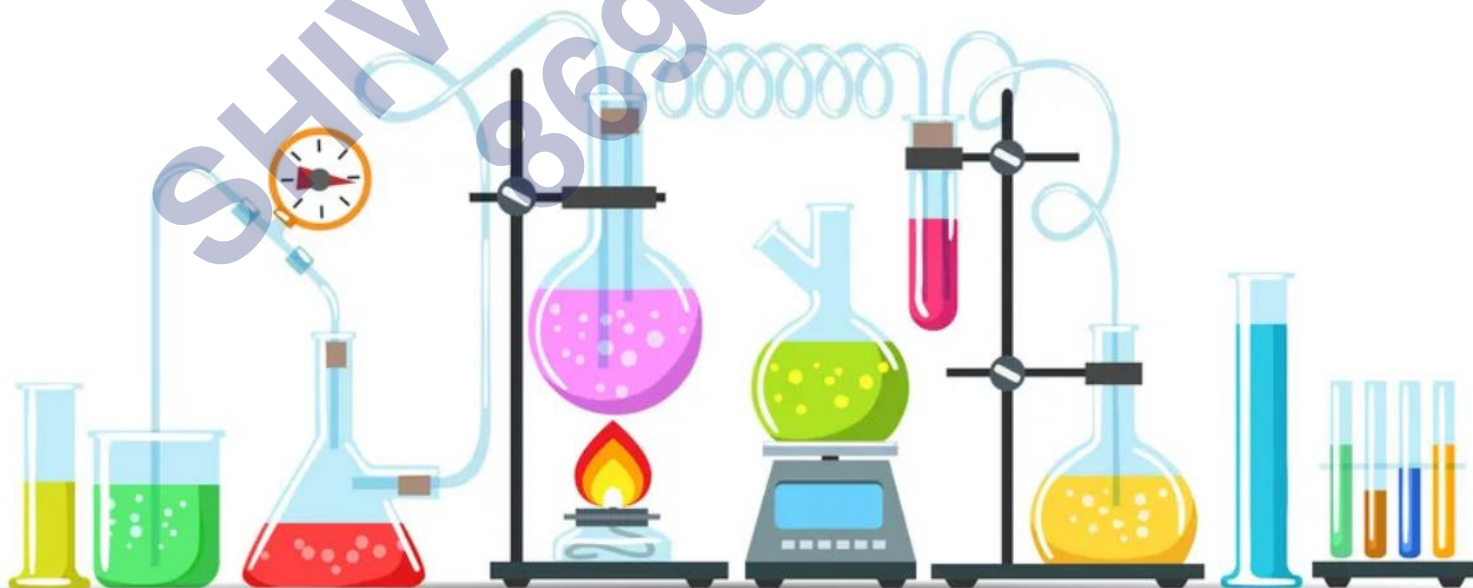


CHEMISTRY

CHAPTER 10: HALOALKANES AND HALOARENES



HALOALKANES AND HALOARENES

Based on the structure i.e depending upon the number of halogen atoms in a compound, Alkyl/ Aryl halides are classified as mono, di, and polyhalogen. When compared to carbon, halogen atoms are more electronegative. Therefore

- The bond (carbon-halogen bond) of alkyl halide is polarised.
- Halogen atom carries a partial negative charge
- Carbon atom carries a partial positive

Preparation Of Alkyl Halides

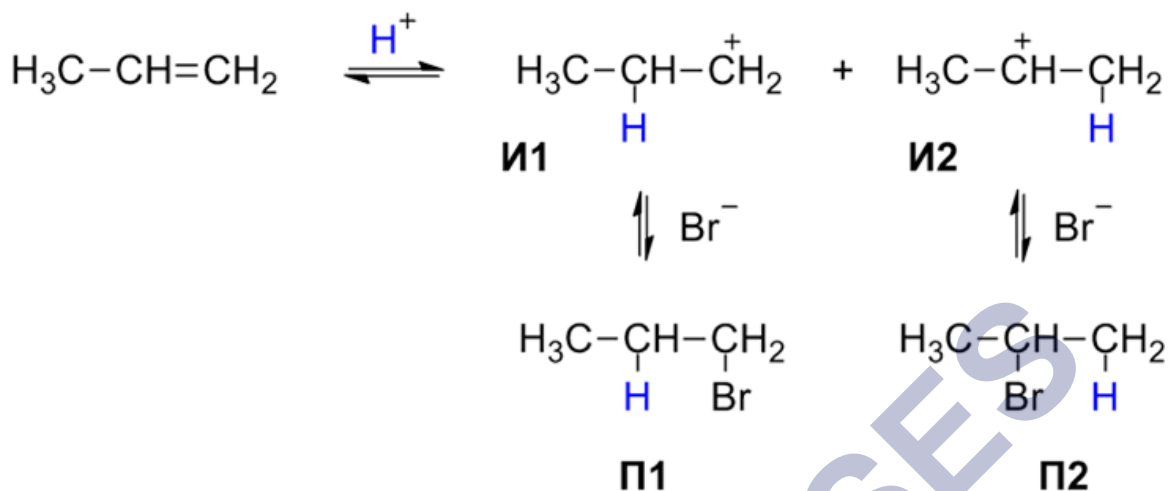
Alkyl halides are produced by the free radical halogenation of alkanes-

Step 1 – Adding halogen acids to alkenes

Step 2 – Replacing –OH group of alcohols by halogens with the use of phosphorus halides or halogen acids or thionyl chloride.

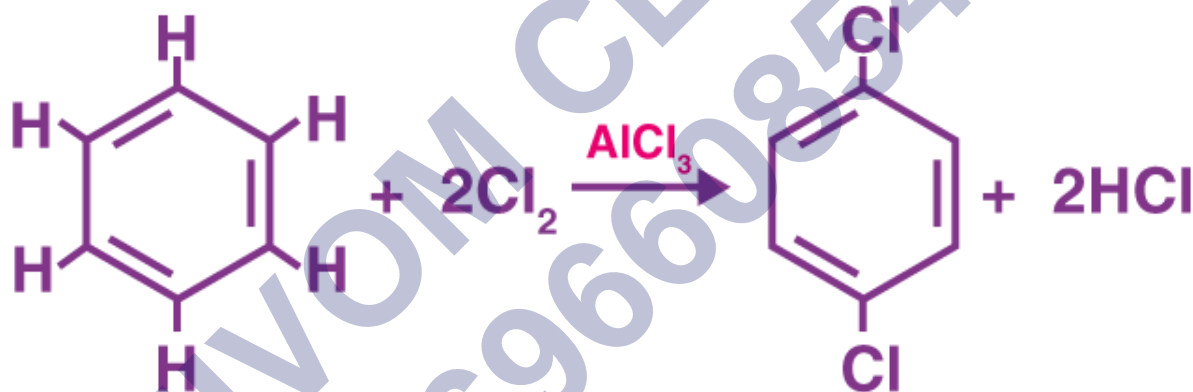
Aryl halides are prepared with the help of electrophilic substitution to arenes. Iodides and Fluorides are prepared with halogen exchange method. Organohalogenes have a higher boiling point when compared hydrocarbons due to strong van der Waals forces and dipole-dipole forces. They partial dissolve in water but completely dissolve in organic solvents.

Organometallic compounds are formed by the nucleophilic substitution, elimination, and reaction with metal atoms which occurs due to the polarity of a carbon-halogen bond of alkyl halides. Based on the kinetic properties Nucleophilic substitution reactions are classified as S_N1 and S_N2 . Chirality plays a very important in S_N2 reactions of understanding the reaction mechanisms of these reactions. S_N2 reactions are characterized by inversion configuration whereas S_N1 reactions are characterised by racemisation.



Substitution Reaction

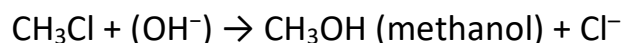
The substitution reaction is defined as a reaction in which the functional group of one chemical compound is substituted by another group or it is a reaction which involves the replacement of one atom or a molecule of a compound with another atom or molecule.



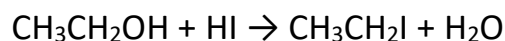
Substitution Reaction

Substitution Reaction Example

These type of reactions are said to possess primary importance in the field of organic chemistry. For example, when CH_3Cl is reacted with the hydroxyl ion (OH^-), it will lead to the formation of the original molecule called methanol with that hydroxyl ion. The following reaction is as shown below-



One more example would be the reaction of Ethanol with the hydrogen iodide which forms iodoethane along with water. The reaction is as shown-



Substitution Reaction Conditions

In order to substitution reaction to occur there are certain conditions that have to be used.

They are-

- Maintaining low temperatures such as room temperature.
- The strong base such as NaOH has to be in dilute form. Suppose if the base is of a higher concentration, there are chances of dehydrohalogenation taking place.
- The solution needs to be in an aqueous state such as water.

Substitution Reactions – Types

Substitution Reactions are of two types namely nucleophilic reaction and electrophilic reactions. These two types of reactions mainly differ in the kind of atom which is attached to its original molecule. In the nucleophilic reactions the atom is said to be electron-rich species, whereas, in the electrophilic reaction, the atom is an electron-deficient species. A brief explanation of the two types of reactions is as given below.

nucleophiles

Nucleophiles are those species in the form of an ion or a molecule which are strongly attracted to the region of a positive charge. These are said to be fully charged or have negative ions present on a molecule. The common examples of nucleophiles are cyanide ions, water, hydroxide ions, and ammonia.

Nucleophilic substitution reaction

A Nucleophilic substitution reaction in organic chemistry is a type of reaction where a nucleophile gets attached to the positively charged atoms or molecules of the other substance.

Nomenclature Of Haloalkanes And Haloarenes

Initially, there was no proper system for the naming of compounds. Mostly there were trivial names that were used depending upon the country and region. These trivial names were based on the discoverer or the nature of the compound or its place of discovery.

The system of trivial names was not standard and led to much confusion, thus raising the need for a standard system for the naming of organic compounds. IUPAC came up with a set of rules that are used universally for the naming of organic compounds.

There are two names associated with every compound:

Common name – It is different from a trivial name in the sense that it also follows a rule for its nomenclature.

IUPAC name – The IUPAC (International Union of Pure and Applied Chemistry) naming system is the standard naming system that chemists generally use.

Rules of Nomenclature

- Find the longest carbon chain.
- Number the longest carbon chain such that the carbon atom(s) to which the halogen(s) is/are attached get the lowest number(s).

- Multiple halogen atoms are labelled with the Greek numerical prefixes such as di, tri, tetra, to denote the number of identical halogen atoms attached to a carbon atom. If more than one halogen atoms attached to the same carbon atom, the numeral is repeated that much time.
- In case, different types of halogens are attached, they are named alphabetically.
- The position of the halogen atom is indicated by writing the position and name of the halogen just before the name of the parent hydrocarbon.

The Methodology of Writing Name

- First, write the root word for the parent hydrocarbon (depending upon the no. of carbon atoms in the longest carbon chain).
- Secondly, calculate the number of halogen atoms present. If there are multiple halogen atoms present, then arrange the halogens alphabetically in the prefix, labelling them with their respective positions. But, if the same halogen atom is present more than once then use the prefixes di, tri, tetra, etc.

