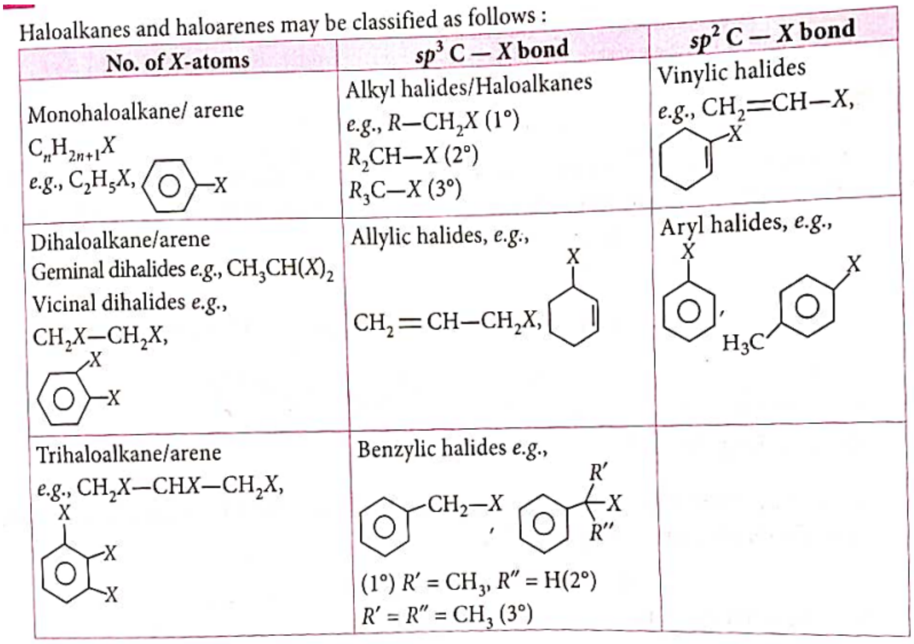
10. Haloalkanes and Haloarenes

10.1 Introduction

- Haloalkane – compound obtained from alkane by the replacement of hydrogen by halogen. Halogen is attached to the SP^3 hybridized carbon.
- Haloarene – hydrogen atom of benzene ring is substituted by a halogen. Halogen is attached to the SP^2 hybridized carbon.

10.2 Classification



Haloalkanes and haloarenes may be classified as follows :

No. of *X*-atoms	sp^3 C — *X* bond	sp^2 C — *X* bond
Monohaloalkane/ arene $C_nH_{2n+1}X$ *e.g.*, C_2H_5X,	Alkyl halides/Haloalkanes *e.g.*, $R—CH_2X$ (1°) $R_2CH—X$ (2°) $R_3C—X$ (3°)	Vinylic halides *e.g.*, $CH_2{=}CH—X$,
Dihaloalkane/arene Geminal dihalides *e.g.*, $CH_3CH(X)_2$ Vicinal dihalides *e.g.*, $CH_2X—CH_2X$,	Allylic halides, *e.g.*, $CH_2{=}CH—CH_2X$,	Aryl halides, *e.g.*,
Trihaloalkane/arene *e.g.*, $CH_2X—CHX—CH_2X$,	Benzylic halides *e.g.*, (1°) $R' = CH_3$, $R'' = H$(2°) $R' = R'' = CH_3$ (3°)	

10.3 Nomenclature

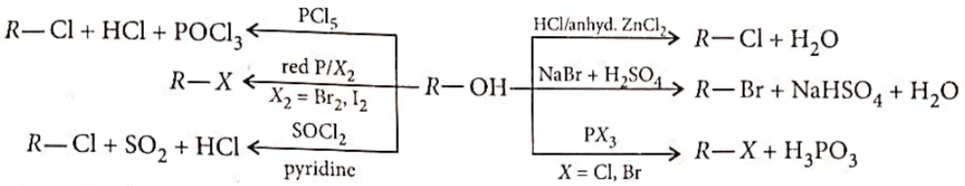
- Common name: alkylhalide
- IUPAC name: haloalkane
- For monohalogen derivatives of benzene, common and IUPAC names are the same. For dihalogen derivatives, the prefixes o-, m-, p- are used in common names; the numerals 1,2 1,3 and 1,4 are used in IUPAC system.
- Dihaloalkanes are classified as geminal (X on the same C) and vicinal halides (X present on the adjacent C). gem-dihalides are named as alkylidene halide and vic-dihalides as alkylene dihalides. In IUPAC system, they are named as dihaloalkanes.

