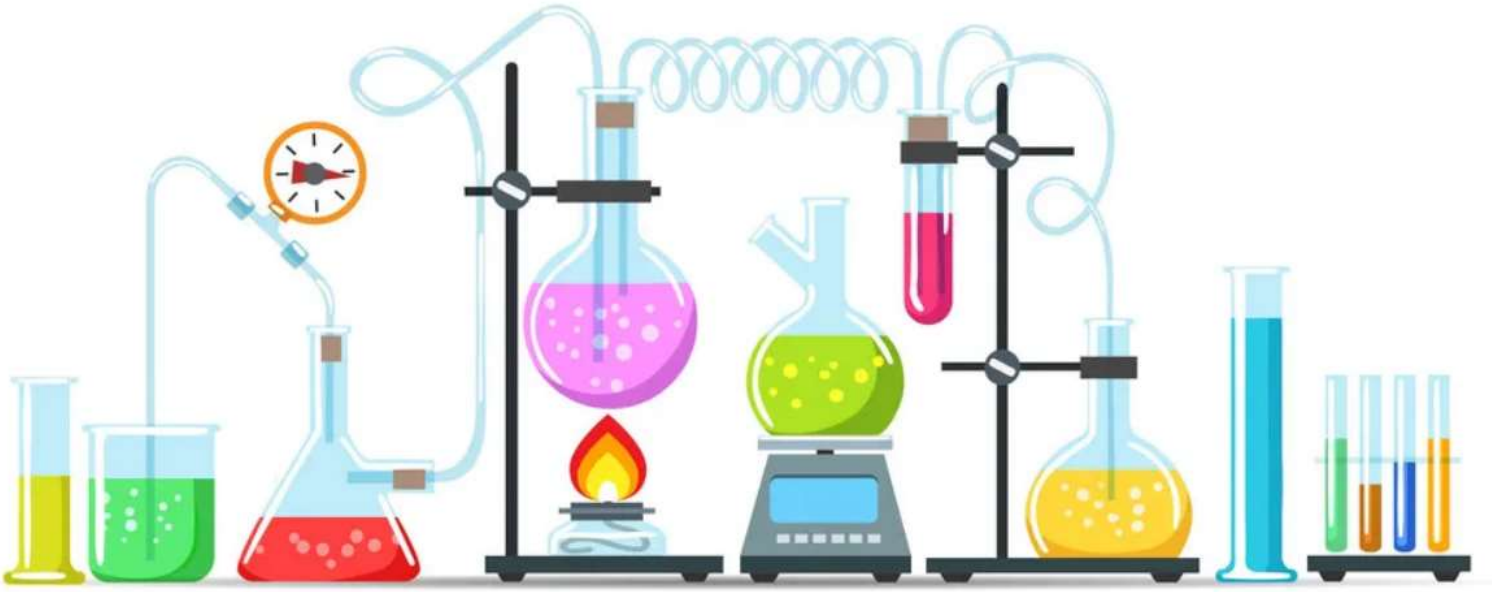
CHEMISTRY

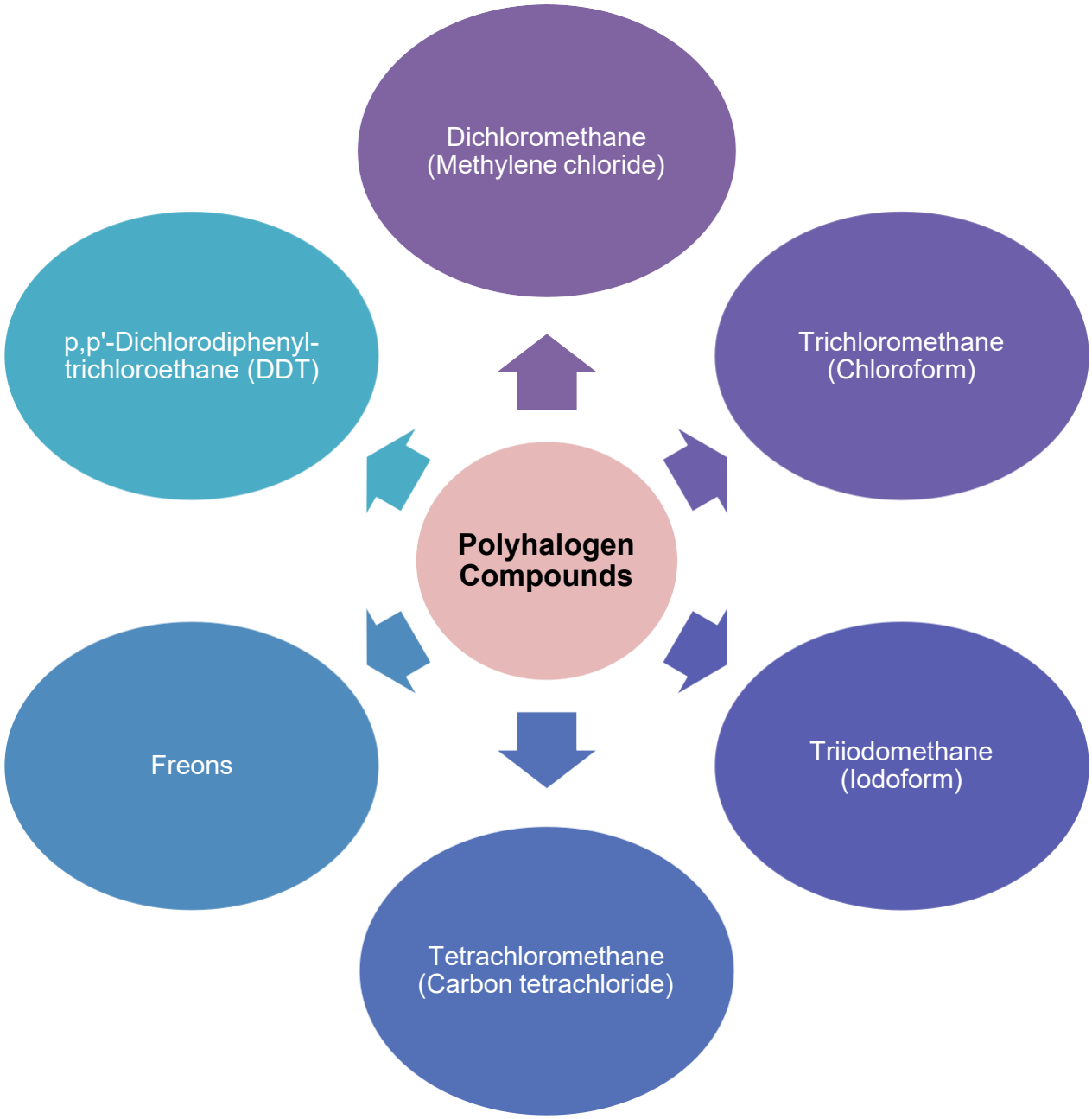


HALOALKANES AND HALOARENES

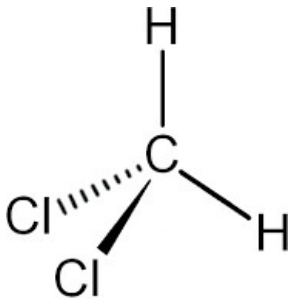
Polyhalogen Compounds

Polyhalogen compounds: Carbon compounds containing more than one halogen atom permolecule.

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



Dichloromethane (Methylene chloride)



Uses:

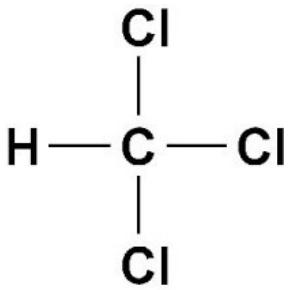
Dichloromethane (methylene chloride) is used as a:

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 andvision.
3. High levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in thefingers and toes.
4. In humans, direct skin contact with methylene chloride causes intense burning and mild rednessof 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 It was once used as a general anaesthetic in surgery but has been replaced by less toxic, saferanaesthetics such as ether.

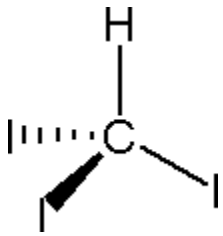
Harmful effects:

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 inchloroform.
4. Chloroform is slowly oxidised by air (oxygen) in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

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

Triiodomethane (Iodoform)



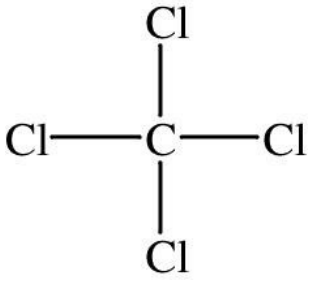
Uses:

- It was used earlier as an antiseptic, but the antiseptic properties are due to the liberation of freeiodine 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:

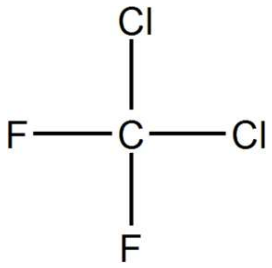
1. It is produced in large quantities for use in the manufacture of refrigerants and propellants foraerosol cans.
2. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, inpharmaceutical manufacturing and general solvent use.
3. Until the mid-1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasingagent, 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 cancause 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 immunesystem.

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.

