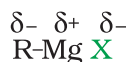




Victor Grignard had a strange start in academic life for a chemist - he took a maths degree. When he eventually switched to chemistry, it was not to the mathematical province of physical chemistry but to organic chemistry. While attempting to find an efficient catalyst for the process of methylation, he noted that Zn in diethyl ether had been used for this purpose and wondered whether the Mg/ether combination might be successful. Grignard reagents were first reported in 1900 and Grignard used this work for his doctoral thesis in 1901. In 1910, Grignard obtained a professorship at the University of Nancy and in 1912, he was awarded the Nobel prize for Chemistry which he shared with Paul Sabatier who had made advances in nickel catalysed hydrogenation.

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium halogen bond is essentially ionic.



Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols, amines are sufficiently acidic to convert them to corresponding hydrocarbons.



It is therefore necessary to avoid even traces of moisture from a Grignard reagent. That is why reaction is carried out in dry ether. On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

Wurtz reaction

Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction (Unit 13, Class XI).

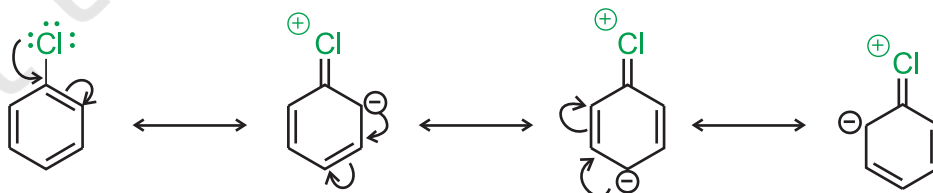


10.7.2 Reactions of Haloarenes

1. Nucleophilic substitution

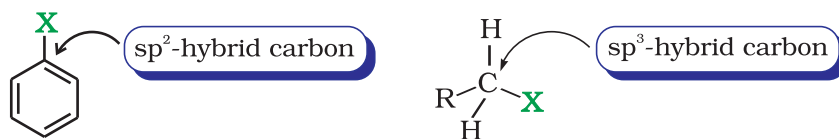
Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

- (i) *Resonance effect* : In haloarenes, the electron pairs on halogen atom are in conjugation with π -electrons of the ring and the following resonating structures are possible.



C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

- (ii) *Difference in hybridisation of carbon atom in C—X bond:* In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2 -hybridised.

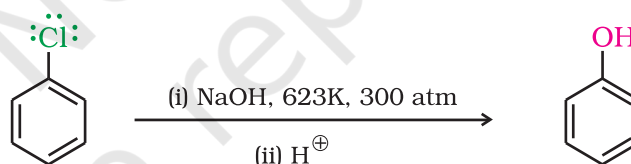


The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3 -hybridised carbon in haloalkane with less s-character. Thus, C—Cl bond length in haloalkane is 177pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

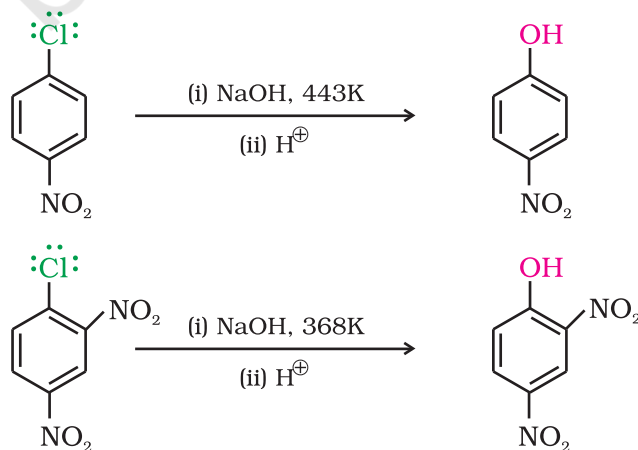
- (iii) *Instability of phenyl cation:* In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out.
- (iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

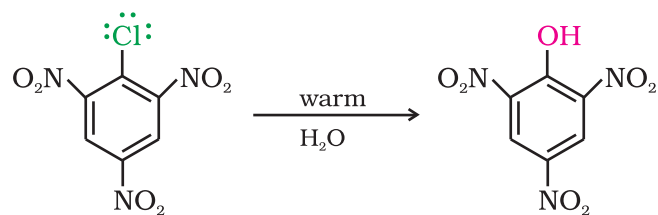
Replacement by hydroxyl group

Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres.