10.4 Nature of C-X bond

- X is more electronegative than C making the C-X bond polar (dipole moment = 1.8). Varies irregularly in a group because in a group the size of halogens increases down the group and electronegativity decreases.
- With increase in size of halogen atom, bond length increases and bond enthalpy decreases.

10.5 Methods of preparation of Haloalkanes

From Alcohols



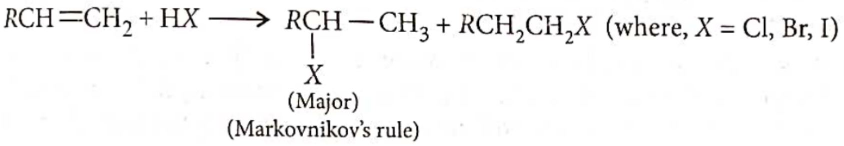
The order of reactivity of alcohols with a given haloacid is $3^0 > 2^0 > 1^0$

From Hydrocarbons

- **By free radical halogenation :**

$$CH_4 + Cl_2 \xrightarrow[\text{or heat}]{\text{UV light}} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$$

- The ease of replacement of hydrogen follows the order : 3° > 2° > 1°
- **By electrophilic addition of HX to alkene :**



$$RCH{=}CH_2 + HX \longrightarrow \underset{\substack{\text{(Major)}\\ \text{(Markovnikov's rule)}}}{\underset{X}{\underset{|}{RCH}}-CH_3} + RCH_2CH_2X \text{ (where, } X = \text{Cl, Br, I)}$$

$$RCH{=}CH_2 + HBr \xrightarrow{\text{Peroxide}} RCH_2-CH_2Br \text{ (Anti-Markovnikov's rule)}$$

- **By addition of halogens to alkene :**

$$CH_2{=}CH_2 + Br_2 \xrightarrow{CCl_4} \underset{\textit{Vic}\text{-dibromide}}{BrCH_2-CH_2Br}$$

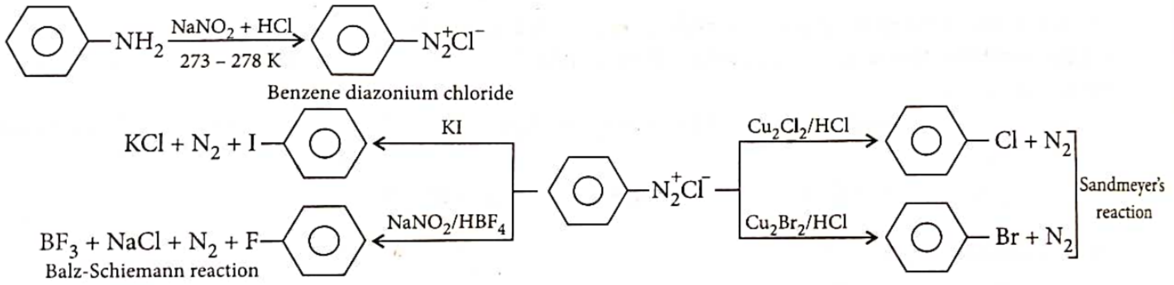
Halogen Exchange

- **Finkelstein reaction :** $R-X + NaI \xrightarrow{\text{dry acetone}} R-I + NaX$ (Where, X = Cl, Br)
  - NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's principle.
- **Swarts reaction :** $\underset{(X = \text{Cl, Br})}{RX} + \underset{\substack{(\text{or } Hg_2F_2 \text{ or}\\ CoF_2 \text{ or } SbF_3)}}{AgF} \longrightarrow RF + AgX$

10.6 Preparation of Haloarenes

- Aryl chlorides and bromides are prepared by electrophilic substitution of arenes with Cl_2 or Br_2 in the presence of Lewis acid catalyst like Fe or $FeCl_3$
- Mono substituted arenes produce ortho or para haloarenes depending on the nature of the substituent. The Ortho and para isomers can be easily separated due to large difference in their melting points.

