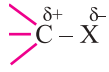
UNIT 9

HALOALKANES AND HALOARENES

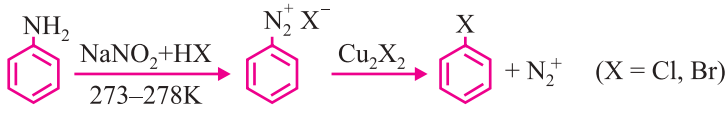
Points to Remember

1. Haloalkanes (Alkyl halides) are halogen derivatives of alkanes with general formula $[C_nH_{2n+1}X]$. (X = F, Cl, Br or I)
2. Haloarenes (Aryl halides) are halogen derivatives of arenes with general formula Ar – X.
3. Since halogen is more electronegative than C, hence C – X bond is polar.



4. **Named Reactions :**

(a) Sandmeyer Reaction :



(b) Finkelstein Reaction :

$$R - X + NaI \xrightarrow{\text{dry acetone}} R - I + NaX \quad (X = Cl, Br)$$

(c) Swartz Reaction :

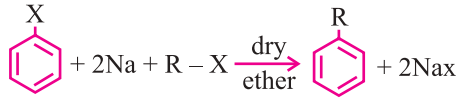
$$CH_3 - Br + AgF \rightarrow CH_3 - F + AgBr$$

Instead of Ag – F, other metallic fluoride like Hg_2F_2, CoF_2 or SbF_3 can also be used.

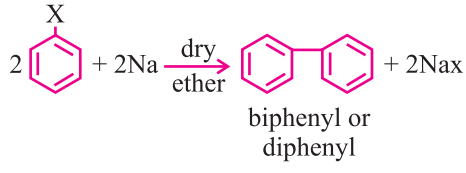
(d) Wurtz Reaction :

$$2R - X + 2Na \xrightarrow{\text{dry ether}} R - R + 2NaX$$

(e) Wurtz-Fittig Reaction :

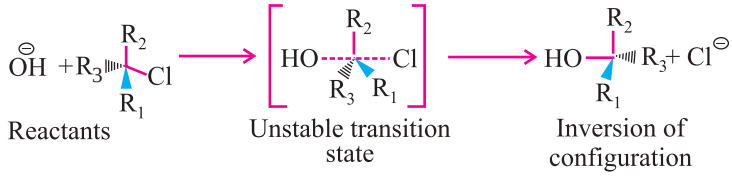


(f) Fittig Reaction :



5. Nucleophilic Substitution Reactions :

(a) Substitution nucleophilic bimolecular (S_N^2) :

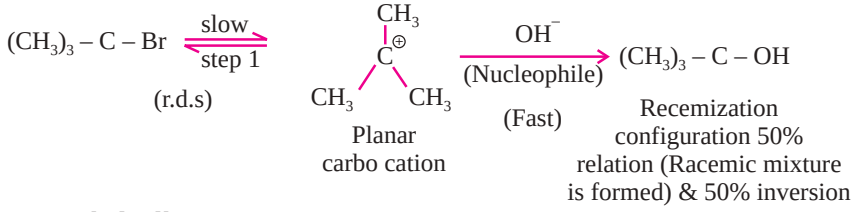


1. 1º haloalkane
2. Bimolecular, 2nd order
3. One step

Order of reactivity : 1º > 2º > 3º

Deciding factor : Steric hindrance

(a) Substitution nucleophilic unimolecular (S_N^1) :



1. 3º haloalkane
2. Unimolecular, 1st order
3. Two steps

Order of reactivity : 3º > 2º > 1º

Deciding factor : Stability of carbo cation

* Allylic $\left[CH_2=CH-\overset{\oplus}{C}H_2\right]$ and benzylic $\left[C_6H_5\overset{\oplus}{C}H_2\right]$ halides undergo reaction via SN^1 mechanism as the corresponding carbo cations are resonance stabilized.

6. Aryl halides are much less reactive towards nucleophilic substitution reactions than haloalkanes.

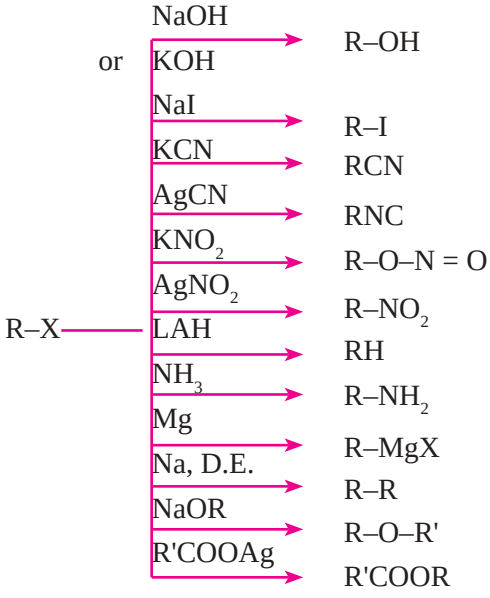
7. Halogen is deactivating but *o*, *p*-directing in electrophilic substitution reaction of haloarenes.

