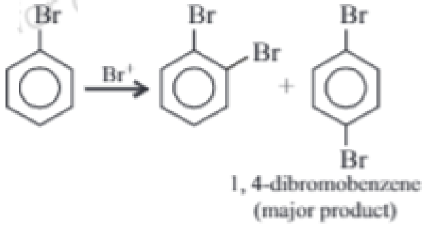
Bond strength decreases as the size of the halogen increases. $CH_3F > CH_3Cl > CH_3Br > CH_3I$ and stability decreases as the strength of C–X bond decreases.

14. (c): Bromobenzene shows both –*I* effect as well as +*M* effect; but mesomeric effect dominates the –*I* character and becomes the directing factor for incoming electrophile.

Formation of electrophile :

$Br - Br + FeBr_3 \rightarrow Br^+ + FeBr_4^-$

Bromobenzene acts as an *ortho-para* director for upcoming electrophiles.



15. (a): Branching of chain makes molecule more compact and therefore, decreases the surface area. Due to decreases in surface area, the magnitude of van der Waals' force of attraction decreases and consequently, the boiling points of branched chain are less than those of straight chain compounds.

16. (c): Aryl halides undergo nucleophilic substitution with difficulty.

17. (b): Among dichlorobenzenes, the *p*-isomer being symmetrical, packs closely in the crystal lattice and hence has much higher melting point than *o*- and *m*- isomers.

18. (d): Even though haloalkanes are polar molecules, still they are insoluble in water. This is due to the fact that haloalkanes can neither form hydrogen bonds with water nor they can break the hydrogen bonds already existing between water molecules.

19. (b): Vinyl chloride itself shows resonance structure and thus stabilized.

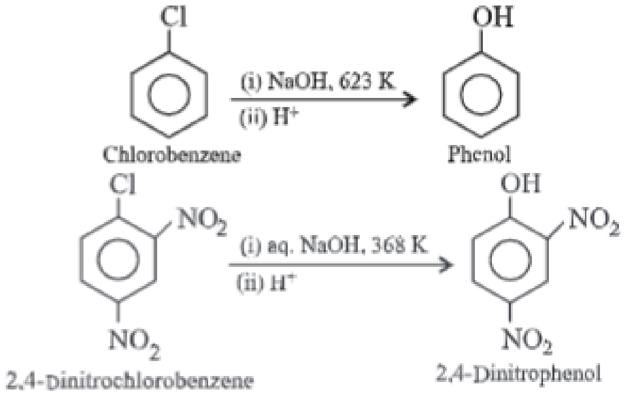
As vinyl chloride has partial double bond character thus breaking of C – Cl bond is difficult which makes vinyl chloride less reactive than alkyl chloride.

$$\overset{\frown}{CH_2}{=}CH\overset{\frown}{-}\ddot{Cl} \leftrightarrow H_2\overline{C} - CH = Cl^+$$

20. (c): Halogens are somewhat deactivating but *o*, *p*-directing. As a result, aryl halides undergo the usual electrophilic substitution reactions less readily than benzene.

21. (c): In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation. The carbocation formed is sp^2 hybridised and planar. The attack of the nucleophile may be accomplished from either side resulting in a mixture of products with opposite configuration *i.e.*, racemic mixture.

22. (d): Halobenzenes become reactive to nucleophilic substitution reactions when electron withdrawing groups (nitro, cyano) are present at ortho/para position. This is evident from the milder conditions required for hydrolysis in 2, 4-dinitrochlorobenzene than chlorobenzene.



23. (b): *p*-Dichlorobenzene being more symmetrical than *o*-isomer fits closely in the crystal lattice and hence greater amount of energy is needed to break the crystal lattice. Thus, *p*-isomer is less soluble than *o*-isomer.

24. (c): Carbocation intermediate obtained from $C_6H_5CH(C_6H_5)$ Br is more stable than that obtained from $C_6H_5CH(CH_3)Br$ because it is stabilized by two phenyl groups due to resonance. Therefore, the former bromide is reactive than the latter in S_N1 reactions.

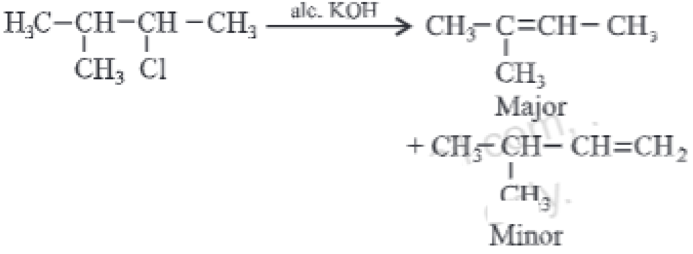
25. (a): Due to steric hindrance, tertiary haloakanes do not prefer to undergo substitution but instead undergo elimination.

26. (d): Vinylic halides are very less reactive towards nucleophilic substitution reactions because of resonance effect. Resonance gives rise to partial double bond character to the carbon-halogen bond making it stronger and therefore more difficult to cleave than a Csp^3 – *X* bond. It also reduces the polarity of the carbon-halogen bond thereby making heterolysis difficult.

$$\overset{\frown}{CH_2}{=}CH\overset{\frown}{-}\underset{..}{\ddot{X}}{:} \longleftrightarrow \overset{-}{C}H_2 - CH = \underset{..}{\overset{+}{X}}{:}$$

27. (a)

28. (a) **:** 2-Chloro-3-methylbutane on treatment with alcoholic potash gives 2-methylbut-2-ene as main product.



$$H_3C-\underset{CH_3}{CH}-\underset{Cl}{CH}-CH_3 \xrightarrow{\text{alc. KOH}} \underset{\text{Major}}{CH_3-\underset{CH_3}{C}=CH-CH_3} + \underset{\text{Minor}}{CH_3-\underset{CH_3}{CH}-CH=CH_2}$$

Elimination occurs according to Saytzeff rule, "the major product is one which involves elimination of H from less hydrogenated carbon".

29. (c) **:** Alkyl iodides in general turn brown due to liberation of I_2 on decomposition by the action of air and light.

30. (b) **:** As the size of the alkyl groups increases, the S_N2 reactivity decreases, further C–Cl bond is stronger and more difficult to cleave than C–Br bond. So CH_3Br is more reactive than $(CH_3)_2CHCl$.