From Benzene Diazonium Chloride



10.7 Physical properties

- Alkyl halides are colourless when pure. Bromides and iodides develop colour when exposed to light.
- Lower members are gases while higher members are either liquids or solids.
- Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction are stronger in alkyl or aryl halides. So, have higher boiling point compared to parent hydrocarbon.
- For the same alkyl group, the boiling points of alkyl halides decrease in the order: RI > RBr > RCl > RF. With increase in size of halogen atom the intermolecular forces increase.
- The boiling points of isomeric haloalkanes decrease with increase in branching.
- The para dihalobenzene have higher melting point compared to their ortho and meta isomers. Due to high symmetry of p – isomer that fits in crystal lattice better as compared to ortho- and meta- isomers.
- They are denser than water and the density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.

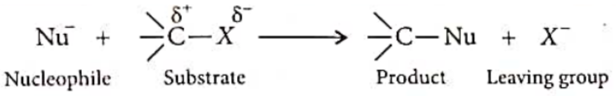
- Very slightly soluble in water but more soluble in organic solvents due to similar intermolecular force of attraction.

10.7 Chemical reactions

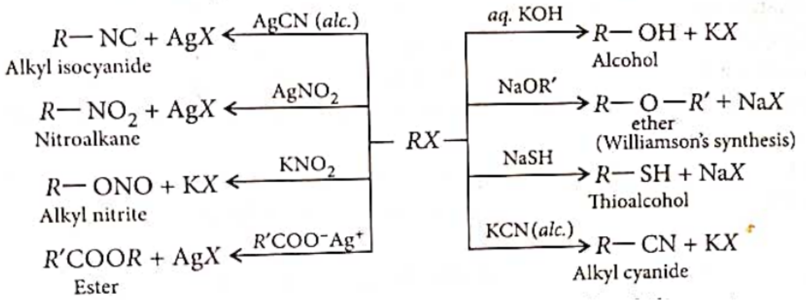
- Divided into 3 main categories: (i) Nucleophilic, (ii) Elimination and (iii) Reaction with metals

10.7a Nucleophilic substitution

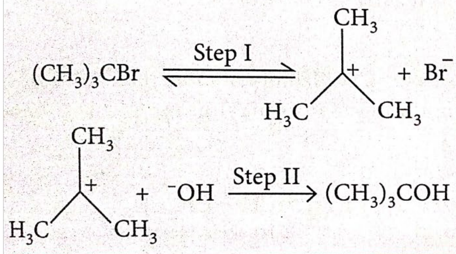
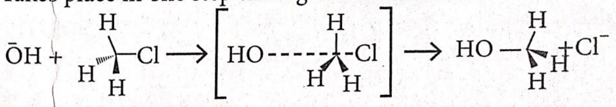
- The polarity of C – X bond is responsible for the nucleophilic substitution reactions



Some of the nucleophilic substitution reactions of haloalkanes are



- Groups like cyanides and nitrites is a hybrid of two contributing structures and therefore can act as a nucleophile in two different ways ($^{-}C \equiv N \leftrightarrow :C \equiv N^{-}$), i.e., linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides. Similarly, nitrite ion also represents an ambident nucleophile [$^{-}$O-N=O]. The linkage through oxygen results in alkyl nitrite while through nitrogen atom, it leads to nitroalkane.
- The nucleophilic substitution can proceed via S_N1 or S_N2 mechanism.
- For a given alkyl group, the reactivity of the halide, R-X, follows the same order in both the mechanisms. R-I > R-Br > R-Cl > R-F

