

Haloalkanes and Haloarenes

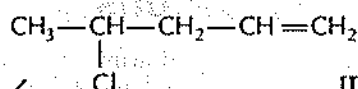
Previous Years' Examination Questions

Practice the Real Questions

1 Mark Questions

1. Write the IUPAC name of $(\text{CH}_3)_2\text{CH}\cdot\text{CH}(\text{Cl})\text{CH}_3$ [Delhi 2013]

2. Write the IUPAC name of

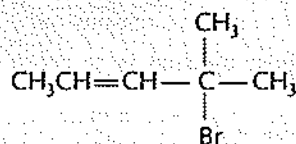


[Delhi 2013]

3. What happens when CH_3Br is treated with KCN? [Delhi 2013]

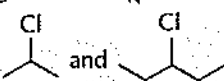
4. What happens when ethyl chloride is treated with aqueous KOH? [Delhi 2013]

5. Write the IUPAC name of



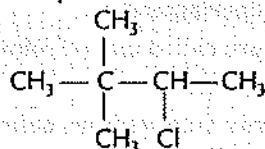
[Delhi 2013]

6. Which compound in the following pair undergoes faster $\text{S}_{\text{N}}1$ reaction?



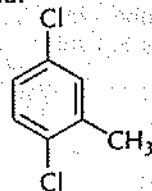
[Delhi 2013]

7. Write the IUPAC name of the following compound



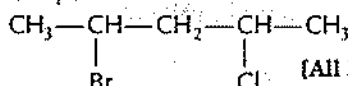
[All India 2013]

8. Write the IUPAC name of the following compound.



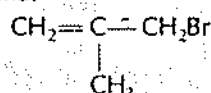
[All India 2013]

9. Write the IUPAC name of the following compound



[All India 2013]

10. Give the IUPAC name of the following compound.



[Delhi 2012]

11. What happens when bromine attacks $\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}\equiv\text{CH}$?

[All India 2012]

12. Write the IUPAC name of the following compound $(\text{CH}_3)_3\text{CCH}_2\text{Br}$. [Delhi 2011]

13. Write the IUPAC name of the following compound $\text{CH}_2=\text{CHCH}_2\text{Br}$.

[All India 2011]

14. Write the structure of 1,4-dibromobut-2-ene.

[Delhi 2011C; All India 2010C]

15. Write the structure of 2-(2-bromophenyl)butane. [Delhi 2011C]

16. Write the structure of 2-(2-chlorophenyl)-1-iodooctane.

[All India 2011C]

17. Write the structure of the following compound: 1-bromo-4-sec butyl-2-methylbenzene. [All India 2011C]

18. Write the structure of the following organic compound: 2-chloro-3-methylpentane.

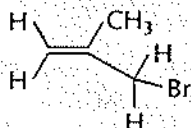
[All India 2011C, 2009C]

19. Which will react faster in $\text{S}_{\text{N}}2$ displacement, 1-bromopentane or 2-bromopentane and why? [Foreign 2011, 2010]

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20. Write the structure of the following compound 3-(4-chlorophenyl)-2-methyl propane. [Delhi 2011C]

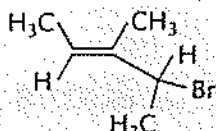
21. Write the IUPAC name of the following.



[All India 2010; Delhi 2008]

22. A solution of KOH hydrolysis $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$. Which one of these is more easily hydrolysed? [Foreign 2010, Delhi 2010]

23. Give the IUPAC name of the following.

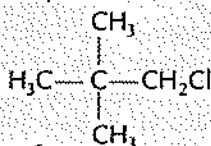


[All India 2010; Foreign 2009]

24. Write the structure of the compound 4-tert-butyl-3-iodoheptane.

[All India 2010C]

25. Write the IUPAC name of the following compound.



[All India 2010C]

26. Write the structure of the compound 1-chloro-4-ethylcyclohexane.

[All India 2010C]

27. Draw the structure of the following compound: 4-bromo-3-methylpent-2-ene.

[Foreign 2010]

28. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

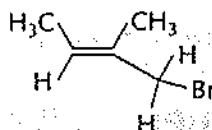
[All India 2008; Delhi 2008]

29. Complete the following chemical equation $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{Peroxide}}$

[Delhi 2008]

30. Write the IUPAC name of $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Br}$ [All India 2008C]

31. Write IUPAC name of



[Foreign 2008]