8. $CHCl_3$ is stored in dark bottles upto brim so that formation of poisonous gas phosgene in presence of air and light can be avoided.

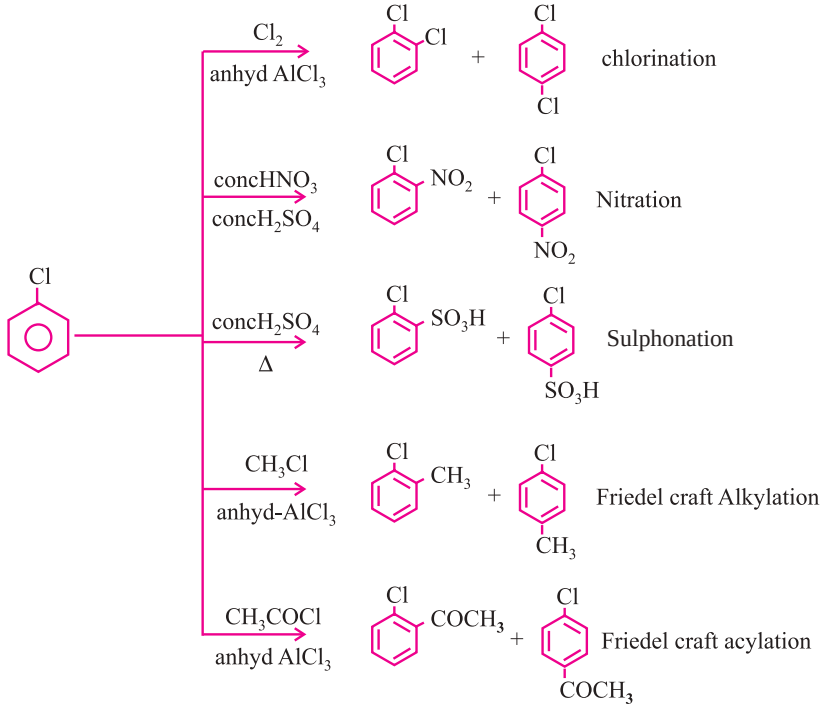
$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$$

Chloroform Carbonyl chloride (phosgene)

9. Reaction of Haloalkanes :



10. Electrophilic Substitution Reaction of Haloarenes :

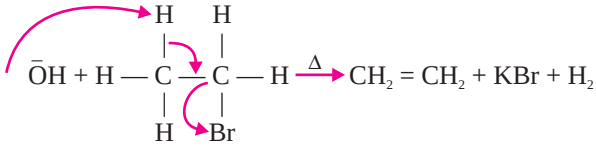


11. Elimination reaction: Two groups or atoms attached to two adjacent carbon atom and simultaneous formation of multiple bonds between these carbon atom. [Reverse of addition]

Two types (*i*) β-Elimination ⟶ (E_1 ⟶ Two step eliminate; E_2 ⟶ One step eliminate)

(*ii*) α-elimination

Saytzaff's Rule



$$CH_3 - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3 \xrightarrow{\text{Aloc.KOH}} CH_2 = CH_2 + KBr + H_2$$

(81% More highly substituted Alkenes, More stable)

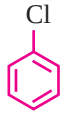
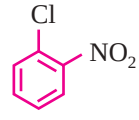
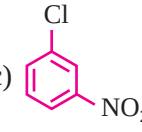
12. Distinguishing test for alkyl chlorides, bromides and iodide : Alkyl chlorides react with $AgNO_3$ to give white precipitate which is soluble in alcoholic ammonium hydroxide. Alkyl bromides react with $AgNO_3$ to give a yellow precipitate which is sparingly soluble in alcoholic ammonium hydroxide. Alkyl iodides react with $AgNO_3$ to give dirty yellow precipitate, which is insoluble in alcoholic ammonium hydroxide.

E.g., $CH_3 - Cl \xrightarrow[AgNO_3]{HNO_3} AgCl\downarrow$ White ppt.

Vinyl and aryl halides do not yield silver halide under these conditions.