Nomenclature of Haloalkanes

Alkyl halides are named in two ways. In the common system, the alkyl group is named first followed by an appropriate word chloride, bromide, etc. The common name of an alkyl halide is always written as two separate words. In the IUPAC system, alkyl halides are named as haloalkanes. The other rules followed in naming compounds is that

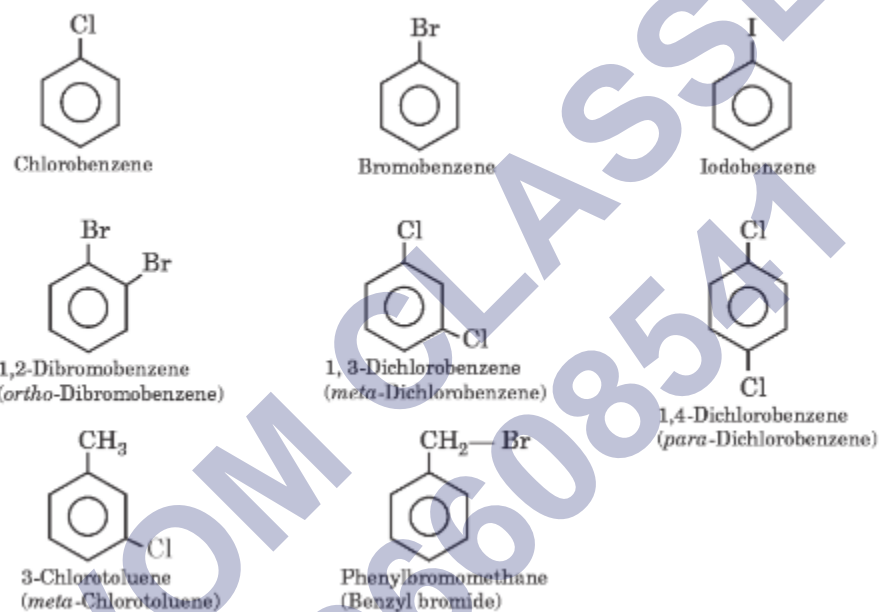
- Select the longest chain of carbon atoms containing the halogen atom.
- Number the chain to give the minimum number to the carbon carrying halogen atom.
- If multiple bonds (double or triple bond) is present, then it is given the preference in numbering the carbon chain.
- The IUPAC name of any halogen derivative is always written as one word.

Compound	Common Name	IUPAC Name
$\text{CH}_3\text{-Cl}$	Methyl Chloride	Chloromethane
$\text{CH}_3\text{-CH}_2\text{-Br}$	Ethyl bromide	Bromoethane
$\text{CH}_3\text{-C}(\text{CH}_3)_2\text{-Br}$	tert-Butyl bromide	2-Bromo-2-methylpropane
CHCl_3	Chloroform	Trichloromethane
$\text{CH}_3\text{-CH}(\text{Br})_2$	Ethylidene bromide	1,1-Dibromoethane
$\text{CH}_2=\text{CH-CH}_2\text{-I}$	Allyl iodide	3-Iodoprop-1-ene

Nomenclature of Haloarenes

- Aryl halides are named by prefixing “halo” to the name of the parent aromatic hydrocarbon.
- If there is more than one substituent on the ring then the relative positions of the substituents are indicated by mathematical numerals.
- In the common system, the relative position of two groups is shown by prefixes ortho, meta or para.

The common and IUPAC names of some representative haloarenes are given below.



Haloarenes: Nature of C-X bond

Haloarenes are the chemical compounds containing arenes, where one or more hydrogen atoms bonded to an aromatic ring are replaced with halogens. The nature of C-X bond depends on both the nature of carbon in the aromatic ring and the halogen attached. Halogens are generally denoted by “X”.

As we know halogens are group 17 elements having high electronegativity namely, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Out of them, Fluorine has the highest electronegativity. The elements in this group are just one electron short of completing their nearest noble gas configuration.

Carbon in haloarenes is a 14th group element with comparatively lesser electronegativity in comparison to halogen molecules. This is due to the fact that electronegativity increase across a period from left to right.

Salient Points on the Nature of C-X Bond in Haloarenes are:

- The C-X bond in haloarenes is polarized, as halogens are more electronegative than

carbon. Due to the high electronegativity of halogen, it attracts the electron cloud more towards itself and thus gains a slight negative charge, on the other hand, carbon obtains a slight positive charge.

- As halogens need only one electron to achieve their nearest noble gas configuration, only one sigma bond is formed between one carbon and one halogen atom.
- Due to the increase in atomic size from fluorine to astatine, the C-X bond length in haloarenes increases from fluorine to astatine and bond dissociation strength decreases.
- Dipole moment depends on the difference in electronegativity of carbon and halogens (group 17 trends properties) and as we know that the electronegativity of halogens decreases down the group, the dipole moment also decreases. There is an exception to C-Cl and C-F dipole moments. Though the electronegativity of Cl is less than F, the dipole moment of a C-Cl bond is more than C-F.

S_N1 and S_N2 Reaction of Haloalkanes

Haloalkanes are converted into alcohols using hydroxide ion in aqueous media through S_N1 and S_N2 Reactions. Alcohols can efficiently be prepared by substitution of haloalkanes and sulfonic esters with good leaving groups. The choice of reagents and reaction conditions for the hydrolysis is important because competitive elimination reactions are possible especially at high temperatures leading to alkenes.

The hydrolysis of haloalkanes depends on the structure of the haloalkanes, primary haloalkanes typically undergo S_N2 reactions whereas tertiary haloalkanes react an S_N1 mechanism for tertiary haloalkanes or tertiary alkyl halides. There are two kinds of reactions of haloalkanes naming S_N1 And S_N2 Reaction.

S_N1 Reaction

The S_N1 reaction is a substitution nucleophilic unimolecular reaction. It is a two-step reaction. In the first step, The carbon-halogen bond breaks heterolytically with the halogen retaining the previously shared pair of electrons. In the second step, the nucleophile reacts rapidly with the carbocation that was formed in the first step.

This reaction is carried out in polar protic solvents such as water, alcohol, acetic acid etc. This reaction follows first order kinetics. Hence, this is named as substitution nucleophilic unimolecular. This reaction takes place in two steps as described below.

Step-1:

- The bond between carbon and halogen breaks due to the presence of a nucleophile and formation of carbocation takes place.
- It is the slowest and the reversible step as a huge amount of energy is required to break the bond.
- The bond is broken by solvation of the compound in a protic solvent, thus this step is

slowest of all.

- The rate of reaction depends only on haloalkane, not on nucleophile.

Step-2:

- The nucleophile attacks the carbocation formed in step 1 and the new compound is formed.
- Since, the rate defining step of the reaction is the formation of a carbocation, hence greater the stability of formation of an intermediate carbocation, more is the ease of the compound undergoing substitution nucleophilic unimolecular or S_N1 reaction.
- In the case of alkyl halides, 3° alkyl halides undergo S_N1 reaction very fast because of the high stability of 3° carbocations.
- Hence allylic and benzylic halides show high reactivity towards the S_N1 reaction.

S_N2 Reaction

This reaction follows second order kinetics and the rate of reaction depends upon both haloalkane and participating nucleophile. Hence, this reaction is known as substitution nucleophilic bimolecular reaction. In this reaction, the nucleophile attacks the positively charged carbon and the halogen leaves the group.

It is a one-step reaction. Both the formation of carbocation and exiting of halogen take place simultaneously. In this process, unlike the S_N1 mechanism, the inversion of configuration is observed. Since this reaction requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon atom has a dramatic inhibiting effect.

So opposite to S_N1 reaction mechanism, this is favoured mostly by primary carbon, then secondary carbon and then tertiary carbon. Nucleophilic substitution reaction depends on a number of factors. Some important factors include.

- Effect of the solvent
- Effect of the structure of the substrate
- Effect of the nucleophile
- Effect of leaving - group.

Comparing S_N1 and S_N2 Reactions

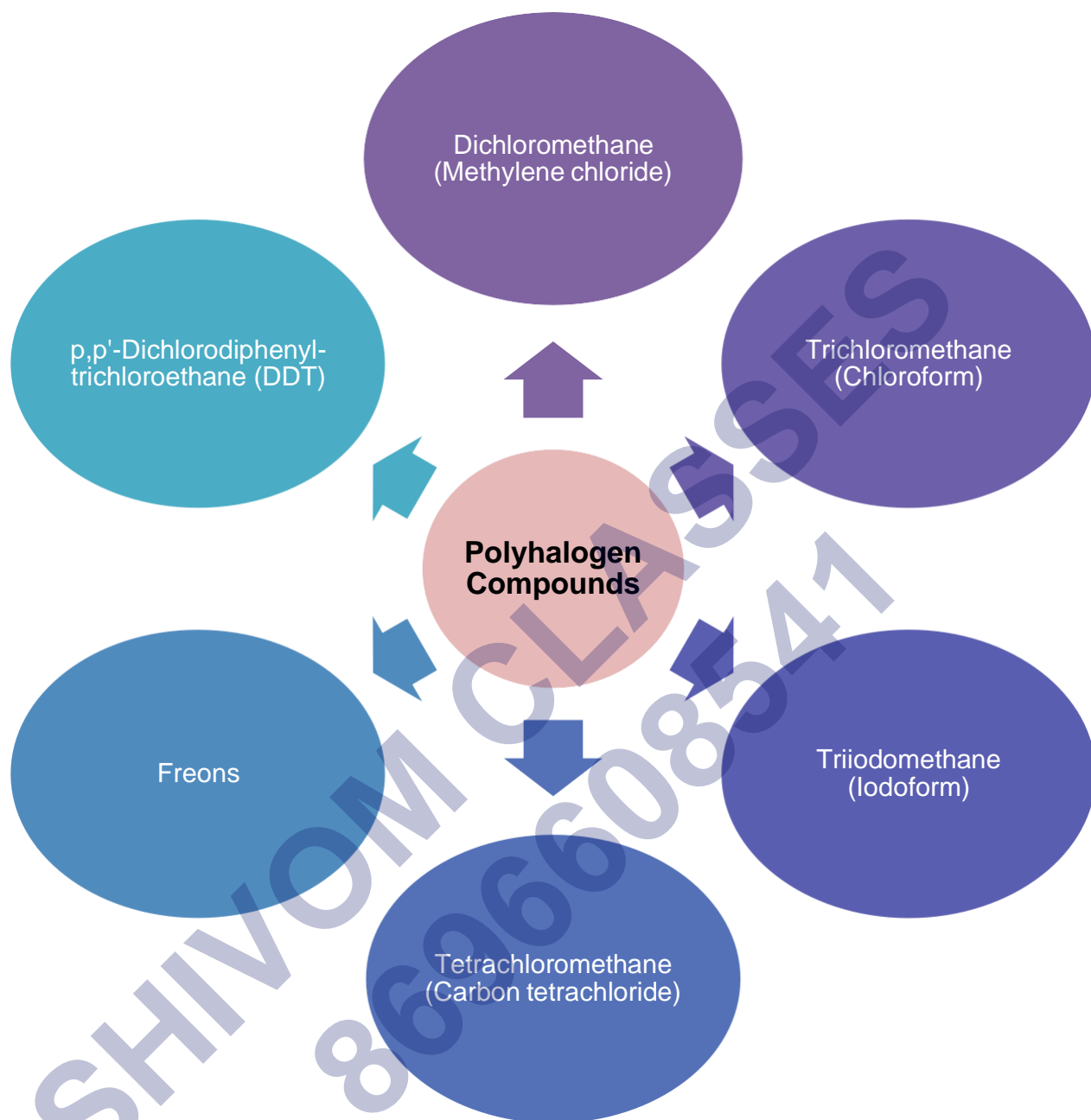
Related Concepts	S _N 1 Reaction	S _N 2 Reaction
Rate law	Unimolecular	Bimolecular
Haloalkane reactivity (electrophile)	3° > 2° > 1°	3° < 2° < 1°
Solvent	Polar solvent (protic solvent)	Polar aprotic solvent
Nucleophile	Weak nucleophile	Strong nucleophile
Stereochemistry	A mix of retention and inversion	Inversion

The solvent in which the nucleophilic substitution reaction is carried out also has an influence on whether an S_N2 or an S_N1 reaction will predominate. Before understanding how a solvent favours one reaction over another we must understand how solvents stabilize organic molecules.