Unimolecular (S_N1)	**Bimolecular (S_N2)**
It is first order reaction.	It is second order reaction.
Generally carried out in polar protic solvents like water, alcohol and acetic acid.	Carried out in polar aprotic solvents like acetone, DMSO, acetonitrile or DMF.
Takes place in two steps through carbocation as the intermediate. 	Takes place in one step through transition state. 
Rate of reaction : 3° > 2° > 1° > $^{+}CH_3$ (fastest) (slowest) Greater the stability of carbocation, faster will be the reaction.	Rate of reaction : CH_3 > 1° > 2° > 3° halides (fastest) (slowest) Less the steric hindrance in transition state, faster will be the reaction.
Tends to proceed with weak nucleophiles, e.g., CH_3OH, H_2O, CH_3CH_2OH, etc.	Tends to proceed with strong nucleophiles, e.g., CH_3O^-, CN^-, OH^-, etc.
Configuration is retained but in front attack inversion takes place (racemisation and inversion).	Inversion of configuration takes place (Walden inversion).

To draw any nucleophilic substitution product:

- Find the sp^3 hybridized carbon with the leaving group.
- Identify the nucleophile, the species with a lone pair or π bond.

- Substitute the nucleophile for the leaving group

- Optical activity - the ability of a substance to rotate the plane of polarization of a beam of light towards the right (clockwise) or towards the left (anticlockwise) that is passed through it.
- dextro isomer rotates the light to the right (In Latin dexter means right) (d – form or +ve)
- laevo isomer rotates the light to the left (in Latin laevo mean left) (*l*-form or -ve)
- Enantiomer or d and l isomer(in Greek enantion, means "opposite") – optical isomers which are non-superimposable mirror images (or dissymmetric). They have similar physical, chemical properties. Two enantiomers rotate plane-polarized light to an equal extent but in the opposite direction.
- Diastereomers – optical isomers which are not mirror images of each other. They have different physical properties and
- racemic mixture - An equimolar mixture of the d and l form and is optically inactive (dl form or (±) form)
- racemisation – The process of conversion of an enantiomer into racemic mixture.
- Resolution – The process of separating a racemic mixture into individual enantiomers.
- Chirality – A compound is said to have chirality if the central atom is attached to four different groups and this centre is called chiral centre (asymmetric/stereogenic/streo centre)
- Mesocompounds have two or more even number of chiral carbon atoms and have an internal plane of symmetry. These are optically inactive due to internal compensation.
- No relationship exists between the R and S prefixes that designate configuration and the (+) and (–) designations indicating optical rotation. For example, the S enantiomer of lactic acid is dextrorotatory (+), whereas the S enantiomer of glyceraldehyde is laevorotatory (–)

10.7b Elimination reactions

- Elimination of hydrogen from β – carbon and halogen from α – carbon when heated with alcoholic KOH.
- Saytzeff's rule - major alkene is one which contains maximum number of alkyl groups.

10.7c Reaction with Metals

- $R-X + Mg \longrightarrow RMgX$ (Grignard reagent)
- Grignard reagents are highly reactive and react with any source of proton to form hydrocarbons.
- $R-X + Li \longrightarrow RLi + LiX$
- $R-X + Na \longrightarrow R-R + NaX$

