

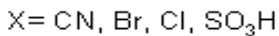
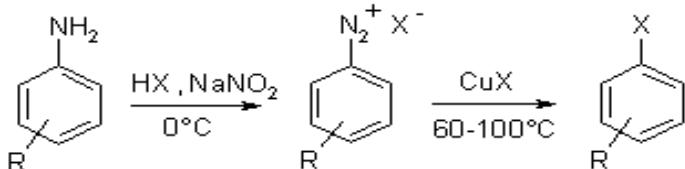
HALOALKANES AND HALOARENES

KEY NOTES

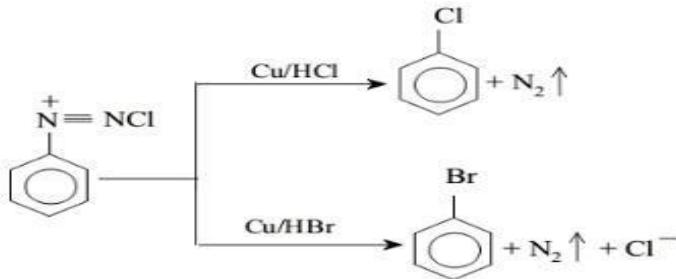
- Haloalkanes are classified as fluoro, chloro, bromo or iodo compounds according to the type of halogen present and as mono-, di-, tri-, tetra- haloalkanes, etc., according to the one, two, three, four, etc., halogen atoms respectively present in their molecule.
- Alkyl halides are further classified as primary (1°), secondary (2°) and tertiary (3°) according to the halogen atom attached to primary, secondary and tertiary carbon atoms, respectively. Due to electronegativity difference between the carbon and the halogen, the shared pair of electron lies closer to the halogen atom. As a result, the halogen carries a small negative charge, while the carbon carries a small positive charge.
- Methods of Preparation of Haloalkanes:** Haloalkanes can be prepared from displacement of alcoholic group in alkyl alcohol by halogen acid, PCl_5 or PCl_3 . Haloalkanes can also be prepared by addition of halogen acids or halogens on alkene and alkyne.
- Methods of preparation of Haloarenes**

From diazonium salts:

- (i) By Sandmeyer reaction:



- (ii) By Gattermann reaction:



- Chemical reactions of haloalkanes**

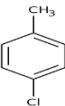
(a) Nucleophilic Substitution Reactions:

- (i) C-X bond in alkyl halide is more polar due to electron repelling nature of alkyl group and thus readily undergo nucleophilic substitution reaction. These are of two types:

(1) **S_{N}^1 (Substitution Nucleophilic Unimolecular)**: In such type of reactions, rate = $k [\text{RX}]$, i.e., rate, is independent of concentration of nucleophile and occurs in two steps. Such reactions are favoured by polar solvents.

(2) **S_{N}^2 (Substitution Nucleophilic Bimolecular)**: In such type of reactions, rate = $k [\text{RX}] [\text{Nu}]^-$, i.e., rate of reaction depends on concentration of nucleophile and take place in one step.

MULTIPLE CHOICE QUESTIONS

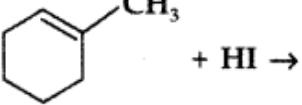
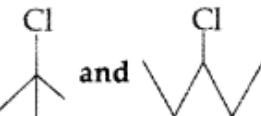
1.	Which of the following is most reactive towards aqueous NaOH? (a) C_6H_5Cl (b) $C_6H_5CH_2Cl$ (c) C_6H_5Br (d) BrC_6H_4Br
2.	Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to (a) formation of a less stable carbonium ion in aryl halides (b) resonance stabilization in aryl halides (c) presence of double bonds in alkyl halides (d) inductive effect in aryl halides
3	The main difference between C – X bond of a haloalkane and a haloarene is (a) C – X bond in haloalkanes is shorter than haloarenes (b) In haloalkanes the C attached to halogen in C – X bond is sp^3 hybridised while in haloarenes it is sp^2 hybridised. (c) C – X bond in haloalkanes acquires a double bond character due to higher electronegativity of X than haloarenes. (d) haloalkanes are less reactive than haloarenes due to difficulty in C – X cleavage in haloalkanes.
4.	Which of the following is a primary halide? (a) Isopropyl iodide (b) Secondary butyl iodide (c) Tertiary butyl iodide (d) Neohexyl chloride
5.	Which is the correct IUPAC name for  (a) Methylchlorobenzene (b) Toluene (c) 1-Chloro-4-methylbenzene

ASSERTION REASON TYPE QUESTIONS

- (a) Both Assertion and reason are true and Reason is correct explanation of assertion.
- (b) Assertion and reason both are true but Reason is not the correct explanation of assertion.
- (c) Assertion is true, Reason is false.
- (d) Assertion is false, Reason is true.

