

HALOALKANES AND HALOARENES

UNIT 10

Learning Outcomes

After studying this Unit, you will be able to

- Name haloalkanes and haloarenes according to the IUPAC system of nomenclature from their given structures;
- Describe the reactions involved in the preparation of haloalkanes and haloarenes and understand various reactions that they undergo;
- Correlate the structures of haloalkanes and haloarenes with various types of reactions;
- Use stereochemistry as a tool for understanding the reaction mechanism;
- Appreciate the applications of organo-metallic compounds;
- Highlight the environmental effects of polyhalogen compounds

Classification of Halogen Derivatives

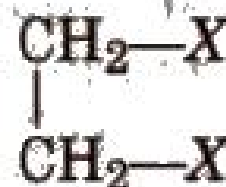
On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.,



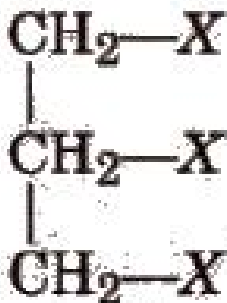
monohaloalkane



monohaloarene

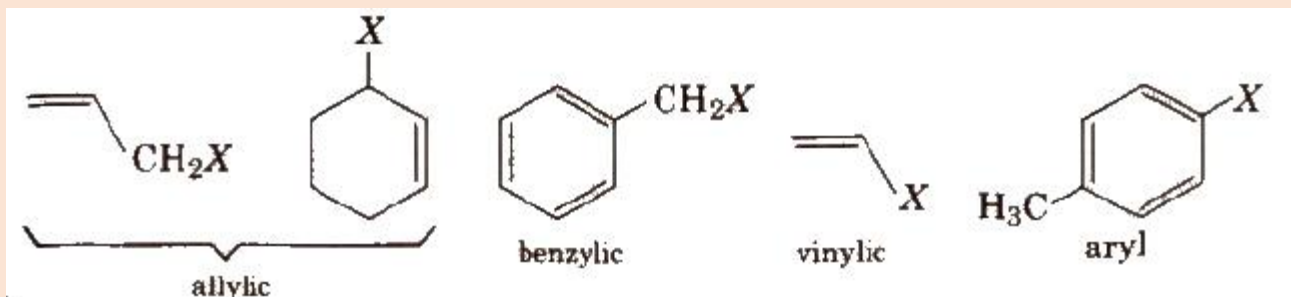
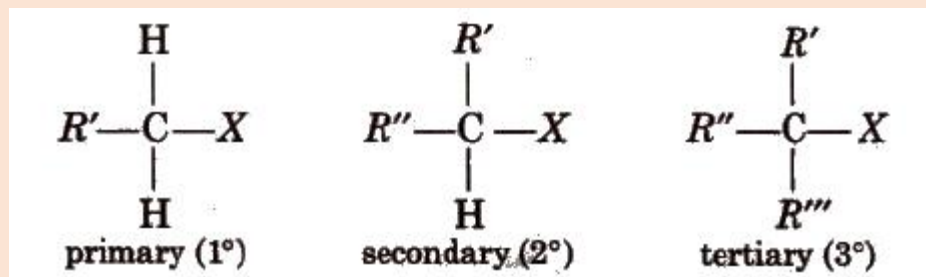


dihaloalkanes



trihaloalkane

On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as 1°, 2°, 3°, allylic, benzylic, vinylic and aryl derivatives, e.g.,



DIFFERENTIATION

LA

Write the structure of 1-bromo-4chlorobut-2-ene.

MA

Write the structure of 3-bromo-2-methylprop-1-ene.

HA

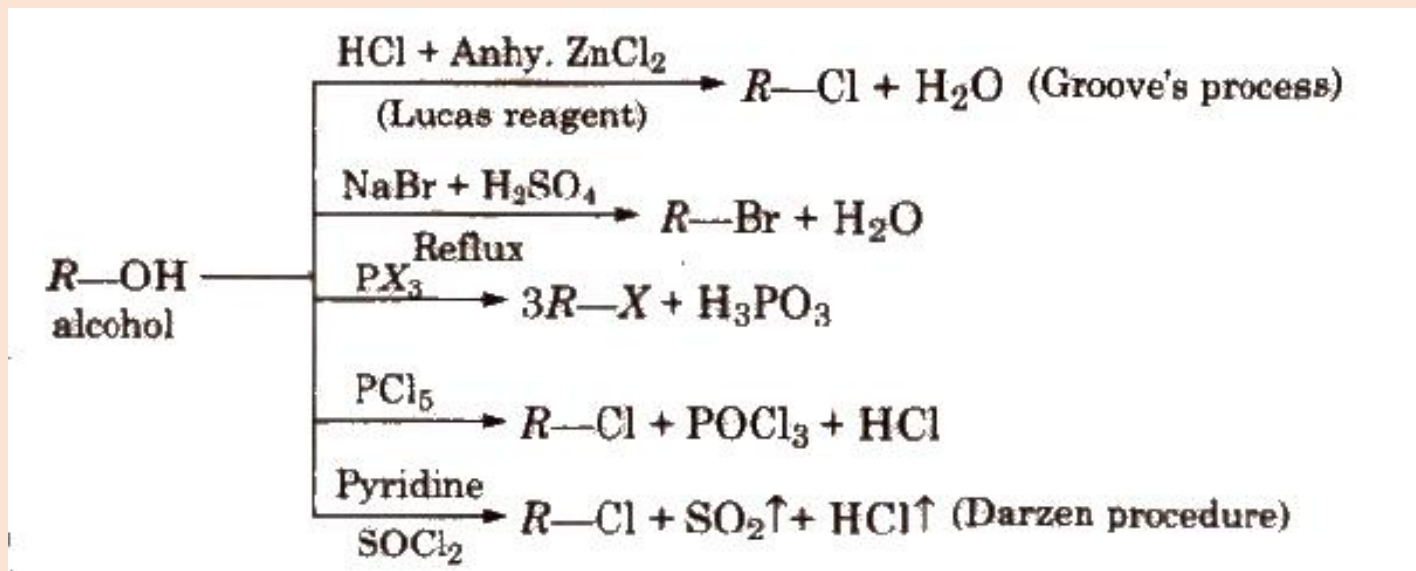
Write the structure of an isomer of compound C_4H_9Br , which is most reactive towards S_N1 reaction.