32. Which one of the two compounds CH_3Br and CH_3I will react faster in an $\text{S}_\text{N}2$ reaction with $-\text{OH}^-$? [Foreign 2007]

2 Marks Questions

33. Account for the following

(i) The C—Cl bond length in chlorobenzene is shorter than that in $\text{CH}_3\text{—Cl}$

(ii) Chloroform is stored in closed dark brown bottles. [Delhi 2013]

34. Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction. Give two reasons for the same. [Delhi 2013]

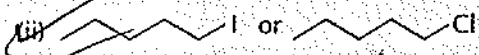
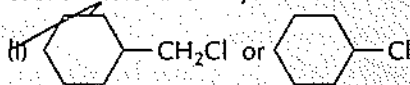
35. Explain as to why

(i) alkyl halides, though polar, are immiscible with water?

(ii) Grignard's reagent should be prepared under anhydrous conditions? [Foreign 2012]

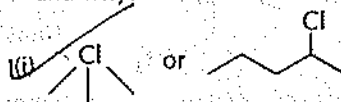
36. What are ambident nucleophiles? Explain giving an example. [Foreign 2012]

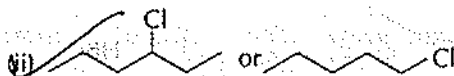
37. Which one in the following pairs of substances undergoes $\text{S}_\text{N}2$ substitution reaction faster and why?



[Delhi 2009]

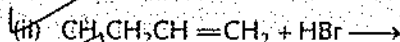
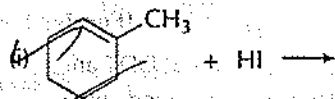
38. Which one in the following pairs undergoes $\text{S}_\text{N}1$ substitution reaction faster and why?





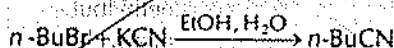
[All India 2009]

39. Complete the following reaction equations.



[All India 2009]

40. Suggest a possible mechanism for the following reaction.



[Delhi 2009C; All India 2008C]

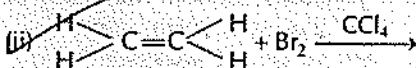
41. Suggest a possible reason for the following observations.

(i) The order of reactivity of haloalkanes is $\text{RI} > \text{RBr} > \text{RCl}$.

(ii) Neo-pentyl chloride, $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Cl}$ does not follow $\text{S}_{\text{N}}2$ mechanism.

[Delhi 2009C]

42. Complete the following reaction equation.



[Delhi 2008; All India 2008]

43. Which compound in each of the following pairs will react faster in $\text{S}_{\text{N}}2$ reaction with OH^- ? why?

[Delhi 2008]

(i) CH_3Br or CH_3I

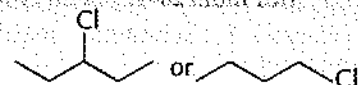
(ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl [All India 2010C]

44. Discuss the mechanism of $\text{S}_{\text{N}}1$ reaction of haloalkanes.

[Delhi 2008C]

45. (i) Why is it that haloalkanes are more reactive than haloarenes towards nucleophiles?

(ii) Which one of the following react faster in an $\text{S}_{\text{N}}1$ reaction and why?



[Delhi 2008]

46. Give one example of

(i) Wurtz reaction

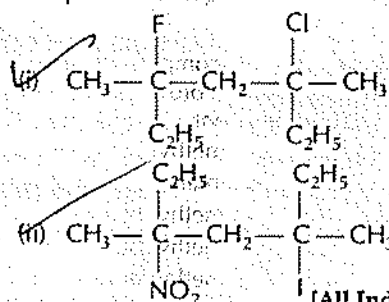
(ii) Wurtz Fittig reaction

[Delhi 2007]

47. What happens when iodoform is heated with silver powder? Write chemical reaction. [All India 2007]

48. What type of reaction are known as nucleophilic substitution reaction? Give one example. [Delhi 2006]

49. Write IUPAC name of the following compound.



[All India 2006]

3 Marks Questions

50. Give reasons for the following

(i) Ethyl iodide undergoes $\text{S}_{\text{N}}2$ reaction faster than ethyl bromide.

(ii) (\pm) 2-Butanol is optically inactive.

(iii) $\text{C}-\text{X}$ bond length in halobenzene is smaller than $\text{C}-\text{X}$ bond length in CH_3-X . [All India 2013]

51. Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*-directing in electrophilic aromatic substitution reactions. Explain, why is it so?

[Delhi 2012]

52. Answer the following questions.

(i) What is meant by chirality of a compound?

