

# **NEET Important Questions with Solutions from Haloalkanes and Haloarenes**

Q.1.	Which of the following is halogen exchange reaction?
A)	$R X + NaI \longrightarrow RI + NaX$
B)	$ C = C < + H X \longrightarrow C - C < $ H X
C)	$R - OH + HX \xrightarrow{ZnCl_2} R - X + H_2O$
D)	$\begin{array}{ c c c c } \hline CH_3 & CH_3 \\ + X_2 & \overrightarrow{\text{dark}} & X \\ \hline X & X \end{array} + X \\ \hline \end{array}$
Answer: $R X + NaI \longrightarrow RI + NaX$	
Solut	${ m lion:}$ Alkyl lodides are often prepared by the reaction of alkyl chlorides/bromides with ${ m NaI}$ in dry acetone. This reaction is known as Finkelstein reaction.
	$NaCl\ or\ NaBr\ $ thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.
	In the given reaction, there happens to be an exchange of halogens between reacting species, hence the reaction is very often termed as Halogen exchange reaction.
Q.2.	Which reagent will you use for the following reaction?
	$\mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_3 \ \rightarrow \ \mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{CI} \ + \ \mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}\mathrm{Cl}\mathrm{CH}_3$
A)	$\mathrm{Cl}_2/\mathrm{UV}$ light
B)	$NaCl + H_2SO_4$
C)	$\mathrm{Cl}_2$ gas in dark
D)	$\mathrm{Cl}_2$ gas in the presence of iron in dark
Answ	ver: $\operatorname{Cl}_2/\operatorname{UV}$ light
Solut	tion: Free radical chlorination or bromination of alkanes gives a complex mixture of isomeric mono and polyhaloalkanes, which is difficult to separate as pure compounds.

In this case, a mixture of the two isomeric forms of butane is obtained by reacting butane with  ${
m CI}_2$  /  ${
m UV}$  light.

$$CH_{2}CH_{2}CH_{2}CH_{3} \xrightarrow{Cl_{2}/UV \text{ light}}$$
or heat

 $\mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{Cl} + \mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}\mathrm{Cl}\mathrm{CH}_3$ 



Q.3. Arrange the following compounds in the increasing order of their densities.



Solution:

A)

B)

C)

D)

The density increases with increase in number of carbon atoms, halogen atoms and atomic masses of the halogen atoms bonded with the alkyl or aryl groups.

In other words, density is related to molecular mass of the compound. Higher the molecular mass, greater will be the density of the compound.

Q.4. Arrange the following compounds in increasing order of their boiling points.

(a)  $\begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \end{array}$  (b)  $CH_3 CH_2 CH_2 CH_2 Br$  (c)  $H_3 C - CH_3 \\ H_3 C - CH_3 \\ CH_$ (b) < (a) < (c)(a) < (b) < (c)(c) < (a) < (b)(c) < (b) < (a)Answer: (c) < (a) < (b)Solution: Molecular forces of attraction get stronger as molecules get bigger in size. Further, as the branching increases, the surface area of the molecule decreases. Because of this, the Van der Waal's force of attraction between the molecule decreases and consequently boiling point decreases. In the above three isomers given Structure (b) is a straight-chain with no branching, structure (c) is branched but has less surface area compared to the structure (a). Hence, the increasing order of their boiling points is, (c) < (a) < (b)

Q.5. In which of the following molecules carbon atom marked with asterisk (\*) is asymmetric?



A) (a), (b), (c), (d)



- B) (a), (b), (c)
- C) (b), (c), (d)
- D) (a), (c), (d)
- Answer: (a), (b), (c)
- Solution: Carbon atom attached with four different groups or atoms is known as asymmetric carbon atom. This condition is satisfied by the compounds (a), (b) and (c) which contain chiral carbon. The compound (d) contains carbon atom which is linked to two similar atoms (H), hence it is not asymmetric carbon atom.

