CHAPTER

# 18

# Haloalkanes and Haloarenes

## Section-A JEE Advanced/ IIT-JEE

### A Fill in the Blanks

1. The halogen which is most reactive in the halogenation of alkanes under sunlight is ..... .
(chlorine, bromine, iodine) *(1981 - 1 Mark)*
2. The compound prepared by the action of magnesium on dry ethyl bromide in ether is known as ..... reagent. *(1982 - 1 Mark)*
3. The interaction of elemental sulphur with Grignard reagent gives ..... . *(1991 - 1 Mark)*
4. Vinyl chloride on reaction with dimethyl copper gives ..... . *(1997 - 1 Mark)*

### B True / False

1. *m*-Chlorobromobenzene is an isomer of *m*-bromochlorobenzene. *(1985 - ½ Mark)*
2. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markovnikov's rule. *(1989 - 2 Marks)*

### C MCQs with One Correct Answer

1. Chlorobenzene can be prepared by reacting aniline with : *(1984 - 1 Mark)*
   (a) hydrochloric acid
   (b) cuprous chloride
   (c) chlorine in presence of anhydrous aluminium chloride
   (d) nitrous acid followed by heating with cuprous chloride
2. The reaction of toluene with chlorine in presence of ferric chloride gives predominantly : *(1986 - 1 Mark)*
   (a) benzoyl chloride
   (b) *m*-chlorotoluene
   (c) benzyl chloride
   (d) *o*- and *p*-chlorotoluene
3. The reaction conditions leading to the best yields of $C_2H_5Cl$ are : *(1986 - 1 Mark)*

   (a) $C_2H_6\,(\text{excess}) + Cl_2 \xrightarrow{\text{uv light}}$

   (b) $C_2H_6 + Cl_2 \xrightarrow[\text{room temperature}]{\text{dark}}$

   (c) $C_2H_6 + Cl_2\,(\text{excess}) \xrightarrow{\text{uv light}}$

   (d) $C_2H_6 + Cl_2 \xrightarrow{\text{uv light}}$

4. n-Propyl bromide on treatment with ethanolic potassium hydroxide produces *(1987 - 1 Mark)*
   (a) Propane (b) Propene
   (c) Propyne (d) Propanol
5. The number of structural and configurational isomers of a bromo compound, $C_5H_9Br$, formed by the addition of HBr to 2-pentyne respectively are *(1988 - 1 Mark)*
   (a) 1 and 2 (b) 2 and 4
   (c) 4 and 2 (d) 2 and 1
6. 1-Chlorobutane on reaction with alcoholic potash gives *(1991 - 1 Mark)*
   (a) 1-butene (b) 1-butanol
   (c) 2-butene (d) 2-butanol
7. The chief reaction product of reaction between *n*-butane and bromine at 130°C is : *(1995S)*
   (a) $CH_3CH_2CH_2CH_2Br$

   (b) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HBr$

   (c) $CH_3 - CH_2\underset{\displaystyle CH_2Br}{\underset{|}{C}}HBr$

   (d) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}Br_2$

8. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives : *(1995S)*
   (a) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$ & $CH_3CH_2MgBr$

   (b) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$ & $MgBr(OC_2H_5)$

   (c) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H, CH = CH_2$ & Mg(OH)Br

   (d) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$ & $CH_3CH_2OMgBr$

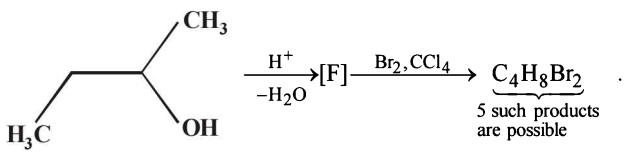
9. $(CH_3)_3CMgCl$ on reaction with $D_2O$ produces : *(1997 - 1 Mark)*
   (a) $(CH_3)_3CD$ (b) $(CH_3)_3OD$
   (c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$.