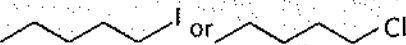
Give an example.

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



or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

(iii) Which one undergoes $\text{S}_{\text{N}}2$ substitution reaction faster and why?



[All India 2012]

Haloalkanes and Haloarenes

53. Answer the following.

(i) Haloalkanes easily dissolve in organic solvents. Why?

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

(iii) Of the two bromo derivatives $C_6H_5CH(CH_3)Br$ and $(C_6H_5)_2CHBr$, which one is more reactive in S_N1 substitution reaction and why? [Delhi 2011]

54. Rearrange the compounds of each of the following sets in order of reactivity towards S_N2 displacement.

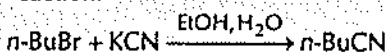
(i) 2-bromo-2-methyl butane, 1-bromopentane, 2-bromopentane.

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

(iii) 1-bromobutane, 1-bromo-2, 2-dimethyl propane, 1-bromo-2-methyl butane, 1-bromo-3-methyl butane

[All India 2011]

55. Write the mechanism of the following reaction.



(i) Why is the dipole moment of chlorobenzene lower than that of cyclohexyl chloride? [Delhi 2011C]

56. (i) Write a chemical test to distinguish between

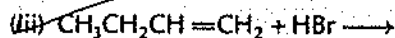
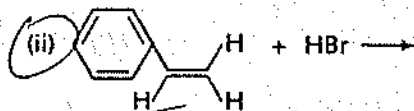
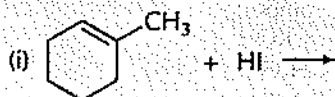
(a) chlorobenzene and benzyl chloride

(b) chloroform and carbon tetrachloride

(ii) Why is methyl chloride hydrolysed more easily than chlorobenzene?

[All India 2011C]

57. Complete the following reaction equations.



[Foreign 2011, 2008]

58. (i) State one use of DDT and iodoform.

(ii) Which compound in the following couples will react faster in S_N2 displacement and why?

(a) 1-bromopentane or 2-bromopentane

(b) 1-bromo-2-methylbutane or 2-bromo-2-methyl butane.

[Delhi 2010]

59. How would you differentiate between S_N1 and S_N2 mechanism of substitution reactions? Give one example of each.

[All India 2010]

60. Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides though polar are immiscible with water?

(iii) in the pair, $(\text{CH}_3)_3\text{C}-\text{Cl}$ and CH_3Cl , CH_3Cl will react faster in S_N2 reaction with $-\text{OH}^-$? [All India 2010C]

61. Give reasons for the following observations.

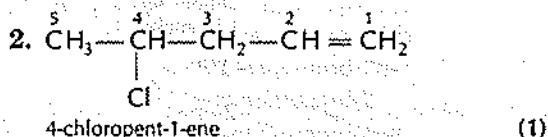
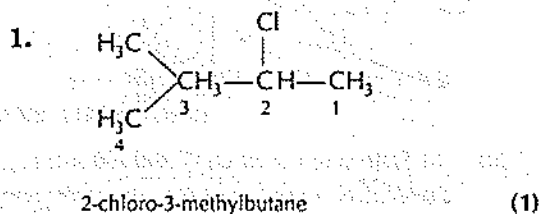
(i) *p*-dichlorobenzene has higher melting point than those of *o* and *m*-isomers.

(ii) Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

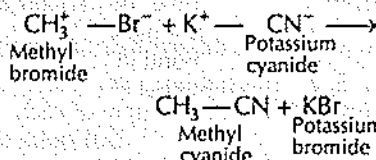
(iii) The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product.

[All India 2009C; Delhi 2008, 2008C]

Step-by-Step Solutions

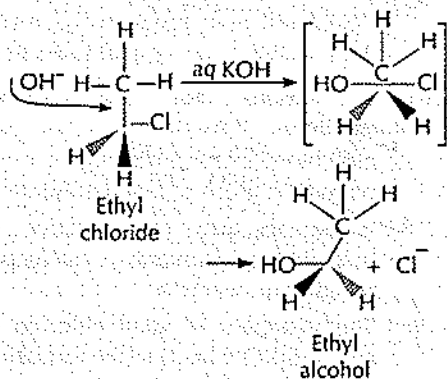
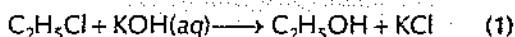