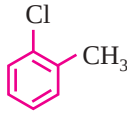
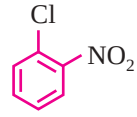
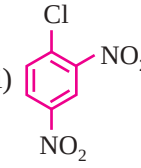
MULTIPLE CHOICE QUESTIONS

1. Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution:

(a) 
(b) 
(c) 

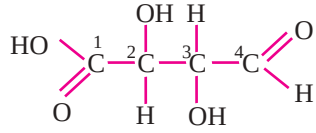
(a) a < b < c (b) a < b < a
(c) a < c < b (d) c < a < b

2. Arrange the following compound in increasing order of rate of reaction towards nucleophilic substitution.

(i) 
(ii) 
(iii) 

(a) i < ii < iii (b) i < iii < ii
(c) ii < i < iii (d) iii < ii < i

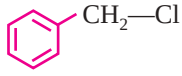
3. Which of the carbon atom present in the molecule given below are asymmetric.

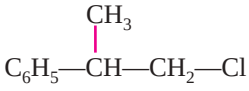
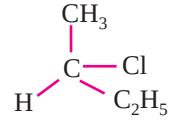


(a) 1, 2 , 3, 4 (b) 2, 3

(c) 1, 4 (d) 1, 2, 3

4. Which of the following compound will undergo recevisation when solution of KOH hydrolyses?

(i)  (ii) $CH_3CH_2—CH_2—Cl$

(iii)  (iv) 

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

(c) iii and iv (d) iv

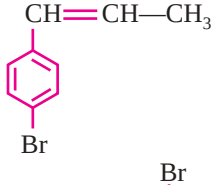
5. In a S_N^1 reaction on chiral centres, there is

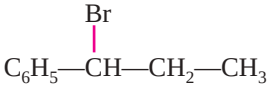
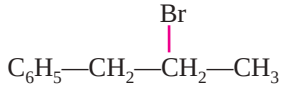
(a) 100 % retention (b) 100 % inversion

(c) 100 % recenisation

(d) inversion is more than retention leading to recenisation

6. The reaction of $C_6H_5—CH=CH—CH_3$ with HBr produces

(a) $C_6H_5—CH_2\ CH_2—CH_2—Br$ (b) 

(c)  (d) 

7. In S_N^2 reactions, the correct order of reactivity fo the following compounds:

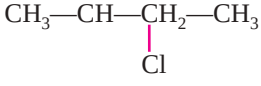
(i) CH_3Cl (ii) $(CH_3)_3CCl$

(iii) $(CH_3)_2CHCl$ (iv) $CH_3CH_2—Cl$

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

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

8. The increasing order of reactivity of the following halides for the S_N^1 reaction is

(i)  (ii) $CH_3—CH_2—CH_2—Cl$

(iii) $P—H_3CO—C_6H_4—CH_2—Cl$

(a) iii < ii < i (b) ii < i < iii

(c) i < iii < ii (d) ii < iii < i

9. Arrange the following compounds in increasing order of their boiling point

(i) $(CH_3)_2CH_2CH_2$—Br (ii) CH_3—$(CH_2)_3$—Br (iii) $(CH_3)_3C$—Br

(a) ii < i < iii (b) i < ii < iii

(c) iii < i < ii (d) iii < ii < i

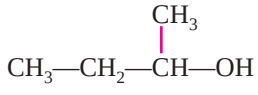
10. Toluene reacts with halogen in thepresence of $FeCl_3$ giving ortho and parabola compound. The reactions is

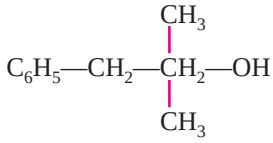
(a) electrophilic elimination reaction (b) electrophilic substitution

(c) free radical addition reaction (d) nucleophilic substitution

11. The order of reactivity of following alcohols with halogen acid (HX) is

(i) CH_3—CH_2—CH_2—OH

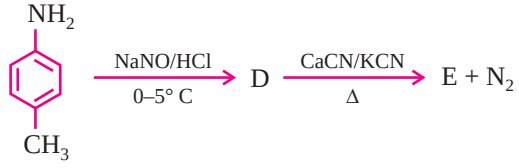
(ii) 

(iii) 

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

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

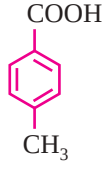
12. In the reaction

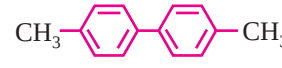


the product is:

(a) 

(b) 

(c) 

(d) 

13. Chlorobenzene is formed by reactionj of chlorine with benzene in presence of $AlCl_3$. Which of the following species attacks the beneze ring in this reaction.