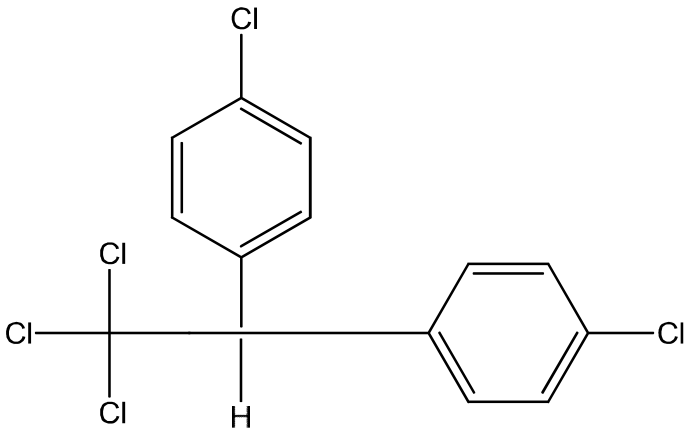
Uses:

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 atmospherewhere 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 theeffectiveness 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 itseffectiveness 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 ofthe world.

MIND MAP : LEARNING MADE SIMPLE

CHAPTER - 10

Haloalkanes and Haloarenes

Polyhalogen compounds

- **Chloroform**
  - Solvent for fats, alkaloids, I etc.
  - Production of Freon
- **Iodoform** — Antiseptic
- **Carbon tetrachloride**
  - Manufacture of refrigerants and propellants.
  - Cleaning fluid
- **Freons** — For aerosol propellants, refrigeration and air conditioning purposes
- **D.D.T.** — As insecticide
- **Dichloromethane**
  - Paint remover
  - Propellant in aerosols
  - Metal cleaning and finishing solvent.

Racemisation S_N1

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

S_N2 Stereochemical inversion

- (a) Dextro (+/d)
- (b) laevo (–/l)

Haloalkanes

- Preparation
  - From alcohol :

$$R\text{–}OH + HCl \xrightarrow{ZnCl_2} R\text{–}Cl + H_2O$$

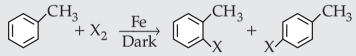
$$3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3$$

$$ROH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$$

  - From hydrocarbons :
    - (a) By free radical halogenations

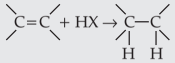
$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

    - (b) By electrophilic substitution



    - (c) Sand meyer's reaction

    - (d) From alkenes

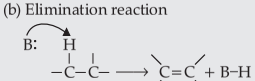


$$H_2C{=}CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2\text{–}CH_2Br$$

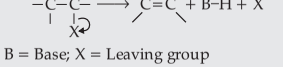
  - Halogen exchange :

$$R\text{–}X + NaI \rightarrow R\text{–}I + NaX$$

- Properties
  - Physical : Colourless, volatile, sweet smell.
    Lower members are gases at room temperature while higher are solids.
    B.P : RI > R Br > 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