10. A solution of (+) –2–chloro–2–phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of *(1999 - 2 Marks)*
(a) carbanion (b) carbene
(c) free-radical (d) carbocation

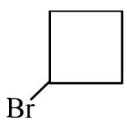
11. Identify the set of reagent / reaction conditions 'X' and 'Y' in the following set of transformations *(2002S)*

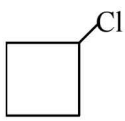
$$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

(a) X = dilute aqueous NaOH, 20°C; Y = HBr/acetic acid, 20°C
(b) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acetic acid, 20°C
(c) X = dilute aqueous NaOH, 20°C ; Y = $Br_2/CHCl_3$, 0°C
(d) X = concentrated alcoholic NaOH, 80°C; Y = $Br_2/CHCl_3$, 0°C

12. 

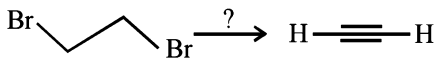
How many structures for F are possible? *(2003S)*
(a) 2 (b) 5
(c) 6 (d) 3

13. What would be the product formed when 1–bromo–3–chlorocyclobutane reacts with two equivalents of metallic sodium in ether? *(2005S)*
(a) 

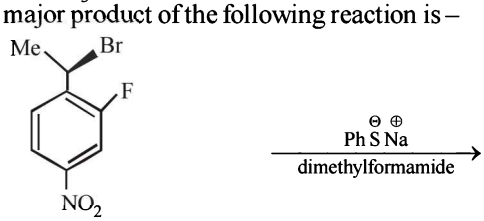
(b) 

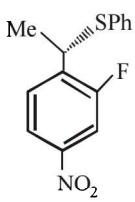
(c) 
(d) 

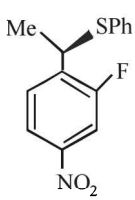
14. When phenyl magnesium bromide reacts with *tert* – butanol, the product would be *(2005S)*
(a) Benzene (b) Phenol
(c) *ter*–butylbenzene (d) *ter*–butyl phenyl ether

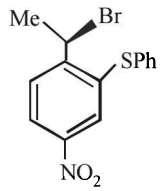
15. The reagent(s) for the following conversion,


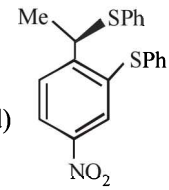
is/are *(2007)*
(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) $Zn/CH_3OH$

16. The major product of the following reaction is – *(2008)*


(a) 

(b) 

(c) 

(d) 

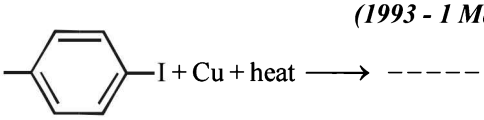

## D MCQs with One or More Than One Correct

1. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to : *(1990 - 1 Mark)*
(a) The formation of less stable carbonium ion
(b) Resonance stabilization
(c) Longer carbon-halogen bond
(d) The inductive effect
(e) $sp^2$ hybridized carbon attached to the halogen.

2. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with *(1998 - 2 Marks)*
(a) $SO_2Cl_2$ (b) $SOCl_2$
(c) $Cl_2$ (d) NaOCl

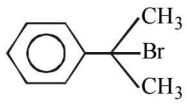
## E Subjective Problems

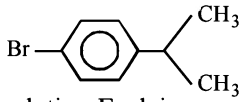
1. (a) Show by chemical equations only, how you would prepare the following from the indicated starting materials. Specify the reagents in each step of the synthesis.
(i) Hexachlorethane, $C_2Cl_6$, from calcium carbide.
(ii) Chloroform from carbon disulphide.
(b) Give one chemical test which would distinguish between $C_2H_5OH$ from $CHCl_3$. *(1979)*

2. Write the structural formula of the major product in each of the following cases :
(*i*) chloroform reacts with aniline in the presence of excess alkali *(1981 - ½ Mark)*
(*ii*) bromoethane reacts with one-half of the molar quantity of silver carbonate. *(1981 - ½ Mark)*
(*iii*) $(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}-CH_2CH_3 \xrightarrow[\text{alc. KOH}]{}$ *(1992 - 1 Mark)*
(*iv*) $CH_3CH_2CHCl_2 \xrightarrow[\text{alkali}]{\text{boil}}$ *(1992 - 1 Mark)*
(*v*) $C_6H_5-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{KOH, }\Delta]{\text{alcoholic}} ? \xrightarrow{HBr} ?$ *(1993 - 1 Mark)*
(*vi*) 

*(1997 - 1 Mark)*
(*vii*) $C_6H_5CH_2CHClC_6H_5 \xrightarrow[\text{heat}]{\text{alcoholic KOH}}$ 2 Products *(1998 - 2 Marks)*
(*viii*) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2Br \xrightarrow[\Delta]{C_2H_5OH}$ *(2000 - 1 Mark)*

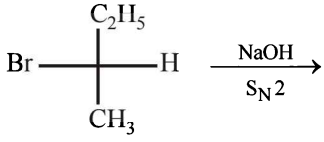
3. Give reasons for the following :
   (*i*) 7-Bromo-1, 3, 5-cycloheptatriene exists as ionic compound, while 5-bromo-1, 3-cyclopentadiene does not ionise even in presence of $Ag^+$ ion. Explain. ***(2004 - 2 Marks)***

   (*ii*)  $\xrightarrow{\text{aq. } C_2H_5OH}$ Acidic solution

    $\xrightarrow{\text{aq. } C_2H_5OH}$ Neutral

   solution. Explain. ***(2005 - 1 Mark)***
4. State the conditions under which the following preparation are carried out. Give the necessary equations which need not be balanced :
   (*i*) Lead tetraethyl from sodium-lead alloy ***(1983 - 1 Mark)***
   (*ii*) Methyl chloride from aluminium carbide ***(1983 - 1 Mark)***
5. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment? ***(1985 - 2 Marks)***
6. What happens when excess chlorine is passed through boiling toluene in the presence of sunlight? ***(1987 - 1 Mark)***
7. What effect should the following resonance of vinyl chloride have on its dipole moment? ***(1987 - 1 Mark)***

   $CH_2=CH-Cl \longleftrightarrow CH_2^- - CH_2=Cl^+$
8. An organic compound X, on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures, Y and Z. Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound while Z on similar treatment gives ethanal. Find out the molecular formula of X and give the structures of Y and Z. ***(1989 - 4 Marks)***
9. Draw the stereochemical structures of the products in the following reaction : ***(1994 - 4 Marks)***

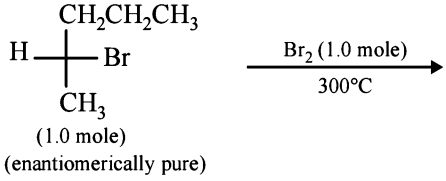
   
10. An alkyl halide, X, of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z ($C_6H_{12}$). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of X, Y and Z. ***(1996 - 3 Marks)***
11. How will you prepare *m*-bromoiodobenzene from benzene (in not more than 5-7 steps)? ***(1996 - 2 Marks)***
12. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic reacts with ethanal to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1–bromo–1–methylcyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B). ***(2001 - 5 Marks)***

## H Assertion & Reason Type Questions

1. Read the following Statement-1 (Assertion) and Statement -2 (Reason) and answer as per the options given below :
   **Statement-1 :** Bromobenzene upon reaction with $Br_2$/Fe gives 1,4-dibromobenzene as the major product. ***(2008S)***
   **Statement-2 :** In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.
   (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
   (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
   (c) Statement-1 is True, Statement-2 is False
   (d) Statement-1 is False, Statement-2 is True

## I Integer Value Correct Type

1. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is ***(2011)***
2. In the following monobromination reaction, the number of possible chiral products is ***(JEE Adv. 2016)***

   
   (1.0 mole)
   (enantiomerically pure)

# Section-B JEE Main / AIEEE

1. Bottles containing $C_6H_5I$ and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute $HNO_3$ and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment ? **[2003]**
   (a) A and $C_6H_5CH_2I$
   (b) B and $C_6H_5I$
   (c) Addition of $HNO_3$ was unnecessary
   (d) A was $C_6H_5I$
2. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid, is
   (a) freon (b) DDT **[2004]**
   (c) gammexene (d) hexachloroethane
3. Tertiary alkyl halides are practically inert to substitution by $S_N2$ mechanism because of **[2005]**
   (a) steric hindrance (b) inductive effect
   (c) instability (d) insolubility
4. Alkyl halides react with dialkyl copper reagents to give
   (a) alkenyl halides (b) alkanes **[2005]**
   (c) alkyl copper halides (d) alkenes

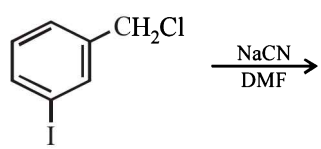
5. Elimination of bromine from 2-bromobutane results in the formation of– [2005]
(a) Predominantly 2-butyne
(b) Predominantly 1-butene
(c) Predominantly 2-butene
(d) equimolar mixture of 1 and 2-butene

6. Phenyl magnesium bromide reacts with methanol to give [2006]
(a) a mixture of toluene and Mg(OH)Br
(b) a mixture of phenol and Mg(Me)Br
(c) a mixture of anisole and Mg(OH)Br
(d) a mixture of benzene and Mg(OMe)Br

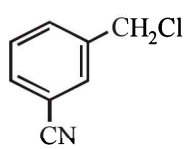
7. Fluorobenzene ($C_6H_5F$) can be synthesized in the laboratory [2006]
(a) by direct fluorination of benzene with $F_2$ gas
(b) by reacting bromobenzene with NaF solution
(c) by heating phenol with HF and KF
(d) from aniline by diazotisation followed by heating the diazonium salt with $HBF_4$

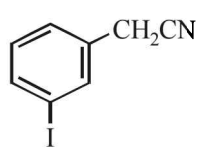
8. Reaction of *trans* 2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces [2006]
(a) 1-phenylcyclopentene (b) 3-phenylcyclopentene
(c) 4-phenylcyclopentene (d) 2-phenylcyclopentene

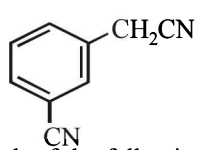
9. The structure of the major product formed in the following reaction [2006]

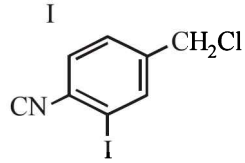



is

(a) 


(b) 

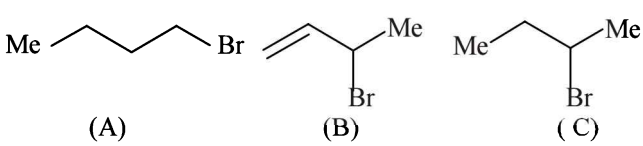

(c) 


(d) 


10. Which of the following is the correct order of decreasing $S_N2$ reactivity? [2007]
(a) $R_2CHX > R_2CX > RCH_2X$
(b) $RCHX > R_2CX > R_2CHX$
(c) $RCH_2X > R_2CHX > R_2CX$
(d) $R_2CX > R_2CHX > RCH_2X$.
(X is a halogen)

11. The organic chloro compound, which shows complete sterochemical inversion during a $S_N2$ reaction, is [2008]
(a) $(C_2H_5)_2CHCl$ (b) $(CH_3)_3CCl$
(c) $(CH_3)_2CHCl$ (d) $CH_3Cl$

12. Consider the following bromides :



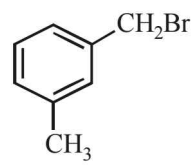

(A) (B) ( C)

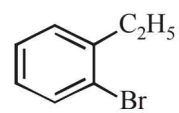
The correct order of $S_N1$ reactivity is [2010]
(a) B > C > A (b) B > A > C
(c) C > B > A (d) A > B > C

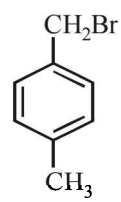
13. How many chiral compounds are possible on monochlorination of 2- methyl butane ? [2012]
(a) 8 (b) 2
(c) 4 (d) 6

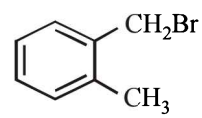
14. What is DDT among the following ? [2012]
(a) Greenhouse gas
(b) A fertilizer
(c) Biodegradable pollutant
(d) Non-biodegradable pollutant

15. Compound (A), $C_8H_9Br$, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). [JEE M 2013]

(a) 


(b) 


(c) 


(d) 


16. In $S_N2$ reactions, the correct order of reactivity for the following compounds: [JEE M 2014]

$CH_3Cl$, $CH_3CH_2Cl$, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is:

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

17. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is: [JEE M 2014]
(a) Acetylene (b) Ethene
(c) 2 - Butyne (d) 2 - Butene

18. The synthesis of alkyl fluorides is best accomplished by : [JEE M 2015]
(a) Finkelstein reaction (b) Swarts reaction
(c) Free radical fluorination (d) Sandmeyer's reaction