Q.6. Which of the following structures is enantiomeric with the molecule (A) given below:

$$H_{5}C_{2} \xrightarrow{C_{1}} Br$$
(A)

A)



B)



C)



D)

 $\begin{array}{c} Br \\ | \\ H_5C_2 \\ CH_3 \end{array}$ 

Answer:





#### Solution:

The stereo isomers of a compound which are non-superimposable on each other are known as enantiomers. The molecule (A) has an asymmetric carbon atom.

The mirror image of the molecule

$$H_{3}C \xrightarrow{H} C_{2}H_{5}$$

is not superimposable on (A).

The other molecules are superimposable on (A).

- Q.7. Which of the following is an example of vic-dihalide?
- A) Dichloromethane
- B) 1,2-dichloroethane
- C) Ethylidene chloride
- D) Allyl chloride

Answer: 1, 2-dichloroethane

Solution: Vic-dihalides or vicinal dihalides are those dihaloalkanes where the halogen atoms are present on two adjacent carbon atoms. In 1, 2 dichloroethane, the two chlorine atoms are attached to two adjacent carbon atoms, therefore, it is a vicdihalide. In Dichloromethane two halogen atoms are attached to the same carbon atom. Ethylidene chloride is geminal dihalide as both the halogen atom are attached to the same carbon atom, while Allyl chloride consists of only one chlorine atom. Q.8. The position of -Br in the compound in  $CH_3$   $CH = CHC(Br)(CH_3)_2$  can be classified as \_ A) Allyl B) Aryl C) Vinyl D) Secondary Answer: Allyl Solution: The compounds in which the halogen atom is bonded to an  $sp^3$ - hybridised carbon atom next to carbon-carbon double bond (C = C) i.e., to an allylic carbon are classified as allylic halides. Therefore,  $CH_3 CH = CHC(Br)(CH_3)_2$  can be considered as allyl halide. Aryl halides are formed when the halogen atom is bonded directly to the  $sp^2$  hybridised carbon atom of an aromatic ring. Vinylic bonds are formed when the halogen atom is bonded to a  $sp^2$  hybridised carbon atom of a carbon-carbon double bond. In Secondary haloalkanes, the halogen is bonded to a secondary carbon atom of the molecule. Q.9. A primary alkyl halide would prefer to undergo \_

A)  $S_N 1$  reaction



- ${\sf B}) \qquad S_N 2 \ \text{reaction}$
- C)  $\alpha$ -Elimination
- D) Racemisation
- Answer: S<sub>N</sub>2 reaction
- Q.10. Which of the following alkyl halides will undergo  $S_{\rm N}1$  reaction most readily?
- A)  $(CH_3)_3C$ —F
- $\mathsf{B}) \quad (\mathrm{CH}_3)_3\mathrm{C}\mathrm{--Cl}$
- C)  $(CH_3)_3C$ —Br
- D)  $(CH_3)_3C-I$
- Answer:  $(CH_3)_3C$ —I
- Q.11. Which of the following is known as freon and is used as a refrigerant?
- A)  $CCl_2F_2$
- B) CHCl<sub>3</sub>
- C)  $CH_2F_2$
- D)  $CF_4$

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Answer: CCl<sub>2</sub>F<sub>2</sub>
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Solution:  $CCl_2F_2$  is known as freon and is used as a refrigerant.

Dichlorodifluoromethane is a colorless, non-flammable gas that can affect you when breathed in. Acute (short-term) exposure to dichlorodifluoromethane can cause dizziness, lightheadedness, and trouble with concentration.

- Q.12. Use of chlorofluorocarbons is NOT encouraged because \_\_\_\_\_
- A) they are harmful to the eyes of people that use it
- B) they damage the refrigerators and air conditioners
- C) they deplete away the ozone in the atmosphere
- D) they destroy the oxygen layer
- Answer: they deplete away the ozone in the atmosphere



- Solution: Chlorofluorocarbons are the cause depletion of the ozone layer in the atmosphere because they react with ozone molecule by releasing chlorine radicals through a chain reaction. Chlorofluorocarbons are broken up by ultraviolet radiations.
- Q.13. In the compound 'X', all the bond angles are exactly 109°28'. 'X' may be \_\_\_\_\_.
- A) Chloroform
- B) Iodoform
- C) Chloromethane
- D) Carbon tetrachloride
- Answer: Carbon tetrachloride

Solution: When all the atoms are attached to carbon atom are same then all the angles between atom-carbon-atom are the same.