ASSIGNMENT

Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

General Methods of Preparation of Haloalkanes

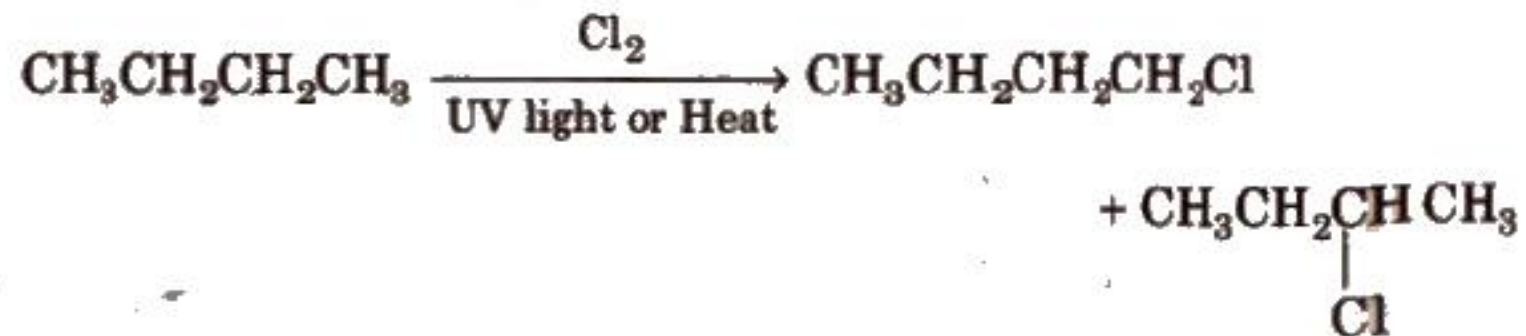
1. From Alcohols



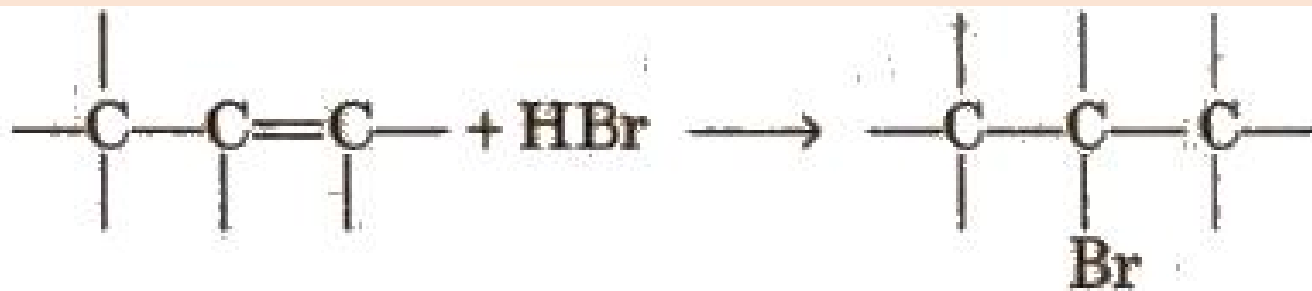
In Groove's method, $ZnCl_2$ is used to weaken the C-OH bond. In case of 3° alcohols, $ZnCl_2$ is not required.

The reactivity order of halogen acids is $HI > HBr > HCl$.

2. Free Radical Halogenation of Alkanes



Addition of Hydrogen Halides on Alkenes



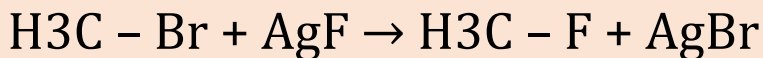
2-bromopropane



1. Finkelstein Reaction



2. Swarts Reaction



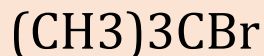
Hg₂F₂, COF₂ and SbF₃ can also be used as a reagent for Swarts reaction.

3. Hunsdiecker Reaction

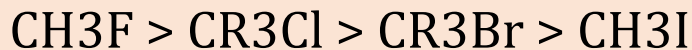


Physical Properties of Haloalkanes

1. Boiling point orders



2. Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is



3. Dipole moment decreases as the electronegativity of the halogen decreases.

4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density order is

$RI > RBr > RCl > RF$ (For the same alkyl group)

$CH_3I > C_2H_5I > C_3H_7I$

DIFFERENTIATION

LA

Write the structure of an isomer of compound C_4H_9Br , which is most reactive towards S_N1 reaction.

MA

Write the IUPAC name of $(CH_3)_2CH\cdot CH(Cl)CH_3$.

HA

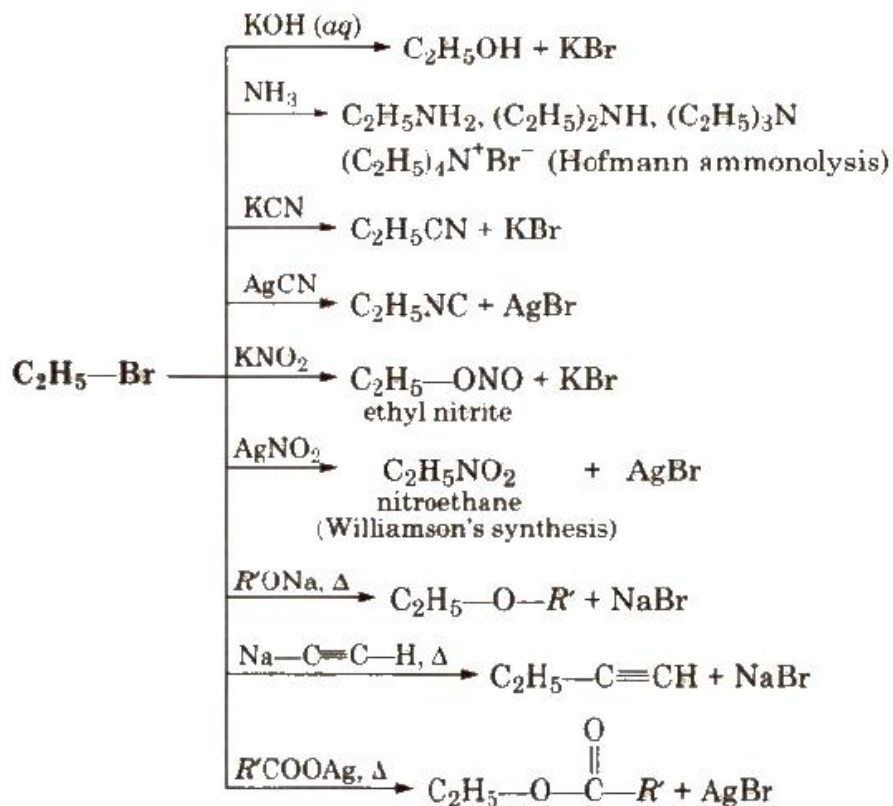
What happens when CH_3-Br is treated with KCN ?

ASSIGNMENT

Arrange each set of compounds in order of increasing boiling points. (i) Bromomethane, Bromoform, Chloromethane, Dibromomethane. (ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

Chemical Reactions of Haloalkanes

1. Nucleophilic Substitution Reactions (S_N reactions)

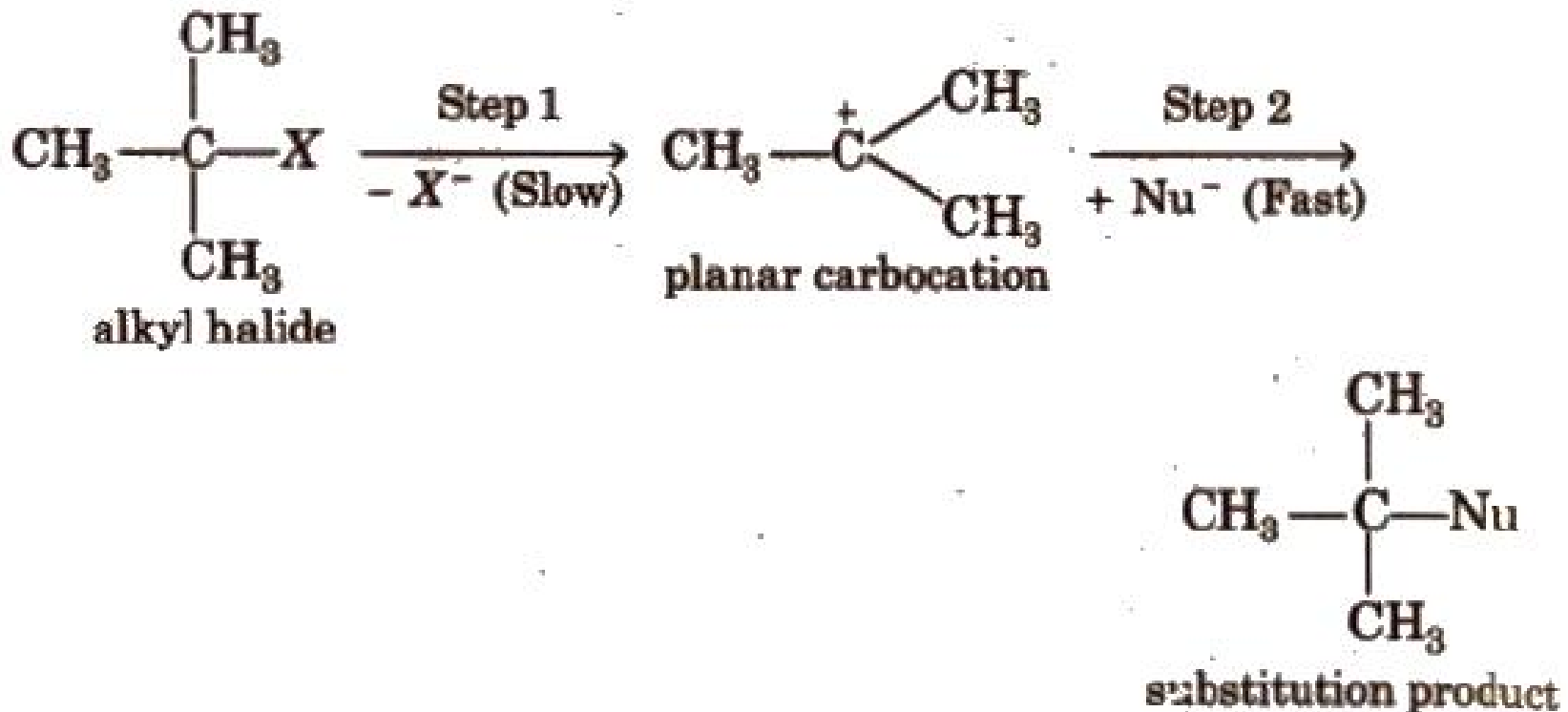


KCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN , KNO_2 form R-ONO while AgNO_2 produces R-NO_2 as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

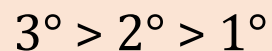
Methodology/Approach used for class room delivery. Nucleophilic substitution reactions are of two types

(a) SN1 type (Unimolecular nucleophilic reactions proceed in two steps):



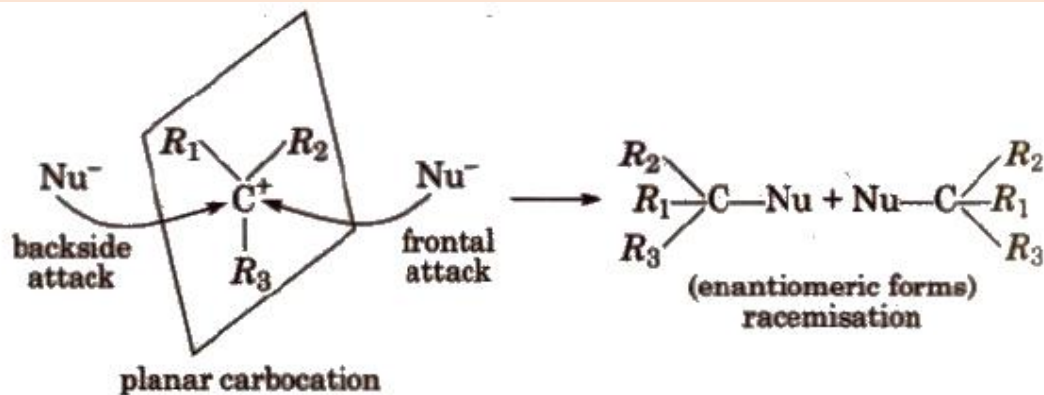
Methodology/Approach used for class room delivery. Rate, $r = k [RX]$. It is a first order reaction.

Reactivity order of alkyl halide towards SN1 mechanism



Polar solvents, low concentration of nucleophiles and weak nucleophiles favour SN1 mechanism.

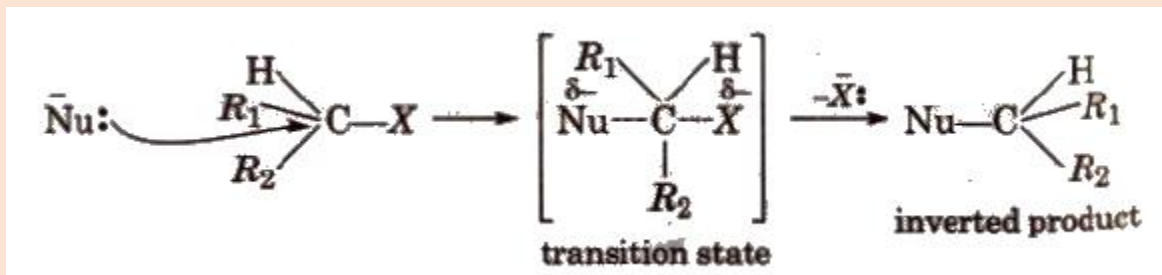
In SN1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.



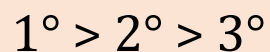
(b) SN2 type (Bimolecular nucleophilic substitution)

These reactions proceed in one step and is a second order reaction with $r = k[\text{RX}][\text{Nu}]$.

During SN2 reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,



Reactivity of halides towards SN2 mechanism is

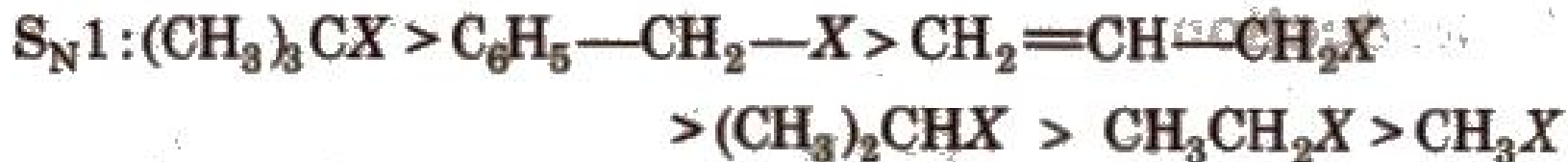


Rate of reaction in SN2 mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is



Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour SN2 mechanism.