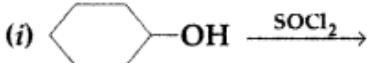
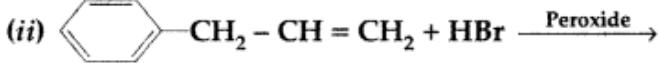
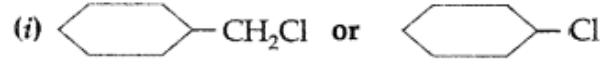
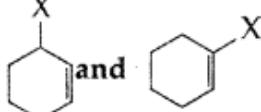
11.	<p>Assertion: Primary benzylic halides are more reactive than primary alkyl halides towards S_N^1 reactions.</p> <p>Reason: Reactivity depends upon the nature of the nucleophile and the solvent.</p>
12.	<p>Assertion: The presence of nitro group facilitates nucleophilic substitution reactions in aryl halides.</p> <p>Reason: The intermediate carbanion is stabilised due to the presence of nitro group.</p>
13.	<p>Assertion: 4-nitrochlorobenzene undergoes nucleophilic substitution more rapidly than chlorobenzene.</p> <p>Reason: Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism while 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.</p>
14.	<p>Assertion: Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution reaction.</p> <p>Reason: Nitro group, being an electron withdrawing group decreases the electron density over benzene ring.</p>
15.	<p>Assertion: In mono chloroarenes, further electrophilic substitution occurs at ortho & para positions.</p> <p>Reason: Halogen atom is a benzene ring deactivator.</p>

SHORT QUESTION ANSWERS (2 MARKS)

16.	<p>Draw the structure of major monohalogen product formed in the following reaction :</p> <p style="text-align: center;"></p>
17.	<p>Predict the order of reactivity of the following compounds in S_N^1 reaction : $C_6H_5CH_2Br$, $C_6H_5C(CH_3)$, $(C_6H_5)Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$</p>
18.	<p>In the following pair of compounds, which will react faster by S_N^1 mechanism and why?</p> <p style="text-align: center;"></p>

19.	Arrange the following in increasing order of boiling point: (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ (ii) $(\text{CH}_3)_3\text{CBr}$ (iii) $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$
20.	What happens when ethyl chloride is treated with aqueous KOH?

SHORT QUESTION ANSWERS (3 MARKS)

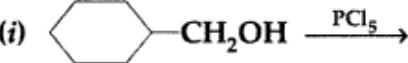
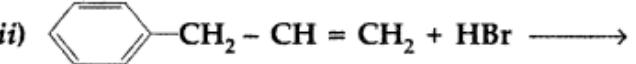
21.	Draw the structure of major product in each of the following reactions : (i)  (ii) 
22.	Which one in the following pairs of substances undergoes S_N^2 substitution reaction faster and why? (i)  or  (ii)  or 
23.	How are the following conversions carried out? (i) Benzyl chloride to benzyl alcohol (ii) Methyl magnesium bromide to 2-methyl-propan-2-ol.
24.	Account for the following: (i) The C–Cl bond length in chlorobenzene is shorter than that in CH_3Cl . (ii) Chloroform is stored in closed dark brown bottles.
25.	Answer the following : (i) Haloalkanes easily dissolve in organic solvents. Why? (ii) What is known as a racemic mixture? Give an example. (iii) Out of  which is an example of allylic halide?