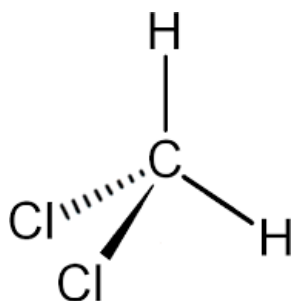
Polyhalogen Compounds

Polyhalogen compounds: Carbon compounds containing more than one halogen atom per molecule.

Polyhalogen compounds are useful in various industries and in agriculture. Some important polyhalogen compounds:



Dichloromethane (Methylene chloride)



Uses:

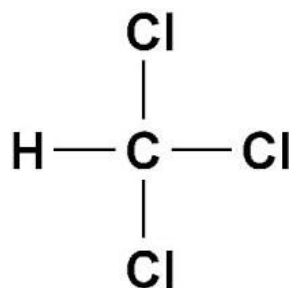
Dichloromethane (methylene chloride) is used as a:

1. Solvent for paint removers
2. Propellant in aerosols
3. Process solvent in the manufacture of drugs
4. Metal cleaning and finishing solvent

Harmful effects:

1. It endangers the human central nervous system.
2. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision.
3. High levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes.
4. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin.
5. Direct contact with the eyes can burn the cornea.

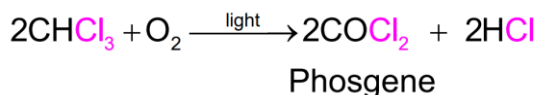
Trichloromethane (Chloroform)

**Uses:**

1. Chemically, chloroform is used as a solvent for fats, alkaloids, iodine and other substances.
2. The major use of chloroform today is in the production of the freon refrigerant R-22.
3. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, safer anaesthetics such as ether.

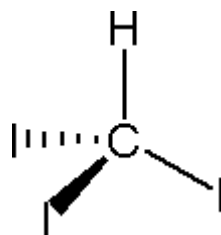
Harmful effects:

1. As might be expected from its use as an anaesthetic, inhaling chloroform vapour depresses the central nervous system.
2. Breathing about 900 parts of chloroform per million parts of air (900 ppm) for a short time can cause dizziness, fatigue and headache.
3. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys. Some people develop sores when the skin is immersed in chloroform.
4. Chloroform is slowly oxidised by air (oxygen) in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene.



It is therefore stored in closed dark-coloured bottles which are completely filled so that air is kept out.

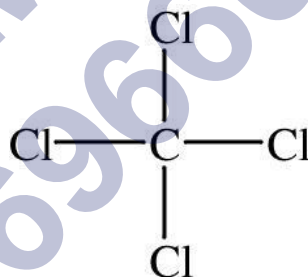
Triiodomethane (Iodoform)

**Uses:**

- It was used earlier as an antiseptic, but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself.

Drawback:

- Because of its objectionable smell, it has been replaced by other formulations containing iodine.

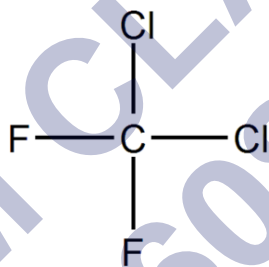
Tetrachloromethane (Carbon tetrachloride)**Uses:**

1. It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans.
2. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, in pharmaceutical manufacturing and general solvent use.
3. Until the mid-1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and fire extinguisher.

Harmful effects:

1. There is evidence that exposure to carbon tetrachloride causes liver cancer in humans.
2. The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells.
3. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to CCl_4 can make the heart beat irregularly or stop.
4. The chemical may irritate the eyes on contact. When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer.
5. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

Freons



- The chlorofluorocarbon compounds of methane and ethane are collectively known as freons.
- They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.
- They are manufactured from tetrachloromethane by Swarts reaction.
- By 1974, the total freon production in the world was about 2 billion pounds annually.

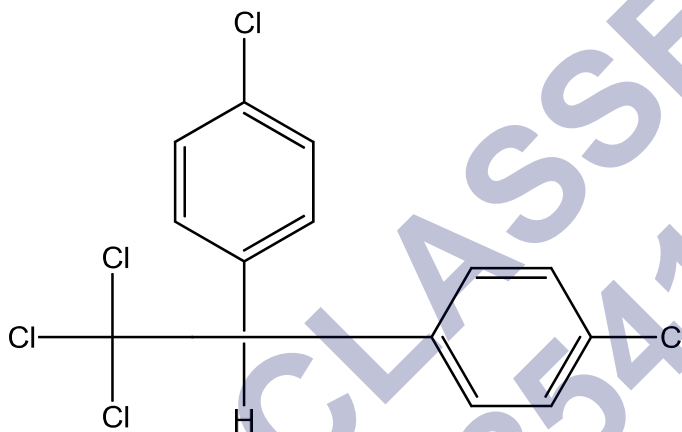
Uses:

1. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.
2. Freon 12 (CCl_2F_2) is one of the most common freons in industrial use.
3. Most freons, even those used in refrigeration, eventually make their way into the atmosphere where it diffuses unchanged into the stratosphere.

Harmful Effect:

- In stratosphere, freons can initiate radical chain reactions which can upset the natural ozonebalance.

p,p'-Dichlorodiphenyltrichloroethane (DDT)



DDT, the first chlorinated organic insecticide, was originally prepared in 1873.

However, it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide.

Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery.



Paul Muller

Uses:

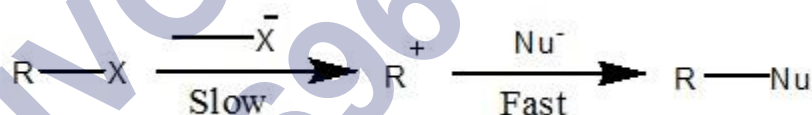
- The use of DDT increased enormously worldwide after World War II, primarily because of its effectiveness against the mosquito which spreads malaria and lice which carry typhus.

Harmful Effects:

Problems related to extensive use of DDT began to appear in the late 1940s.

1. Many species of insects developed resistance to DDT.
2. It has a high toxicity towards fish.
3. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised very rapidly by animals. Instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time.

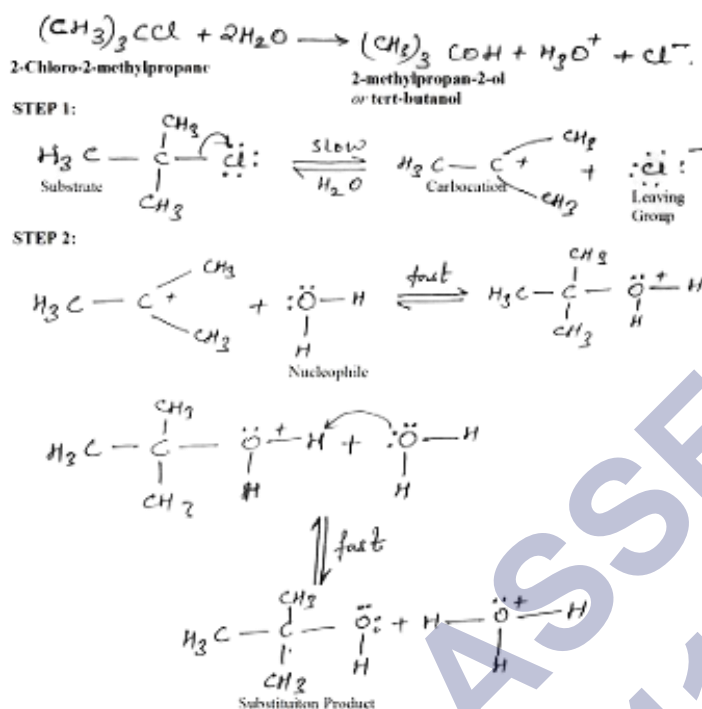
The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world.

S_N¹ mechanism

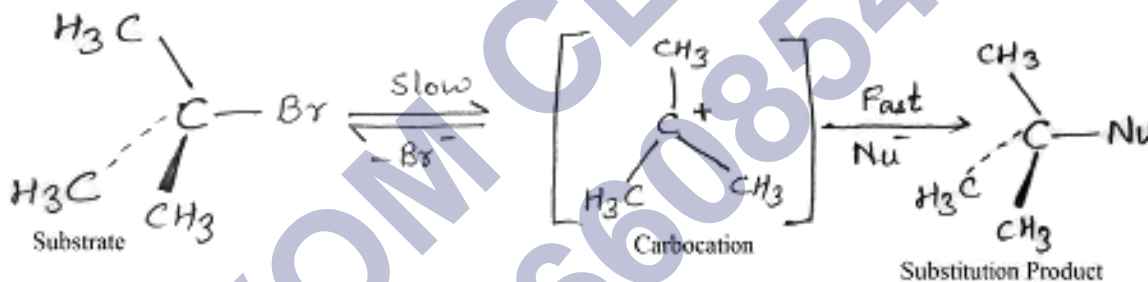
The tertiary alkyl halides react by S_N¹ mechanism via formation of carbocation as intermediate. The reactivity order for S_N¹ reaction is

Benzyl > Allyl > 3° > 2° > 1° > CH₃X.

A mechanism for the reaction of tert-butyl chloride with water apparently involves two steps:



Stereochemistry of S_N1 :



Key features:

More stable will be the carbocation intermediate; faster will be the S_N1 mechanism.

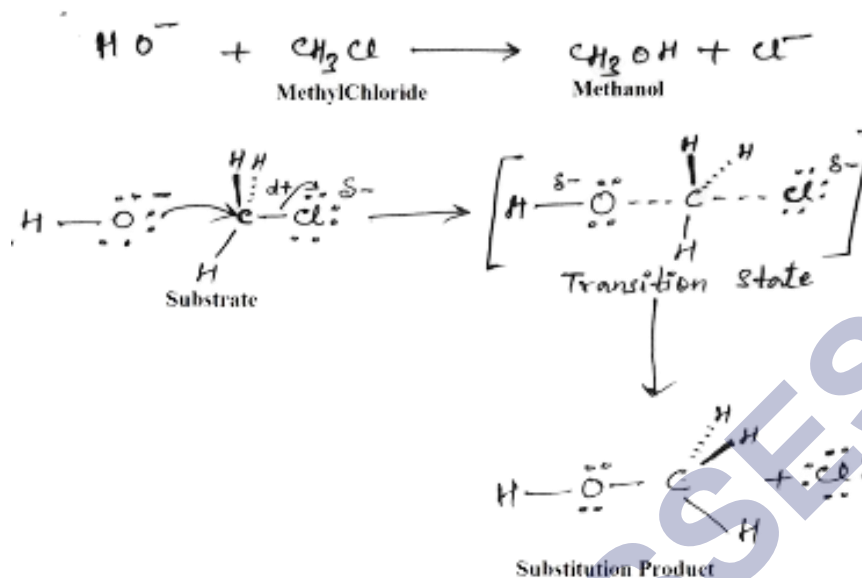
Polar solvents lead to polar transition state which in turn accelerates the S_N1 reaction.

If the initial compound is chiral then S_N1 reaction ends up with racemization of the product.