In carbon tetrachloride, chlorine atom is attached

to carbon is same then all the angles between

 $\mathrm{Cl}-\mathrm{C}-\mathrm{Cl}$  are the same.

- Q.14. Isobutyl bromide may be obtained from isobutylene and HBr in the presence of \_\_\_\_\_.
- A) peroxide
- B) hydroquinone
- C) diffused sunlight
- D) Pyridine

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Answer: peroxide
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Solution:

Isobutyl bromide may be obtained from isobutylene and HBr in the presence of peroxide  $(Anti-Markovnikov\ rule).$ 

$$CH_{3}$$

$$C = CH_{2} + HBr \xrightarrow{H_{2}O_{2}} CH_{3}$$

$$CH_{3} - CH_{2} - Br$$

$$CH_{3}$$

$$CH_{3} - butylbromide$$

$$CH_{3} - butylbromide$$

- Q.15. Heterolysis of carbon-chlorine bond produces \_\_\_\_\_
- A) carbocation and chloride ion
- B) two free radicals
- C) carbanion and chloronium ion
- D) two carbocations
- Answer: carbocation and chloride ion





Heterolysis of carbon-chlorine bond produces carbocation and chloride ion. Heterolysis means that the sharing of the bonding electron takes towards the more electronegative atom when the cleavage of carbon-halogen atom.



Q.16. Which of the following is isobutyl chloride?

A)

$$CH_3 - CH_2 -$$

B)

C)

$$CH_3 - CH - CH_2 - CI$$

D)



### Answer:

 $\substack{CH_3-CH-CH_2-Cl}{\underset{CH_3}{\mid}}$ 

Solution:

'Iso' term is used when, methyl is attached to the second carbon from terminal carbon in the main chain. Isobutyl chloride is a chlorinated derivative of isobutane.

Isobutane is the simplest alkane with one tertiary carbon.

Its IUPAC name is  $1-\!\!\text{chloro}-2-\!\!\text{methylpropane}$  and its structure is given below:

$$CH_3$$
  
|  
 $CH_3 - CH - CH_2 - Cl$   
Isobutyl chloride

Q.17. Arenes, when treated with chlorine or bromine in the presence of Lewis acid as a catalyst, undergo \_\_\_\_\_ reaction.

- A) nucleophilic substitution
- B) electrophilic substitution
- C) rearrangement



## D) dehydrohalogenation

#### Answer: electrophilic substitution

- Solution: Electrophilic substitution reactions are chemical reactions in which an electrophile displaces a functional group in a compound, which is mostly hydrogen atom. Arenes, when treated with chlorine or bromine in the presence of Lewis acid as a catalyst, undergo electrophilic substitution reaction.
- Q.18. State the product formed during the reaction between sodium phenoxide and ethyl iodide on heating:

A) benzyl alcohol

- B) phenol
- C) phenetol
- D) None of these
- Answer: phenetol
- Solution:

The reaction between sodium phenoxide and ethyl iodide on heating gives phenetol. This is 
$$\mathrm{SN}^2$$
 reaction, as the strong nucleophile sodium phenoxide attacks on the less crowded ethyl iodide. Reaction is shown below.

$$PhO^- + C_2H_5I \rightarrow \overset{C_2H_5OPh}{_{phenetol}}$$

Q.19. A particular form of tribromobenzene forms three possible mono nitro tribromobenzenes. The structure of the compound is





B)



C)



D) Both B and C



Answer:





The structure of the compound is,



because it has three positions available to attack  $\overset{\oplus}{NO_2}$  group in the given reaction conditions to form three possible mono nitro tribromobenzene and others form only one type of product.



The above molecule is having two different position to attack electrophile.



The above structure forms single nitro product on nitration.