(a) Cl^- (b) Cl^+

(c) $AlCl_3$ (d) $AlCl_4^-$

14. $H_3C—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH=CH_2 + HBr \longrightarrow A$

(a) $H_3C—\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{CH}}}}—CH_2—CH_3$

(b) $H_3C—\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{CH}}}}—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

(c) $H_3C—\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{CH}}}}—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3$

(d) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{CH}}}}—CH_2—CH_2—Br$

15. The reaction of toluene with Cl_2 in the presence of $FeCl_3$ gives 'X' and the reaction with Cl_2 in presence of light gives 'Y'. Thus 'X' and 'Y' are:

(a) 'X' = benzyl chloride and 'Y' = m-chlorotoluene

(b) 'X' = benzyl chloride and 'Y' = o-chlorotoluene

(c) 'X' = m-chlorotoluene and 'Y' = p-cholorotoluene

(d) 'X' = p-chlorotoluene and 'Y' = benzyl chloride.

16. Anyl halides are less reactive toward nucleophilic substitution reaction than alkyl halides due to

(a) the formation of stable carbonimion

(b) resonance stabilization

(c) longer carbon-halogen bond

(d) sp^2 hybridised carbon attached to halogen

17. A new carbon carbon bond is possible in the following reaction reactions:

(a) $C_6H_6 + CH_3Cl \xrightarrow{\text{anhy. } AlCl_3}$

(b) $CH_3CH_2Br + CH_3CH_2NH_2 \longrightarrow$

(c) $CH_3—Br + CH_3CH_2—ONa \longrightarrow$

(d) $CH_3CH_2—Br + kCN(alc) \longrightarrow$

18. Which of the following state are correct

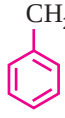
(a) Benzyl halides are more reactive than vinyl and anyl halides

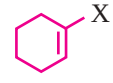
(b) Vinyl/halides are more reactive than alkyl halides

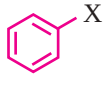
(c) Aryl halides are less reactive than alkylhalide

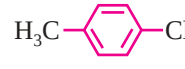
(d) Aryl halides are more reactive than benzyl halides

19. Which of the following contain sp^2 hybridised carbon bonded to X?

(a) 

(b) 

(c) 

(d) 

20. The IUPAC name of the following compound are 

(a) 1-chloro-4-methyl benzene (b) 4-chlorotoluene

(c) 1-methyl-4-chlorobenzene (d) 4-methylchlorobenzene

Note : *In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.*

(a) Both assertion and reason are Correct, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are True, but reason is not the correct explanation of the assertion.

(c) Assertion is Incorrect, but reason is Correct.

(d) Both assertion and reason are Incorrect.

Assertion and Reasoning

21. Assertion : S_N^2 reaction proceeds with inversion of configuration.

Reason : S_N^2 reactionoccurs in one step

22. Assertion : Treatment of chloroethane with saturated solution of AgCN give ethyl isocyanide as major product.

Reason : Cyanide ion (CN^-) is an ambident nucleophile.

Matching Column Type

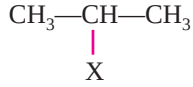
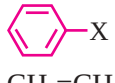
23. Match the items of column 1 and column 2

Column1	**Column 2**
(A) CH_2Cl_2	P. Antiseptic
(B) CCl_4	Q. Insecticide
(C) (p-Cl C_6H_4)$CHCCl_3$	R. Pyrene
(D) CHI_3	S. Refrigerend

(a) A–R, B–Q, C–S, D–P (b) A–S, B–R, C–Q, D–P

(c) A–Q, B–P, C–S, D–R (d) A–P, B–S, C–R, D–Q

24. Match the items of column 1 and column 2

(A) 	P. Anyl halide
(B) CH_2=CH—CH_2—X	Q. Alkyl halide
(C) 	R. Vinyl halide
(D) CH_2=CH—X	S. Allyl halide

(a) A–P, B–Q, C–S, D–P (b) A–S, B–R, C–Q, D–P

(c) A–Q, B–P, C–S, D–R (d) A–P, B–S, C–R, D–Q

Integer Type Question

25. In how many pairs, the second compound reacts faster than the first in S_N1 reaction with OH^-?

(i)  (ii) CH_3I, CH_3Br

(iii) $(CH_3)_3CBr$, $(CH_3)_2HBr$ (iv) 