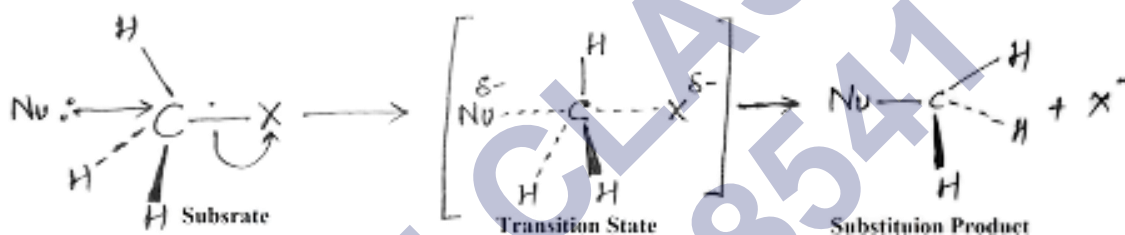
Weaker bases being leaving group favor S_N1 reaction.

S_N2 mechanism

In case of S_N2 reactions the halide ion leaves from the front side whereas the nucleophiles attacks from the back side; due to this reason S_N2 reactions are always accompanied by the inversion of configuration. Thus formation of another enantiomer is lead by S_N2 reaction of an optically active halide i.e. optical activity is retained but with opposite configuration.



Stereochemistry of $\text{S}_{\text{N}}2$:



Key features:

In $\text{S}_{\text{N}}2$ reaction the stereochemistry around carbon atom of the substrate undergoes inversion and is known as Walden inversion.

The rate of reaction depends on the steric bulk of the alkyl group.

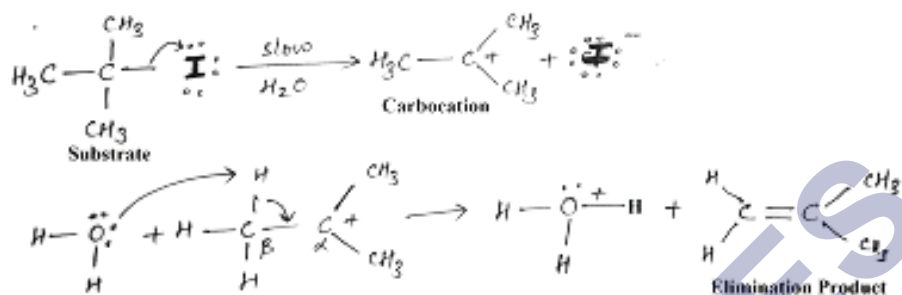
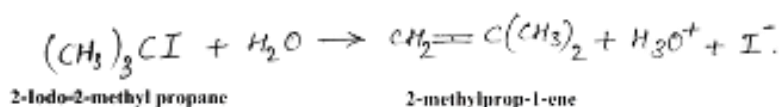
Increase in the length of alkyl group decreases the rate of reaction. Alkyl branching next to the leaving group decreases the rate drastically.

Under the following conditions $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions take place:

- The alkyl is secondary and tertiary.
- The solvent is Protic or Aprotic.
- To stabilize the intermediate stage..

E1 reaction

It is a unimolecular reaction. Rate determining step consist of formation of carbocation intermediate. Stability of carbocation intermediate determines the reactivity of E1 reaction. Order of reactivity for E1 reaction is $3^\circ > 2^\circ > 1^\circ$. Both elimination and substitution reaction involves the use of (same reactive intermediate) carbocation. Therefore both the products are formed in comparable amount. This reaction is favored by entropy of reaction therefore increase in temperature favors the E1 reaction.



Stereochemistry of E1 reaction:

E1 eliminations generally lead to the more stable stereochemistry.

The rate of the E1 reaction depends only on the substrate, therefore more stable the carbocation is, faster will be the reaction. Slowest step is the formation of the carbocation.

Alkenes formation doesn't require strong base, since there is no leaving group that needs to be displaced. So there is no requirement for the stereochemistry of the starting material;

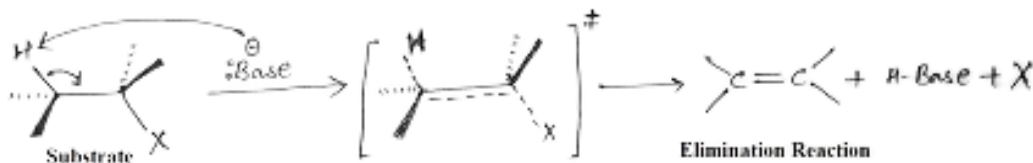
E2 reaction

It's a bimolecular reaction. It is a single step reaction whose rate depends on the concentration of base and substrate. Reactivity depends on both strength of base and nature of alkyl halide. Order of reactivity for E1 reaction is $3^\circ > 2^\circ > 1^\circ$. This reaction proceeds at room temperature.

Example:



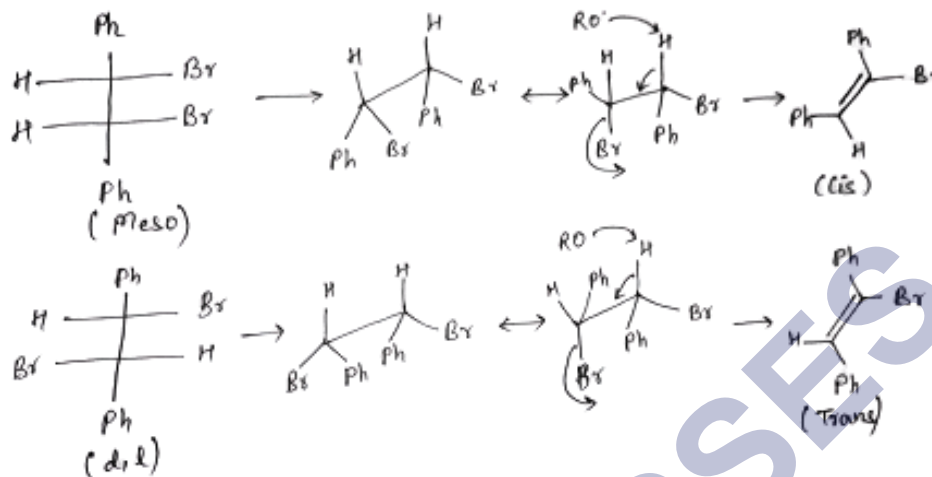
General mechanism:



Stereochemistry of E2 reaction:

E2 eliminations may or may not lead to the more stable stereochemistry. Initial material for this reaction has two sp^3 hybridized carbons which on rehybridization forms two sp^2 hybridized carbons. The C-X bond and the C-H bond lines up in the same plane and faces in

anti directions to each other.



SHIVOM CLASSES
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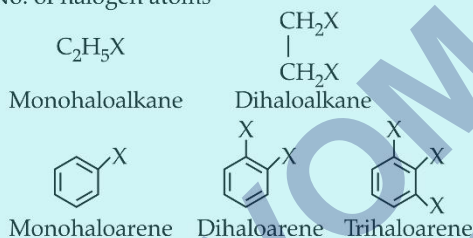
Racemisation S_N1

- Chiral : Objects which are non-superimposable
- Achiral : objects which are superimposable

Haloalkanes and Haloarenes

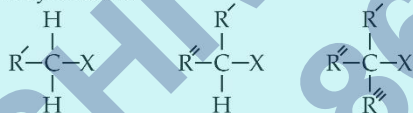
Classification

- No. of halogen atoms

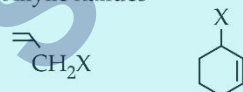


- Compounds containing sp^3 C-X bond

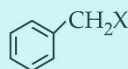
- (a) Alkyl halides



- (b) Allylic halides



- (c) Benzylic halides



- Compounds containing sp^2 C-X bond

- (a) Vinylic halides



- (b) Aryl halides



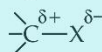
- Nomenclature

Common name : alkyl group followed by halides. Dihalogen derivatives, prefixes o-, m-, p- are used.

IUPAC name : numerals are used

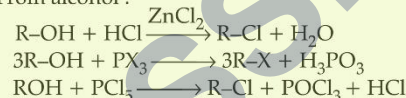
- Nature of C-X bond

: Carbon-halogen bond is polarized

**Haloalkanes**

- Preparation

- From alcohol :

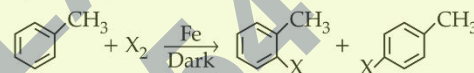


- From hydrocarbons :

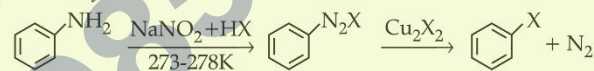
- (a) By free radical halogenations



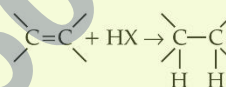
- (b) By electrophilic substitution



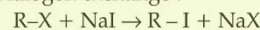
- (c) Sand meyer's reaction



- (d) From alkenes



- Halogen exchange :



- Properties

- Physical : Colourless, volatile, sweet smell.

Lower members are gases at room temperature while higher are solids.

B.P : $RI > RBr > RCl > RF$

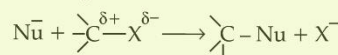
M.P : Para isomers have high m.p. than ortho and meta - isomers.

Density : Increases with increase in number of C/X atoms and atomic masses of the X atoms.

Solubility : Very slightly soluble in water.

- Chemical :

- (a) Nucleophilic substitution

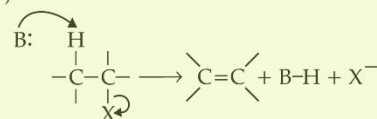


For S_N2 reaction

Tertiary, Secondary, Primary

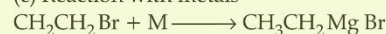
For S_N1 reaction

- (b) Elimination reaction

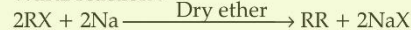


B = Base; X = Leaving group

- (c) Reaction with metals



Wurtz reaction :



Class : 12th Chemistry
Chapter-10 : Haloalkanes And Haloarenes (Part_2)

Carbon tetrachloride

- Manufacture of refrigerants and propellants.
- Cleaning fluid

Chloroform

- Solvent for fats, alkaloids, I etc.
- Production of Freon

Dichloromethane

- Paint remover
- Propellant in aerosols
- Metal cleaning and finishing solvent.