3. Methyl cyanide is obtained.

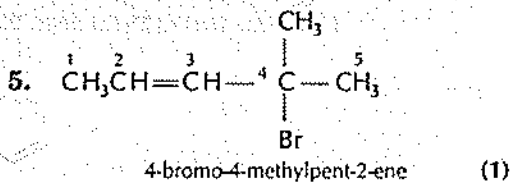


It is a nucleophilic substitution reaction. Nucleophile CN^- substitutes Br^- . (1)

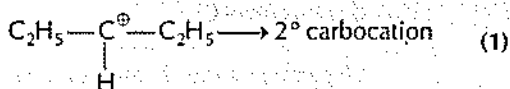
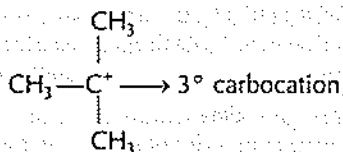
4. Bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$) reaction occurs.



Inversion of configuration takes place.



6. When these compounds I and II undergo $\text{S}_{\text{N}}1$ reaction, they form 3° and 2° carbocation respectively hence compound I undergoes $\text{S}_{\text{N}}1$ reaction fast..

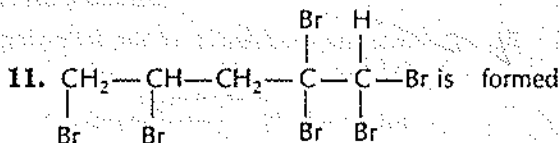


7. 2-chloro-3,3-dimethylbutane as halogen are preferred over alkyl group while naming. (1)

8. 1,4-dichloro-2-methylbenzene (1)

9. 2-bromo-4-chloropentane (1)

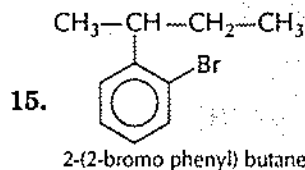
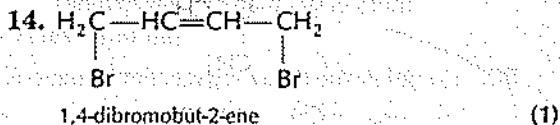
10. 3-bromo-2-methylprop-1-ene (1)



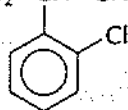
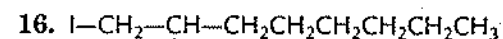
when Br_2 is used in excess. But if only one mole of Br_2 is used, then $\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}(\text{Br})=\text{C}-\text{Br}$ will be formed. (1)

12. 1-bromo-2,2-dimethyl propane (1)

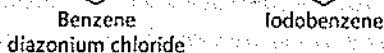
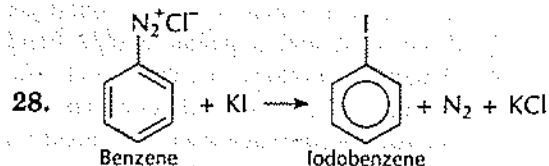
13. 3-bromoprop-1-ene (1)



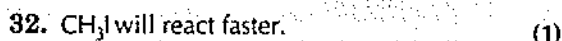
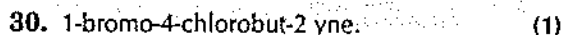
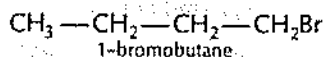
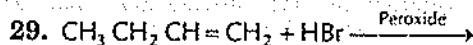
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(1)



(1)

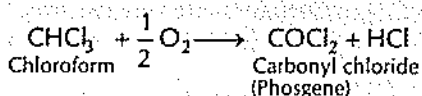


33. (i) Due to partial double bond character of C—Cl bond (due to resonance in $\text{C}_6\text{H}_5\text{Cl}$), bond length of C—Cl [bond in chlorobenzene is shorter than that in methyl chloride (CH_3Cl).

(1)

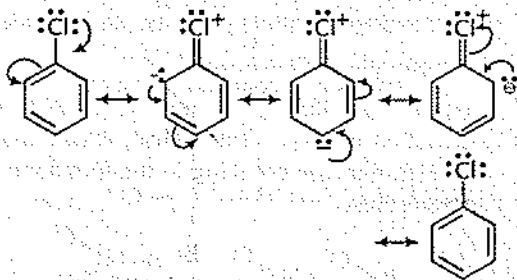
(ii) In the presence of air and sunlight, chloroform get oxidised to phosgene [carbonyl chloride- COCl_2], a poisonous compound. Thus, to check the formation of phosgene, chloroform is stored in dark brown bottles filled up to brim.