(v) CH_3Cl, $(CH_3)_2CHCl$ (vi) $(CH_2)_2CHBr$, CH_3CH_2Br

0	1	2	3	4	5	6	7	8	9

ANSWERS

1. (c) **2.** (a) **3.** (b) **4.** (d) **5.** (d) **6.** (c) **7.** (c) **8.** (b) **9.** (c) **10.** (b)

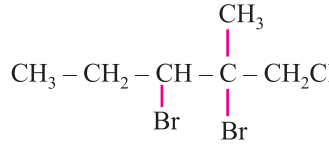
11. (b) **12.** (a) **13.** (b) **14.** (a) **15.** (d)

16. (b, d) **17.** (a, d) **18.** (a, c) **19.** (b, d) **20.** (a, b)

21. (b) **22.** (b) **23.** (b) **24.** (b)

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Give IUPAC name of :



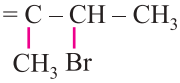
[*Hint :* 1-chloro-2, 3-dibromo-2-methyl pentane]

Q. 2. Identify A and B in each of the following processes :

$$CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{Reduction} B$$

[*Hint :* A : $CH_3 - CH_2 - CN$; B : $CH_3CH_2CH_2NH_2$]

Q. 3. Draw the structure of 4-bromo-3-methylpent-2-ene.

[*Hint :* 

Q. 4. Why Grignard reagent should be prepared under anhydrous conditions ?

Q. 5. Chloroform is stored in dark coloured and sealed bottles. Why ?

Q. 6. An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure ?

[*Hint* 

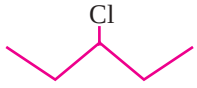
Q.7. An organic compound 'A' on treatment with KCN gave B which on hydrolysis with dil. HCl gave acetic acid. Identify A.

[*Hint :* A : CH_3Cl]

Q. 8. Write IUPAC name of iodoform.

[*Hint :* Triiodomethane]

Q. 9. Which one of the following two substances undergo SN^1 reaction faster and why ?



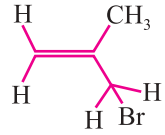
Or

(Hint :

(2º)

Q. 10. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN form isocyanides as the chief product. Explain.

Q. 11. Write the IUPAC name of the following compound :



[*Hint :* 3-bromo-2-methylprop-1-ene]

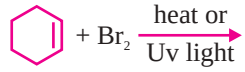
Q. 12. Arrange the following in order of their increasing reactivity in nucleophilic substitution reactions :

$$CH_3F,\ CH_3I,\ CH_3Br,\ CH_3Cl$$

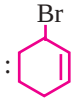
[*Hint :* $CH_3F < CH_3Cl < CH_3Br < CH_3I$]

Q. 13. Allyl chloride is more reactive than n-propyl chloride towards nucleophilic substitution reaction. Explain why ?

Q. 14. Complete the reaction :



(Hint :



)

Q. 15. How will you convert 2-bromo propane into 1-bromo propane ?

Q. 16. Give one chemical test to distinguish between chlorobenzene and benzyl chloride ?

[*Hint :* $AgNO_3$ test]

Q. 17. Why iodoform show antiseptic properties ?

[*Hint :* Due to free liberated iodine.]

Q. 18. The presence of nitro group ($-NO_2$) at ortho or para positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. Explain.

Q. 19. For the preparation of alkyl chlorides from alcohols, thionyl chloride ($SOCl_2$) is preferred. Give reason.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Complete the following reactions :

(i) $C_6H_5N_2Cl + KI \rightarrow$

(ii) $\begin{matrix} H \\ H \end{matrix}\!\!\diagdown\!\!C = C\!\!\diagup\!\!\begin{matrix} H \\ H \end{matrix} + Br_2 \xrightarrow{CCl_4}$

Q. 2. Carry out the following conversions in not more than two steps :

(i) Toluene to benzyl alcohol

(ii) Benzyl alcohol to phenylethanenitrile

Q. 3. Give reasons :

(i) Boiling point of alkyl bromide is higher than alkyl chloride.

(ii) Alkyl halides are better solvents than aryl halides.

[*Hint :* (i) High magnitude of van der Waal's forces in alkyl bromides.

(ii) C – X is more polar in haloalkanes.]

Q. 4. Which of the following compounds would undergo S_N1 reaction faster and why ?

(A) (B)

Hint : B

Q. 5. Identify and indicate the presence of centre of chirality, if any, in the following molecules. How many stereoisomers are possible for those containing chiral centre :

(i) 1, 2-dichloropropane

(ii) 3-bromopent-1-ene

Q. 6. Convert :

(i) Benzene to m-nitrochlorobenzene

(ii) Benzene to diphenyl

Q. 7. What happens when :

(i) Propene is treated with HBr in presence of peroxide.