## Q.20. Predict the product formed in the following reaction:







A)

Answer:



Solution:

First of all Lewis acid reacts with the alkyl chloride and forms the carbocation. Then carbocation will go for rearrangement from less stable form to more stable form. After that benzene will give the electrophilic aromatic substitution reaction and gives the Friedel-Craft Alkylation reaction.



Q.21. Which would be obtained by boiling CHCl<sub>3</sub> with caustic soda?



- A)  $CH_3 COON$
- B) HCOONa
- C)  $Na_2C_2O_4$
- D) CH<sub>3</sub>OH
- Answer: HCOONa
- Solution: Chloroform when boiled with the aqueous solution of caustic soda, first it forms formic acid which reacts further and sodium formate forms.

Hydrolysis in basic medium chloroform converts into sodium formate.

 $CHCl_3 \xrightarrow{4NaOH} HCOONa + 3 NaCl + 2H_2O$ 

- Q.22. Which of the following statement is FALSE for alkyl halides?
- A) They are less reactive by nature.
- B) They give nucleophilic substitution reactions.
- C) The halide group is easily replaced by different functional groups.
- D) All of these
- Answer: They are less reactive by nature.

Solution: The C - X bond is a covalent bond, but, the electronegativity of carbon atom is less than halogen atom. Therefore, due to the difference in electronegativity, the C - X bond is polar in nature. In this way, the partial negative charge appears on the halogen atom and a partial positive charge on the carbon atom.

Due to this, alkyl halide gives nucleophilic substitution reaction.

Q.23.



Reagent [Y] can be:

- A) AgF
- B)  $Hg_2F_2$
- C)  $SbF_3$
- D) All
- Answer: All

Solution:

The given reaction is the halide exchange reaction in which alkyl fluoride is formed.

This is Swart's reaction.

Swarts' reaction is generally used to get alkyl fluorides from alkyl chlorides or alkyl bromides. This is done by heating of the alkyl chloride/bromide in the presence of the fluoride of some heavy metals like  $AgF, \ Hg_2F_2, \ SbF_5$  etc.

The reaction will proceed if sodium fluoride or potassium fluoride is used, but the resulting yield will be significantly lower.



- Q.24. The best leaving group (nucleofuge) is:
- A)  $(CH_3)_2S$
- $\mathsf{B}) \quad (\mathrm{CH}_3)_2 \mathrm{NH}$
- C)  $(CH_3)_2O$
- D)  $CH_3OH$
- Answer:  $(CH_3)_2S$
- Solution: According to the question, leaving group is an atom or group of atoms which breaks away from the rest of the molecule, taking with it the electron pair which used to be the bond between the leaving group and the rest of the molecule. The bond dissociation occurs through heterolytic bond fission.

The leaving power of the group is indirectly proportional to the basicity of group. As electronegativity of centre atom of nucleophile decreases then its leaving ability increases.

For example- order of increasing of basicity: or decreasing in leaving ability.  $I^- > \ Br^- \ > Cl^- > F^-$ . So dimethyl sulphide is better leaving group among these options.

Q.25. What is the product C obtained in the following sequence of reactions?

$$\begin{array}{c} \text{Br} \xrightarrow{\text{NH}_2} \text{Br} \xrightarrow{(1) \text{ HONO}} \text{A} \xrightarrow{\text{Sn}/\text{HCl}} \text{B} \xrightarrow{(1) \text{ HONO}} \text{Cl} \\ \xrightarrow{(2) \text{ CuCl}} \text{A} \xrightarrow{(1) \text{ HONO}} \text{B} \xrightarrow{(2) \text{ H}_3\text{PO}_2} \text{Cl} \end{array}$$





B)



C)



D) None of these



Answer:

Br 、 Br

Solution:

The first reaction is the Sandmeyer reaction which is used to synthesise aryl halide (A) from aryl diazonium salt using copper salt as a reagent or a catalyst. It is an example of radical-nucleophilic aromatic substitution.

The next step is the reduction of  $-NO_2$  group of A by tin and HCl to  $-NH_2$  to form the product B.

B reacts with  $HNO_2$  to give diazonium salt and  $H_3PO_2$  replaces it by  $H_{\cdot}$ 



Practice more on Haloalkanes and Haloarenes