(1)



34. Two reasons for the less reactivity of chlorobenzene towards a nucleophilic substitution reaction are as follows

(i) Resonance effect The electron pair of chlorine atom is involved in conjugation with the π -electrons of the benzene ring and the following resonating structures are obtained.

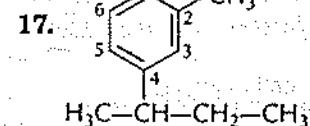


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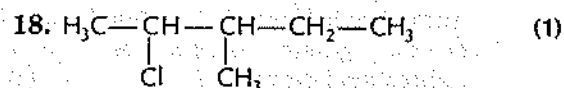
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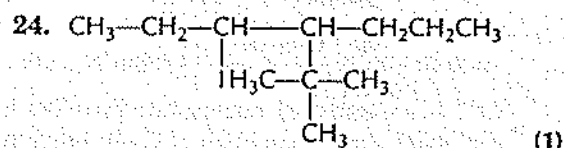
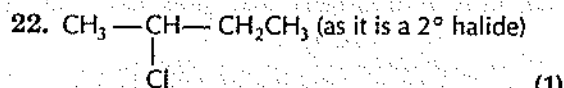
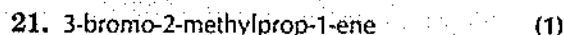
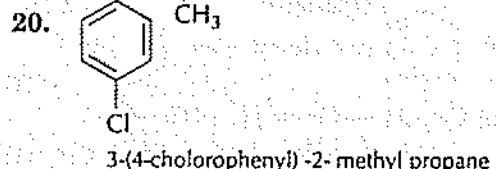
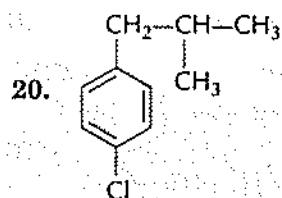


(1)

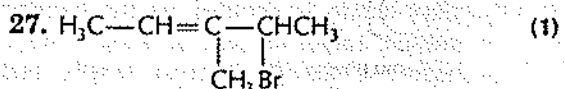
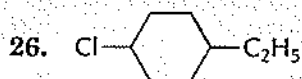
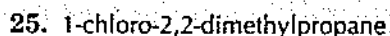


(1)

19. 1-bromo pentane reacts fastest in $\text{S}_{\text{N}}2$ displacement because it is a primary halide, i.e., less hindered. (1)



(1)



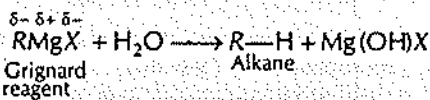
(1)

As a result electrons of C—Cl bond get delocalized and a partial double bond character develops in the bond and hence, it becomes difficult for the nucleophile to cleave the C—Cl bond. (1)

- (ii) **Increased electron density** A repulsion is suffered by the nucleophile due to increased electron density on the benzene ring which prohibits the nucleophile to make a close access for the attack on the molecule. (1)

35. (i) To be miscible with water, the solute-water force of attraction must be stronger than the solute-solute and water-water forces of attraction. Alkyl halides are polar molecules and so held together by dipole-dipole interactions. Similarly, strong H-bonds exist between the water molecules. The new force of attraction between the alkyl halides and water molecules is weaker than the alkyl halide-alkyl halide and water-water forces of attraction. Hence, alkyl halides (though polar) are immiscible with water. (1)

- (ii) Grignard reagents are very reactive. In the presence of moisture, they react to give alkanes. (1)

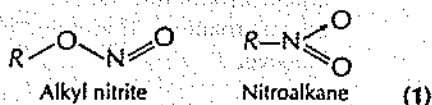



Therefore, Grignard reagents should be prepared under anhydrous conditions. (1)


36. Ambident nucleophiles have two nucleophilic sites through which they can attack. (1)


For example, nitrite ion is an ambident nucleophile. $[\overset{\ominus}{\text{O}}-\overset{\ominus}{\text{N}}=\overset{\ominus}{\text{O}}]$

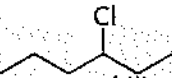
It can attack through oxygen resulting in the formation of alkyl nitrites. Also, it can attack through nitrogen resulting in the formation of nitroalkanes.

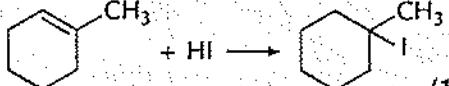


37. (i)  CH_2Cl , it is a primary halide and therefore undergoes $\text{S}_{\text{N}}2$ reaction faster.