(ii) Benzene is treated with methyl chloride in presence of $AlCl_3$.

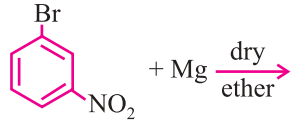
Q. 8. (i) Alkyl iodides develop colouration on long standing particularly in light. Explain.

[*Hint :* (i) Due to decomposition by light and produce I_2.]

Q. 9. Tert-butyl bromide reacts with aq. NaOH by S_N1 mechanism while n-butylbromide reacts with S_N2 mechanism. Why ?

Q. 10. Although chlorine is an electron withdrawing group, yet it is o, p-directing in electrophilic aromatic substitution reactions. Explain, why is it so ?

Q. 11. Identify the products :

(i) 

(ii) $CH_3 - \underset{\underset{Br}{|}}{CH} - CH_3 \xrightarrow{alc.KOH} A \xrightarrow[H_2O_2]{HBr} B$

Q. 12. (i) Arrange the following halides in order of increasing S_N1 reactivity :

CH_3Cl, CH_3Br, CH_3CH_2Cl, $(CH_3)_2CHCl$

(ii) Which out of 1-bromobutane & 2-bromobutane would react faster by S_N2 pathway and why ?

Q. 13. Identify the products :

$$C_6H_6 \xrightarrow[anhy.AlCl_3]{CH_3Cl} A \xrightarrow[hv]{Cl_2\,(1\,mole)} B \xrightarrow{aq.KOH} C \xrightarrow{HBr} D$$

Q. 14. Carry out the following conversions :

(i) But-1-ene to n-butyliodide

(ii) Isopropyl alcohol to iodoform

Q. 15. An organic compound A reacts with PCl_5 to give compound B. Compound B reacts with Na/ether to give n-butane. What are compounds A and B ?

[*Hint :* A = C_2H_5OH, B = C_2H_5Cl]

Q. 16. Write short note on :

(i) Sandmeyer reaction

(ii) Finkelstein reaction

Q. 17. Name the reagents used to convert :

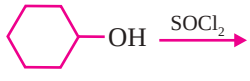
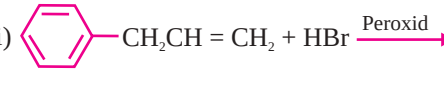
(i) 2-chloropropane to 2-nitropropane

(ii) Chloroethane to n-butane

[*Hint :* (i) $AgNO_2$

(ii) Na/dry ether]

Q. 18. Draw structure of monohalo product in each of the following :

(i)  (ii) 

Ans. (i)  (ii) 

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Rearrange the compounds of each of the following sets in order of reactivity towards S_N2 displacement :

(i) 2-bromo-2-methyl butane, 1-bromopentane, 2-bromopentane

(ii) 1-bromo-3-methylbutane, 2-bromo-2-methyl butane, 2-bromo-3-methyl butane

(iii) 1-bromobutane, 1-bromo-2, 2-dimethyl propane, 1-bromo-2-methyl butane

Q. 2. Answer the following :

(i) Haloalkanes easily dissolve in organic solvents, why ?

(ii) What is known as racemic mixture ? Give example.

(iii) Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_N1 substitution reaction and why ?

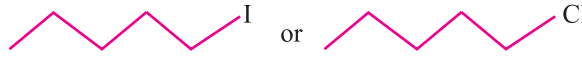
Q. 3. Answer the following :

(i) What is meant by chirality of a compound ? Give an example.

(ii) Which one of the following compounds is more easily hydrolysed by KOH and why ?

$$CH_3CHClCH_3CH_3 \text{ or } CH_3CH_2CH_2Cl$$

(iii) Which one undergo S_N2 substitution reaction faster and why ?



Q. 4. Complete the following reactions :

(i) $CH_3CH_2OH \xrightarrow{SOCl_2} A \xrightarrow{KCN} B$

(ii) $(CH_3)_2CHBr + Na \rightarrow$

(iii) $CH_3CH_2Cl \xrightarrow{AgNO_3}$

Q. 5. How the following conversions can be carried out ?

(i) But-1-ene to n-butyl iodide

(ii) Tert-butyl bromide to isobutyl bromide

(iii) Ethanol to but-1-yne

Q. 6. Write short notes on :

(i) Wurtz-Fittig reaction

(ii) Fittig reaction

(iii) Dehydrohalogenation reaction

Q. 7. An organic compound 'A' having molecular formula C_4H_8 on treatment with dil. H_2SO_4 give another compound 'B'. B on treatment with conc. HCl and anhy. $ZnCl_2$ gives 'C'. C on treatment with sodium ethoxide gives back 'A'. Identify the compound. Write the equations involved.