Freon's

For aerosol propellants, refrigeration and air conditioning purposes

D. DT.

As insecticide

Iodoform

Antiseptic

Polyhalogen compounds

Haloalkanes and Haloarenes

S_N2 Stereochemical inversion

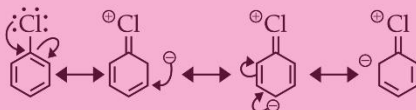
- (a) Dextro (+/d)
- (b) laevo (-/l)

Haloarenes

Reactions :

(a) Nucleophilic substitution

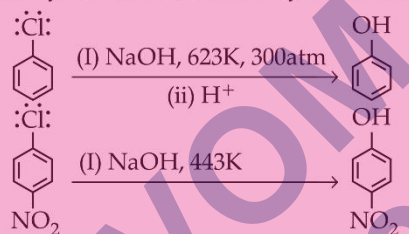
(i) Resonance effect



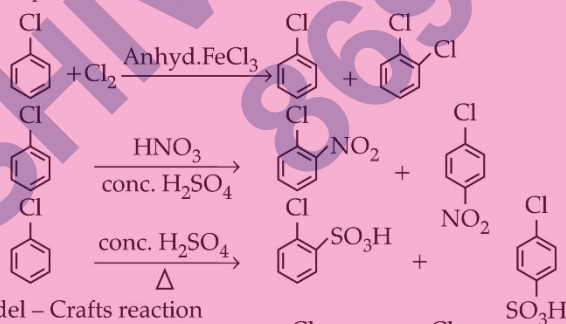
(ii) Hybridization of C - X bond in :

Haloalkane $-sp^3$; Haloarene $-sp^2$

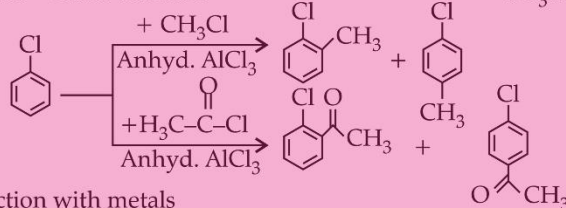
(iii) Phenyl cation unstabilised by resonance



(b) Electrophilic substitution

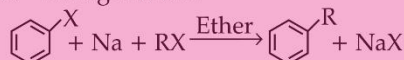


Friedel - Crafts reaction

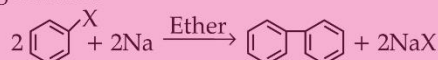


(c) Reaction with metals

Wurtz - Fittig reaction



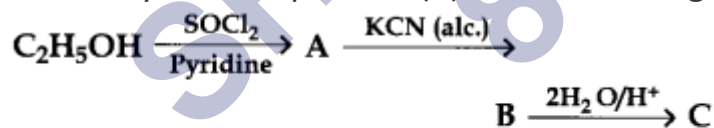
Fittig reaction



Important Questions

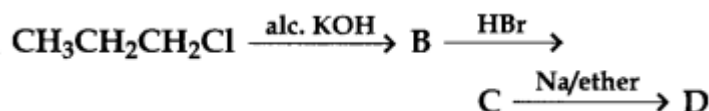
Multiple Choice questions-

- S_N1 reaction of alkyl halides lead to
 - Retention of configuration
 - Racemisation
 - Inversion of configuration
 - None of these
- p-dichlorobenzene has higher melting point than its o- and m- isomers because
 - p-dichlorobenzene is more polar than o- and m- isomer.
 - p-isomer has a symmetrical crystalline structure.
 - boiling point of p-isomer is more than o- and m-isomer.
 - All of these are correct reasons.
- Chloropicrin is formed by the reaction of
 - steam on carbon tetrachloride.
 - nitric acid on chlorobenzene.
 - chlorine on picric acid.
 - nitric acid on chloroform.
- Fitting reaction can be used to prepare
 - Toluene
 - Acetophenone
 - Diphenyl
 - Chlorobenzene
- Identify the end product (C) in the following sequence:



- (a) $\text{C}_2\text{H}_5\text{CH}_2\text{NH}_2$ (b) $\text{C}_2\text{H}_5\text{CONH}_2$
 (c) $\text{C}_2\text{H}_5\text{COOH}$ (d) $\text{C}_2\text{H}_5\text{NH}_2 + \text{HCOOH}$

6.

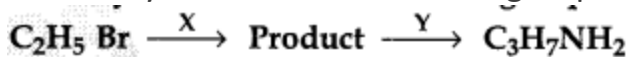


In the above reaction, the product D is

- Propane
- 2, 3-Dimethylbutane

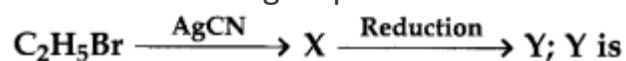
- (c) Hexane
(d) Allyl bromide

7. Identify X and Y in the following sequence



- (a) X = KCN, Y = LiAlH₄
(b) X = KCN, Y = H₃O⁺
(c) X = CH₃Cl, Y = AlCl₃ HCl
(d) X = CH₃NH₂, Y = HNO₂

8. In the following sequence of reactions:

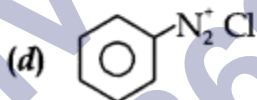
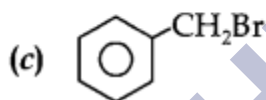
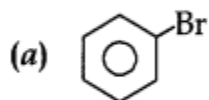


- (a) n-propylamine
(b) isopropylamine
(c) ethylamine
(d) ethylmethanamine

9.

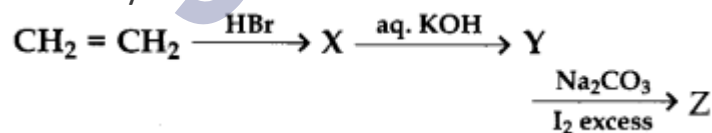


Which of the following cannot be X?



10.

Identify Z in the series

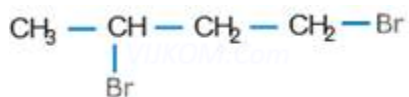


- (a) C₂H₅I
(b) C₂H₅OH
(c) CH₃
(d) CH₃CHO

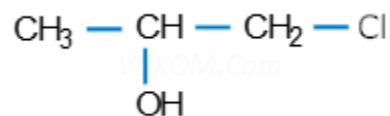
Very Short Questions-

1. Give IUPAC names of following compounds

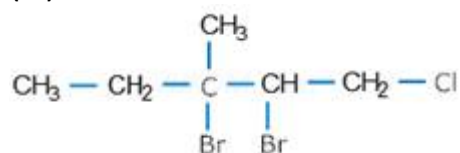
(i).



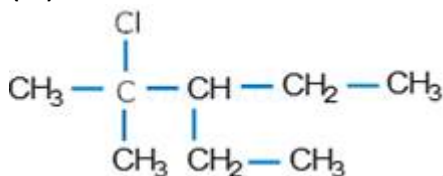
(ii).



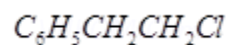
(iii).



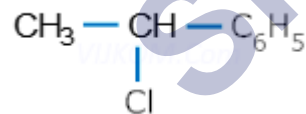
(iv).



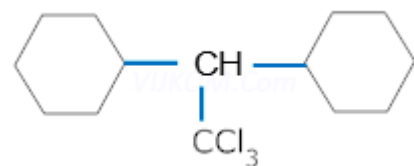
(v).



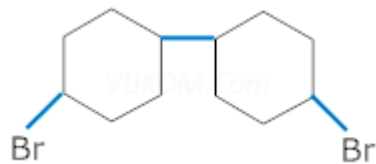
(vi).

(vii). $\text{C}_6\text{H}_6\text{Cl}_6$

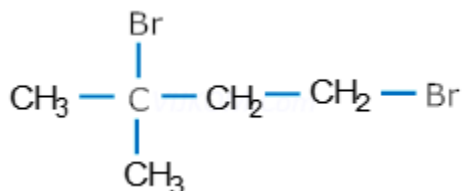
(viii).



(ix).



(x).



Short Questions-

1. Thionyl chloride is preferred for converting alcohol to haloalkane.
2. Phenol cannot be converted to chlorobenzene by reacting with HCl.
3. HNO_3 is added during iodination of benzene.
4. p- dichlorobenzene has higher melting point than meta – dichlorobenzene.
5. The boiling points of isomeric haloalkenes decrease with increase in branching.
6. Hydrolysis of optically active 2- bromobutane forms optically inactive butan – 2 – ol.
7. Chlorobenzene is less reactive towards nucleophilic substitution reaction.
8. Chloroform is stored in dark coloured bottles.
9. The order of boiling points is $RCl < RBr < RI$.
10. Vinyl chloride is less reactive than allyl chloride.

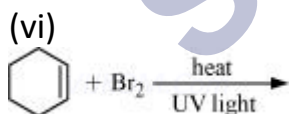
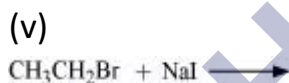
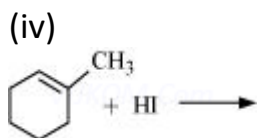
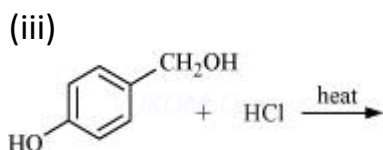
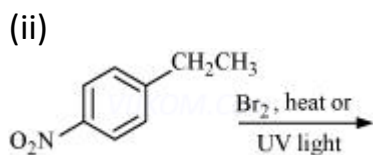
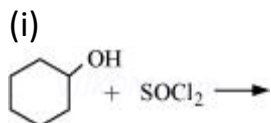
Long Questions-

1. Write structures of the following compounds:
 - (i) 2-Chloro-3-methylpentane
 - (ii) 1-Chloro-4-ethylcyclohexane
 - (iii) 4-tert. Butyl-3-iodoheptane
 - (iv) 1,4-Dibromobut-2-ene
 - (v) 1-Bromo-4-sec. butyl-2-methylbenzene
2. Write structures of different dihalogen derivatives of propane.
3. Among the isomeric alkanes of molecular formula C_5H_{12} , identify the one that on photochemical

chlorination yields

- (i) A single monochloride.
- (ii) Three isomeric monochlorides.
- (iii) Four isomeric monochlorides.

4. Draw the structures of major monohalo products in each of the following reactions:

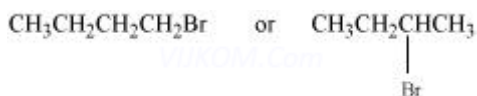


5. Arrange each set of compounds in order of increasing boiling points.

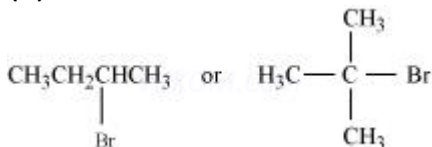
- (i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.
- (ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

6. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

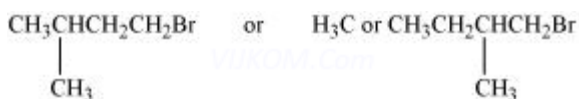
(i)



(ii)

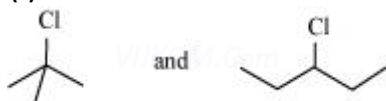


(iii)

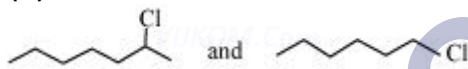


7. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

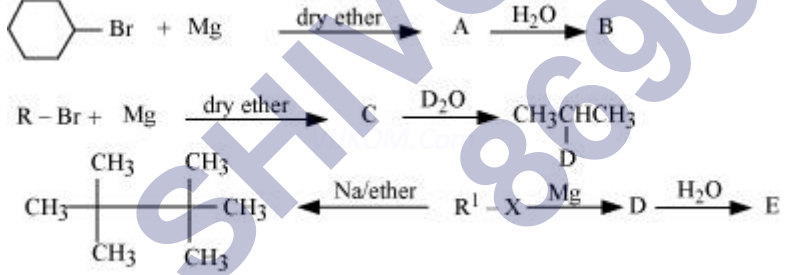
(i)



(ii)



8. Identify A, B, C, D, E, R and R^1 in the following:



Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
- a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 - b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 - c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

Assertion: Isopropyl chloride is less reactive than CH_3Br in $\text{S}_{\text{N}}2$ reactions.

Reason: $\text{S}_{\text{N}}2$ reactions are always accompanied by inversion of configuration.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- Assertion and reason both are correct statements and reason is correct explanation for assertion.
- Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- Assertion is correct statement but reason is wrong statement.
- Assertion is wrong statement but reason is correct statement.

Assertion: Lower members of alkyl halides are colourless gases.

Reason: Alkyl iodides in general turn black on exposure to air and light.