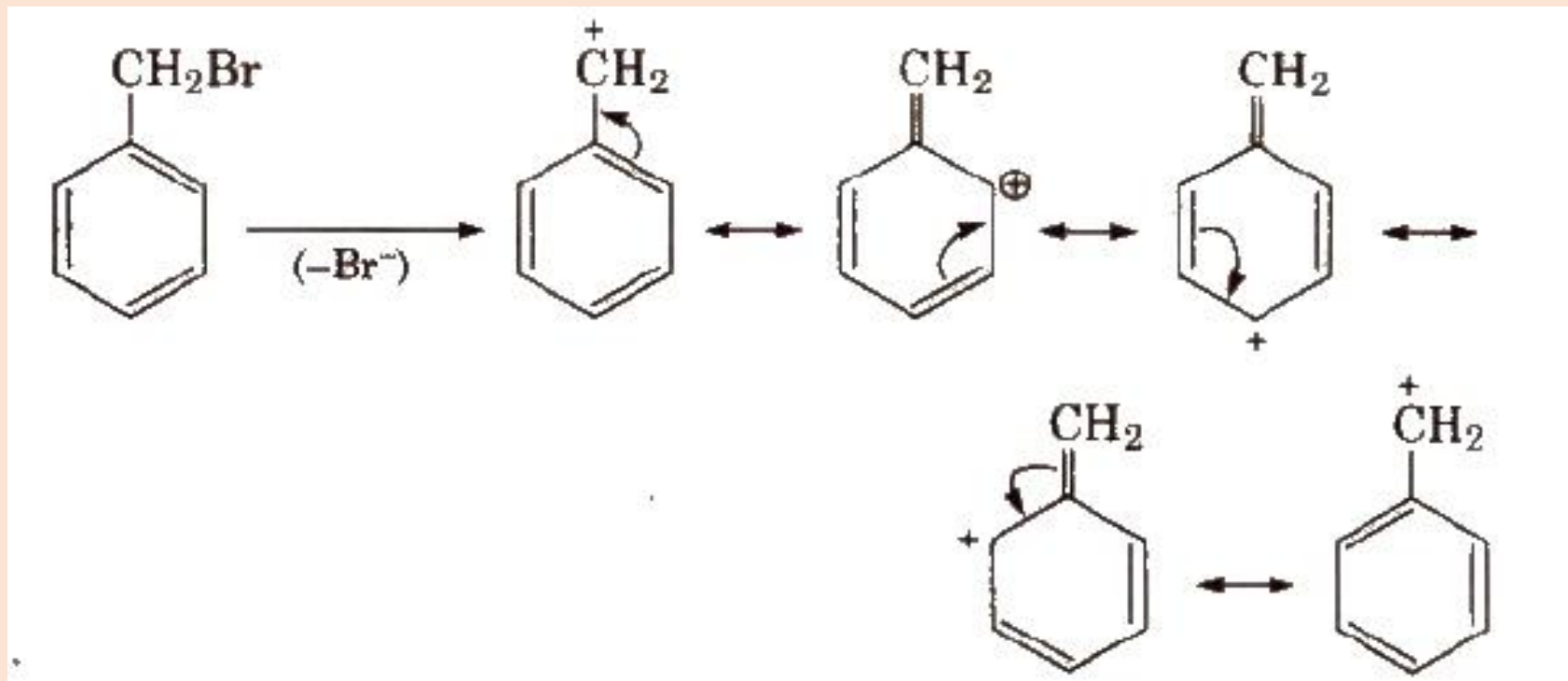
Relative rates of some alkyl halides in SN1 and SN2 reactions are in the order



resonance stabilised



Resonating structure of benzyl carbocations are



DIFFERENTIATION

LA

Predict the order of reactivity of the following compounds in SN 1 and SN2 reactions: (i) The four isomeric bromobutanes (ii) C₆H₅CH₂Br, C₆H₅CH(C₆H₅)Br, C₆H₅CH(CH₃)Br, C₆H₅C(CH₃)(C₆H₅)Br

MA

1. Which would undergo S_N2 reaction faster in the following pair and why?



HA

Which would undergo S_N1 reaction faster in the following pair?



ASSIGNMENT

Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides: (i) $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{CH}_3$

(ii) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)\text{Cl}$

(iii) $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{I}$

(iv) $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{Br})\text{C}_6\text{H}_5$

(v) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{Br})\text{CH}_3$

(vi) $\text{CH}_3\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{Br}$

(vii) $\text{CH}_3\text{C}(\text{Cl})(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3$

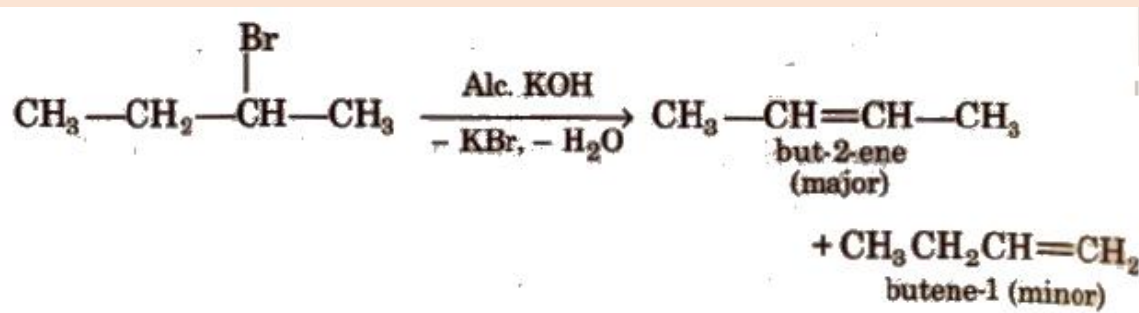
(viii) $\text{CH}_3\text{CH}=\text{C}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$

(ix) $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$

(x) $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)$

2. Elimination Reactions

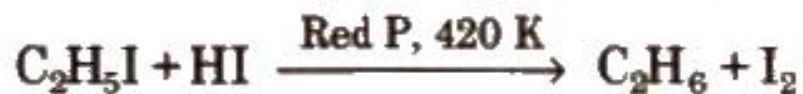
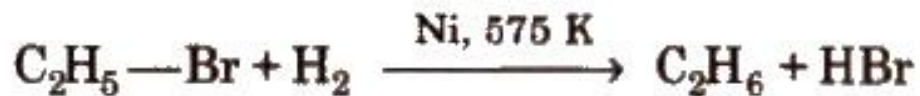
Dehydrohalogenation is a β - elimination reaction in which halogen is from α -carbon atom and the hydrogen from the β -carbon according to Saytzeff rule, e.g.



Ease of dehydrohalogenation among halides $3^\circ > 2^\circ > 1^\circ$

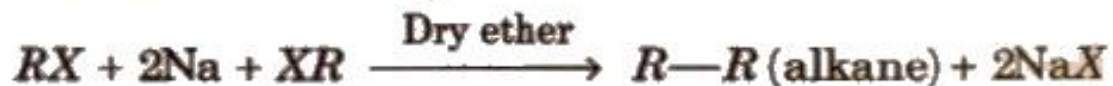


3. Reduction



4. Reaction with Metals

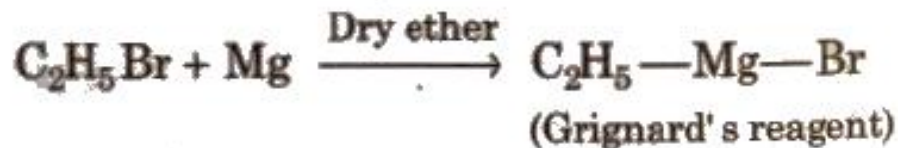
(i) Wurtz reaction



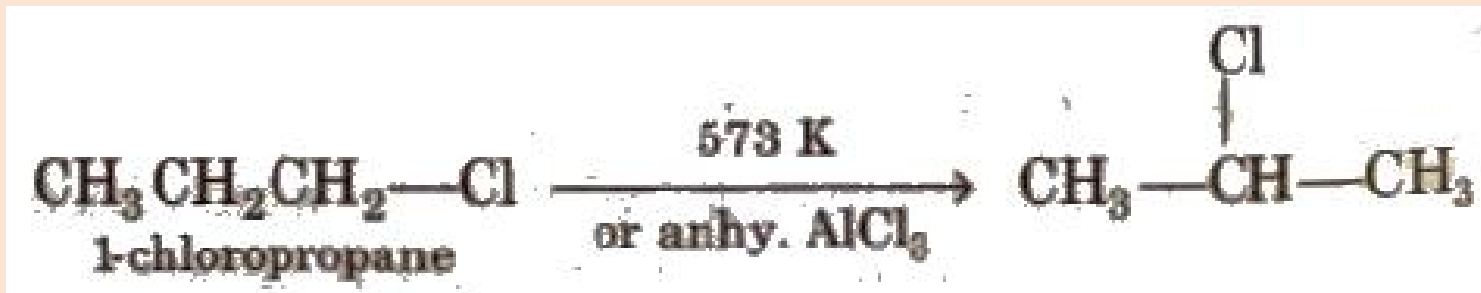
(ii) Wurtz-Fittig reaction



(iii) Reaction with Mg



5. Isomerisation



DIFFERENTIATION

LA

Which one of the following has the highest dipole moment? (i) CH_2Cl_2 (ii) CHCl_3 (iii) CCl_4

MA

A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound $\text{C}_5\text{H}_9\text{Cl}$ in bright sunlight. Identify the hydrocarbon.

HA

Write the isomers of the compound having formula $\text{C}_4\text{H}_9\text{Br}$.

ASSIGNMENT

How will you bring about the following conversions? (i) Ethanol to but-1-yne

(ii) Ethane to bromoethene

(iii) Propene to 1-nitropropane

(iv) Toluene to benzyl alcohol

(v) Propene to propyne

(vi) Ethanol to ethyl fluoride

(vii) Bromomethane to propanone

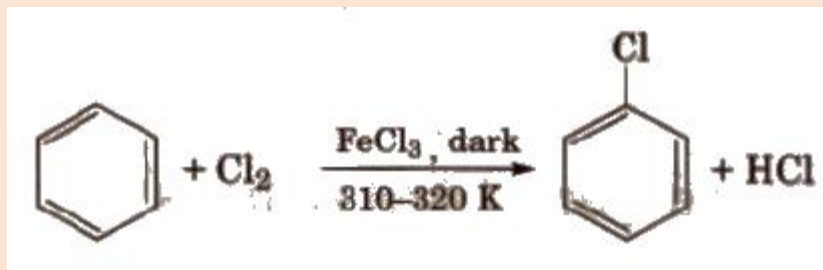
(viii) But-1-ene to but-2-ene

(ix) 1-Chlorobutane to n-octane

(x) Benzene to biphenyl.

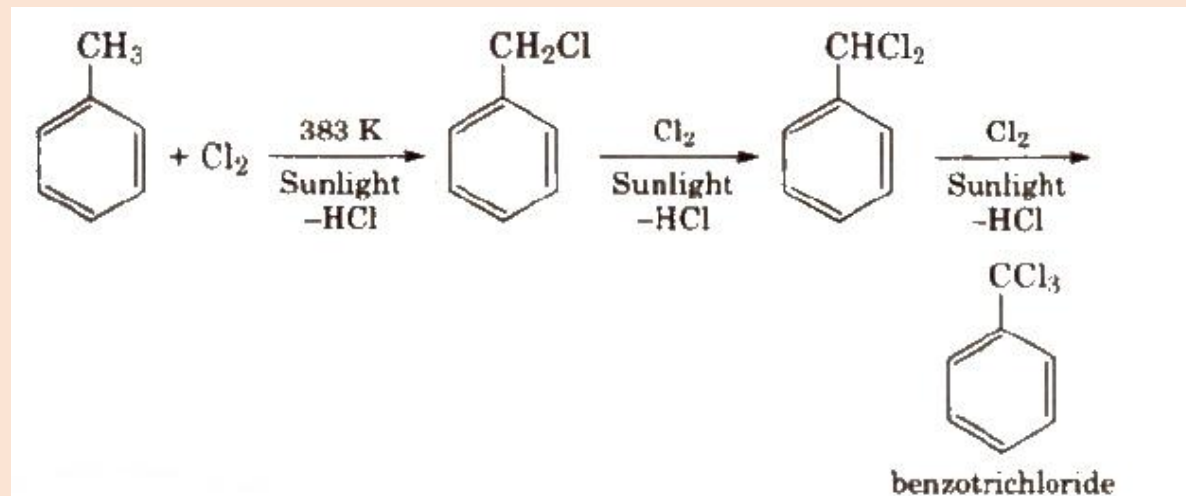
General Methods of Preparation of Aryl Halides

1. By Halogenation of Aromatic Hydrocarbons

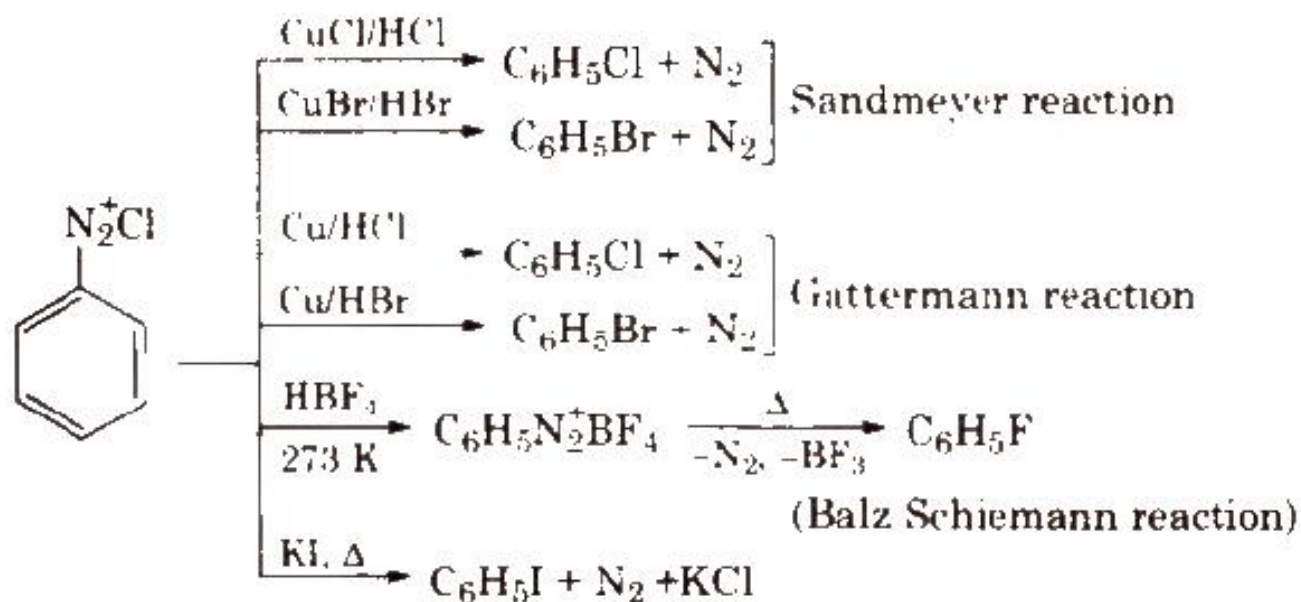


It is an electrophilic substitution reaction

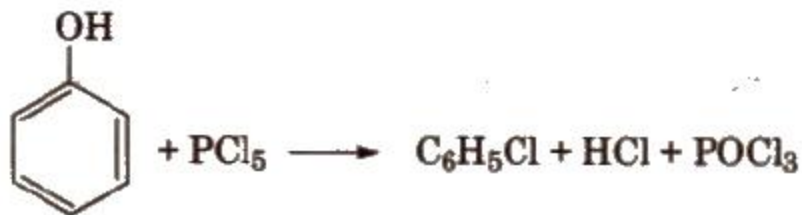
2. By Side Chain Halogenation



3. From Benzene Diazonium Salt



4. From Phenol



Physical Properties of Aryl Halides

- Aryl halides are colourless liquids or colourless solids with characteristic odour.
- Boiling point generally increases with increase in the size of aryl group or halogen atom. Boiling point order



- The melting point of p-isomer is more than o- and m-isomer.
- This is because of more symmetrical nature of p-isomer.

. Due to resonance in chlorobenzene, C-Cl bond is shorter and hence, its dipole moment is less than that of cyclohexylchloride.

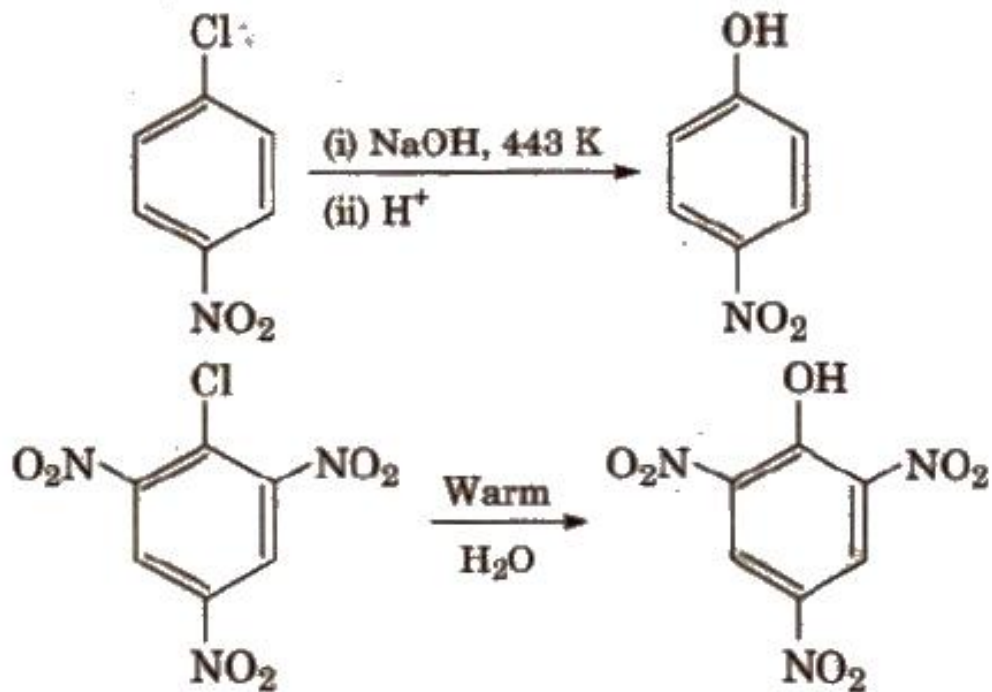
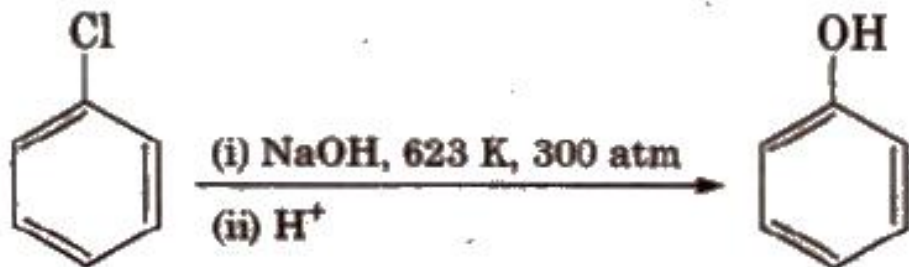
Chemical Properties of Aryl Halides

1. Nucleophilic Substitution Reaction

Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

Due to resonance, C-X bond has partial double bond character. Stabilisation of the molecule by delocalisation of electrons.
(Instability of phenyl carbocation.)

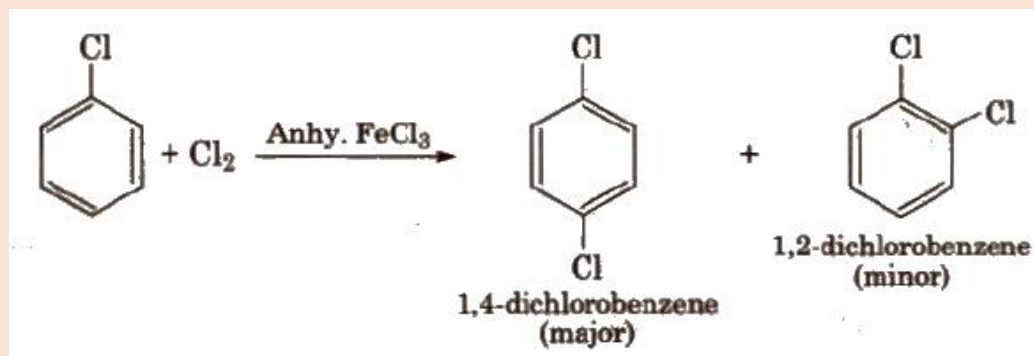
However, aryl halides having electron withdrawing groups (like - NO₂, - SO₃H, etc.) at ortho and para positions undergo nucleophilic substitution reaction easily.



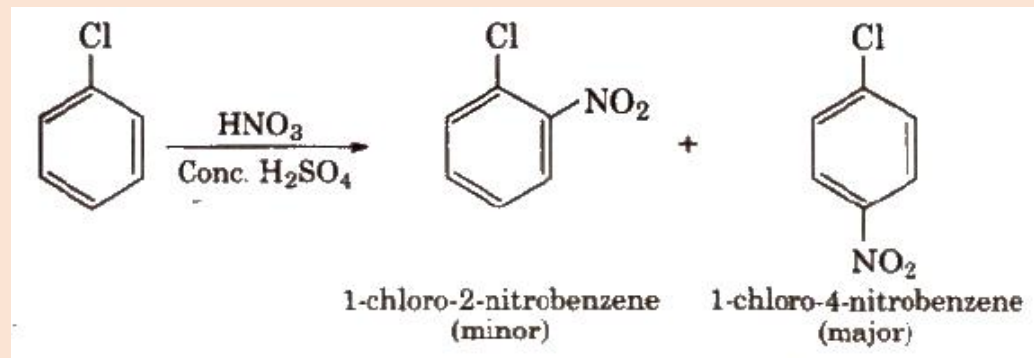
2. Electrophilic Substitution Reactions

Halogens are deactivating but O, p-directing. Thus, chlorination, nitration, sulphonation and Friedel Craft's reaction give a mixture of o- and p-chloro substituted derivatives.

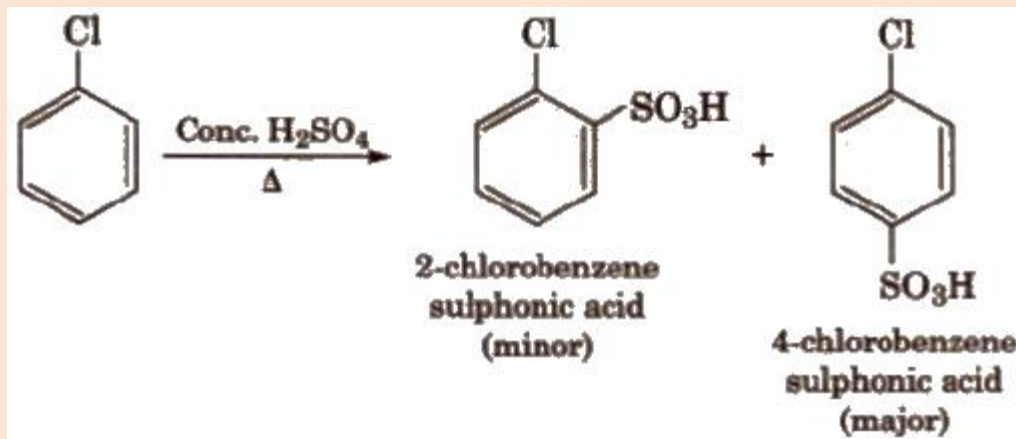
(i) Halogenation



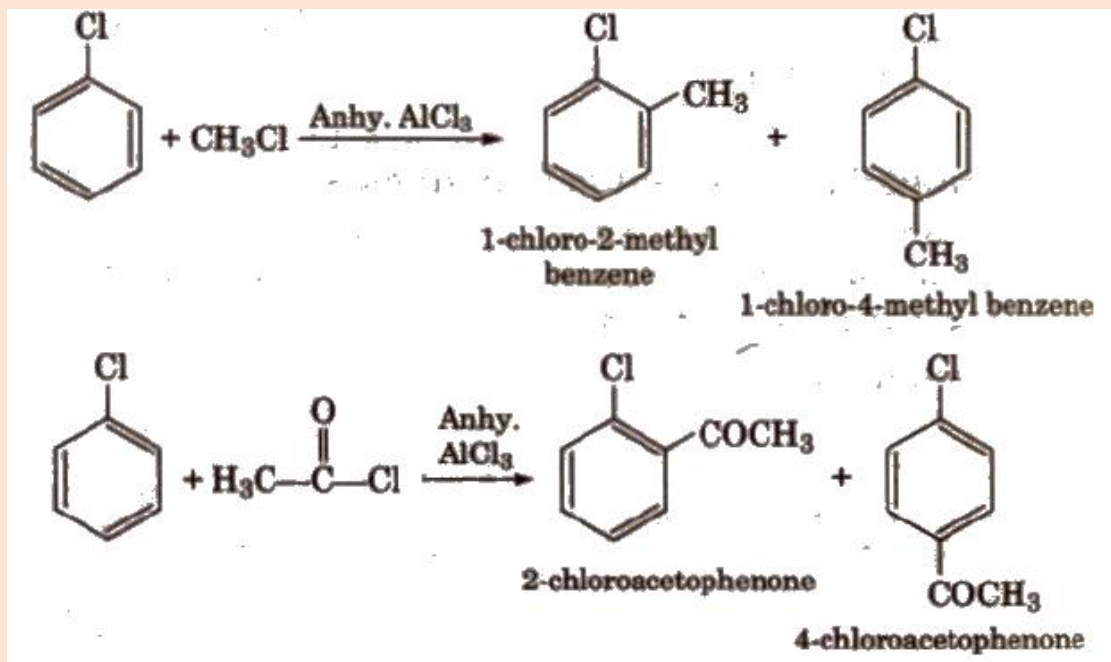
(ii) Nitration



(iii) Sulphonation

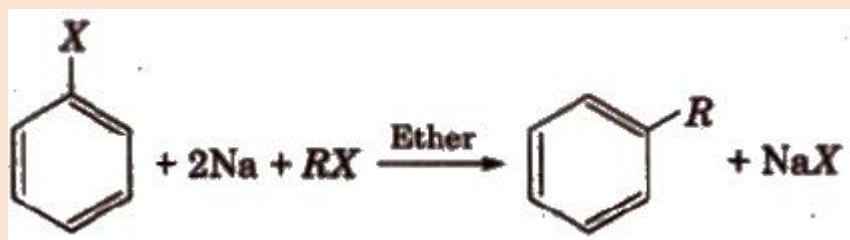


(iv) Friedel-Crafts reaction

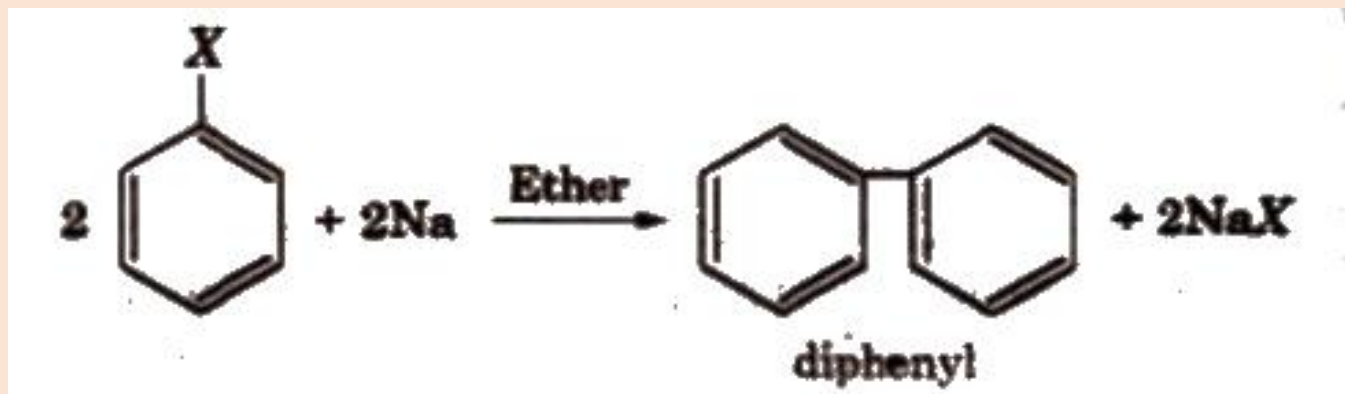


3. Reaction with Metals

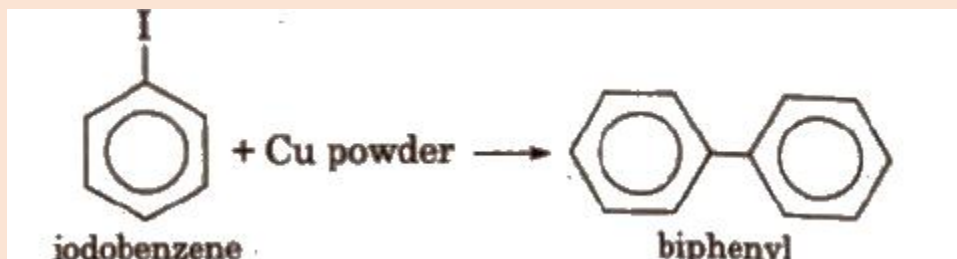
(i) Wurtz Fittig reaction



(ii) Fitting reaction

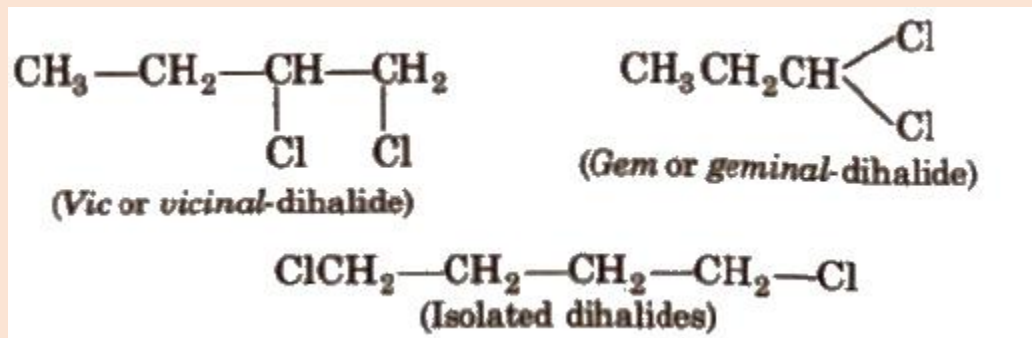


(iii) Ullmann reaction



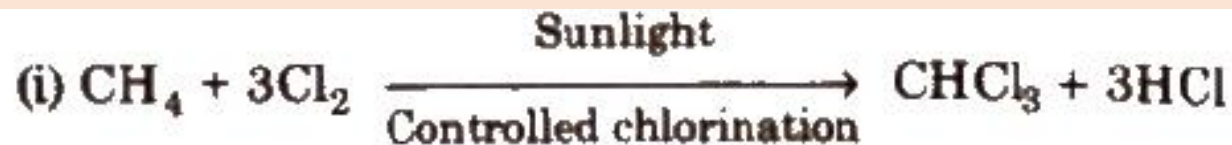
Dihalogen Derivatives

Dichloromethane (CH_2Cl_2) is widely used as a solvent, as a propellant in aerosols. Direct contact of dichloromethane in humans causes intense burning and milk redness of the skin.

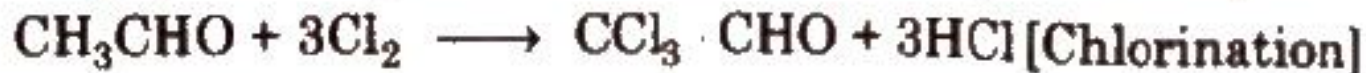


Trihalogen Derivatives

1. Chloroform [Trichloromethane, CHCl₃]



(ii) Haloform reaction



[Hydrolysis]

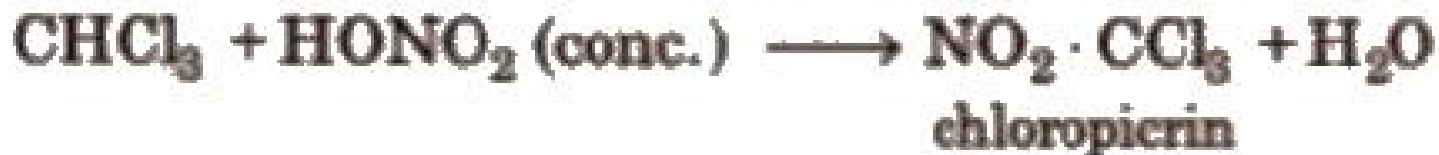
Properties

1. Oxidation of CHCl_3 gives poisonous gas phosgene (carbonyl chloride).



To avoid this oxidation CHCl_3 is stored in dark brown bottles and filled to the brim. 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

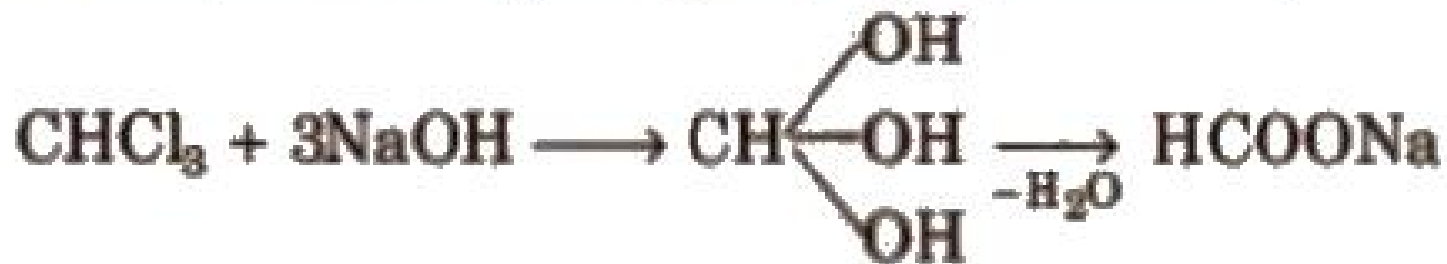
2. CHCl_3 is widely used in the production of freon refrigerant R-22.
3. On nitration, it gives tear producing insecticide substance chloropicrin



4. On dehalogenation, it gives C_2H_2 (acetylene).

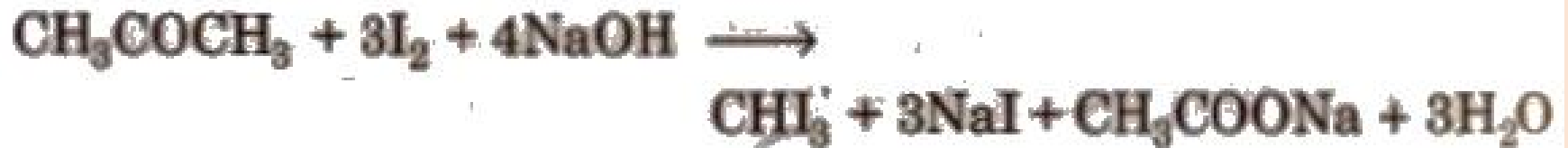


5. When subjected to hydrolysis, it gives formate.



2. Iodoform (tri-iodomethane, CHI_3)

Iodoform is prepared by iodoform reaction.



Compounds containing either CH_3CO - or $\text{CH}_3\text{CH}(\text{OH})$ group form yellow colour iodoform with I_2 and NaOH .

Iodoform when comes in contact with organic matter, decomposes easily to free iodine, an antiseptic. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

DIFFERENTIATION

Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

LA

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

MA

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane
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HA

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

ASSIGNMENT

How the following conversions can be carried out?

(i) Propene to propan-1-ol

(ii) Ethanol to but-1-yne

(iii) 1-Bromopropane to 2-bromopropane

(iv) Toluene to benzyl alcohol

(v) Benzene to 4-bromonitrobenzene

(vi) Benzyl alcohol to 2-phenylethanoic acid

(vii) Ethanol to propanenitrile

(viii) Aniline to chlorobenzene

(ix) 2-Chlorobutane to 3, 4-dimethylhexane

(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane

Polyhalogen Derivatives

1. Tetrachloromethane (Carbon Tetrachloride, CCl₄)

Preparation



CCl₄ is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether.

Uses

Carbon tetrachloride is used as a solvent for oils, fats, resins in dry cleaning as fire extinguisher under the name 'pyrene'.

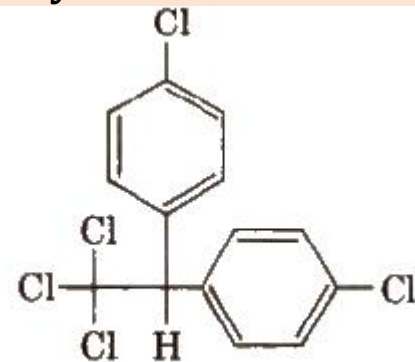
2. Freons

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. Carbon tetra chloride when reacts with antimony trifluoride in the presence of $SbCl_5$ as catalyst, dichlorofluoromethane (freon) is obtained.

3. DDT (p, p'-Dichlorodiphenyltrichloroethane)

DDT is the first chlorinated organic insecticide. Its stability and fat solubility is a great problem.

It is prepared from chloral and chlorobenzene in the presence of conc. H_2SO_4 .



2,2-bis (4-chlorophenyl) -1,1,1- trichloroethane

DIFFERENTIATION

Give the uses of

LA

Freon 12, DDT

MA

Carbon tetrachloride

HA

Iodoform.

ASSIGNMENT

Draw the structure of

- Freon 12
- DDT
- Carbon tetrachloride

PRACTICE QUESTIONS/ASSESSMENT

- Write the equations for the preparation of 1-iodobutane from (i) 1-butanol (ii) 1-chlorobutane (iii) but-1-ene.
 - What are ambident nucleophiles? Explain with an example.
 - Which compound in each of the following pairs will react faster in SN 2 reaction with -OH^- ? (i) CH_3Br or CH_3I (ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl
- 10.10 Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene: (i) 1-Bromo-1-methylcyclohexane (ii) 2-Chloro-2-methylbutane (iii) 2,2,3-Trimethyl-3-bromopentane.

- How will you bring about the following conversions? (i) Ethanol to but-1-yne (ii) Ethane to bromoethene (iii) Propene to 1-nitropropane (iv) Toluene to benzyl alcohol (v) Propene to propyne (vi) Ethanol to ethyl fluoride (vii) Bromomethane to propanone (viii) But-1-ene to but-2-ene (ix) 1-Chlorobutane to n-octane (x) Benzene to biphenyl.
- 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) Grignard reagents should be prepared under anhydrous conditions?
- Give the uses of freon 12, DDT, carbon tetrachloride and iodoform