CASE BASED QUESTION

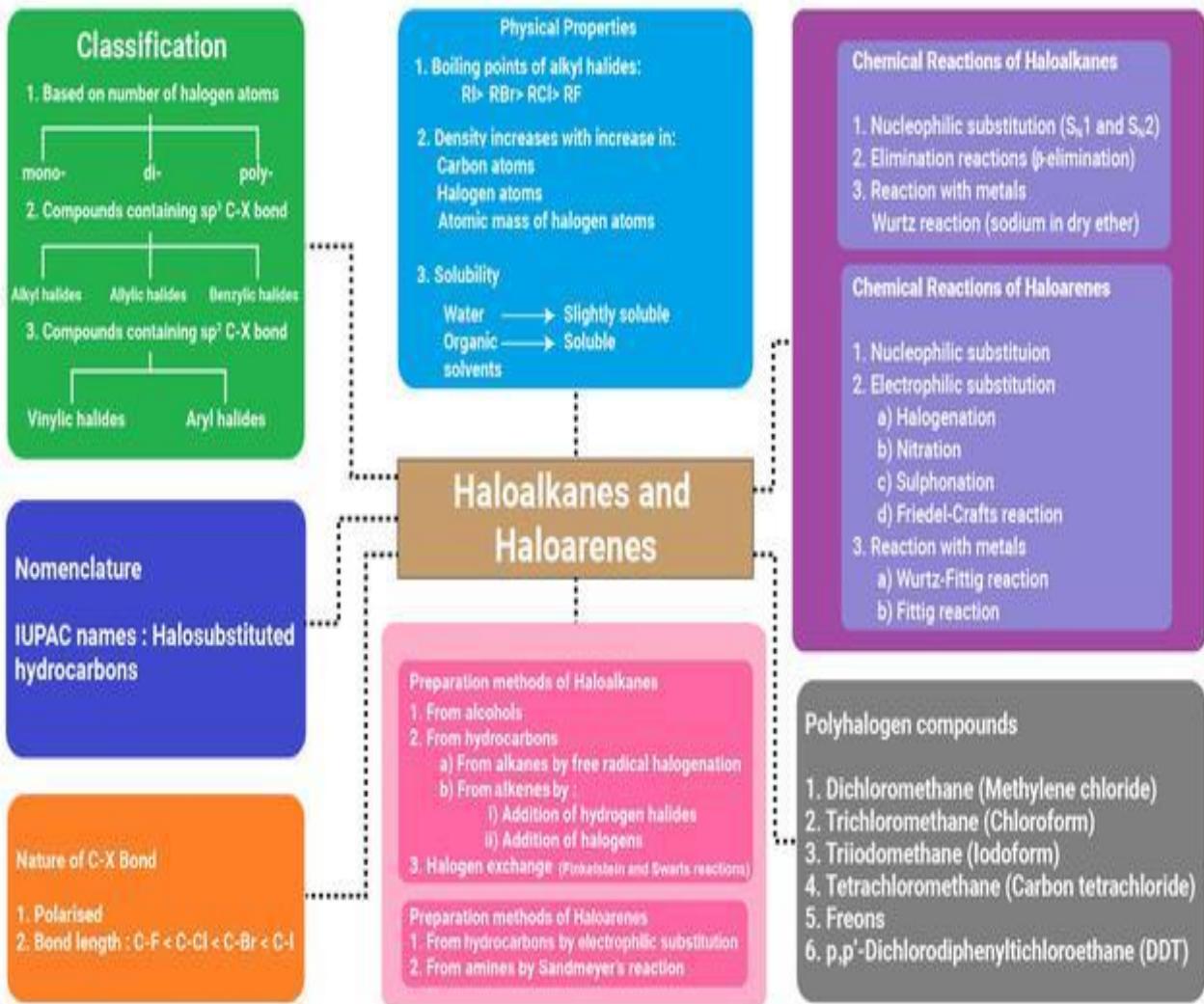
26.	CASE STUDY - A The substitution reaction of alkyl halides occurs in S_N^1 and S_N^2 mechanism, whatever mechanism alkyl halide follow for substitution reaction to occur, the polarity of the carbon halogen bond is responsible for the substitution reaction. The rate of S_N^1 reactions are governed by stability of carbocation whereas for S_N^2 reactions steric factor is a deciding
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	<p>factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide.</p> <p>Question 1: Among 1-bromo propane and 2-methyl-2-bromo propane, which will follow S_N^1 mechanism?</p> <p>Question 2: In which of the following inversion of configuration will occur on reaction with aq. alkali :</p> <p>1-bromopropane or 2-methyl-2-bromo propane?</p> <p>Question 3: What is the role of polar protic solvent in S_N^1 reaction?</p> <p>Question 4: Write example of an alkyl halide having chiral carbon atom.</p>
27.	<p>CASE STUDY - B</p> <p>An organic compound X which is manufactured by heating a mixture of chloral and chlorobenzene in the presence of concentrated H_2SO_4 is used as an insecticide. The use of compound X is banned in many countries. The compound is very effective against mosquitoes which spread malaria. Answer the following questions based on the information:</p> <p>Question 1: Name the compound X.</p> <p>Question 2: Give its structural formula.</p> <p>Question 3: Write the IUPAC name of compound X.</p> <p>Question 4: Why is the use of compound X banned in many countries? Should we also advocate the ban of this compound though it is banned in many countries?</p>
28.	<p>CASE STUDY - C</p> <p>The substitution reaction of alkyl halides occurs in S_N^1 or S_N^2 mechanism. Whatever mechanism alkyl halide follow for substitution reaction to occur, the polarity of the carbon-halogen bond is responsible for the substitution reaction. The rate of S_N^1 reactions are governed by the stability of carbocation where as for S_N^2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.</p> <p>Question 1. Predict the stereochemistry of the product formed if optically active alkyl halide undergoes substitution reaction by S_N^1 mechanism.</p> <p>Question 2. Name the instrument used for measuring the angle by which the plane polarised light is rotated.</p> <p>Question 3. Predict the major product formed when 2-bromopentane reacts with alcoholic KOH.</p> <p>Question 4. Write the structure of the products formed when anisole is treated with HI.</p>