    - (b) Elimination reaction



    B = Base; X = Leaving group
    - (c) Reaction with metals

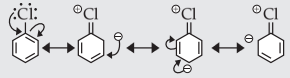
$$CH_2CH_2Br + M \longrightarrow CH_3CH_2MgBr$$

    Wurtz reaction :

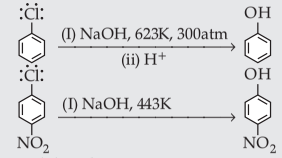
$$2RX + 2Na \xrightarrow{\text{Dry ether}} RR + 2NaX$$

Haloarenes

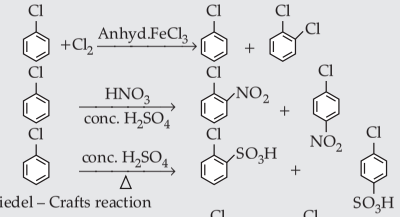
- Reactions :
  - (a) Nucleophilic substitution
    - (i) Resonance effect



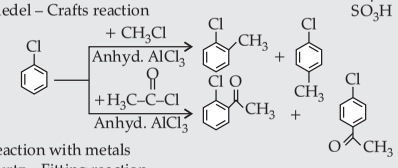
    - (ii) Hybridization of C – X bond in :
      Haloalkane –sp^3; Haloarence –sp^2
    - (iii) Phenyl cation unstabilised by resonance



  - (b) Electrophilic substitution

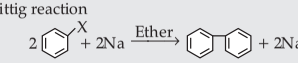


    Friedel – Crafts reaction



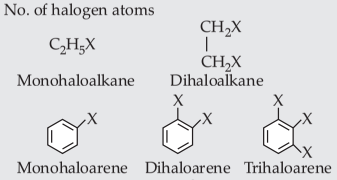
  - (c) Reaction with metals
    Wurtz – Fitting reaction

    Fittig reaction

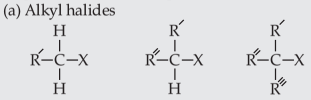


Classification

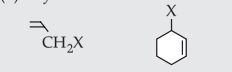
- No. of halogen atoms



- Compounds containing sp^3 C–X bond
  - (a) Alkyl halides

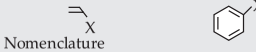


  - (b) Allylic halides



  - (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

Important Questions

Multiple Choice questions-

1. S_N1 reaction of alkyl halides lead to
(a) Retention of configuration
(b) Racemisation
(c) Inversion of configuration
(d) None of these

2. p-djchlorobenzene has higher melting point than its o- and m- isomers because
(a) p-dichlorobenzene is more polar than o- and m- isomer.
(b) p-isomer has a symmetrical crystalline structure.
(c) boiling point of p-isomer is more than o- and m-isomer.
(d) All of these are correct reasons.

3. Chloropicrin is formed by the reaction of
(a) steam on carbon tetrachloride.
(b) nitric acid on chlorobenzene.
(c) chlorine on picric acid.
(d) nitric acid on chloroform.

4. Fitting reaction can be used to prepare
(a) Toluene
(b) Acetophenon
(c) Diphenyl
(d) Chlorobenzene

5. Identify the end product (C) in the following sequence:

$$C_2H_5OH \xrightarrow[\text{Pyridine}]{SOCl_2} A \xrightarrow{KCN\ (alc.)} B \xrightarrow{2H_2O/H^+} C$$

(a) $C_2H_5CH_2NH_2$ (b) $C_2H_5CONH_2$
(c) C_2H_5COOH (d) $C_2H_5NH_2 + HCOOH$

6.

$$CH_3CH_2CH_2Cl \xrightarrow{\text{alc. KOH}} B \xrightarrow{HBr} C \xrightarrow{Na/ether} D$$

In the above reaction, the product D is
(a) Propane
(b) 2, 3-Dimethylbutane

(c) Hexane
(d) Allyl bromide

7. Identify X and Y in the following sequence

$$C_2H_5Br \xrightarrow{X} \text{Product} \xrightarrow{Y} C_3H_7NH_2$$

(a) X = KCN, Y = $LiAlH_4$
(b) X = KCN, Y = H_3O^+
(c) X = CH_3Cl, Y = $AlCl_3$ HCl
(d) X = CH_3NH_2, Y = HNO_2

8. In the following sequence of reactions:

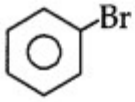
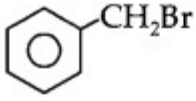
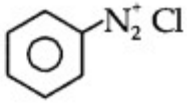
$$C_2H_5Br \xrightarrow{AgCN} X \xrightarrow{\text{Reduction}} Y;\ Y \text{ is}$$

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

9.

$$X \xrightarrow[HNO_3]{AgNO_3} \text{Yellow or While ppt}$$

Which of the following cannot be X?

(a) 
(b) $(CH_3)_3$ Cl
(c) 
(d) 

10.
Identifay Z in the series

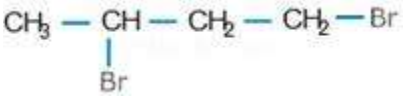
$$CH_2 = CH_2 \xrightarrow{HBr} X \xrightarrow{\text{aq. KOH}} Y \xrightarrow[I_2 \text{ excess}]{Na_2CO_3} Z$$

(a) C_2H_5I
(b) C_2H_5OH
(c) CHI_3
(d) CH_3CHO

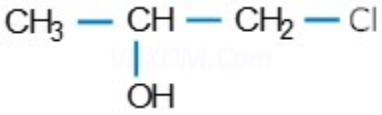
Very Short Questions-

1. Give IUPAC names of following compounds

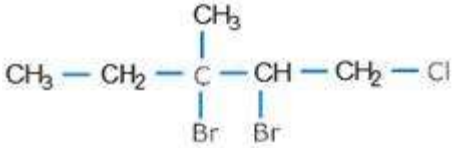
(i).