Q. 8. What happens when :

(i) 1-bromopropane reacts with metallic sodium.

(ii) Bromoethane is treated with caustic potash.

(iii) Iodomethane is treated with ammonia.

Q. 9. Identify A, B and C :

$$\text{2-propanol} \xrightarrow{SOCl_2} A \xrightarrow{Mg} B \xrightarrow{H_2O} C$$

Q. 10. Account for the following :

(i) A small amount of ethyl alcohol is added to $CHCl_3$ stored for use as an anaesthetic.

(ii) After using CCl_4 as a fire extinguisher inside a closed space, the space is thoroughly ventilated.

(iii) When 2-chloro-3-methylbutane is treated with alcoholic potash, 2-methyl-2-butene is the main product.

[*Hint :* (i) To convert harmful $COCl_2$ to ethyl carbonate.

(ii) To sweep out $COCl_2$ formed by CCl_4 vapour and H_2O vapour.

(iii) Saytzeff rule.

Q. 11. How will you distinguish between :

(i) Vinyl chloride and ethyl chloride

(ii) Chlorobenzene and cyclohexyl chloride

(iii) Ethyl chloride and ethyl bromide

Q. 12. Explain the following :

(i) The dipole moment of chloroethane is higher than that of chlorobenzene.

(ii) Although haloalkane are polar in character yet they are insoluble in water.

(iii) Vinyl chloride is unreactive in nucleophilic substitution reactions.

Q. 13. (i) Which will have a higher boiling point ?

1-chloroethane or 2-chloro-2-methyl butane. Give reason.

(ii) p-chloronitrobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving resonating structure as well.

Q. 14. (i) What are ambident nucleophiles ? Explain with an example.

(ii) Convert ethyl bromide to diethyl ether.

(iii) What are freons ?

Q. 15. A hydrocarbon 'A' (C_4H_8) is added with HBr in accordance with Markonikov's rule to give compound 'B' which on hydrolysis with aqueous alkali forms tertiary alcohol 'C' ($C_4H_{10}O$). Identify A, B and C.

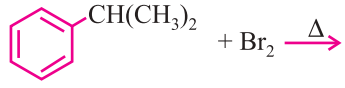
Q. 16. (i) Which isomer of C_4H_9Cl will have the lowest boiling point ?

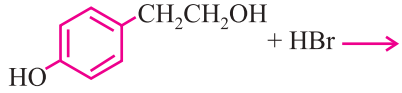
(ii) Predict the alkenes that would be formed by dehydrohalogenation with sodium ethoxide and ethanol. Predict major alkenes :

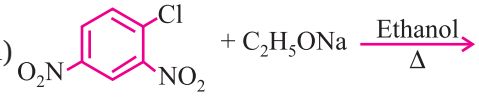
(a) 2-chloro-2-methylbutane

(b) 3-bromo-2, 2, 3-trimethylpentane

Q. 17. Write the structure of major product in each of the following :

(i) 

(ii) 

(iii) 

Q. 18. Write the main products when :

(i) n-butyl chloride is treated with alcoholic KOH

(ii) 2, 4, 6-trinitrochlorobenzene is subjected to hydrolysis.

(iii) Methyl chloride is treated with AgCN.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. How would you bring about the following conversions :

(i) Propene to 2-bromopropane

(ii) Bromoethane to propanoic acid

(iii) 1-chloropropane to 1-propanol

(iv) Ethanol to chloroethane

(v) 1-iodopropane to propene

Q. 2. What happens when : (Give chemical reactions)

(i) Cyclohexanol is treated with thionyl chloride

(ii) p-hydroxybenzyl alcohol is heated with HCl.

(iii) Ethyl bromide is refluxed with NaI in acetone.

(iv) Ethyl bromide is treated with mercurous fluoride.

(v) Chlorobenzene is subjected to hydrolysis.

Q. 3. Complete the following reactions :

(i) $C_6H_6 \xrightarrow{Cl_2/Fe} X \xrightarrow[Pyridine]{CuCN} Y \xrightarrow{H^+, H_2O}$

(ii) $C_2H_4 \xrightarrow{HBr} X \xrightarrow{aq.\ KOH} Y \xrightarrow{I_2, NaOH} Z$

(iii) $CH_3CH_2Br \xrightarrow{AgCN} A$

(iv) 3-ethylpent-2-ene $\xrightarrow{Br_2/H_2O}$ B

Q. 4. Account for the following :

(i) Sulphuric acid is not used during the reaction of alcohols with KI.