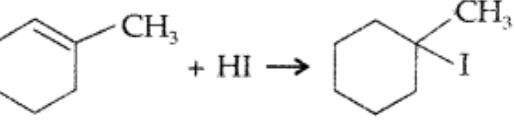
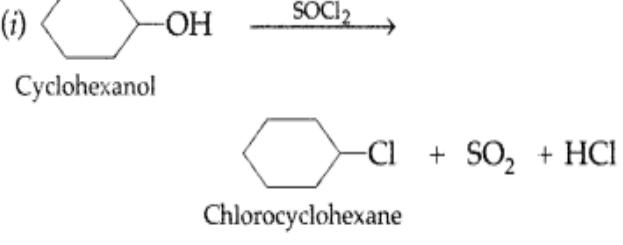
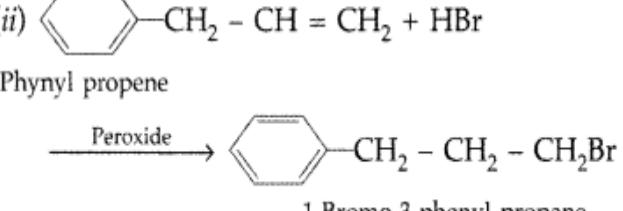
LONG QUESTION ANSWERS (FIVE MARKS)

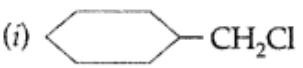
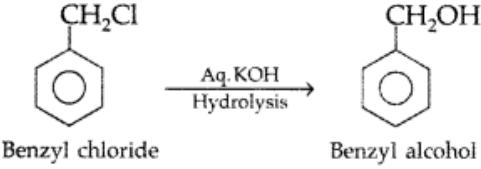
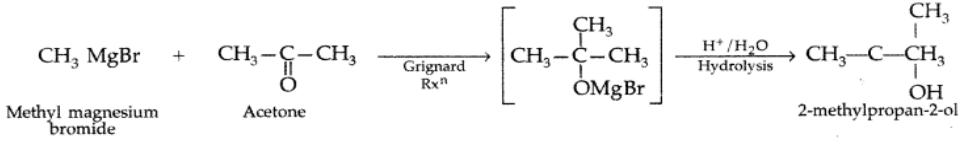
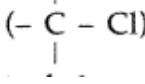
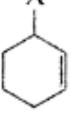
29.	<p>(a) Draw the structures of major products in each of the following reactions :</p> <p>(i) </p> <p>(ii) </p> <p>(b) Which halogen compound in each of the following pairs will react faster in S_N^2 reaction:</p> <p>(i) CH₃Br or CH₃I (ii) (CH₃)₃C–Cl or CH₃–Cl</p>
30.	<p>(a) Give reasons :</p> <p>(i) n-Butyl bromide has higher boiling point than t-butyl bromide. (ii) Racemic mixture is optically inactive.</p> <p>(b) How can the following conversions be carried out :</p> <p>(i) Aniline to bromobenzene (ii) Chlorobenzene to 2-chloroacetophenone (iii) Chloroethane to butane</p>