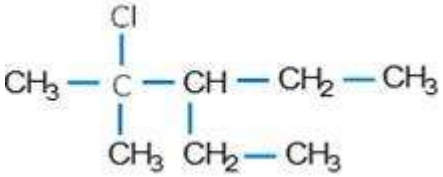
(ii).



(iii).



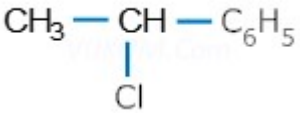
(iv).



(v).

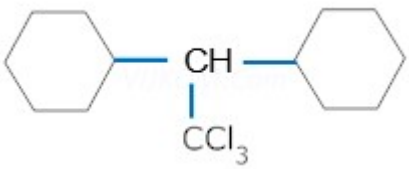
$C_6H_5CH_2CH_2Cl$

(vi).

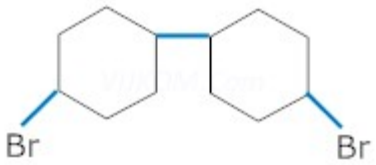


(vii). $C_6H_6Cl_6$

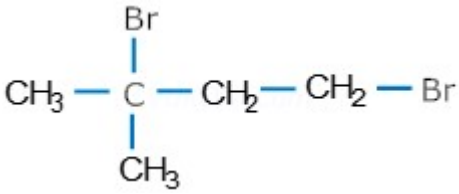
(viii).



(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-

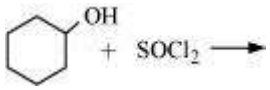
1. Write structures of the following compounds:
(i) 2-Chloro-3-methylpentane
(ii) 1-Chloro-4-ethylcyclohexane
(iii) 4-tert. Butyl-3-iodoheptane
(iv) 1,4-Dibromobut-2-ene
(v) 1-Bromo-4-sec. butyl-2-methylbenzene

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

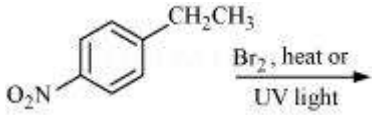
chlorination yields
(i) A single monochloride.
(ii) Three isomeric monochlorides.
(iii) Four isomeric monochlorides.

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

(i)



(ii)



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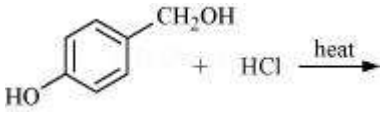

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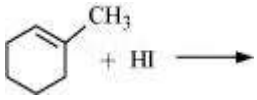
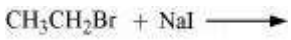
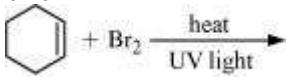


(v)



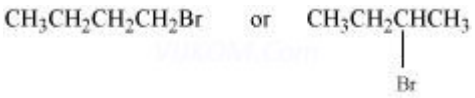
(vi)



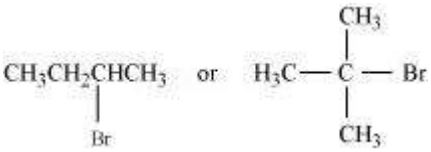
5. Arrange each set of compounds in order of increasing boiling points.
(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.
(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

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

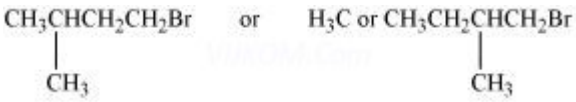
(i)



(ii)

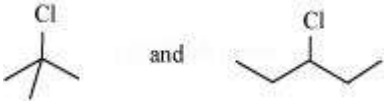


(iii)

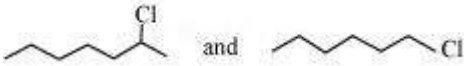


7. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

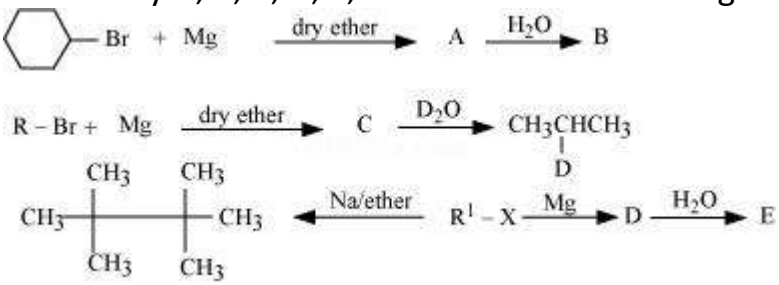
(i)



(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 CH3 Br in S_N2 reactions.

Reason: S_N2 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.

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: 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 (-NO^2) group at o/ p positions increases the reactivity of haloarenes towards nucleophilc substitution reactions.

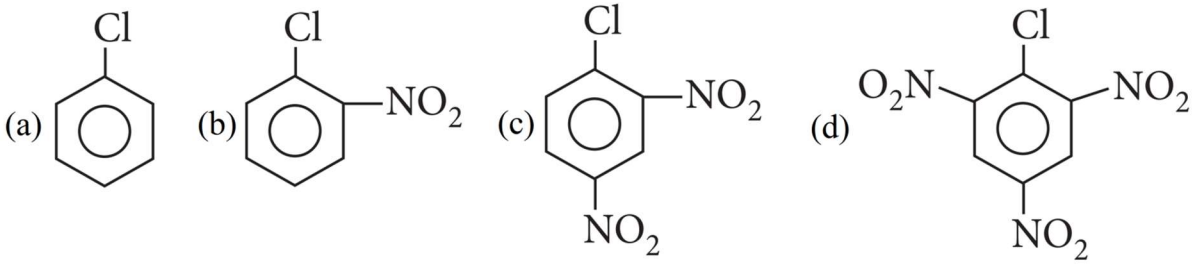
The following questions are multiple choice questions Choose the most appropriate answer:

(i) Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to

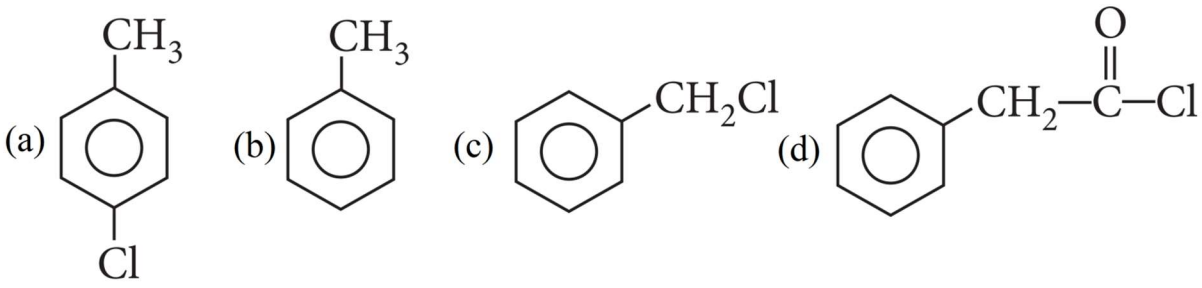
a) The formation of less stable carbonium ion.
b) Resonance stabilisation.
c) Larger carbon-halogen bond.

d) Inductive effect.

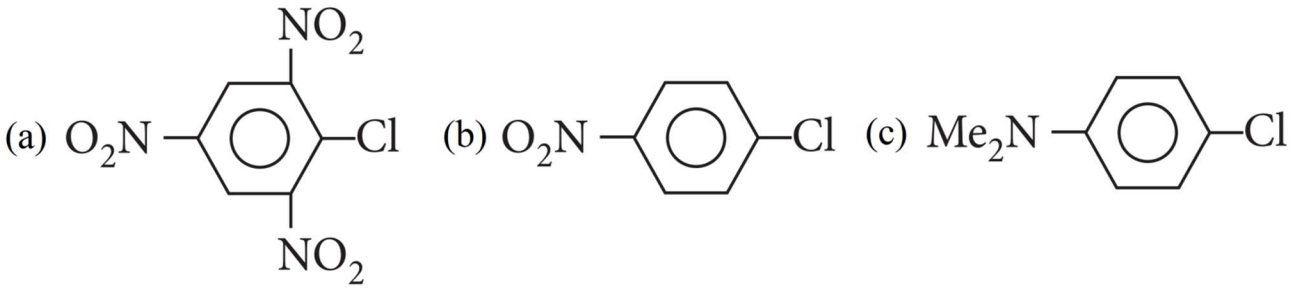
(ii) Which of the following aryl halides is the most reactive towards nucleophilic substitution?



(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) $PhCH_2Br$, (iii) MeCl, (iv) p-$MeOC_6H_4Br$ 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, C_2H_5OH gives:

a) $(CH_3)_3C\ CH_2CONH_2$
b) $(CH_3)_3C\ NH_2$
c) $(CH_3)_3C\ CH_2CH_2NH_2$
d) $(CH_3)_2CHCH_2NH_2$

(iii) The reaction of (C) with Na, C_2H_5OH 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) E_1 mechanism.
d) E_2 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- Cholopropan-2-ol
(iii). 2, 3 – Dibromo-1-chloro-3-methylpentane
(iv). 2-Choloro-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-

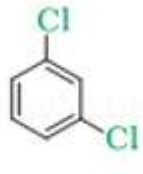
Ans 1. Thionyl chloride is preferred for converting alcohol to haloalkane because the bi-products formed are all gases which escape into the atmosphere.

$$R-OH + SOCl_2 \rightarrow RCl + SO_2 + HCl$$

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, and oxidizing agent like HNO_3 oxidizes the HI formed in the reaction and keeps the reaction in forward direction.

Ans 4.

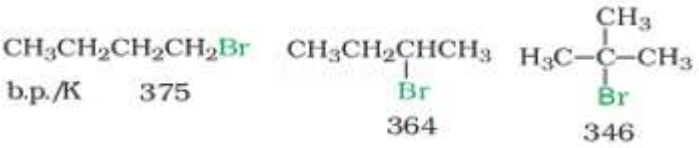


m – dichlorobenzene

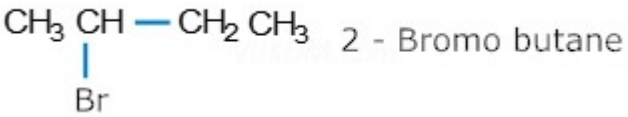
p - dichlorobenzene

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

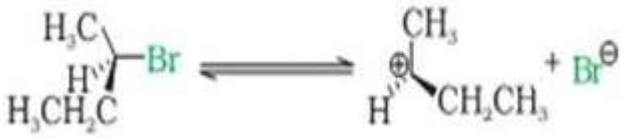
Ans 5. The boiling points of isomeric haloalkanes decreases with branching due to decrease in surface areas with branching. As branching increasing the structure becomes more spherical and the surface area decreases. e.g. the boiling points of isomers of C_4H_9Br follows the order.



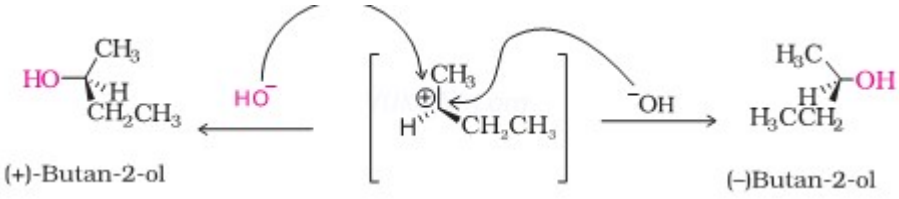
Ans 6.