(ii) p-methoxybenzyl bromide reacts faster than p-nitrobenzyl bromide with sodium ethoxide to form an ether product.

(iii) Organic halogen compounds used as solvents in industry are chlorides rather than bromides and iodides.

(iv) Wurtz reaction fails in case of tert-alkyl halides.

(v) Alkyl halides are insoluble in water though they contain a polar C – X bond.

(vi) Use of $CHCl_3$ as anaesthetic is not preferred.

Q. 5. (i) A primary alkyl halide (A), C_4H_9Br reacted with hot alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give (C), which is an isomer of (A). When (A) was reacted with sodium metal, it gave a compound (D), C_8H_{18} which was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (A) and write equations of all the reactions.

(ii) Iodoform gives a precipitate with $AgNO_3$ on heating while $CHCl_3$ does not. Why ?

[*Hint :* A : $\Rightarrow CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2Br$]

CONCEPTUAL QUESTIONS

Q. 1. Why haloalkanes are more reactive than haloarenes?

Ans. In haloarenes, there is partial double bond character b/w carbon and halogen due to resonance effect which makes him less reactive.

(ii) In benzene, carbon being sp^2 hybridised which is smaller in size than sp^3 present in haloalkanes. So C–Cl bond in aryl halides is shorter and stronger.

Q. 2. Why do haloalkenes under go nucleophillic substitution whereas haloarenes under go electophillic substitution?

Ans. Due to more electro negative nature of halide atom in haloalkanes carbon atom becomes slightly positive and is easily attacked by nucleophillic reagents.

While in haloarenes due to resonance, carbon atom becomes slightly negative and attacked by electrophillic reagents.

Q. 3. When an alkyl halide is treated with ethanolic solution of KCN, the major product is alkyl cyanide where as if alkyl halide is treated with AgCN,the major product is alkyl isocyanide?

Ans. Refer NCERT

Q. 4 The treatment of alkyl chlorides with aqueous KOH lead to the formation of alcohols but in presence of alcoholic KOH alkenes are major products. Explain?

Ans. In aqueous KOH,OH^- is nucleophile which replaces another nucleophile.

$R\text{-}X + KOH \longrightarrow R\text{-}OH + KX$

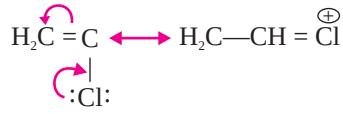
Where as in alcoholic KOH, $C_2H_5O^-$ ion is produced which is a strong base hence β-elimination took place to form alkane

$C_2H_5OH + KOH \longrightarrow C_2H_5O\text{-} + K^+$

$CH_3CH_2\text{-}Cl$ + alcoholic KOH $\longrightarrow CH_2 = CH_2 + C_2H_5OH$

Q. 5 Explain why vinyl chloride is unreactive in nucleophillic substitution reaction?

Ans. Vinyl chloride is unreactive in nucleophillic substitution reaction because of double bond character between C–Cl bond which is difficult to break.



Q. 6 Arrange the following compounds according to reactivity towards nucleophillic substitution reaction with reagents mentioned :-

(i) 4-nitrochlorobenzene> 2,4 dinitrochlorobemzene > 2,4,6, trinitrochlorobenzene with CH_3ONa

Ans. 2,4,6, trinitrochlorobenzene > 2,4 dinitrochlorobemzene > 4- nitrochlorobenzene

Q. 7 Why Grignard reagent should be prepared under an hydrous conditions?

Ans. Grignard reagent react with H_2O to form alkanes, therefore they are prepared under anhydrous condition.

Q. 8 Why is Sulphuric acid not used during the reaction of alcohols wiht KI?

Ans. It is because HI formed will get oxidized to I_2 by concentrated Sulphuric acid which is an oxidizing agent.

Q. 9 p-dichlorobenzene has highest m.p. than those of ortho and m-isomers?

Ans. p-dichlorobenzene is symmetrical, fits into crystal lattice more readily and has higher melting point.

Q. 10. Give reasons:

(i) C–Cl bond length in chlorobenzene is shorter than C–Cl bond in CH_3Cl.

(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(iii) S_N1 reactions are accompained by racemization in optically active alkyl halides.

Ans. (i) In chlorobenzene, each carbon atom is sp^2 hybridised/ resonating structures / partial donable bond character.

(ii) Due to + R effect in chlorobenzene / difference in hybridization i.e., sp^2 and sp^3 respectively.

(iii) Due to formation of planer carbocation.