Case Study Questions-

1. Read the passage given below and answer the following questions:

Haloarenes are less reactive than haloalkanes. The low reactivity of haloarenes can be attributed to:

- Resonance effect.
- sp^2 hybridisation of C - X bond.
- Polarity of C - X bond
- Instability of phenyl cation (formed by self-ionisation of haloarene).
- Repulsion between the electron rich attacking nucleophiles and electron rich arenes.

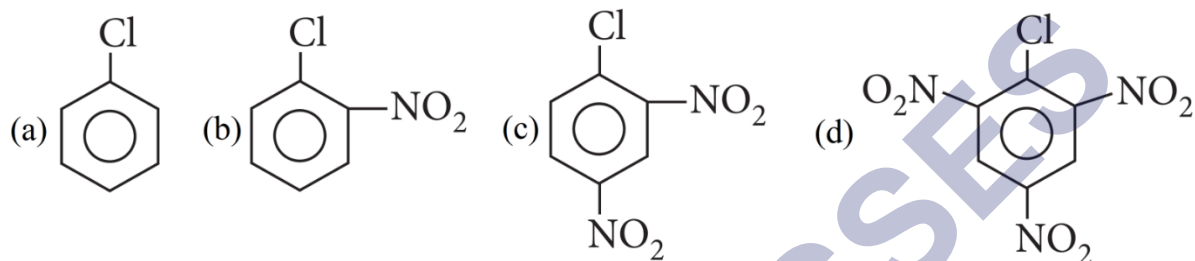
Reactivity of haloarenes can be increased or decreased by the presence of certain groups at certain positions for example, nitro ($-\text{NO}_2$) group at o/ p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

The following questions are multiple choice questions Choose the most appropriate answer:

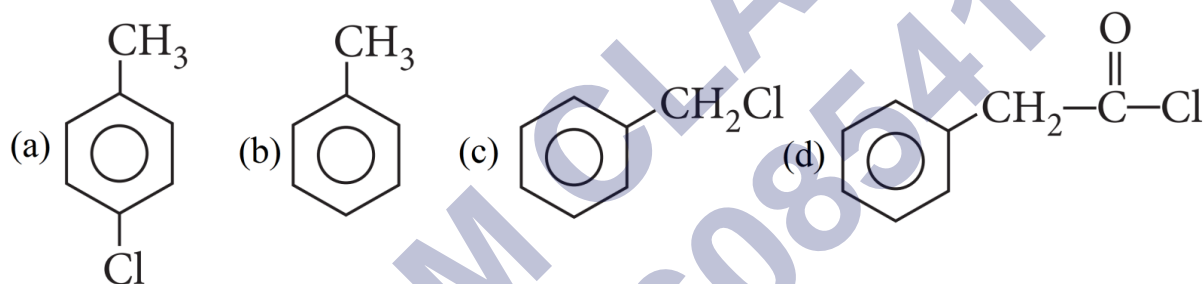
- Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to
 - The formation of less stable carbonium ion.

- b) Resonance stabilisation.
- c) Larger carbon-halogen bond.
- d) Inductive effect.

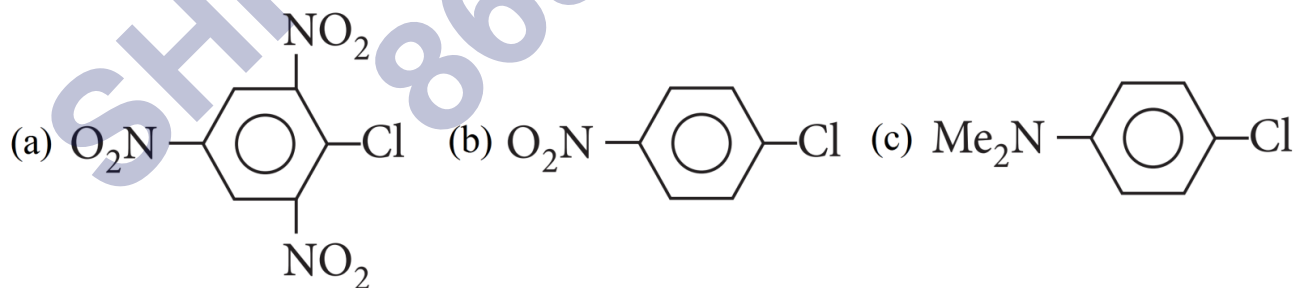
(ii) Which of the following aryl halides is the most reactive towards nucleophilic substitution?



(iii) Which one of the following will react fastest with aqueous NaOH?



(iv) Which chloro derivative of benzene among the followings would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?



d. C_6H_5Cl

(v) The reactivity of the compounds (i) MeBr, (ii) PhCH₂Br, (iii) MeCl, (iv) p-MeOC₆H₄Br decreases as:

- a) (i) > (ii) > (iii) > (iv)
- b) (iv) > (ii) > (i) > (iii)
- c) (iv) > (iii) > (i) > (ii)

d) (ii) > (i) > (iii) > (iv)

2. Read the passage given below and answer the following questions:

A chlorocompound (A) on reduction with Zn-Cu and ethanol gives the hydrocarbon (B) with five carbon atoms. When (A) is dissolved in dry ether and treated with sodium metal it gave 2, 2, 5, 5 - tetramethylhexane. The treatment of (A) with alcoholic KCN gives compound (C).

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The compound (A) is:

- a) 1-chloro-2, 2-dimethylpropane.
- b) 1-chloro-2, 2-dimethyl butane.
- c) 1-chloro-2-methyl butane.
- d) 2-chloro-2-methyl butane.

(ii) The reaction of (C) with Na, C₂H₅OH gives:

- a) (CH₃)₃C CH₂CONH₂
- b) (CH₃)₃C NH₂
- c) (CH₃)₃C CH₂CH₂NH₂
- d) (CH₃)₂CHCH₂NH₂

(iii) The reaction of (C) with Na, C₂H₅OH is called:

- a) Gilman reaction.
- b) Mendius reaction.
- c) Grooves process.
- d) Swart's reaction.

(iv) The reaction of (A) with aq. KOH will preferably favour:

- a) S_N1 mechanism.
- b) S_N2 mechanism.
- c) E₁ mechanism.
- d) E₂ mechanism.

(v) Compound (B) is:

- a) N-pentane.

- b) 2, 2-dimethylpropane.
- c) 2-methylbutane.
- d) None of these.

MCQ Answers-

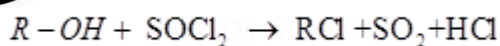
- 1. Answer: b
- 2. Answer: b
- 3. Answer: d
- 4. Answer: c
- 5. Answer: c
- 6. Answer: b
- 7. Answer: a
- 8. Answer: d
- 9. Answer: a
- 10. Answer: c

Very Short Answers-

- (i) 1, 3- Dibromobutane
- (ii). 1- Chloropropan-2-ol
- (iii). 2, 3 – Dibromo-1-chloro-3-methylpentane
- (iv). 2-Chloro-3-ethyl-2-methyl pentane
- (v). 1-Chloro-2-phenylethane
- (vi). 1-Chloro-1-phenyl ethane
- (vii). 1, 2, 3, 4, 5, 6- hexachlorocyclohexane
- (viii). 2, 2- Dihexyl 1, 1, 1-Trichloro ethane
- (ix). 4, 4-dibromobiphenyl
- (x). 1, 3-Dibromo -3- methyl butane

Short Answers-

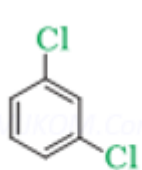
Ans 1. Thionyl chloride is preferred for converting alcohol to haloalkane because the by-products formed are all gases which escape into the atmosphere.



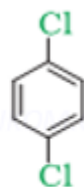
Ans 2. In phenol, due to resonance, the carbon-oxygen bond has a partial double bond character and is difficult to break being stronger than a single bond. Therefore, it can-not be converted to chlorobenzene by reacting with HCl.

Ans 3. When benzene is reacted with iodine, the reaction is reversible in nature. It leads to the formation of reactants back. Therefore, an oxidizing agent like HNO_3 oxidizes the HI formed in the reaction and keeps the reaction in forward direction.

Ans 4.



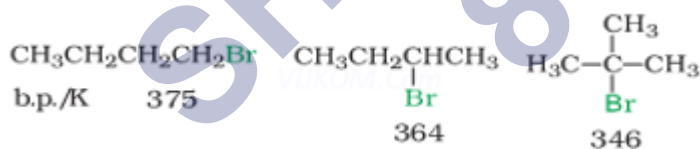
m - dichlorobenzene



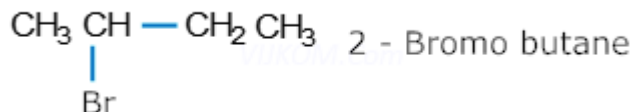
p - dichlorobenzene

p-dichlorobenzene is having symmetrical structure therefore it can fit better into the crystal lattice which increases its melting point.

Ans 5. The boiling points of isomeric haloalkanes decreases with branching due to decrease in surface areas with branching. As branching increasing the structure becomes more spherical and the surface area decreases. e.g. the boiling points of isomers of C_4H_9Br follows the order.



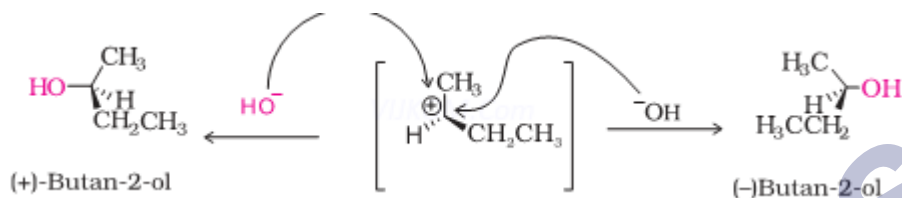
Ans 6.



The compound undergoes hydrolysis by S_N1 mechanism via the formation of carbocation which is planar.

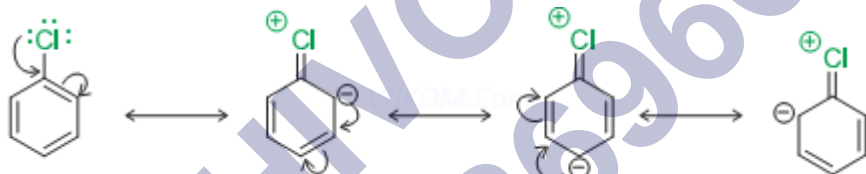


The attack of nucleophile can result in product which is a mixture of compounds both with same configuration and inverted configuration.



Therefore it results in the formation of racemic mixture which is optically inactive.

Ans 7. Chlorobenzene is less reactive towards nucleophilic substitution due to –
 i. resonance, C-Cl bond acquires a double bond character and becomes stronger than a single bond.

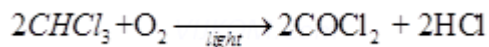


ii. sp^2 hybridisation in C of C-X bond, the carbon becomes more electronegative and holds the electron pair of C-X bond more tightly decreasing the bond length.

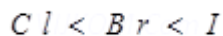
iii. Instability of phenyl cation.

iv. Repulsion for incoming nucleophile from electron rich ring.

Ans 8. Chloroform gets oxidised slowly by air in the presence of light to an extremely poisonous gas phosgene. Therefore, to avoid any exposure to air and sunlight, it is kept in dark coloured bottles.



Ans 9. The boiling points of alkyl halides depends on dipole and van-der-waal's interaction. These attractions get stronger as the molecules get bigger in size and have more electrons. As the size of halogens increases in the order –



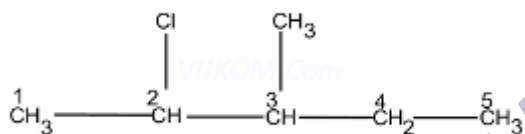
The boiling points also follow the order



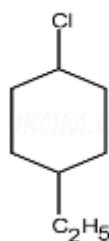
Ans 10. Due to resonance C-Cl bond gets double bond character and becomes stronger than a single bond, making vinyl chloride less reactive than allyl chloride.