- (ii)  As iodide is a better leaving group because of its larger size therefore, it undergoes $\text{S}_{\text{N}}2$ reaction faster. (1 + 1 = 2)

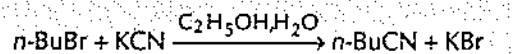
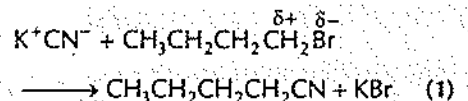
38. (i)  tertiary halide reacts faster than secondary halide in $\text{S}_{\text{N}}1$ reaction because of the greater stability of tertiary carbocation intermediate. (1)

- (ii)  reacts faster because of greater stability of secondary carbocation than primary. (1)

39. (i)  (1)

- (ii) $\text{CH}_3\text{CH}_2-\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow \text{CH}_3-\text{CH}_2-\underset{\text{Br}}{\text{CH}}-\text{CH}_3$ (1)

40. KCN is a reagent that gives CN^- ion as nucleophile in aqueous medium.

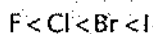


CN^- is an ambident nucleophile therefore it can attack the carbon atom of C—Br bond in $n\text{-BuBr}$. Since, C—C is a stronger bond than C—N bond, therefore, attack occurs through C to form n -butyl cyanide. (1)

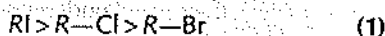
41. (i) When alkyl group is same, the reactivity of alkyl halide is decided by the halogen present. Larger the size of halogen atom, higher is the R—X bond length, and weaker is the bond. Thus, more reactive is the alkyl halide.

Haloalkanes and Haloarenes

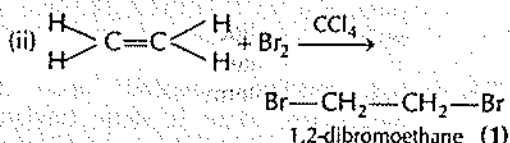
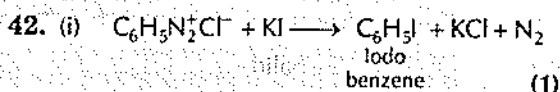
The order of size is



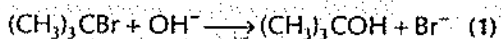
Thus, the order of reactivity is



- (ii) There is steric hinderance in the case of *neo*-pentyl chloride so it does not follow S_N2 mechanism. (1)

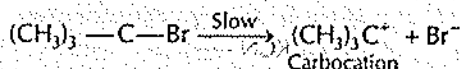


43. (i) CH_3I will react faster as compared to CH_3Br , because CH_3I has lower bond dissociation energy and iodine is better leaving group. In the presence of nucleophile, it will be released at a faster rate. (1)
- (ii) CH_3Cl will react faster as compared to $(CH_3)_3CCl$, because i halides undergo S_N2 mechanism faster than 3° halides. (1)
44. S_N1 reaction are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc). The reaction between *tert*.butyl bromide and hydroxide ion yields *tert*.butyl alcohol and follows the first order kinetics.

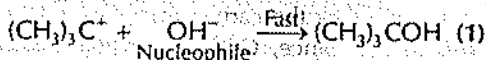


The steps involved are

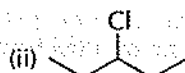
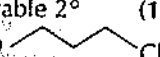
1. Formation of carbocation intermediate



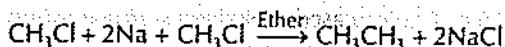
2. Attack of nucleophile on carbocation formed



45. (i) In haloalkanes, there is single bond between $R-X$, which needs less bond dissociation energy, hence they are more reactive towards nucleophiles. In haloarenes, there is double bond character between $C-X$ bond due to resonance, therefore, has more bond dissociation energy. (1)

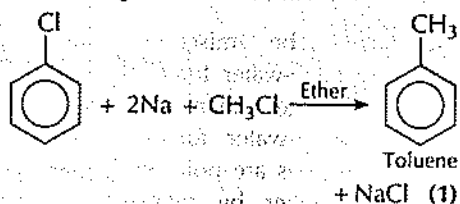
- (ii)  will react faster is S_N1 reaction because i will form more stable 2° carbo-cation as compared to  Cl which forms 1° carbocation. (1)

46. (i) Wurtz reaction

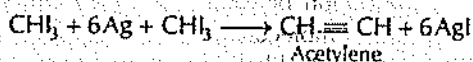


We get alkane from alkyl halide. (1)