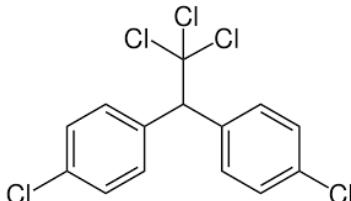
MIND MAP



Answers

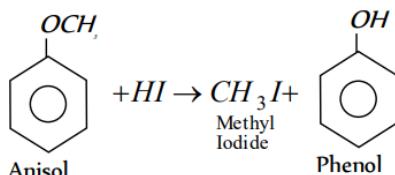
1.	B
2.	B
3.	B
4.	D
5.	C
6.	A
7.	D
8.	B
9.	A
10.	A
11.	B
12.	A
13.	B
14.	A
15.	B
16.	
17.	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br} > \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br} > \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br} > \text{C}_6\text{H}_5\text{CH}_2\text{Br}$
18.	 reacts faster by S _N 1 mechanism as it is a tertiary halide and it produces a stable tertiary carbocation.
19.	$(\text{CH}_3)_3\text{CBr} < (\text{CH}_3)_2\text{CHCH}_2\text{Br} < \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
20.	$\text{C}_2\text{H}_5\text{Cl} + \text{aq. KOH} \xrightarrow{\Delta} \text{C}_2\text{H}_5\text{OH} + \text{KCl}$ Chloroethane Ethanol
21.	(i)  Cyclohexanol  + SO_2 + HCl Chlorocyclohexane
	(ii)  3-Phenyl propene  Peroxide \rightarrow 1-Bromo-3-phenyl propane

22.	(i)  (ii) 	
23.	(i) Benzyl chloride to benzyl alcohol  (ii) Methyl magnesium bromide to 2-methylpropan-2-ol 	
24.	(i)  In haloalkanes, the halogen atom is attached to sp^3 -hybridized carbon while in haloarenes it is attached to sp^2 -hybridized carbon whose size is smaller than sp^3 orbital carbon. Therefore C – Cl bond in chloro-benzene is shorter than alkyl chloride. (ii) $CHCl_3$ is stored in dark coloured bottles to cut off light because $CHCl_3$ is slowly oxidised by air in presence of light to form an extremely poisonous gas, carbonyl chloride, popularly known as phosgene.	
25.	(i) Because the new forces of attraction set up between haloalkanes and solvent molecules are of the same strength as the forces of attraction being broken. (ii) A mixture which contains the equal proportions of two enantiomers of a compound in equal proportions is called racemic mixture Example : (\pm) butan-2-ol (iii)  is an allylic halide.	
26.	Answer 1: 2-methyl-2-bromo propane Answer 3: to facilitate breaking of C-X bond	Answer 2: 1-bromo propane Answer 4: any example
27.	Answer 1: DDT Answer 2:	

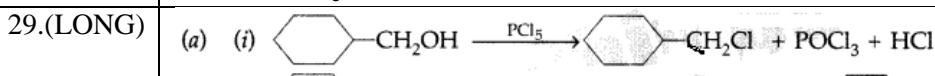


Answer 3: IUPAC NAME: 2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane
 Answer 4: It is banned in many countries as it has harmful effects on microorganisms and vegetation. Yes, we should advocate the ban of DDT

28. ANSWER 1. Racemic mixture will be formed
 ANSWER 2. Polarimeter
 ANSWER 3. Pent-2-ene will be major product.
 $\text{CH}_3\text{—CH(Br)—CH}_2\text{—CH}_2\text{—CH}_3 + \text{KOH(alc)} \rightarrow \text{CH}_3\text{—CH=CH—CH}_2\text{—CH}_3 + \text{KBr} + \text{H}_2\text{O}$
 ANSWER 4.



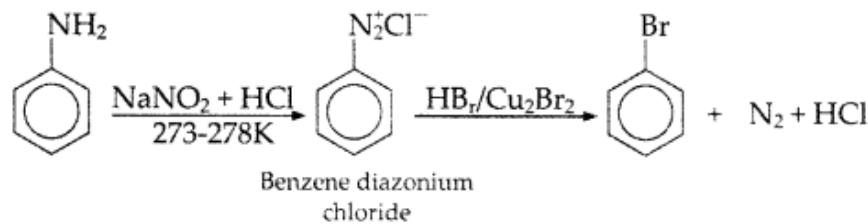
Phenol and CH₃I are formed.



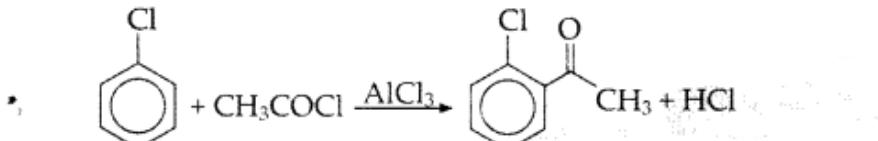
- (ii) 3-Phenyl-2-bromopropane
 (b) (i) CH₃I will react faster in S_N² reaction.
 (ii) CH₃—Cl will react faster in S_N² reaction

30. (a)(i) n-Butyl bromide has higher boiling point than t-butyl bromide because it has larger surface area hence have more Van der Waals' forces.
 (ii) Rotation due to one enantiomer is cancelled by another enantiomer.

(b) (i) **Aniline to bromobenzene**



(ii) **Chlorobenzene to 2-chloroacetophenone**



(iii) **Chloroethane to butane**