Long Answers-

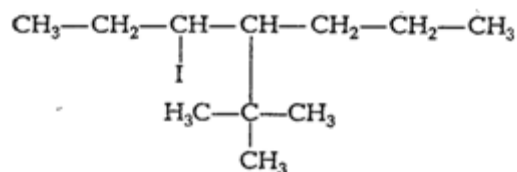
Ans 1. (i) 2-Chloro-3-methyl pentane



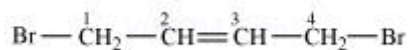
(ii) 1-Chloro-4-ethylcyclohexane



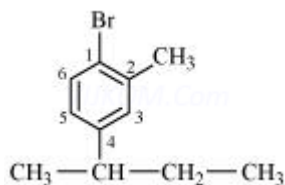
(iii) 4- tert-Butyl-3-iodoheptane



(iv) 1, 4-Dibromobut-2-ene

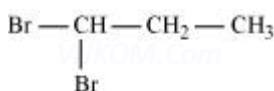


(v) 1-Bromo-4-sec-butyl-2-methylbenzene

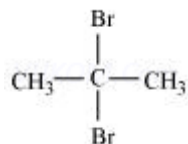


Ans 2. There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.

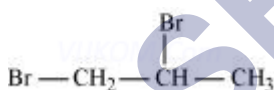
(i) 1, 1-Dibromopropane



(ii) 2, 2-Dibromopropane



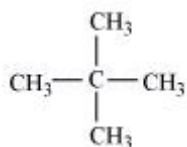
(iii) 1, 2-Dibromopropane



(iv) 1, 3-Dibromopropane



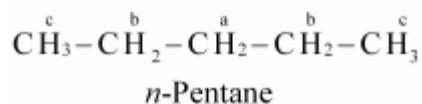
Ans 3. (i) To have a single monochloride, there should be only one type of H-atom in the isomer of the alkane of the molecular formula C_5H_{12} . This is because, replacement of any H-atom leads to the formation of the same product. The isomer is neopentane.



Neopentane

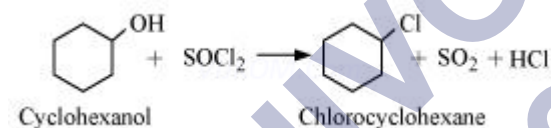
(ii) To have three isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain three different types of H-atoms.

Therefore, the isomer is *n*-pentane. It can be observed that there are three types of H atoms labelled as *a*, *b* and *c* in *n*-pentane.

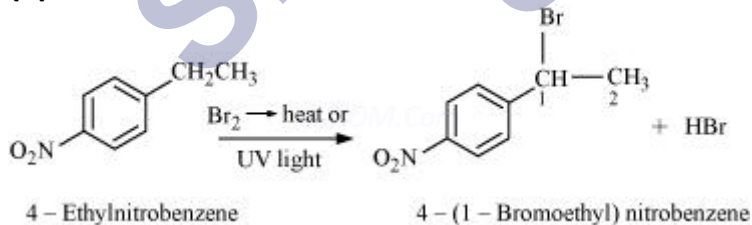


(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of H-atoms labelled as *a*, *b*, *c*, and *d* in 2-methylbutane.

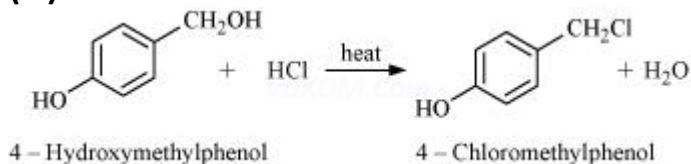
Ans 4. (i)



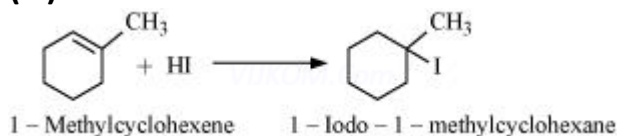
(ii)



(iii)



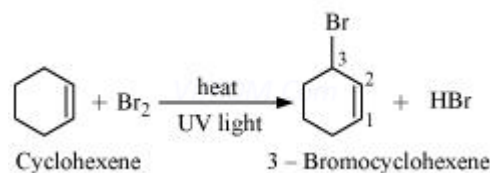
(iv)



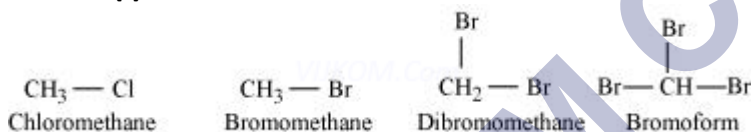
(v)



(vi)



Ans 5. (i)



For alkyl halides containing the same alkyl group, the boiling point increases with an increase in the atomic mass of the halogen atom.

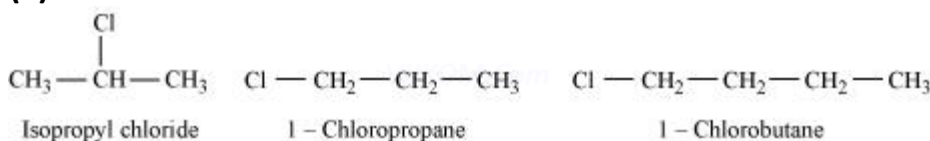
Since the atomic mass of Br is greater than that of Cl, the boiling point of bromomethane is higher than that of chloromethane.

Further, for alkyl halides containing the same alkyl group, the boiling point increases with an increase in the number of halides. Therefore, the boiling point of Dibromomethane is higher than that of chloromethane and bromomethane, but lower than that of bromoform.

Hence, the given set of compounds can be arranged in the order of their increasing boiling points as:

Chloromethane < Bromomethane < Dibromomethane < Bromoform.

(ii)



For alkyl halides containing the same halide, the boiling point increases with an increase in

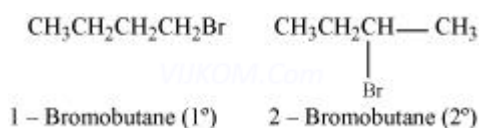
the size of the alkyl group. Thus, the boiling point of 1-chlorobutane is higher than that of isopropyl chloride and 1-chloropropane.

Further, the boiling point decreases with an increase in branching in the chain. Thus, the boiling point of isopropyl alcohol is lower than that of 1-chloropropane.

Hence, the given set of compounds can be arranged in the increasing order of their boiling points as:

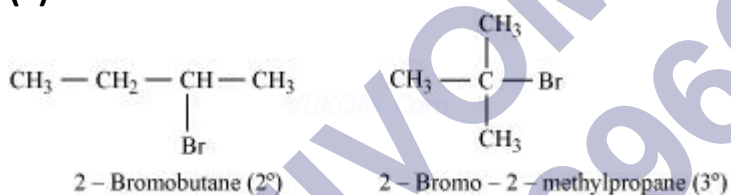
Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

Ans 6. (i)



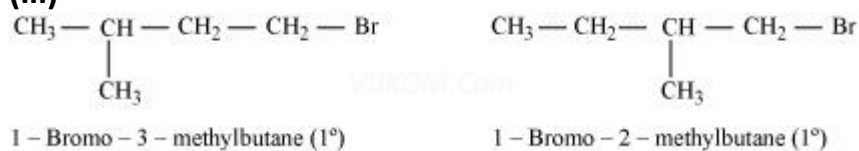
2-bromobutane is a 2° alkylhalide whereas 1-bromobutane is a 1° alkyl halide. The approaching of nucleophile is more hindered in 2-bromobutane than in 1-bromobutane. Therefore, 1-bromobutane reacts more rapidly than 2-bromobutane by an S_N2 mechanism.

(ii)



2-Bromobutane is 2° alkylhalide whereas 2-bromo-2-methylpropane is 3° alkyl halide. Therefore, greater numbers of substituents are present in 3° alkyl halide than in 2° alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S_N2 mechanism.

(iii)

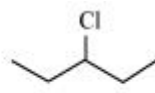


Both the alkyl halides are primary. However, the substituent $-\text{CH}_3$ is at a greater distance to the carbon atom linked to Br in 1-bromo-3-methylbutane than in 1-bromo-2-methylbutane. Therefore, the approaching nucleophile is less hindered in case of the former than in case of the latter. Hence, the former reacts faster than the latter by S_N2 mechanism.

Ans 7. (i)

2 - Chloro - 2 - methylpropane (3°)

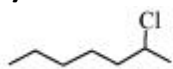
(I)

3 - chloropentane (2°)

(II)

S_N1 reaction proceeds via the formation of carbocation. The alkyl halide (I) is 3° while (II) is 2° . Therefore, (I) forms 3° carbocation while (II) forms 2° carbocation. Greater the stability of the carbocation, faster is the rate of S_N1 reaction. Since 3° carbocation is more stable than 2° carbocation, (I), i.e. 2-chloro-2-methylpropane, undergoes faster S_N1 reaction than (II) i.e., 3-chloropentane.

(ii)

2 - chloroheptane (2°)

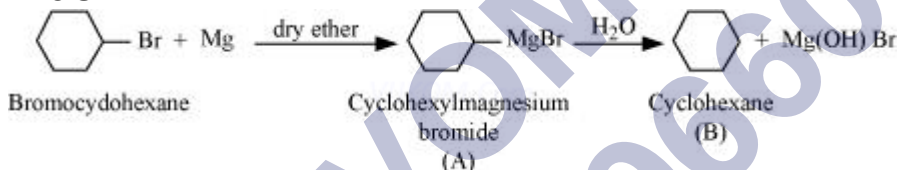
(I)

1 - chlorohexane (1°)

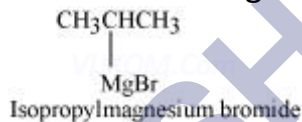
(II)

The alkyl halide (I) is 2° while (II) is 1° . 2° carbocation is more stable than 1° carbocation. Therefore, (I), 2-chloroheptane, undergoes faster S_N1 reaction than (II), 1-chlorohexane.

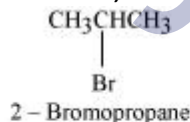
Ans 8.



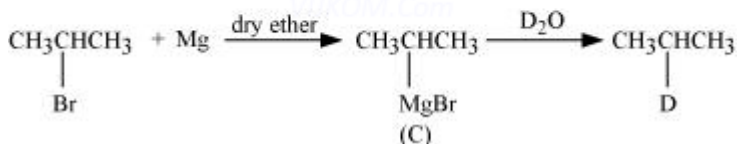
Since D of D_2O gets attached to the carbon atom to which MgBr is attached, C is



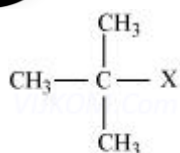
Therefore, the compound R - Br is



2 - Bromopropane

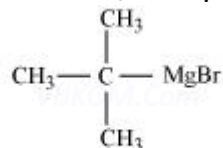


When an alkyl halide is treated with Na in the presence of ether, a hydrocarbon containing double the number of carbon atoms as present in the original halide is obtained as product. This is known as Wurtz reaction. Therefore, the halide, $R^1 - X$, is



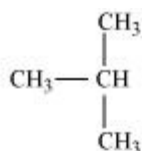
tert - Butylhalide

Therefore, compound D is

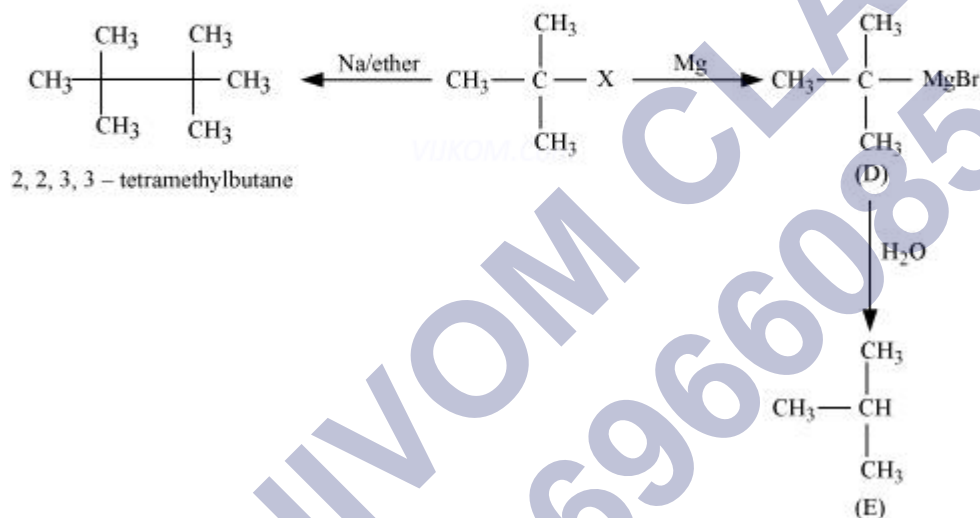


tert - Butylmagnesiumbromide

And, compound E is



2 - Methylpropane



Assertion and Reason Answers-

1. (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

Explanation:

As the size of the alkyl groups increases, the S_N2 reactivity decreases, further C - Cl bond is stronger and more difficult to cleave than C - Br bond. So CH_3Br is more reactive than $(\text{CH}_3)_2\text{CHCl}$.

2. (c) Assertion is correct statement but reason is wrong statement.

Explanation:

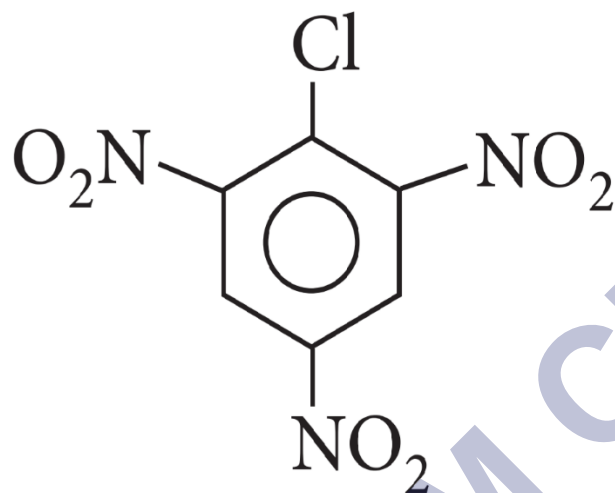
Alkyl iodides in general turn brown due to liberation of I^2 on decomposition by the action of air and light.

Case Study Answers-

1. Answer :

(i) (b) Resonance stabilisation.

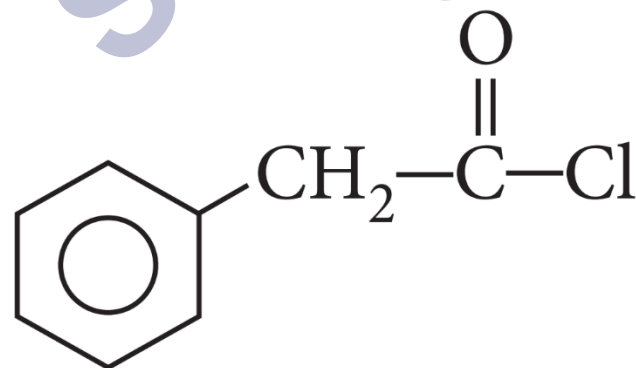
(ii) (d)



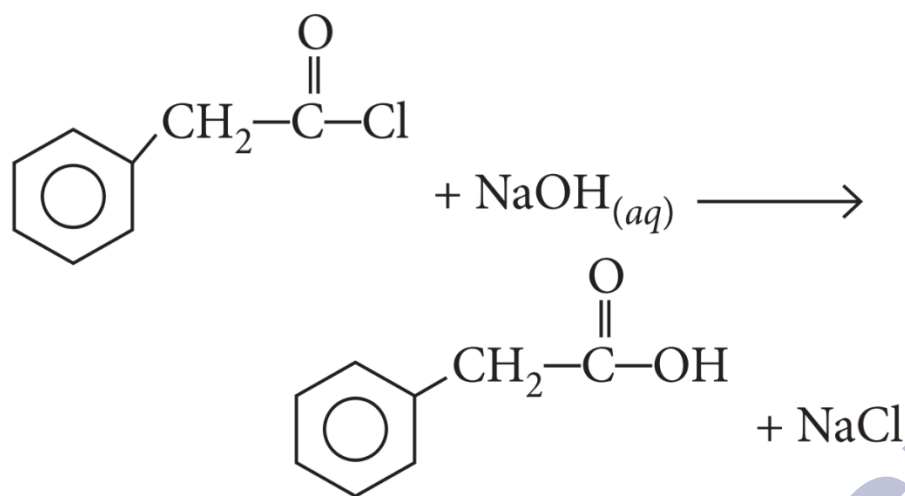
Explanation:

When in aryl halides the electron withdrawing groups are attached at ortho and para positions to the chlorine atom then the removal of chlorine atom as Cl^- ion becomes easy, therefore, 2,4,6-trinitro chlorobenzene is the most reactive among given aryl halides.

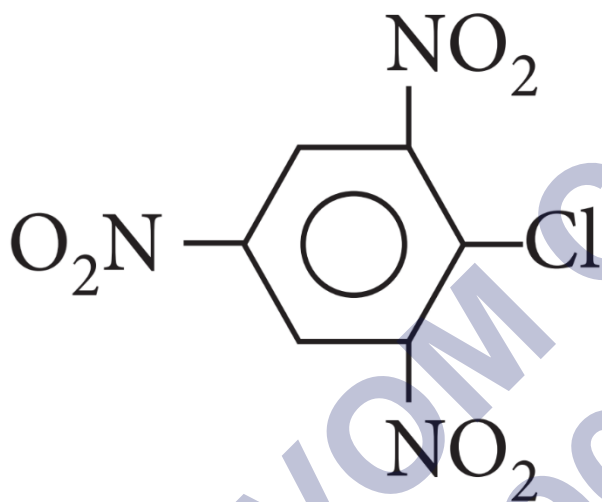
(iii) (d)



Explanation:



(iv) (a)

**Explanation:**

Cl in 2,4,6-trinitrochlorobenzene is activated by three NO_2 groups at o, and p-positions and hence undergoes hydrolysis most readily.

(v) (d) (ii) > (i) > (iii) > (iv)

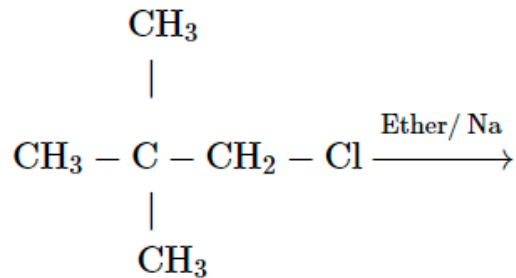
Explanation:

The order of reactivity follows the sequence: benzyl halides > alkyl halides > aryl halides. Out of chlorides and bromides, bromides are more reactive. Therefore, the correct order of reactivity is PhCH_2Br (ii) > MeBr (i) > MeCl (iii) > p - $\text{MeOC}_6\text{H}_4\text{Br}$ (iv).

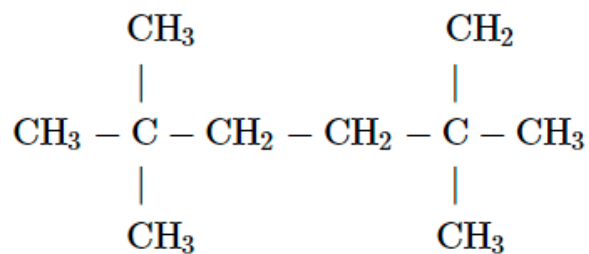
2. Answer :

i. (a) 1-chloro-2, 2-dimethylpropane.

Explanation:



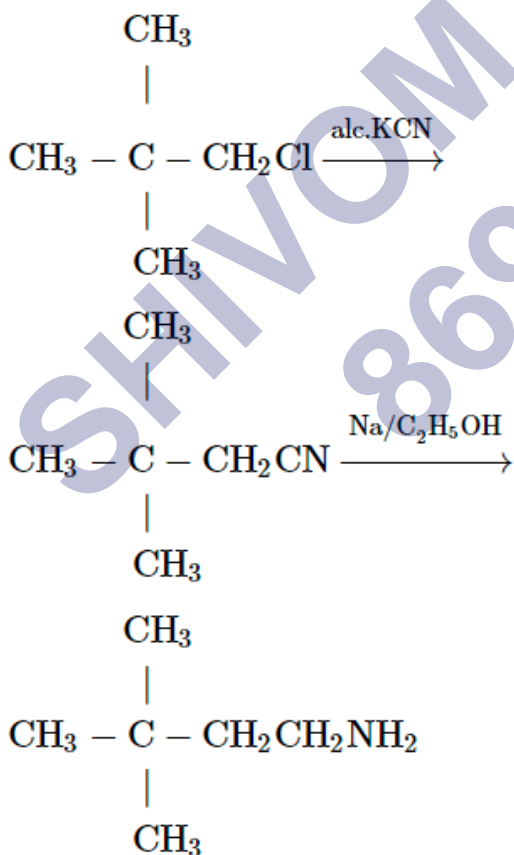
I-Chloro-2, 2-di methylpropane



2, 2, 5, 5-Tetramethylhexane

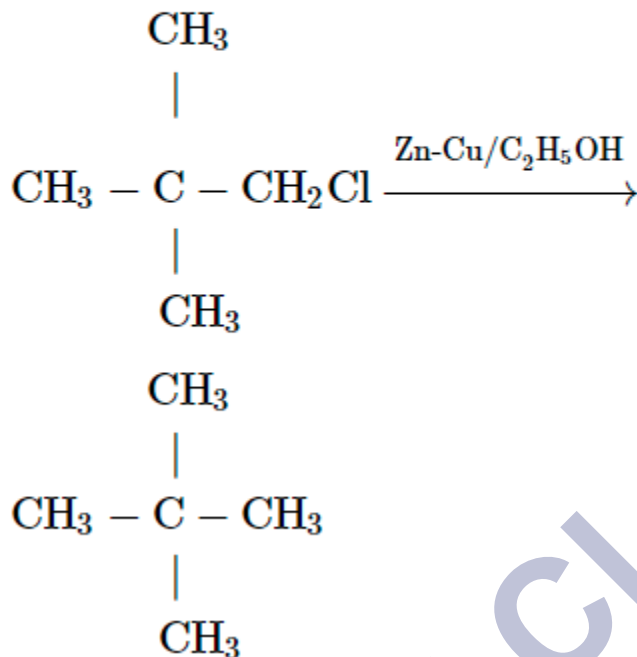
ii. (c) $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{NH}_2$

Explanation:



- iii. (b) Mendius reaction.
iv. (a) S_N1 mechanism.
v. (b) 2, 2-dimethylpropane.

Explanation:



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