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

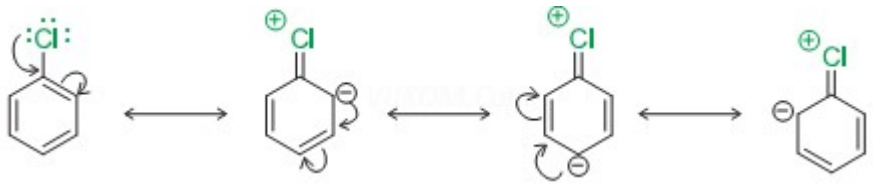


The attack of nucleophile can result in product which is a mixture of compounds both with same configuration and inverted configuration.



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 oxidsed 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.

$$2CHCl_3 + O_2 \xrightarrow[light]{} 2COCl_2 + 2HCl$$

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 –

$Cl < Br < I$

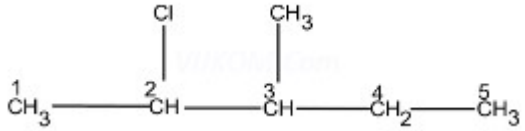
The boiling points also follow the order

RCl < RBr <RI

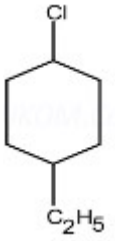
Ans 10. Due to resonance C- Cl bond gets double bond character and becomes stronger than a single bond, making vinyl chloride less reactive than allyl chloride.

Long Answers-

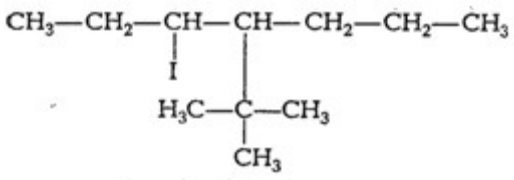
Ans 1. (i) 2-Chloro-3-methyl pentane



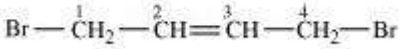
(ii) 1-Chloro-4-ethylcyclohexane



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



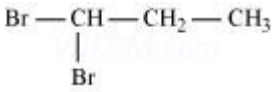
(iv) 1, 4-Dibromobut-2-ene



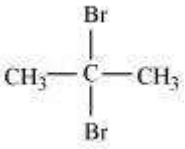
(v) 1-Bromo-4-sec-butyl-2-methylbenzene

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

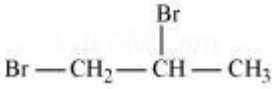
(i) 1, 1-Dibromopropane



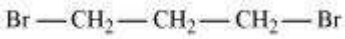
(ii) 2, 2-Dibromopropane



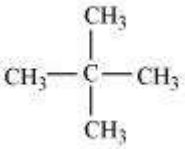
(iii) 1, 2-Dibromopropane



(iv) 1, 3-Dibromopropane

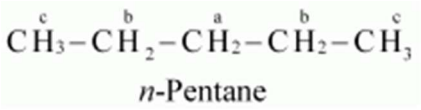


Ans 3. (i) To have a single monochloride, there should be only one type of H-atom in the isomer of the alkane of the molecular formula C_5H_{12}. This is because, replacement of any H-atom leads to the formation of the same product. The isomer is neopentane.



Neopentane

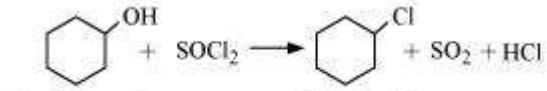
(ii) To have three isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain three different types of H-atoms.
Therefore, the isomer is *n*-pentane. It can be observed that there are three types of H atoms labelled as *a*, *b* and *c* in *n*-pentane.



n-Pentane

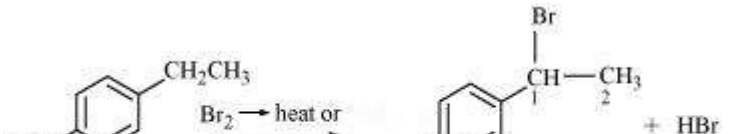
(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12}should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of H-atoms labelled as *a*, *b*, *c,* and *d* in 2-methylbutane.

Ans 4. (i)



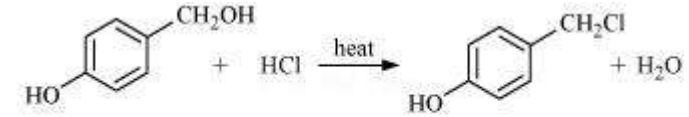
Cyclohexanol Chlorocyclohexane

(ii)



4 – Ethylnitrobenzene 4 – (1 – Bromoethyl) nitrobenzene

(iii)



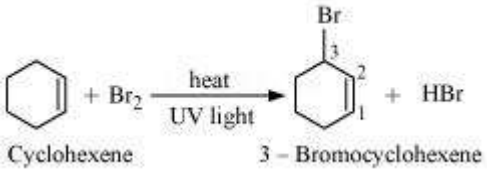
4 – Hydroxymethylphenol 4 – Chloromethylphenol

(iv)

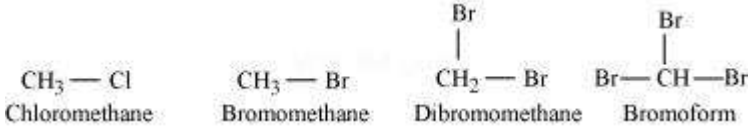
1 – Methylcyclohexene 1 – Iodo – 1 – methylcyclohexane

(v)

(vi)

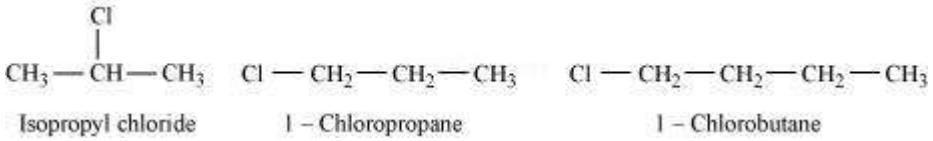


Ans 5. (i)



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.