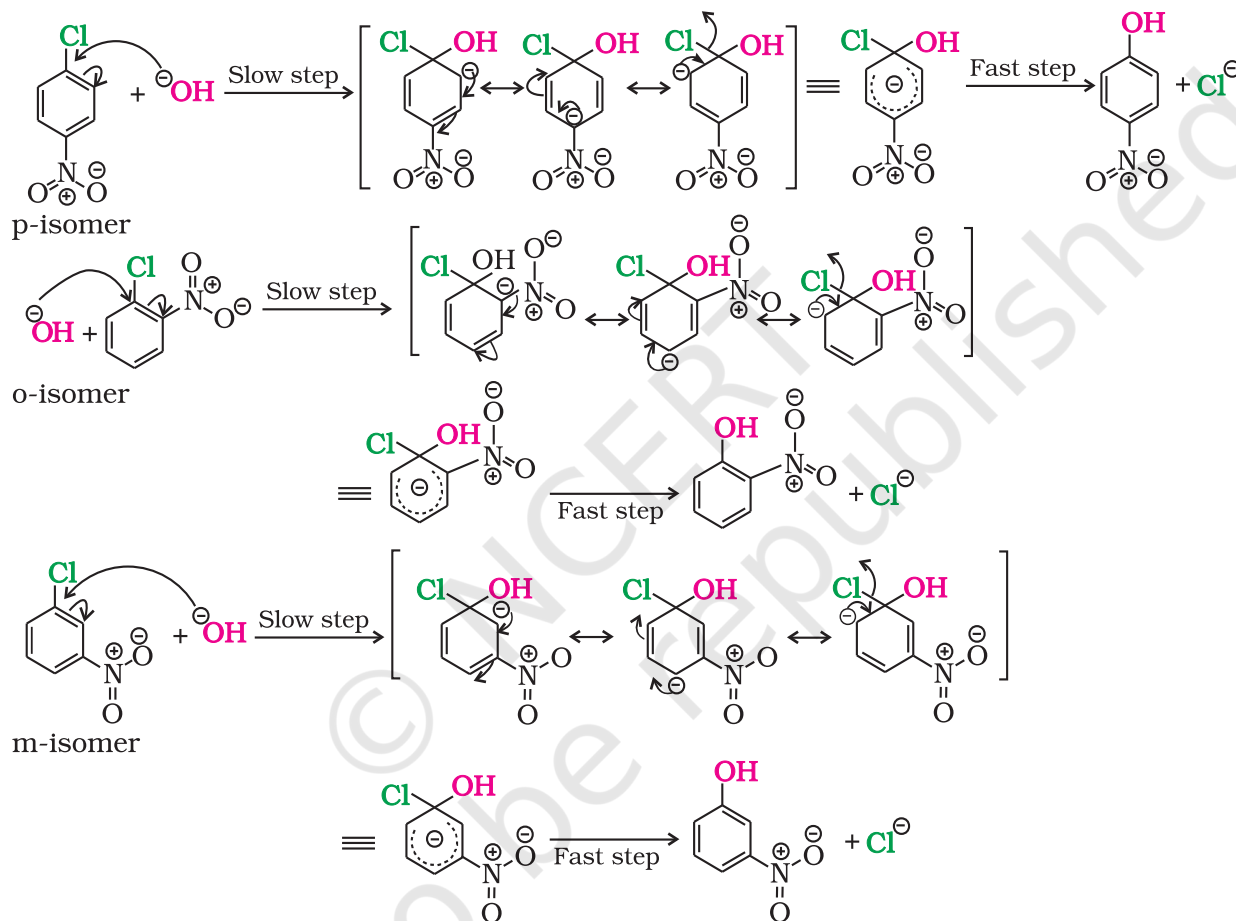


The presence of an electron withdrawing group ($-NO_2$) at *ortho*- and *para*-positions increases the reactivity of haloarenes.





The effect is pronounced when (-NO₂) group is introduced at *ortho*- and *para*- positions. However, no effect on reactivity of haloarenes is observed by the presence of electron withdrawing group at *meta*-position. Mechanism of the reaction is as depicted:

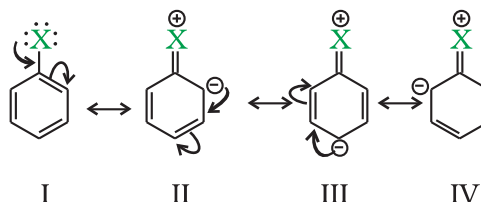


Can you think why does NO₂ group show its effect only at *ortho*- and *para*- positions and not at *meta*- position?

As shown, the presence of nitro group at *ortho*- and *para*-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho*- and *para*- positions with respect to the halogen substituent is stabilised by -NO₂ group while in case of *meta*-nitrobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the -NO₂ group. Therefore, the presence of nitro group at *meta*- position does not stabilise the negative charge and no effect on reactivity is observed by the presence of -NO₂ group at *meta*-position.

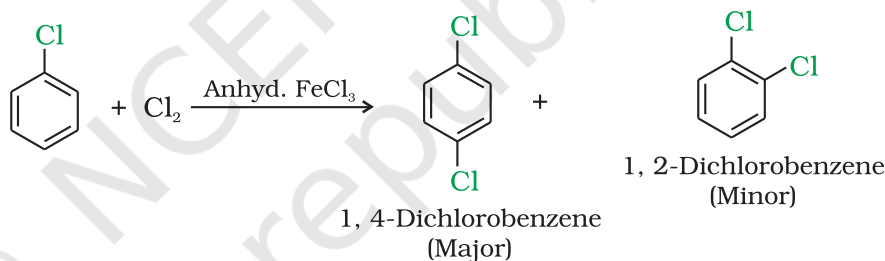
2. Electrophilic substitution reactions

Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. Halogen atom besides being slightly deactivating is *o*, *p*-directing; therefore, further substitution occurs at *ortho*- and *para*-positions with respect to the halogen atom. The *o*, *p*-directing influence of halogen atom can be easily understood if we consider the resonating structures of halobenzene as shown:

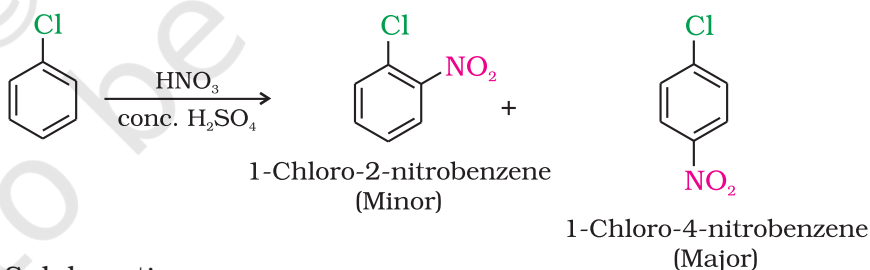


Due to resonance, the electron density increases more at *ortho*- and *para*-positions than at *meta*-positions. Further, the halogen atom because of its $-I$ effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

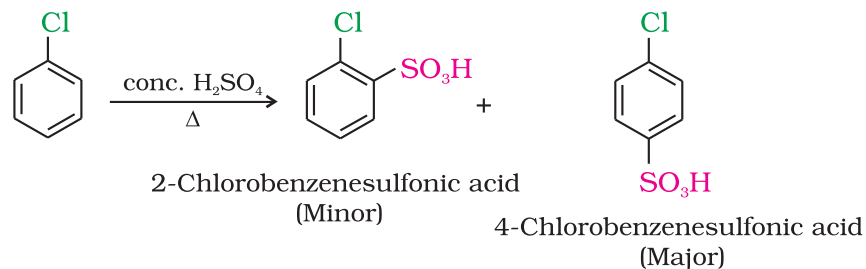
(i) Halogenation



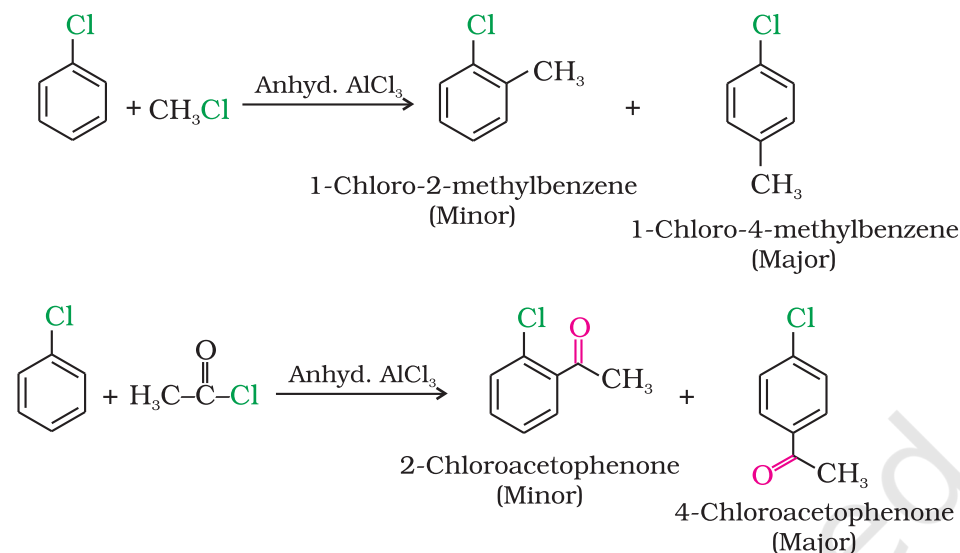
(ii) Nitration



(iii) Sulphonation



(iv) Friedel-Crafts reaction

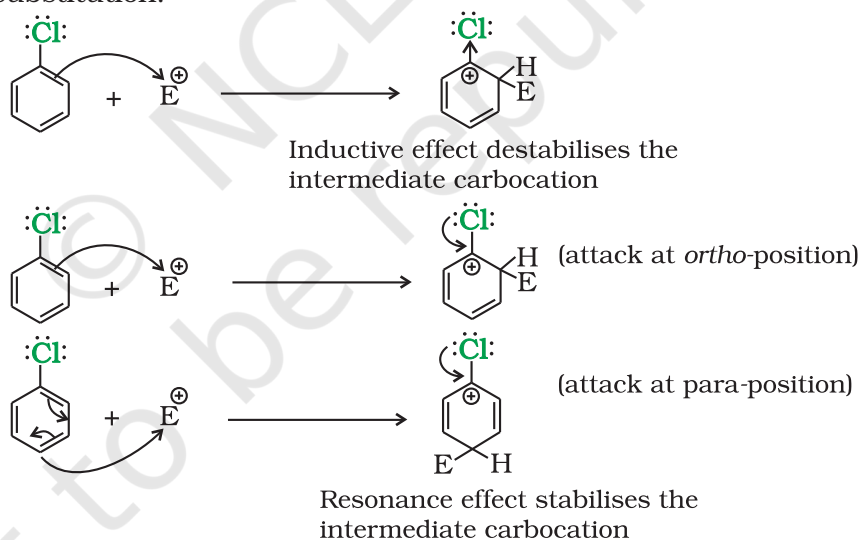


Example 10.9

Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*- directing in electrophilic aromatic substitution reactions. Why?

Solution

Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.

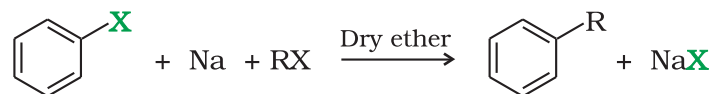


Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at *ortho*- and *para*- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *ortho*- and *para*- positions and hence makes the deactivation less for *ortho*- and *para*- attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

3. Reaction with metals

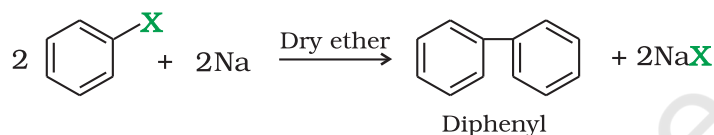
Wurtz-Fittig reaction

A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.



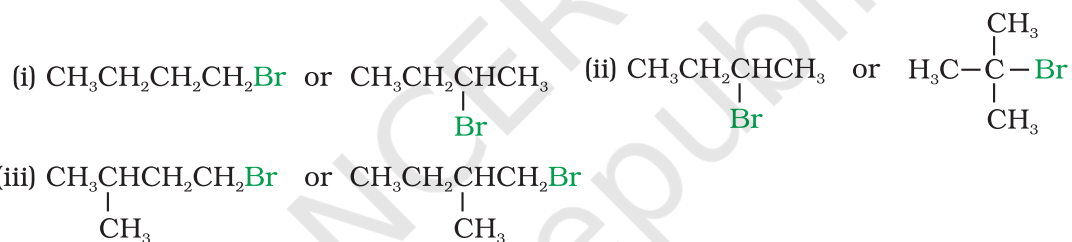
Fittig reaction

Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.

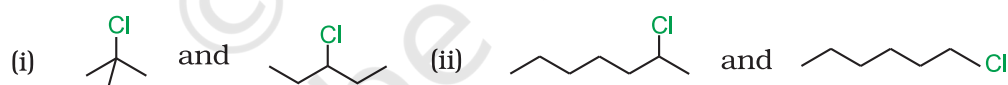


Intext Questions

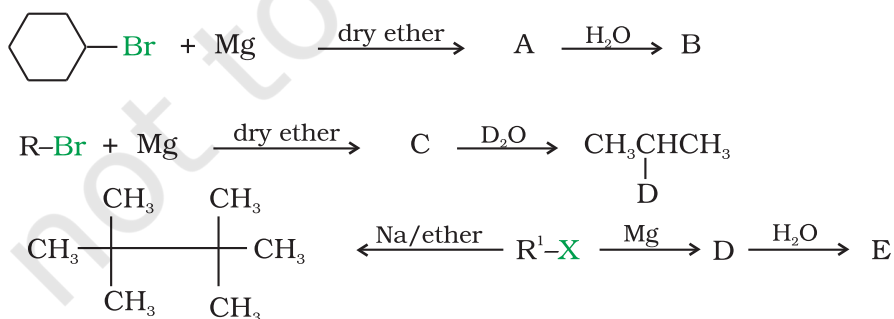
10.7 Which alkyl halide from the following pairs would you expect to react more rapidly by an $\text{S}_{\text{N}}2$ mechanism? Explain your answer.



10.8 In the following pairs of halogen compounds, which compound undergoes faster $\text{S}_{\text{N}}1$ reaction?



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



10.8 Polyhalogen Compounds

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture. Some polyhalogen compounds are described in this section.

10.8.1 Dichloromethane (Methylene chloride)

Dichloromethane is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent. Methylene chloride harms the human central nervous system. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision. Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

10.8.2 Trichloromethane (Chloroform)

Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the freon refrigerant R-22. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, safer anaesthetics, such as ether. As might be expected from its use as an anaesthetic, inhaling chloroform vapours depresses the central nervous system. Breathing about 900 parts of chloroform per million parts of air (900 parts per million) for a short time can cause dizziness, fatigue, and headache. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys, and some people develop sores when the skin is immersed in chloroform. Chloroform is slowly oxidised by air 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 completely filled so that air is kept out.



10.8.3 Triiodomethane (Iodoform)

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. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

10.8.4 Tetrachloromethane (Carbon tetrachloride)

It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use. 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 as fire extinguisher. There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells. 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. 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. Depletion of the

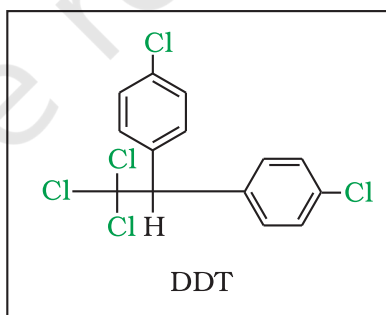
ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

10.8.5 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. Freon 12 (CCl_2F_2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by **Swarts reaction**. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. By 1974, total freon production in the world was about 2 billion pounds annually. Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance (Unit 14, Class XI).

10.8.6 *p,p'*-Dichlorodiphenyl-trichloroethane(DDT)

DDT, the first chlorinated organic insecticides, was originally prepared in 1873, but 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. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish. 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.



Summary

Alkyl/ Aryl halides may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge, and the halogen atom bears a partial negative charge.

Alkyl halides are prepared by the **free radical halogenation** of alkanes, addition of halogen acids to alkenes, replacement of $-\text{OH}$ group of alcohols with halogens using