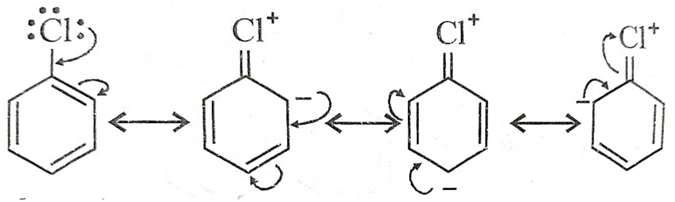
10.8 Reactions of Haloarenes

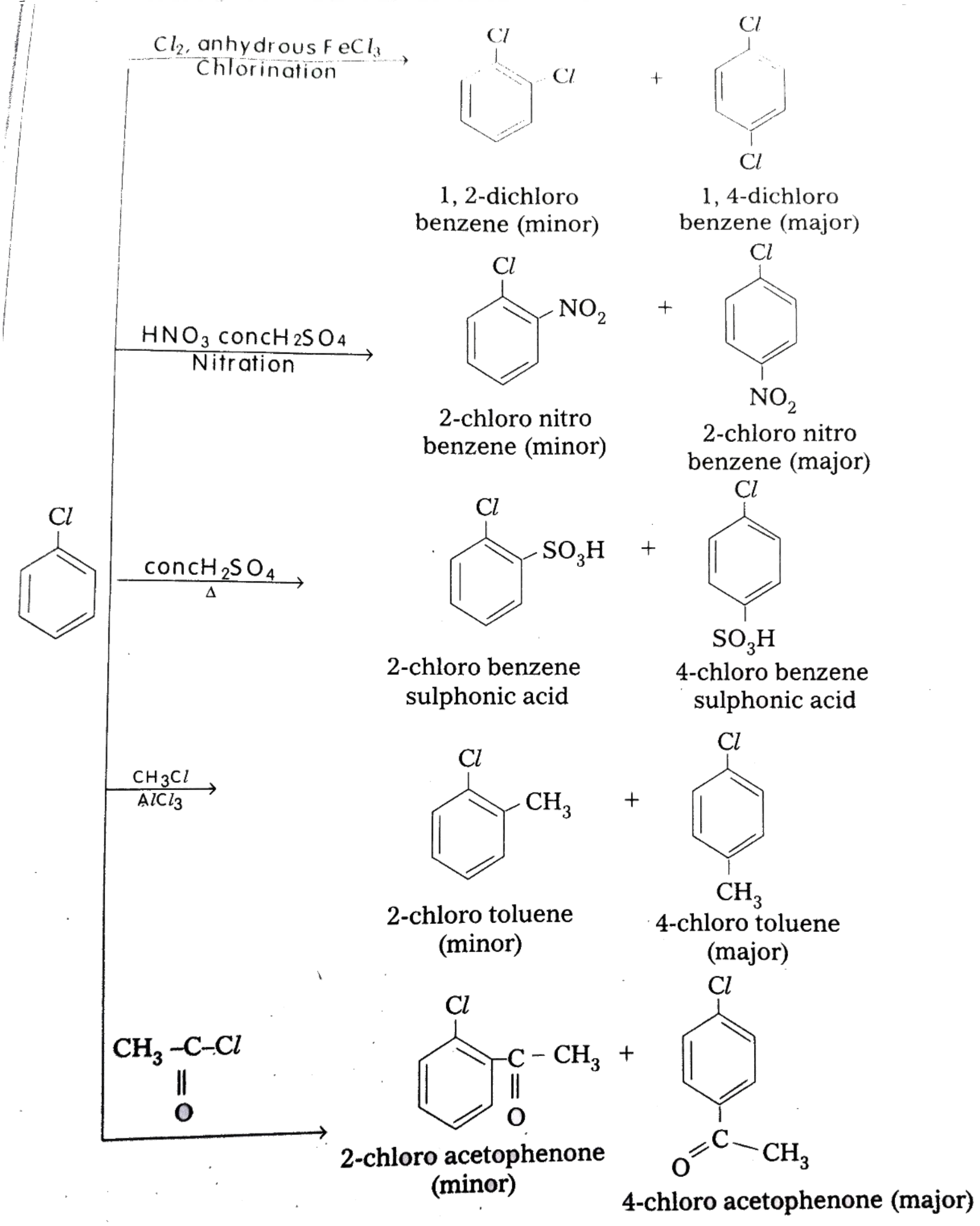
(i) Nucleophilic substitution reaction

- The aryl halides are relative less reactive towards nucleophilic substitution as compared to alkyl halides.
- The low reactivity is attributed due to,
  - The C – X bond in halobenzene has a partial double bond character due to resonance of halogen lone pair electron with benzene ring.
  - The C – X bond in halobenzene is less polar as sp^2 hybridized carbon is more electronegative than sp^3 carbon.
  - Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arene.
  - In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not stabilised by resonance and therefore, S_N1 mechanism is ruled out.