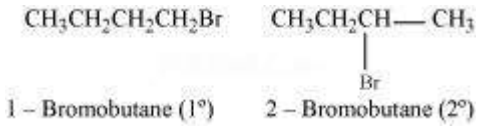
(ii)



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

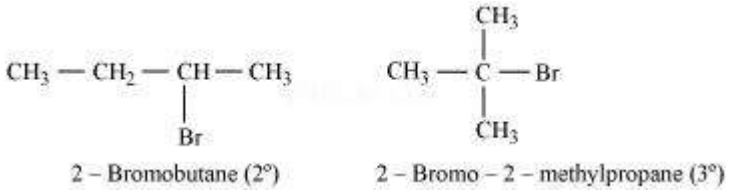
points as:
Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

Ans 6. (i)



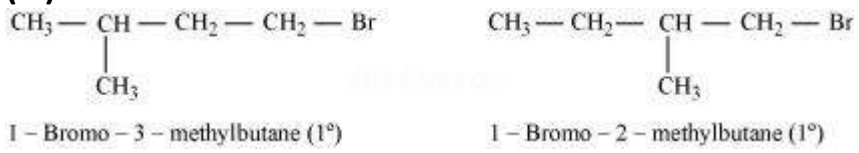
2-bromobutane is a 2° alkylhalide whereas 1-bromobutane is a 1° alkyl halide. The approaching of nucleophile is more hindered in 2-bromobutane than in 1-bromobutane. Therefore, 1-bromobutane reacts more rapidly than 2-bromobutane by an S_N2 mechanism.

(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.

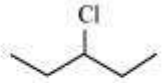
(iii)



Both the alkyl halides are primary. However, the substituent $-CH_3$ 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.

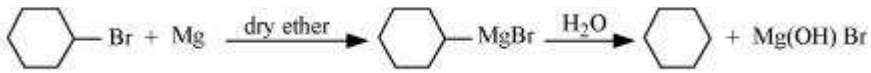
(ii)

2 – chloroheptane (2°)
(I)

1 – chlorohexane (1°)
(II)

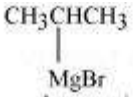
The alkyl halide (I) is 2° while (II) is 1°. 2° carbocation is more stable than 1° carbocation. Therefore, (I), 2-chloroheptane, undergoes faster S_N1 reaction than (II), 1-chlorohexane.

Ans 8.



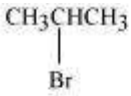
Bromocydohexane — Cyclohexylmagnesium bromide (A) — Cyclohexane (B)

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

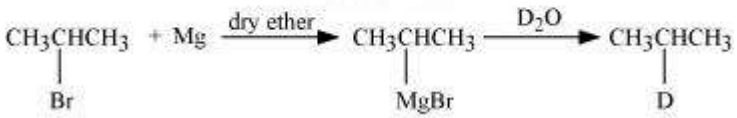


Isopropylmagnesium bromide

Therefore, the compound R – Br is

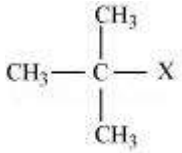


2 – Bromopropane



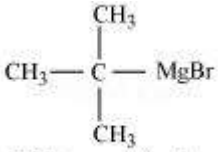
(C)

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



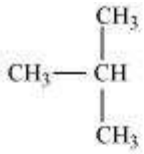
tert – Butylhalide

Therefore, compound D is

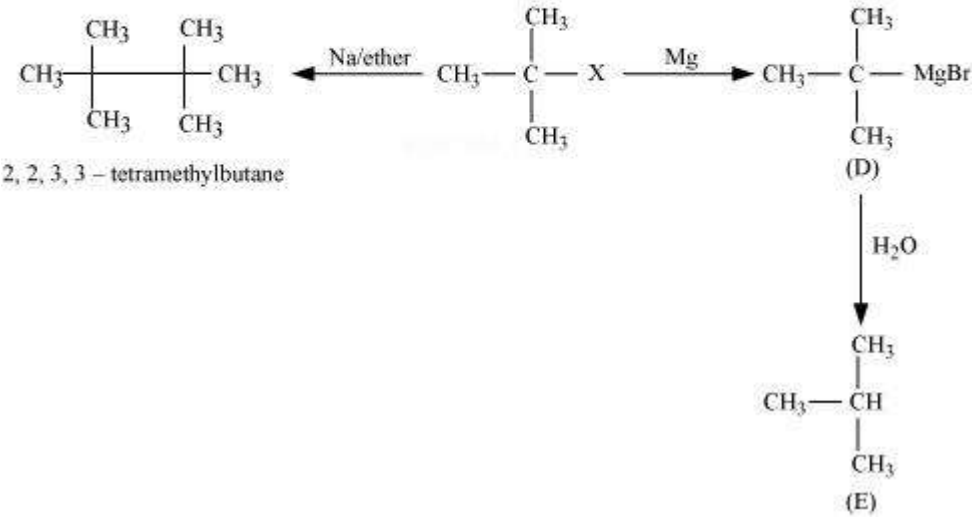


tert – Bulytmagnesiumbromide

And, compound E is



2 – Methylpropane



2, 2, 3, 3 – tetramethylbutane

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 $(CH_3)_2CHCl$.

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

Explanation:

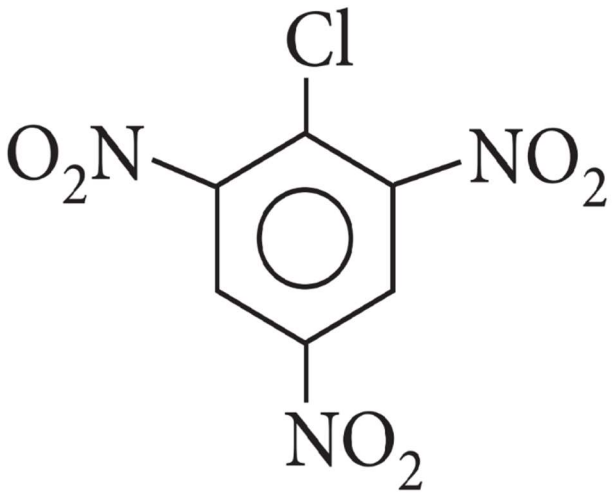
Alkyl iodides in general turn brown due to liberation of I^2 on decomposition by the action of air and light.