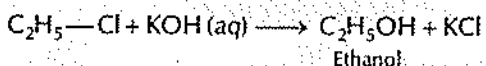
- (ii) Wurtz-Fittig reaction



47. When iodoform is heated with silver powder acetylene is formed. (2)



48. The reactions, in which attacking reagent is a nucleophile and causes substitution are known as nucleophilic substitution reactions. For example (1)



In this reaction, OH^- is a nucleophile which replaces Cl^- ion of chloroethane. (1)

49. (i) 3-chloro-5-fluoro-3, 5-dimethyl heptane (1)

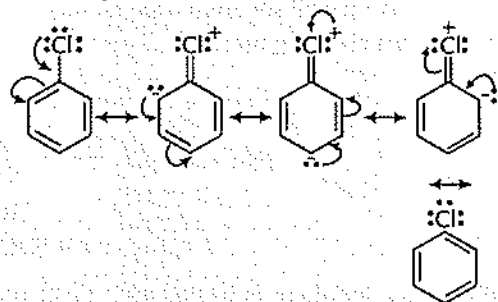
- (ii) 3-iodo-5-nitro-3, 5-dimethyl heptane. (1)

50. (i) Iodide is a better leaving group because of its larger size, than bromide, therefore, ethyl iodide undergoes S_N2 reaction faster than ethyl bromide. (1)

- (ii) (\pm) 2-butanol is a racemic mixture. It is a mixture which contains two enantiomers in equal proportion and thus, have zero optical rotation. Therefore, it is optically inactive. (1)

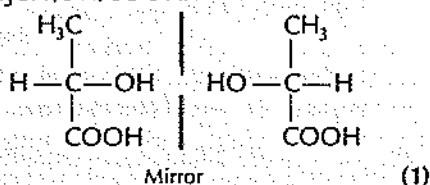
- (iii) Due to delocalisation of lone pairs of electrons of the X atom over the benzene ring, C—X bond in halobenzene acquires some double bond character while in $\text{CH}_3\text{—X}$, C—X bond is a pure single bond. Therefore, C—X bond in halobenzene is shorter than in $\text{CH}_3\text{—X}$. (1)

51. Chlorobenzene is the resonance hybrid of the following structures

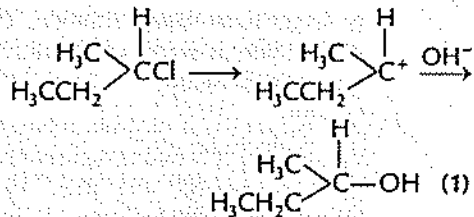


Since electron density is maximum at *o*- and *p*-positions due to +R effect, therefore electrophilic substitution will take place at *o*- and *p*-positions. [3]

52. (i) Chirality An object or molecule which is non-superimposable on its mirror image is called chiral and the property of being chiral is known as chirality. e.g., lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$.



(ii) $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ is more reactive than $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ as the former one gives more stable carbocation intermediate.



(iii) Refer ans. 37 (ii). (1)

53. (i) Haloalkanes easily dissolve in organic solvents because the steric effect is not more as seen in the case of haloarenes and both are covalent in nature (like dissolves like). (1)

(ii) A mixture containing two enantiomers in equal proportion will have zero optical rotation. Such mixtures are called racemic mixtures e.g., (\pm) butan-2-ol. (1)

(iii) The carbocation intermediate from $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ is more stable because it is stabilised by two phenyl groups due to resonance, so $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ is more reactive in $\text{S}_{\text{N}}1$ reaction. (1)

54. (i) $\text{S}_{\text{N}}2$ reactions depend upon steric hinderance. More is steric hinderance, slower the reaction. So, order of reactivity is $1^\circ > 2^\circ > 3^\circ$.

\therefore 1-bromopentane > 2-bromopentane > 2-bromo-2-methyl butane (1)

(ii) 1-bromo-3-methyl butane > 3-bromo-2-methyl butane > 2-bromo-2-methyl butane (1)

(iii) 1-bromobutane > 1-bromo-3-methyl butane > 1-bromo-2-methyl butane > 1-bromo-2, dimethyl propane (1)

55. (i) Refer ans. 40 (1)