(ii) Electrophilic substitution reactions

- - I effect of halogen atom withdraw electrons from the benzene ring. Hence, haloarenes are less reactive than benzene towards electrophilic substitution reaction, i.e., haloarenes are deactivating.
- +R effect of halogen increases electron density at ortho and para position of benzene ring. Thus halogen redirects the coming electrophile to ortho and para positions (o,p- directing)





1, 2-dichloro benzene (minor)

1, 4-dichloro benzene (major)

2-chloro nitro benzene (minor)

2-chloro nitro benzene (major)

2-chloro benzene sulphonic acid

4-chloro benzene sulphonic acid

2-chloro toluene (minor)

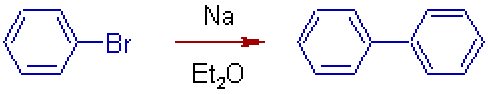
4-chloro toluene (major)

2-chloro acetophenone (minor)

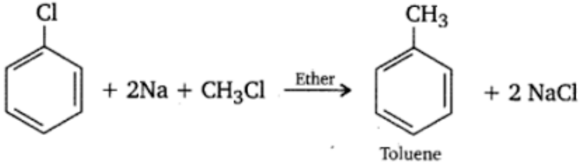
4-chloro acetophenone (major)

(iii) Reaction with metals

- Fitting reaction: In Fittig reaction, two aryl halides are coupled in presence of sodium metal in dry ether or tetrahydrofuran to furnish biphenyl



- A modification of reaction which involves, an alkyl halide and an aryl halide is called **Wurtz-Fittig reaction**

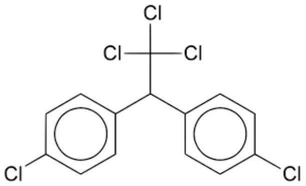


- Polyhalogen compounds – carbon compounds containing more than one halogen atom

- Dichloromethane (Methylene Chloride), CH_2Cl_2
  - Widely used as solvent, as paint remover, as propellant in aerosol.
- Trichloromethane (Chloroform), $CHCl_3$
  - Widely used in the production of freon(used as refrigerant)
  - Used as solvent for resins, rubbers, oils and fats, alkaloids, iodine and many other substances
  - It is oxidised to phosgene, a poisonous gas, in presence of light

$$CHCl_3 \xrightarrow{[O]} 2COCl_2 + H_2O + Cl_2$$

  - Inhaling chloroform vapour depresses the central nervous system, causes dizziness, fatigue and headache.
- Triiodomethane (Iodoform), CHI_3
  - It is used as an antiseptic due to liberation of iodine. Used as methylating agent in organic synthesis
- Iodoform on heating with $AgNO_3$ gives yellow precipitate of AgI whereas chloroform does not give this test because of stable nature of chloroform.
- Tetrachlomethane (carbontetrachloride) CCl_4
  - Used in the manufacture of refrigerants and propellants for aerosol cans.
  - Used as cleaning agent and spot remover. Also used as fire extinguisher under the name of pyrene.
  - It causes liver cancer, dizziness, light headedness, nausea, irritation in the eyes and vomiting in humans. It can cause permanent damage to nerve cells, which can lead to unconsciousness or even death.
  - It and depletes the ozone layer.
- Freons
  - The chlorofluorocarbon compounds of methane & ethane with chlorine & fluorine are known as freons.
  - Freon-12 (CCl_2F_2) is manufactured by the reaction of CCl_4 with metal fluoride (Swarts reaction) $CCl_4 + 2AgF_2 \longrightarrow CCl_2F_2 + 2AgCl$
  - Freons are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.
  - Used for aerosol propellants, refrigeration and air conditioning purposes.
  - Freon is stable and it diffuses into the stratosphere. There it initiates free radical chain reactions with ozone and it causes depletion of ozone layer.
- P,P' – Dichlorodiphenyl Trichloroethane, DDT



  - It is prepared by the condensation of chloral with chlorobenzene in presence of conc.H_2SO_4
  - DDT is powerful insecticide. It is very effective against the mosquitoes that spreads malaria
  - Many species of insects developed resistance to DDT and it is not metabolised very rapidly. It is chemically stable and fat soluble. It is deposited and stored in the fatty tissues.
  - It has high toxicity towards fish.