Case Study Answers-

1. Answer :

(i) (b) Resonance stabilisation.

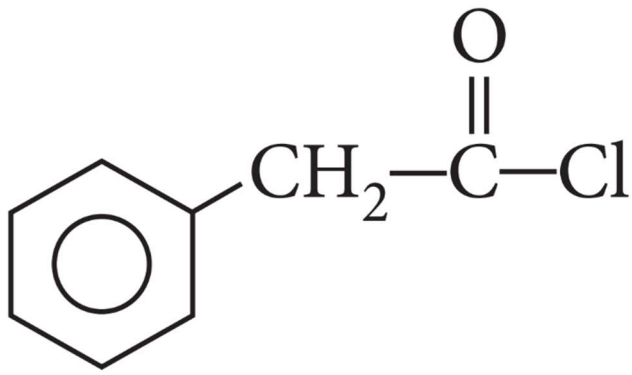
(ii) (d)



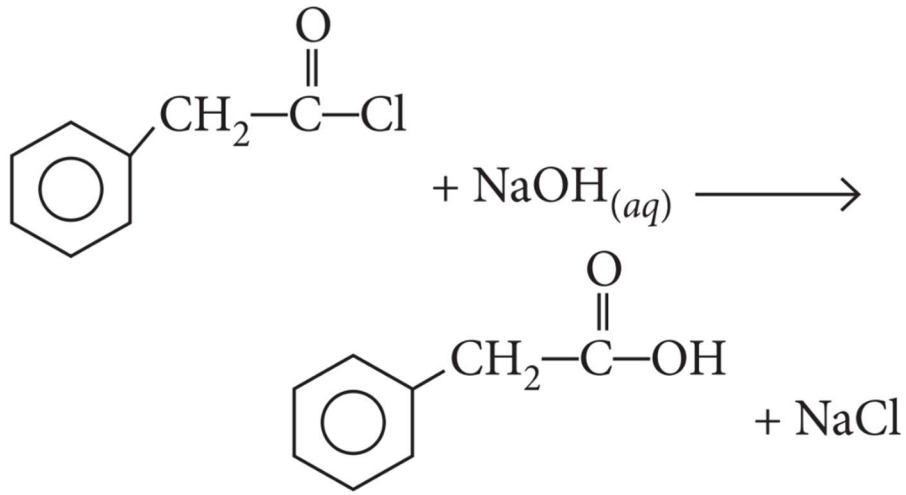
Explanation:

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 Cll- ion becomes easy, therefore, 2,4,6-trinitro chlorobenzene is the most reactive among given aryl halides.

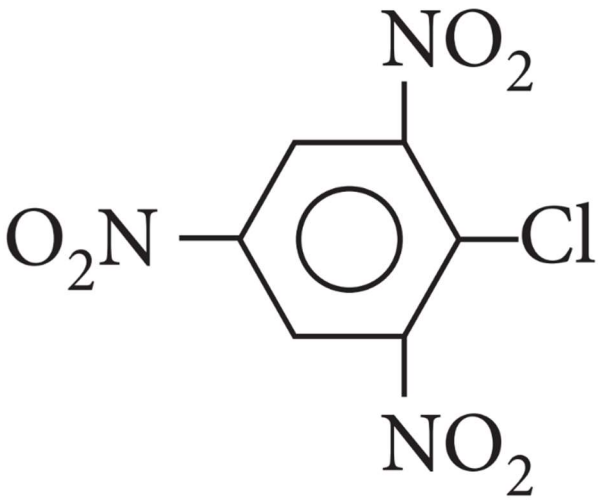
(iii) (d)



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)

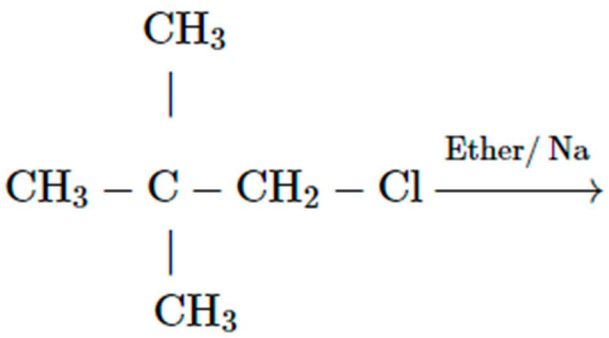
Explanation:

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 - $MeOC_6H_4Br$ (iv).

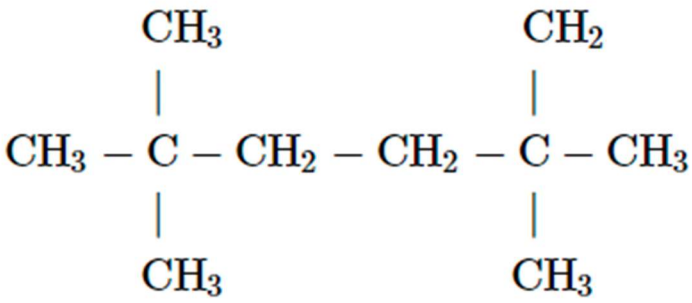
2. Answer :

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

Explanation:



I -Chloro-2, 2-di methylpropane



2, 2, 5, 5-Tetramethylhexane

ii. (c) $(CH_3)_3C\ CH_2CH_2NH_2$

Explanation:

$$\begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ CH_3 - C - CH_2Cl \xrightarrow{\text{alc.KCN}} \\ \quad\quad | \\ \quad\quad CH_3 \end{array}$$

$$\begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ CH_3 - C - CH_2CN \xrightarrow{Na/C_2H_5OH} \\ \quad\quad | \\ \quad\quad CH_3 \end{array}$$

$$\begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ CH_3 - C - CH_2CH_2NH_2 \\ \quad\quad | \\ \quad\quad CH_3 \end{array}$$

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

Explanation: