Electrophilic substitution reactions: Aryl halides undergo usual electrophilic substitution reactions, but these areless reactive than benzene because of deactivating effect of halogens. Halogens are o, p-directing, thus a mixture of o and p-products are obtained, in which p-isomer predominates due to steric effect.

Some of common examples of electrophilic substitution reactions are as follows :

Cl Cl₂'+ Anhyd, AlCl₃
or FeCl₃

Halogenation

Cl Cl
CH₃Cl +
Anhyd, AlCl₃
Friedel-Crafts
alkylation

Cl
CH₃COClor
(CH₃CO)₂O
+ Anhyd, AlCl₃
Friedel-Crafts acylation

COCH₃

Conc. HNO₃ +
Conc. HNO₃ +
Conc. H₂SO₄,
$$\Delta$$
Nitration

Cl
Conc. H₂SO₄ + SO₃,
A
Sulphonation

Cl
Cl
Cl
COCH₃
COCH

➤ Fittig reaction: Aryl halides react with sodium metal in dry ether to give biphenyls. The reaction is similar to Wurtz reaction of alkyl halides.

> Wurtz-Fittig reaction: When a mixture of aryl halide and alkyl halide reacts with sodium metal in dry ether, substituted arenes are obtained.

$$-\text{C1} + 2\text{Na} + \text{C1} - \text{CH}_3 \xrightarrow{\text{Dry ether}} -\text{CH}_3 + 2\text{NaCl}$$

> **Ullmann reaction :** Aryl halides especially iodides on reaction with copper metal yield biphenyls.

> Reduction: Aryl halides can be reduced to benzene.

$$CI + 2[H] \xrightarrow{N_1 - AI + N_3OH} + CI$$

Reaction with chloral: Chlorobenzene on reaction with chloral in presence of conc. H₂SO₄ yield DDT.

C1-
$$\bigcirc$$
-H
+ O=CH-CCl₃
Conc. H₂SO₄
C1- \bigcirc -CH-CCl₃
C1- \bigcirc -CH-CCl₃
C1- \bigcirc -CH-CCl₃

POLYHALOGEN COMPOUNDS

- Dihalogens obtained by replacing two hydrogen atoms by halogens.
 - Vicinal dihalides or alkylene halides: When two halogen atoms are attached to different carbon atoms.
 e.g. CH₂ CH₂Br.
 - > Geminal dihalides or alkylidene halides: When two halogen atoms are attached to same carbon atom. e.g. CH₃-CH₂Cl₂.

Trihalogen Derivatives

Chloroform(CHCl₃)

Preparation

Properties

CHCl₃

CHCl₃

$$C_2H_5NH_2$$
 C_2H_5NC
 C_2H_5NC
 C_2H_5NC
 C_2H_5NC
 C_2H_5NC
 C_2H_5NC
 C_2H_5NC
 C_2H_5NC
 C_2H_5NC
 C_2H_5NC

Iodoform (CHI,)

Preparation CH₃CH₂OH + I₂ + NaOH --→ CHI₃ + HCOONa

Properties: Compounds containing CH₃CO – group give yellow ppt of iodoform with sodium hypohalite.
 CH₃COCH₃ + NaOH + I₂ — CHI₃ + CH₃COONa

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Uses and Environmental Effects of Some Important Polyhalogen Compounds

Name	Uses	Environmental effects
1. Dichloromethane (CH ₂ Cl ₂)	As a solvent in a paint remover. An effective solvent for extraction in pharmaceutical in the manufacturing of drugs and food industries. As a propellant in aerosols. As refrigerant and dewaxing agent.	Have harmful effects on the human central nervous system. Cause dizziness, nausea, tingling and numbness in the fingers and the toes. Direct contact with the eyes can even bum the comea.
2. Trichloromethane or Chloroform (CHCl ₃)	As an important solvent particularly for fats, alkaloids, iodine, waxes, rubber, etc. As an anaesthetic. As a laboratory reagent. Used in medicines. In the production of freon of refrigerant.	Breathing of chloroform for a short time causes dizziness, fatigue and headache. May damage liver and kidneys because chloroform is metabolised to poisonous phosgene. The use of chloroform as an anaesthetic has been replaced by less toxic and safer anaesthetic such as ether.
3. Tetrachloromethane (CCl ₄)	In large quantities in the manufacture of refrigerants and propellants for aerosol cans. As a feedstock in the sysnthesis of chlorofluorocarbons. As a solvent for the manufacture of pharmaceuticals and oils, fats, waxes, etc.	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. When carbon tetrachloride is released into air, it rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer increases the human exposure to ultraviolet radiations which may lead to increase skin cancer, eye diseases and disorders and possible disruption of the immune system.
4. Tri-iodomethane (CHI ₃)	As an antiseptic and this nature is due to free iodine that it liberates and not due to iodoform itself. In the manufacture of pharmaceuticals.	Causes nausea, vomiting. Irritating to mucous membranes and respiratory system. May cause eye irritation.
5. Freons (Chloroflouro carbons)	As refrigerants in refrigerators and air conditioners and hence is the name freons. As propellants for aerosols and foams to spray out deodorants, cleansers, shaving creams, hair sprays and insecticides.	In stratosphere, freons undergo photochemical decomposition and initiate radical chain reactions and deplete the protective ozone layer surrounding our earth. Therefore, the use of freons as propellants and refrigerants has been drastically discouraged. It has also been banned in many countries.
6. DDT (Dichloro diphenyl trichloroethane) Cl ₃ C — HC	It is widely used as an insecticide for killing mosquitoes and other insects.	D.D.T. was formed to have high toxicity towards fish. D.D.T. is not biodegradable. Its residues accumulate in environment and its long term effects could be highly dangerous. D.D.T. is not metabolised very rapidly by animals rather it gets deposited and stored in fatty tissues.