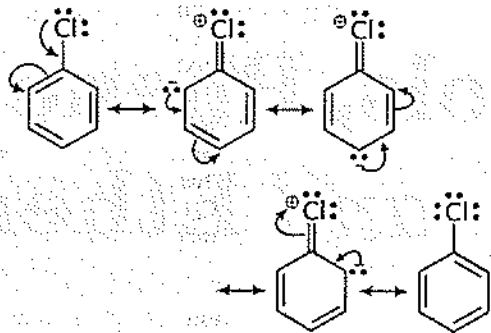
(ii) In chlorobenzene the Cl-atom is linked to a sp^2 hybridized carbon atom. In cyclohexyl chloride the Cl atom is linked to a sp^3 hybridized carbon atom. Now sp^2 hybridized carbon has more s-character so it is more electronegative thus the density of electrons of C—Cl bond near the Cl atom is less in chlorobenzene than in cyclohexyl chloride. Hence, the C—Cl bond of cyclohexyl chloride is more polar, i.e., it has higher dipole moment. (2)

56. (i) (a) Benzyl chloride when treated with AgNO_3 solution will give a white ppt while chlorobenzene will not.

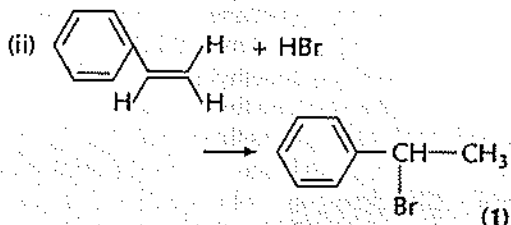
(b) Chloroform when treated with 1° amine and KOH gives offensive smelling isocyanides while CCl_4 does not show this test. (2)

Haloalkanes and Haloarenes

- (ii) Chlorobenzene is stabilized by resonance so has a double bond character between C and Cl. Secondly, the C is sp^2 hybridized so more electronegative thus Cl^- is not replaced easily. (1)



57. (i) Refer ans. 39(i). (1)

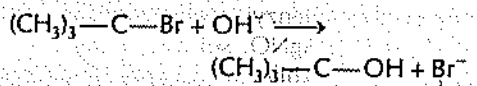


- (iii) Refer ans. 39 (ii). (1)

58. (i) DDT is used as an insecticide and iodoform is used as a mild antiseptic. (1)

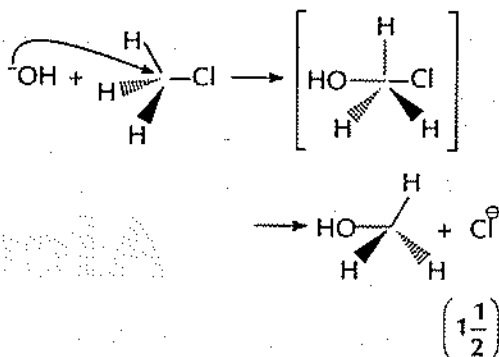
- (ii) (a) 1-bromopentane will react faster because it is a primary alkyl halide. (1)
 (b) 1-bromo-2-methyl butane, as it is a primary alkyl halide. (1)

59. In S_N1 mechanism of substitution reaction, the rate of reaction depends upon the concentration of only one reactant which is tert. butyl bromide. (1)



It involves the formation of carbocation intermediate and inversion as well as retention of configuration.

In S_N2 mechanism of substitution reaction, the rate of reaction depends upon the concentration of both the reactants.



It involves the formation of transition state and inversion of configuration.

60. (i) Refer ans. 55 (ii). (1)

- (ii) Refer ans. 35 (i). (1)

- (iii) CH_3Cl is more reactive than $(CH_3)_3CCl$ because of steric hindrance in case of $(CH_3)_3CCl$. (1)

61. (i) The melting point of *p*-isomer of dichloro benzene is higher than that of *o*-isomer. This is because *p*-isomer has symmetrical structure due to which its molecules can easily pack closely in crystal lattice. Thus, it has stronger intermolecular forces of attraction than *o*-isomer. (1)

- (ii) In haloalkanes, the carbon is bonded to a halogen atom which is more electronegative than carbon. Further polar nature of alkyl halides makes them highly reactive molecules. Also another reason is the carbon atom of haloarenes is sp^2 hybridised so hold the electron pair of the C—X bond more tightly than sp^3 hybridised carbon in haloalkane. (1)

- (iii) In aqueous solution KOH is almost completely ionized to give OH^- ions which being a strong nucleophile gives a substitution reaction on alkyl halide to form alcohol.

But an alcoholic solution of KOH contains alkoxide RO^- ions which being a much stronger base than OH^- ions preferentially eliminates a molecule of HCl from an alkyl chloride to form alkenes. (1)