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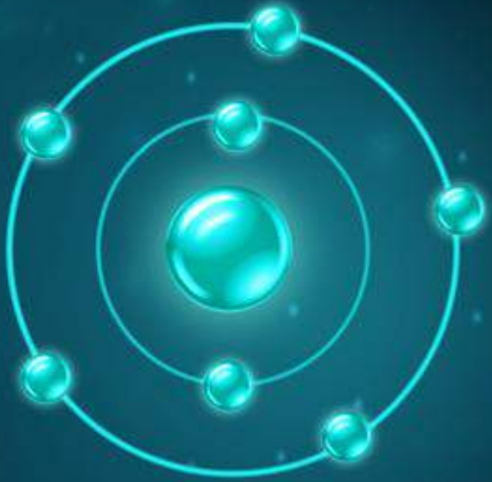
Aakash + BYJU'S LIVE

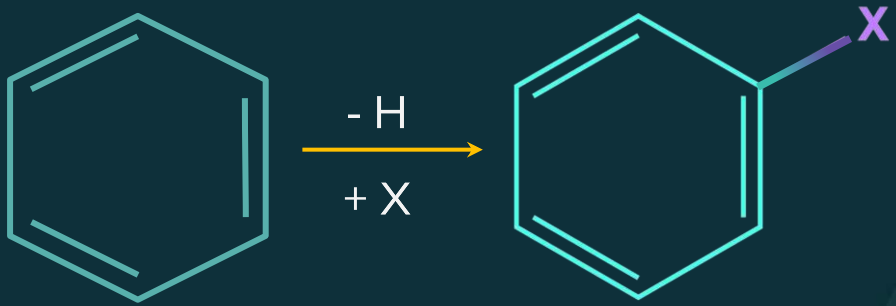
Haloalkanes & Haloarenes



Haloalkanes and Haloarenes

Haloalkanes/haloarenes are compounds in which **at least one halogen atom replaces hydrogen atom** of an alkane/aromatic compound.

$$CH_4 \xrightarrow[+\,X]{-\,H} CH_3X$$



Haloalkanes and Haloarenes in Daily Life

Bromochlorodifluoromethane is used in fire extinguishers.

Dichlorodiphenyltrichloroethane (DDT) is used as pesticides.

Medicinal Uses of Haloalkanes and Haloarenes

Goitre is caused due to the deficiency of hormone. Thyroxine which contains iodine is used to treat it.

Malaria is treated using Chloroquine which contains chlorine.

Halothane is used as an anaesthetic during surgery. It contains fluorine, chlorine, and bromine.

Chloramphenicol – Chlorine containing antibiotic is used for the treatment of typhoid fever.

Classification of Haloalkanes and Haloarenes

Classification

- Number of halogens present
- Hybridisation of 'C' in C—X bond

Depending on the number of halogens present

- Monohaloalkane/ monohaloarene
- Dihaloalkane/ dihaloarene
- Polyhaloalkane/ polyhaloarene

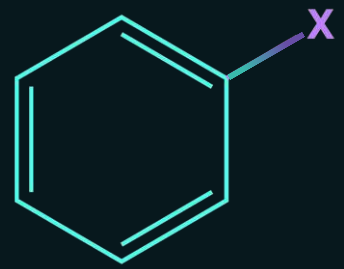
Mono-haloalkanes and Mono-haloarenes

Mono-haloalkanes

H_3C-CH_2-X

Number of halogens (X) = 1

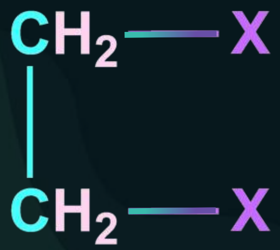
Mono-haloarenes

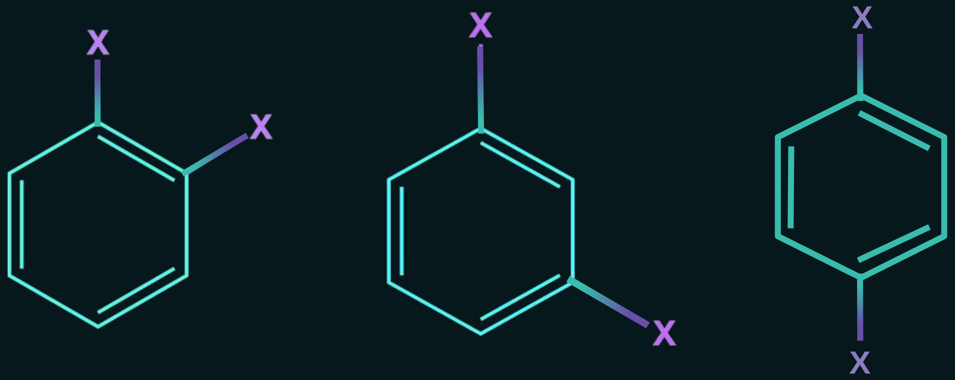


Number of halogens (X) = 1

Di-haloalkanes and Di-haloarenes

Example



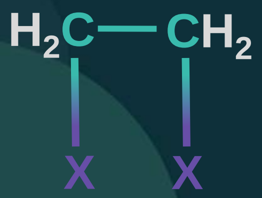


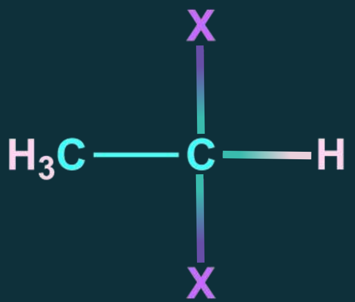
Number of halogens (X) = 2

Classification of Dihaloalkane

Dihaloalkane

- Vicinal dihalide
- Geminal dihalide





Polyhaloalkane/ Polyhaloarene

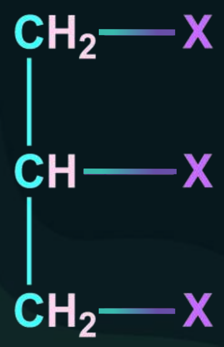
Number of halogens (X) present in the compound > 2

Polyhalogen compounds can be named as **tri, tetra**, etc.

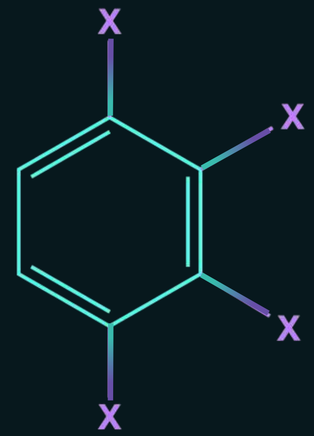
Trihaloalkane | **Trihaloarene**

Polyhaloalkanes and Polyhaloarene

Polyhaloalkanes



Polyhaloarene



Number of halogens (X) = 3

Number of halogens (X) = 4

Halo-compounds

Compound containing sp^3 C-X bond

- Alkyl halides
  - 1°
  - 2°
  - 3°
- Allylic halides
- Benzylic halides

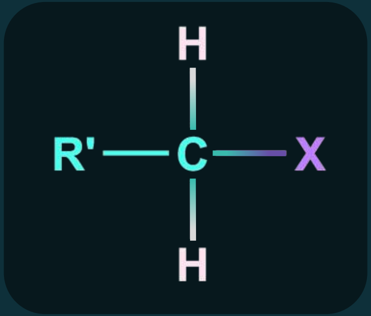
Types of Alkyl Halides

Alkyl halides

- Primary (1°)
- Secondary (2°)
- Tertiary (3°)

Primary Alkyl Halide

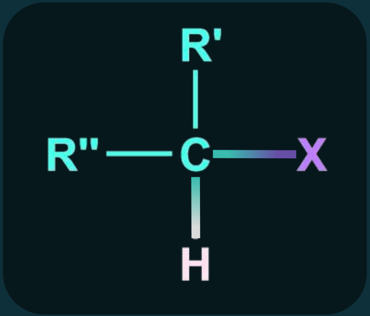
Number of carbons attached to the C-atom of sp^3 C-X bond = 1



Primary (1°)

Secondary Alkyl Halide

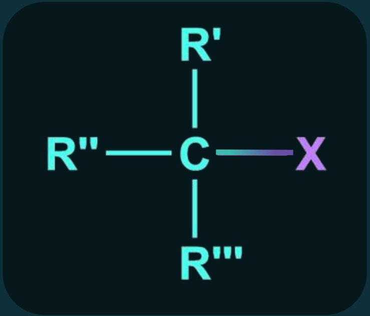
Number of carbons attached to the C-atom of sp^3 C-X bond = 2



Secondary (2°)

Tertiary Alkyl Halide

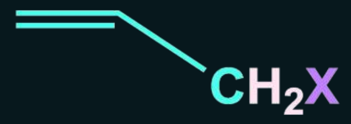
Number of carbons attached to the C-atom of sp^3 C-X bond = 3



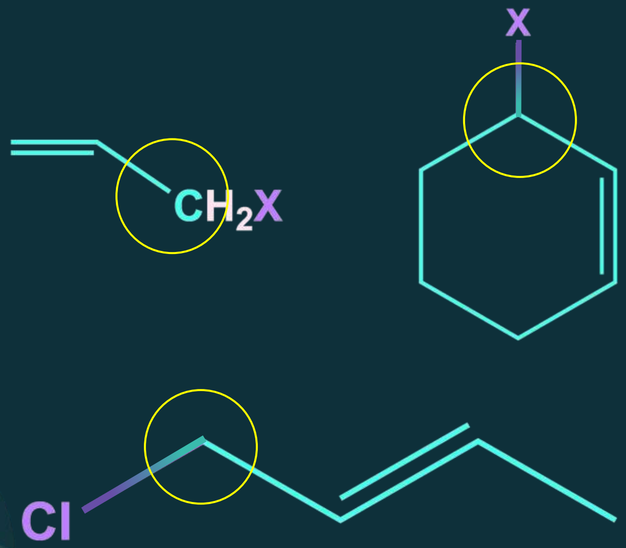
Tertiary (3°)

Allylic Halides

Halogen atom bonded to an sp^3-C atom which is directly attached to a carbon-carbon double bond **(C=C)**



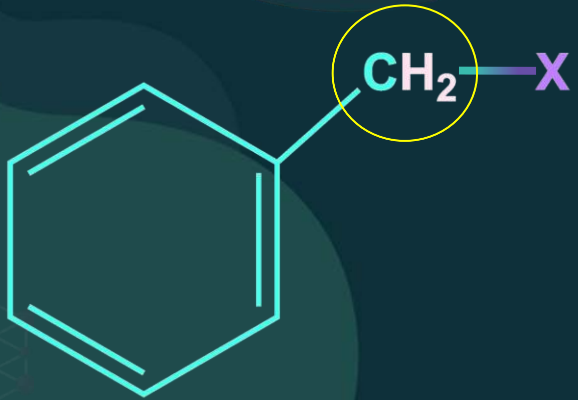
Allylic Carbon

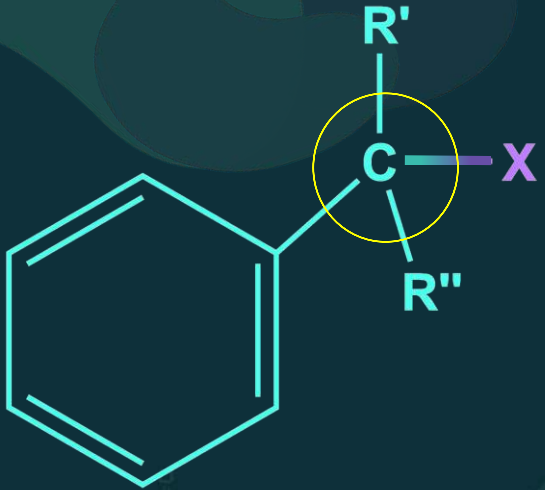


The allylic carbon is highlighted in a circle.

Benzylic Halides

Halogen atom bonded to a sp^3-C atom which is directly attached to a **benzene ring.**



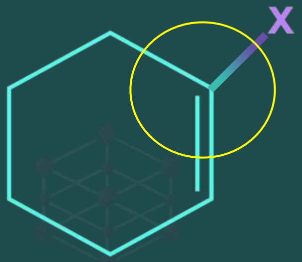


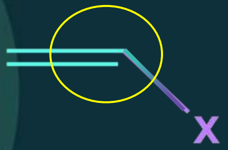
Halo-compounds

Compounds containing sp^2 C-X bond

Vinylic halides

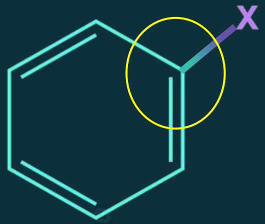
Halogen atom is attached to a sp^2-C atom of **C=C.**

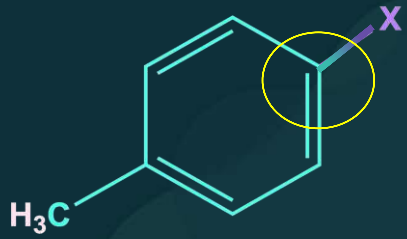




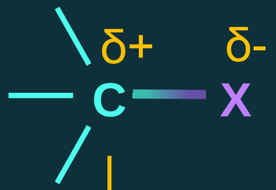
Aryl halides

Halogen atom is **bonded to a sp^2-C atom** of an aromatic ring.





Nature of C-X Bond



More electronegative

Less electronegative

Generally,

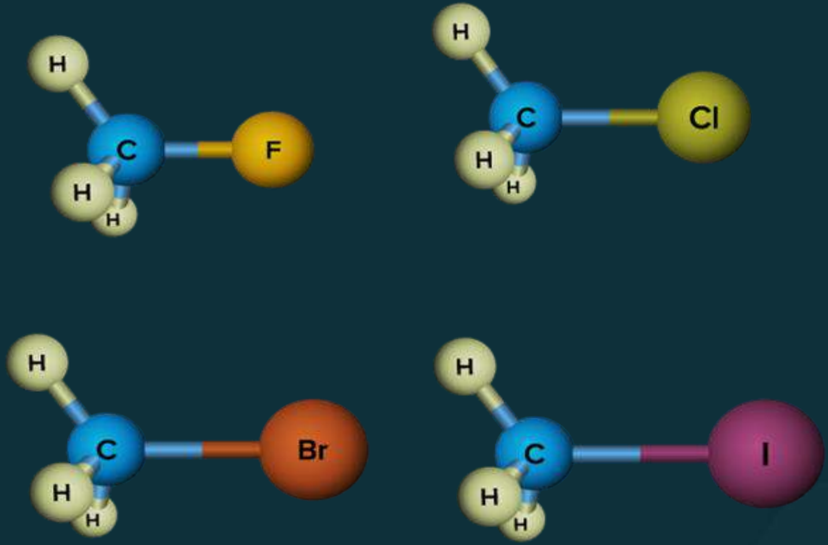
Electronegativity difference ↑ → Polarisation of C-X bond ↑

Bond Length

Down the group → C-X bond length ↑

C-F < C-Cl < C-Br < C-I

Increasing bond length



Bond Enthalpy

Generally, Bond length ↑ → Bond enthalpy ↓

C-F > C-Cl > C-Br > C-I

←

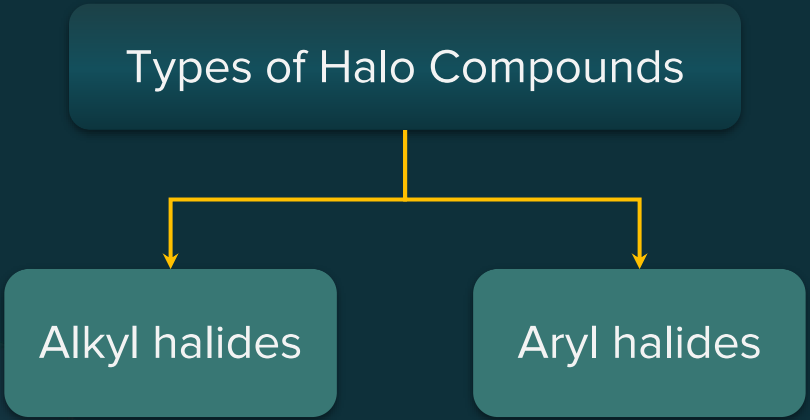
Increasing bond enthalpy

Nature of C-X Bond

Dipole moment of a bond depends on

- |Δ E.N.|
- Bond length

$CH_3 - Cl$ > $CH_3 - F$ > $CH_3 - Br$ > $CH_3 - I$


Types of Halo Compounds
Alkyl halides
Aryl halides

Halo Compounds

Physical Properties

Preparation

Chemical Properties

Let's see preparation of halo compounds

Preparation from Alcohols

R-OH ⟶ R-X

Reagents used

Hydrohalic acid, phosphorus halides and thionyl chloride

Preparation from Alcohols and HX

General reaction

$$CH_3CH_2C(CH_3)_2{-}OH + HCl \longrightarrow CH_3CH_2C(CH_3)_2{-}Cl + H_2O$$

Reactivity of HX

HI > HBr > HCl

Reactivity of ROH

3° > 2° > 1°

Preparation from Alcohols and HCl

Rate of the reaction can be increased by using **$ZnCl_2$** as a **catalyst.**

$$CH_3CH_2CH_2OH + HCl \xrightarrow[\Delta]{ZnCl_2} CH_3CH_2CH_2Cl + H_2O$$

Preparation from Alcohols and HCl

R-OH + HCl → R-Cl + H_2O

When ROH = 3°

Can react without $ZnCl_2$

When ROH = 1°, 2°

$ZnCl_2$ is used

A mixture of concentrated hydrochloric acid and anhydrous zinc chloride is called the **Lucas reagent.**

Preparation from Alcohols and HX

HI and HBr are often **generated in situ** from the **halide ion** and an **acid** such as phosphoric or sulfuric acid.

$$CH_3\underset{\displaystyle OH}{\underset{|}{CH}}CH_3 \xrightarrow[\text{or NaBr, } H_2SO_4]{\text{Conc. HBr}} CH_3\underset{\displaystyle Br}{\underset{|}{CH}}CH_3$$

$$CH_3CH_2CH_2OH + HI \xrightarrow{\Delta} CH_3CH_2CH_2I + H_2O$$

To prepare HI, **KI** is **not** made to react with conc. **H_2SO_4 or HNO_3** as they are **oxidising agents** and thus oxidise iodide ions to iodine (I_2).

HI is generated from **KI** and **H_3PO_4**.

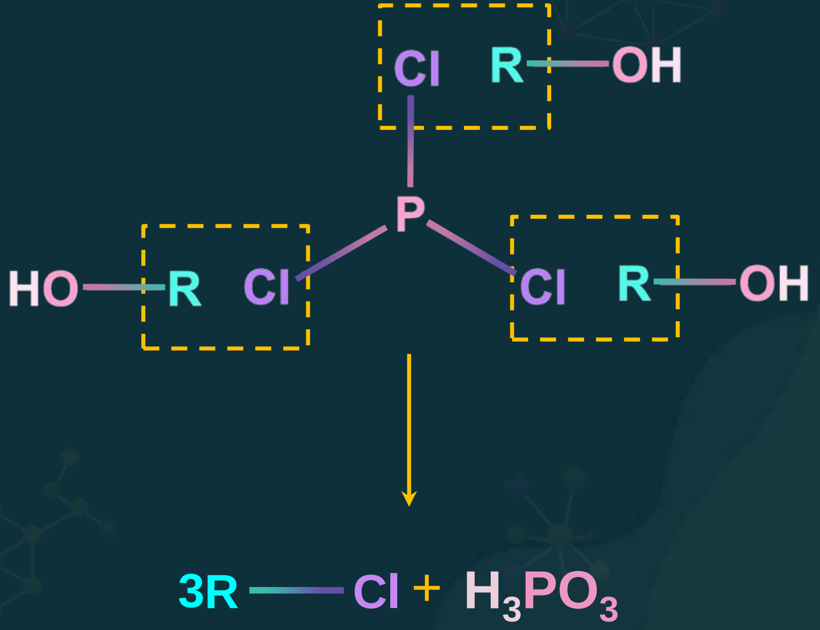
Preparation from Alcohols and PX_5

$$3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$$

$$3ROH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

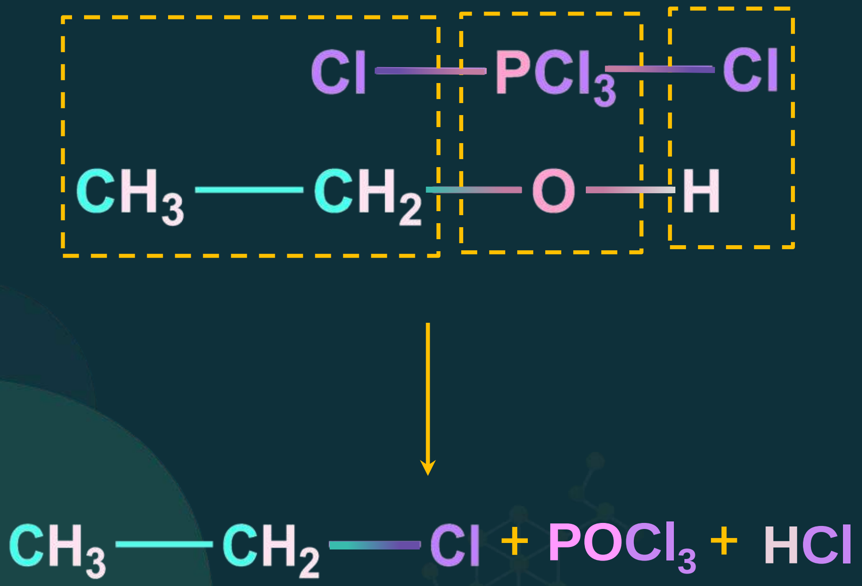
X	Cl, Br, I

$$ROH + PCl_5 \longrightarrow RCl + HCl + POCl_3$$



Preparation from Alcohols and PX_5

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$



Preparation from Alcohols and $SOCl_2$

General reaction

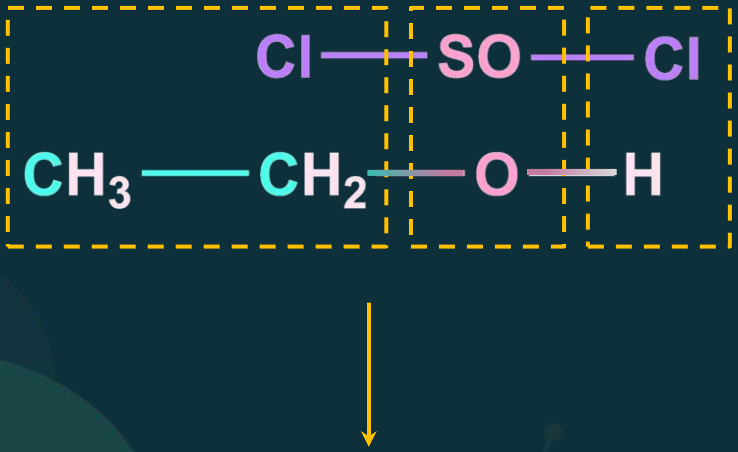
$$ROH + SOCl_2 \xrightarrow{\text{Pyridine, } \Delta} RCl + SO_2\uparrow + HCl\uparrow$$

Good method for the preparation of alkyl halide

By-products are gaseous in nature

Preparation from Alcohols and $SOCl_2$

$$ROH + SOCl_2 \xrightarrow{\text{Pyridine, } \Delta} RCl + SO_2 \uparrow + HCl \uparrow$$



$$CH_3-CH_2-Cl + SO_2 \uparrow + HCl \uparrow$$

Preparation of Alkyl Halides

From Hydrocarbons

- From alkanes
- From alkenes

Free Radical Halogenation

Halogenation of alkanes
by **free radical** mechanism

↓

Generates a mixture of
mono/poly haloalkanes

Mono Halogenation

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[\text{UV light}]{Cl_2} CH_3-CH_2-CH_2-CH_2-Cl$$

$$+$$

$$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

Rate of reaction of **halogens**

F_2 > Cl_2 > Br_2 > I_2

Reactivity of **H**

3° > 2° > 1°

Preparation of Alkyl Halides

Alkyl halides are prepared from alkenes in two ways

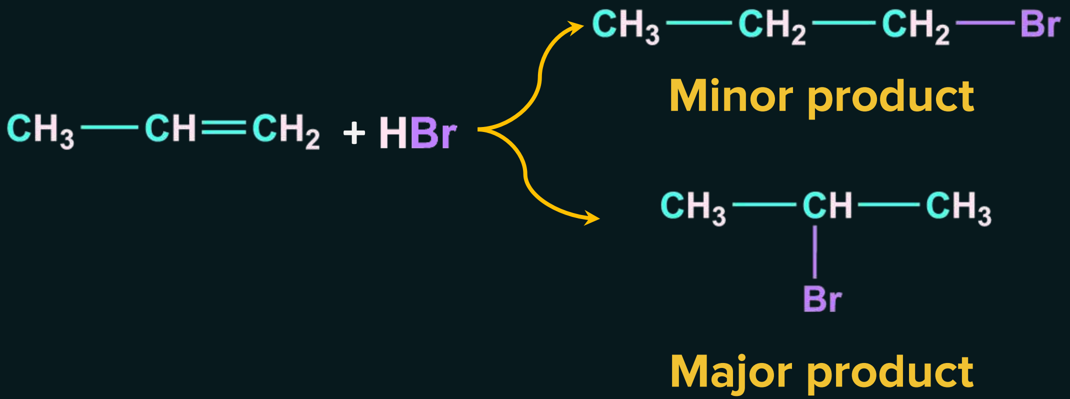
- Mono haloalkanes → Addition of HX
- Dihaloalkanes → Addition of X_2

Addition of Hydrogen Halides (HX)

Addition of HBr to a **symmetrical** alkene

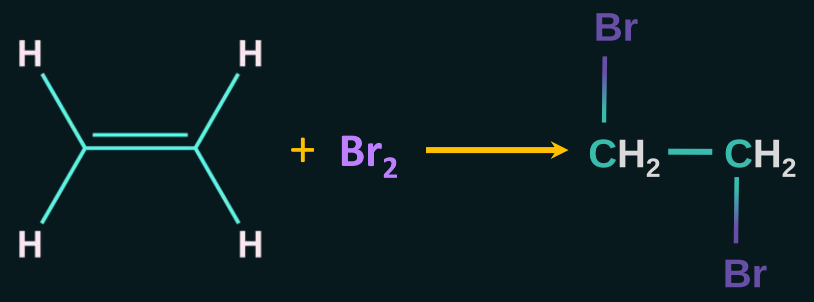
Addition of HBr to **an unsymmetrical** alkene (Markovnikov's rule)

Example



Addition of Halogens

Halogens (Cl_2, Br_2) add up to alkenes to form **vicinal dihalides.**



Anti-addition

Addition of halogens to alkenes is an example of **electrophilic addition reaction.**

Involves **halonium ion** formation

Preparation of Alkyl Halides

Halogen exchange method is used to obtain alkyl halides by

- Finkelstein reaction
- Swarts reaction

Finkelstein Reaction

$$RX + NaI \xrightleftharpoons{\text{Acetone}} RI + NaX$$

X : Cl, Br

Unlike NaI; NaCl or NaBr is **not soluble** in acetone.

When RCl or RBr is treated with a solution of **NaI** in acetone

↓

Equilibrium is shifted by the **precipitation** of NaCl or NaBr

Swarts Reaction

General reaction

$$R\text{-}Br/R\text{-}Cl \longrightarrow R\text{-}F$$

Reagents used: AgF, CoF_2, Hg_2F_2

Example

$$CH_3\text{-}Br + AgF \longrightarrow CH_3\text{-}F + AgBr \downarrow$$

Preparation of Aryl Halide

- Halogenation of arenes
- Via diazonium salts

Preparation of Aryl Halides

Chlorine and bromine in presence of Lewis acid (like $AlCl_3$, $FeCl_3$) react with benzene by **electrophilic substitution reaction.**

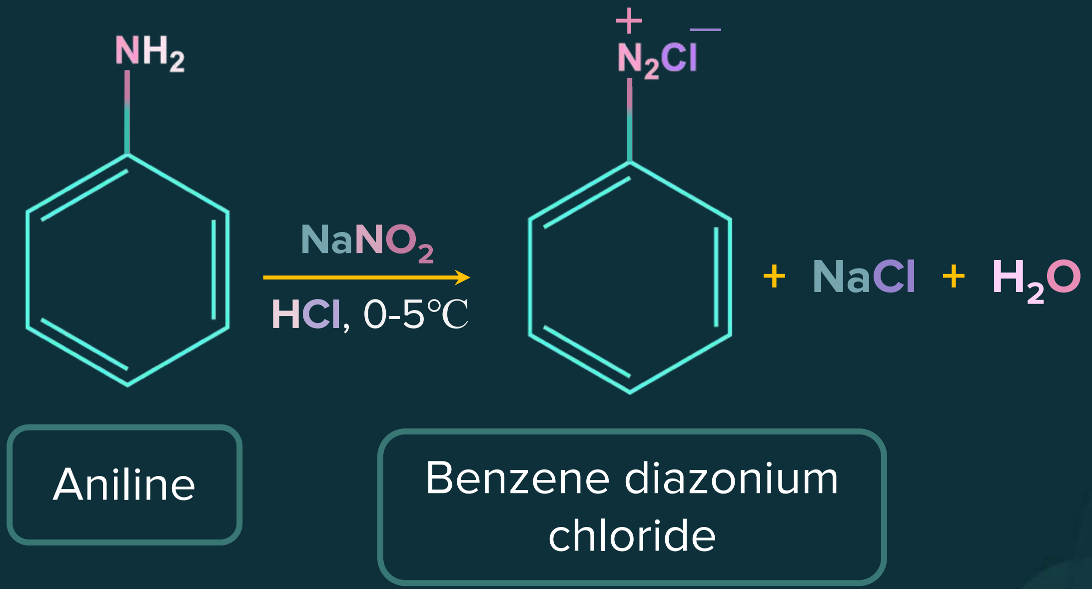
Reactivity of Halogens in ESR

Electrophilic Substitution

- F_2 → Fluorination is highly reactive
- Cl_2, Br_2
- I_2 → Iodination is very slow

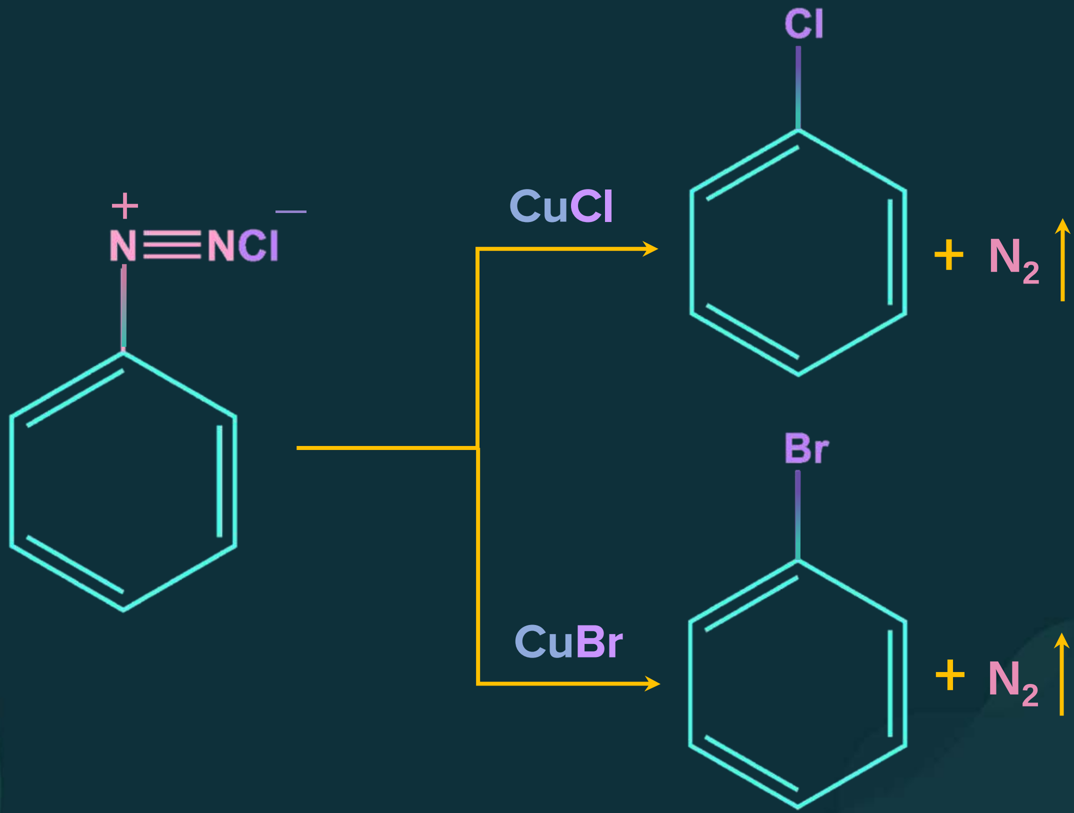
Preparation of Diazonium Salt

Primary aromatic amines react with nitrous acid at low temperature (273-278 K) to give aromatic diazonium salts.



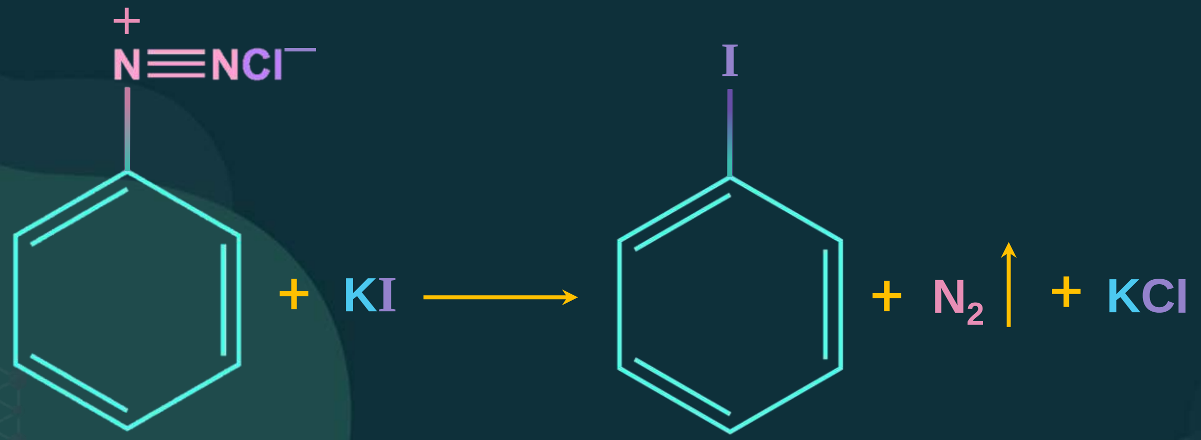
Sandmeyer Reaction

Treatment of **diazonium salts** with cuprous chloride or bromide leads to aryl chlorides or bromides, respectively. It follows **free radical** mechanism.



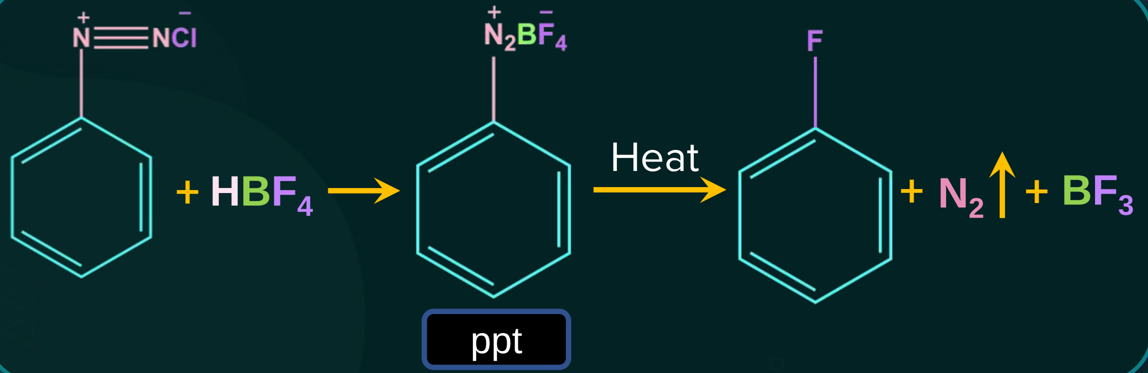
Formation of Iodobenzene

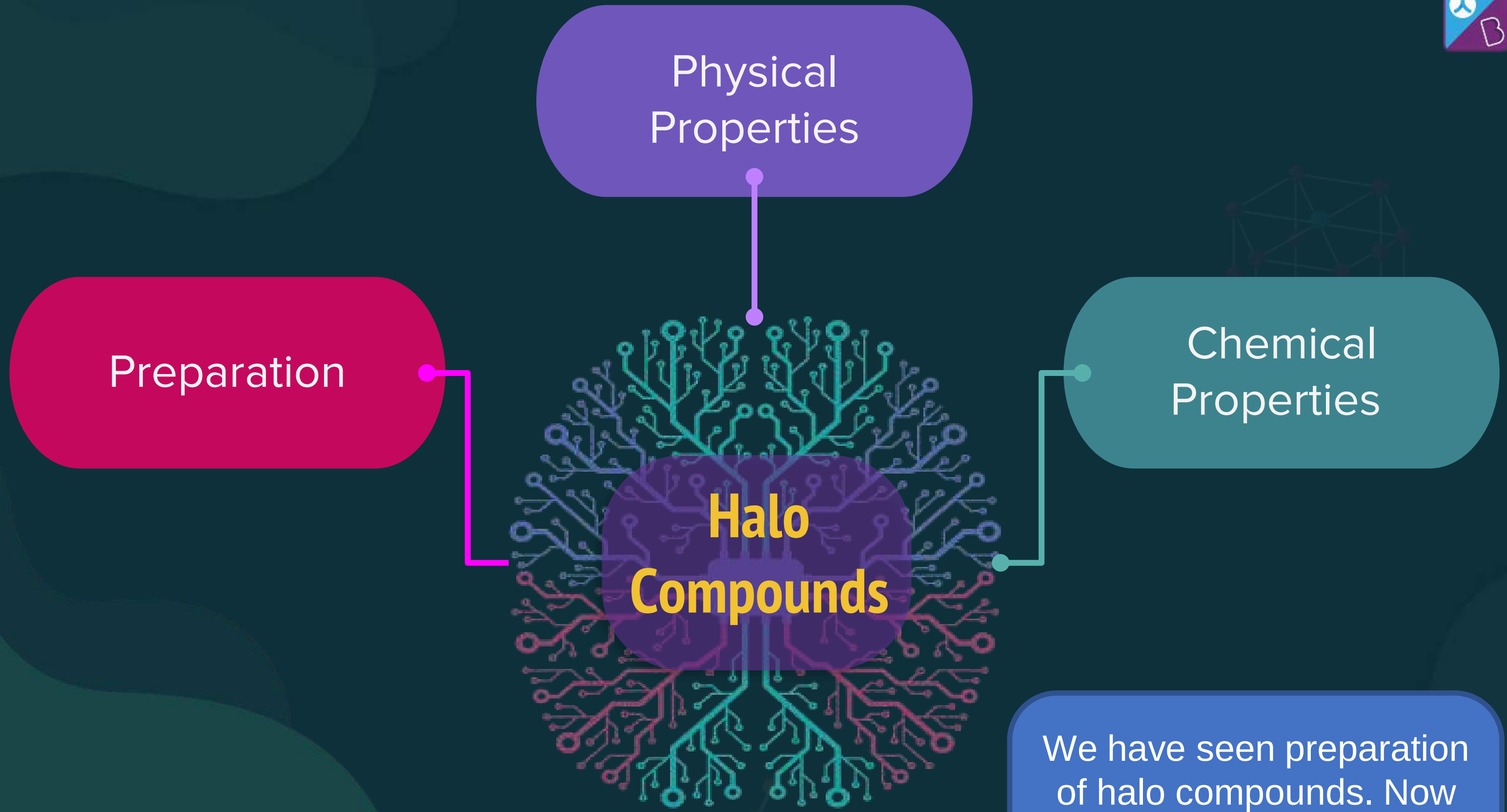
Replacement of diazonium group with iodine doesn't require cuprous iodide. It **can be done with KI.** It also follows **free radical** mechanism.



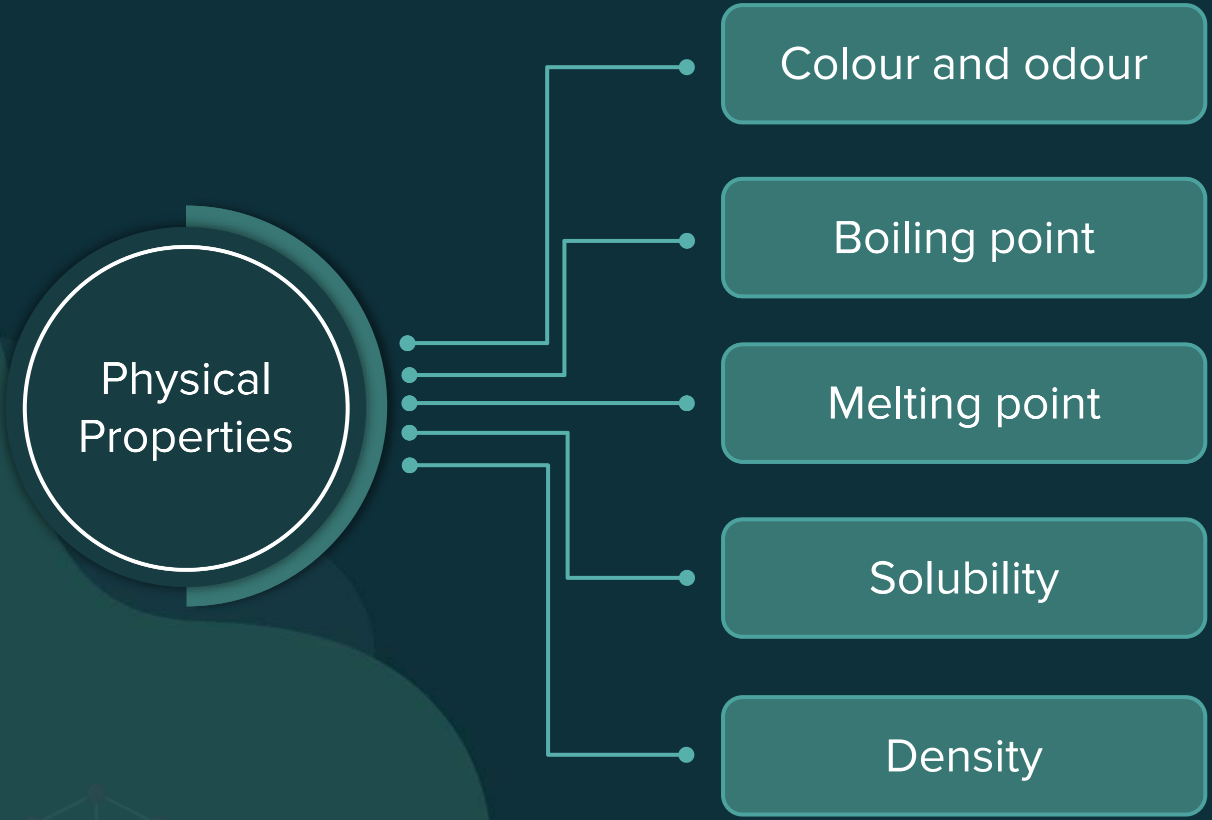
Formation of Fluorobenzene

The diazonium group can be replaced by **fluorine** by treating the diazonium salt with **Fluoroboric acid (HBF_4).** It follows **S_N1** mechanism.





We have seen preparation of halo compounds. Now let’s discuss physical properties of these compounds.


Physical Properties
Colour and odour
Boiling point
Melting point
Solubility
Density

Colour and Odour

Generally, alkyl halides are **colourless** in their pure form.

But **bromides & iodides** develop colour when exposed to light.

Generally, volatile halogen compounds have a **sweet smell**.

Boiling Point

Boiling point is the temperature at which organic liquid overcomes intermolecular forces of attraction and gets converted to gaseous state.

Boiling Point of Haloalkanes depends on

- Polarity and molar mass of the compound
- Branching of parent chain

Boiling Points of Haloalkanes

Polarity of C—X bond

C—I < C—Br < C—F < C—Cl

Polarity of C—X bond ↑ → Dipole-dipole attraction ↑

Order of **van der Waals forces**

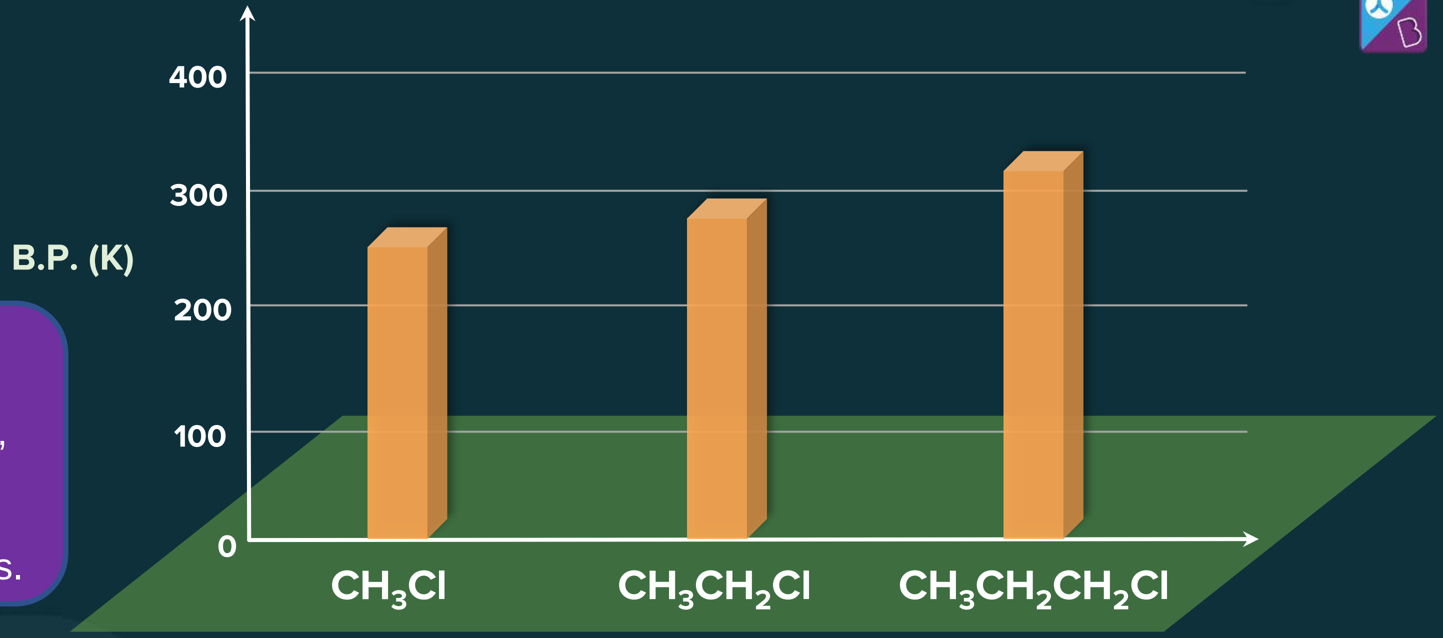
R—F < R—Cl < R—Br < R—I

Boiling Points of Haloalkanes

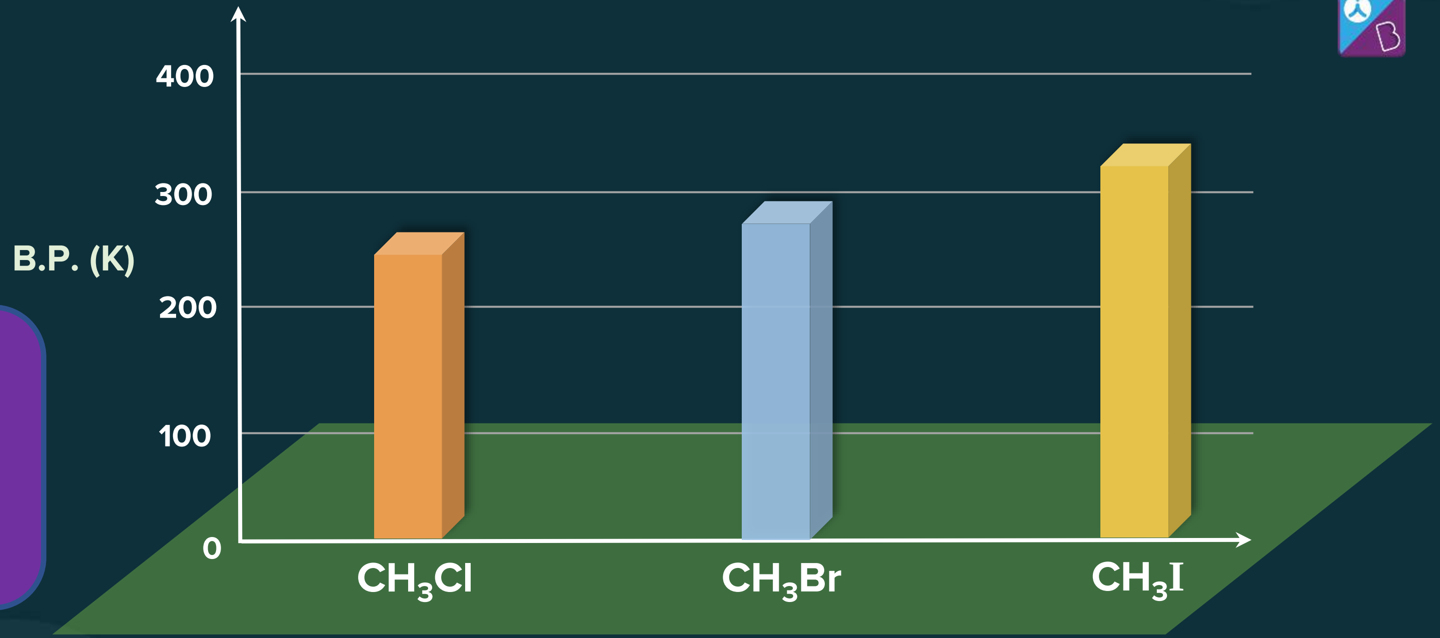
Order of **B.P.**

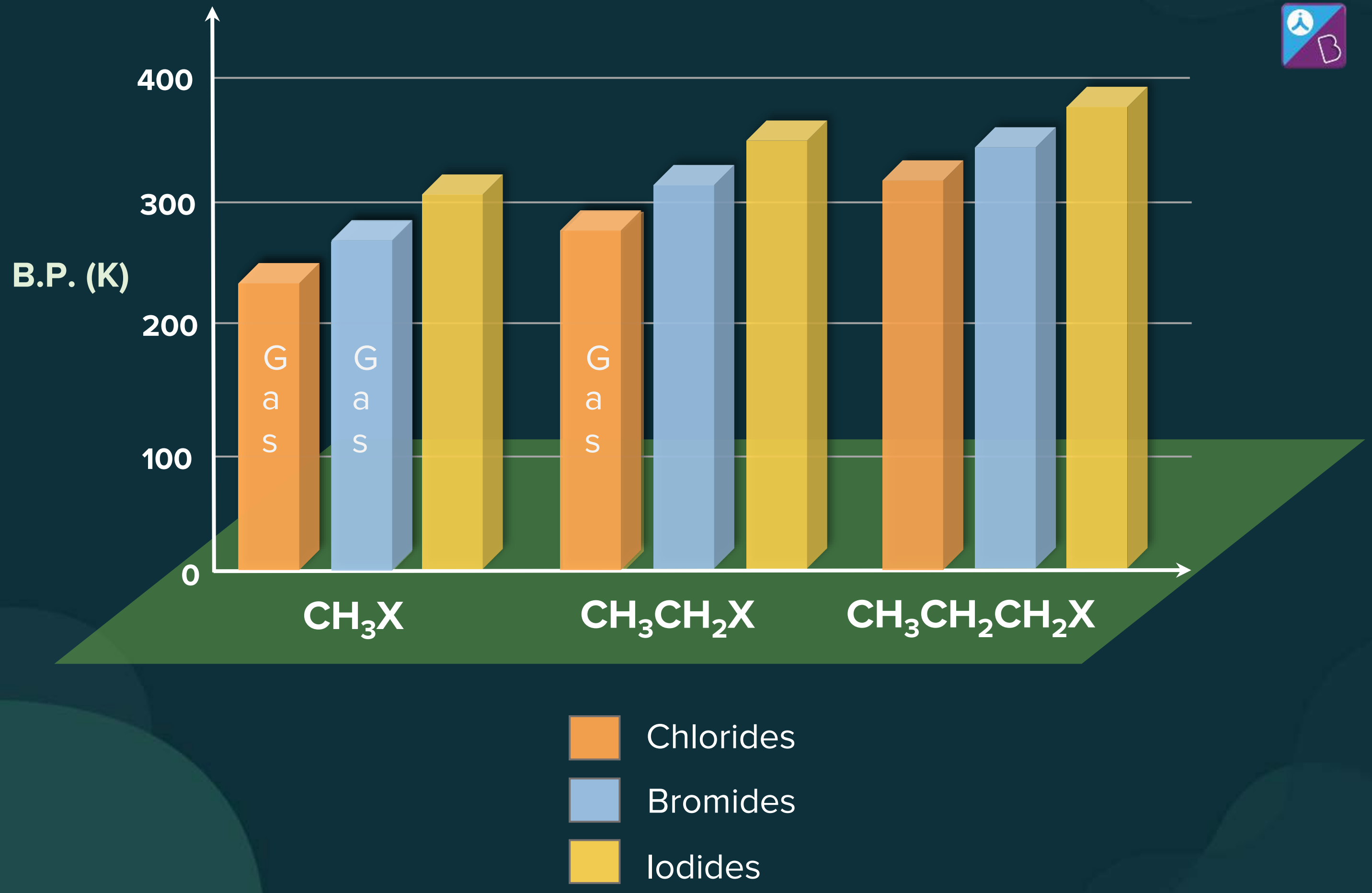
R—F < R—Cl < R—Br < R—I

Here boiling point is shown on the graph: For the same halogen, as the length of hydrocarbon chain increase, b.p. increases.



Here boiling point is shown on the graph: For same hydrocarbon chain, as the size of halogen increase, b.p. increases.

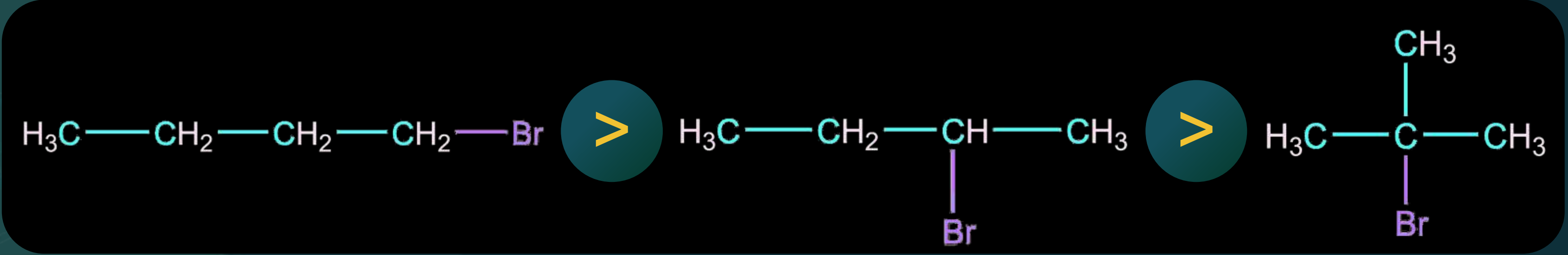




B.P. (K)
400
300
200
100
0
G a s
G a s
G a s
CH_3X
CH_3CH_2X
$CH_3CH_2CH_2X$
Chlorides
Bromides
Iodides

Boiling Points of Haloalkanes

Boiling point $\propto$ $\dfrac{1}{\text{Branching}}$



B.P. (K): 375 | 364 | 346

Boiling point increases

Boiling Points of Haloalkanes vs Hydrocarbon

Haloalkanes have **greater polarity** and **higher molar mass** compared to parent hydrocarbon.

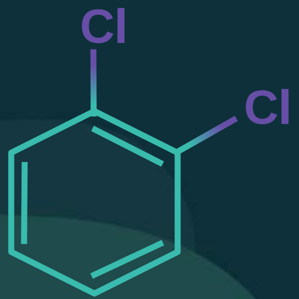
B.P. of haloalkanes is **greater** than their parent hydrocarbon due to

↓

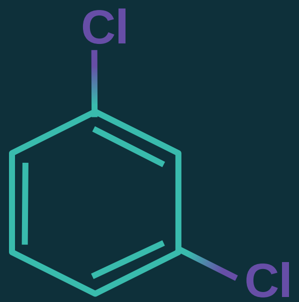
Strong intermolecular force of attraction (**Dipole–dipole** and **van der Waals** forces)

Boiling Points of Haloarenes

Boiling points of isomeric dihalobenzenes are **nearly the same.**



B.P.: 453 K



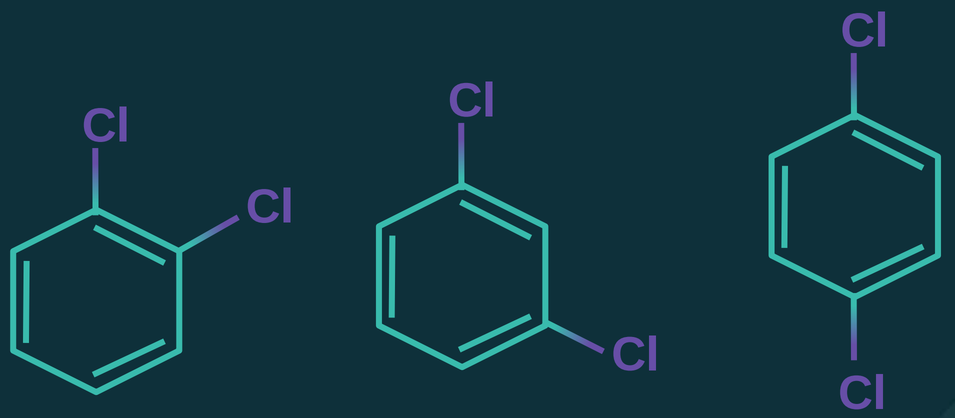
B.P.: 446 K

B.P.: 448 K

Melting Point of Dihalobenzenes

Para-isomers have **high M.P.** as compared to their ortho and meta-isomers.

Molecules with **better packing** have **higher** melting point.



M.P.: 256 K

M.P.: 249 K

M.P.: 323 K

Solubility of Haloalkanes in Water

Energy required to overcome **attractions between haloalkane molecules**

+

Energy required to **break H-bonds between H_2O** molecules

is **greater** than

Energy released when new bonds are setup **between haloalkane and H_2O** molecules

Solubility of Haloalkanes in Water

Hence, solubility of haloalkanes in water is **low.**

Solubility of Haloalkanes in Organic Solvents

Energy required to overcome **attractions between haloalkane molecules**

+

Energy required to overcome interactions between **organic solvent**

is **nearly same** as

Energy released when new bonds are setup **between haloalkanes & organic solvent**

Hence, haloalkanes are **soluble** in organic solvents.

Density of Halo Compounds

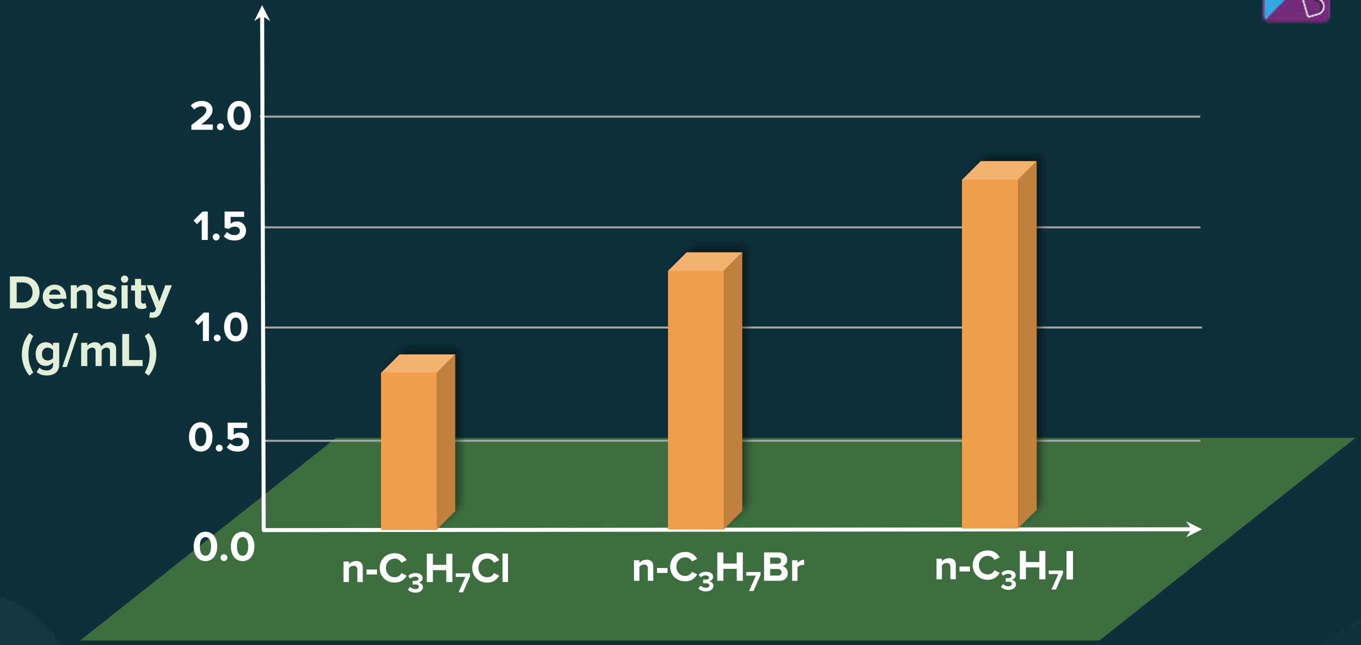
Bromo, iodo, & polychloro derivatives of hydrocarbons are **heavier** than water.

Number of carbon/halogen atoms & atomic mass of the halogen atoms ↑

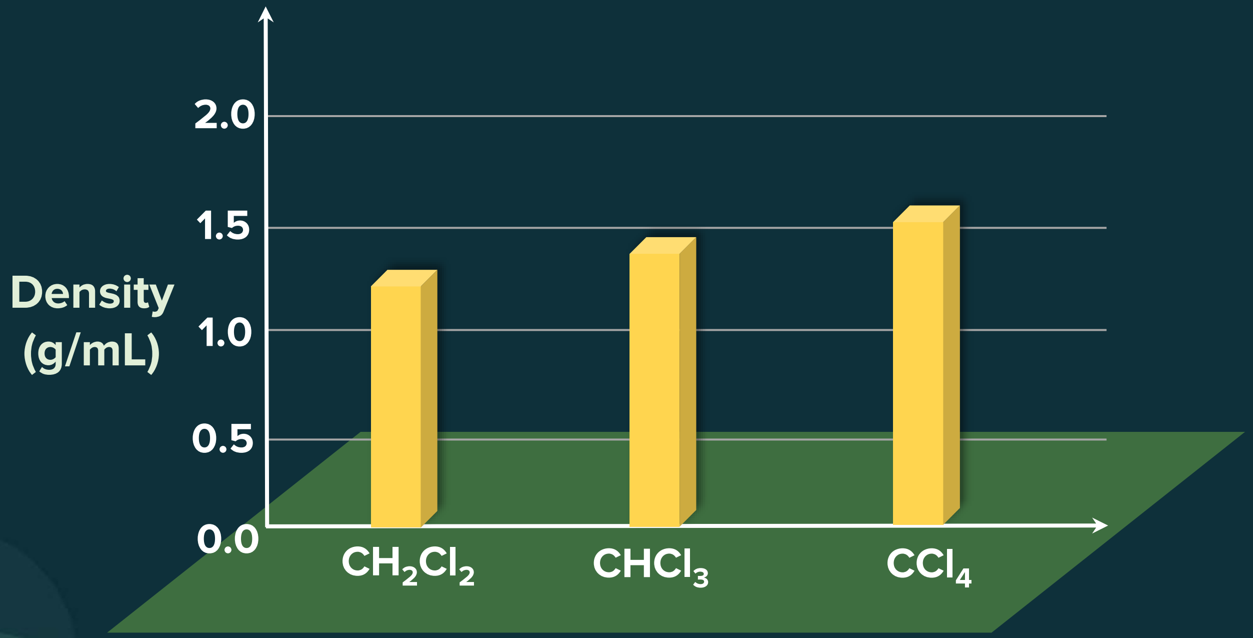
↓

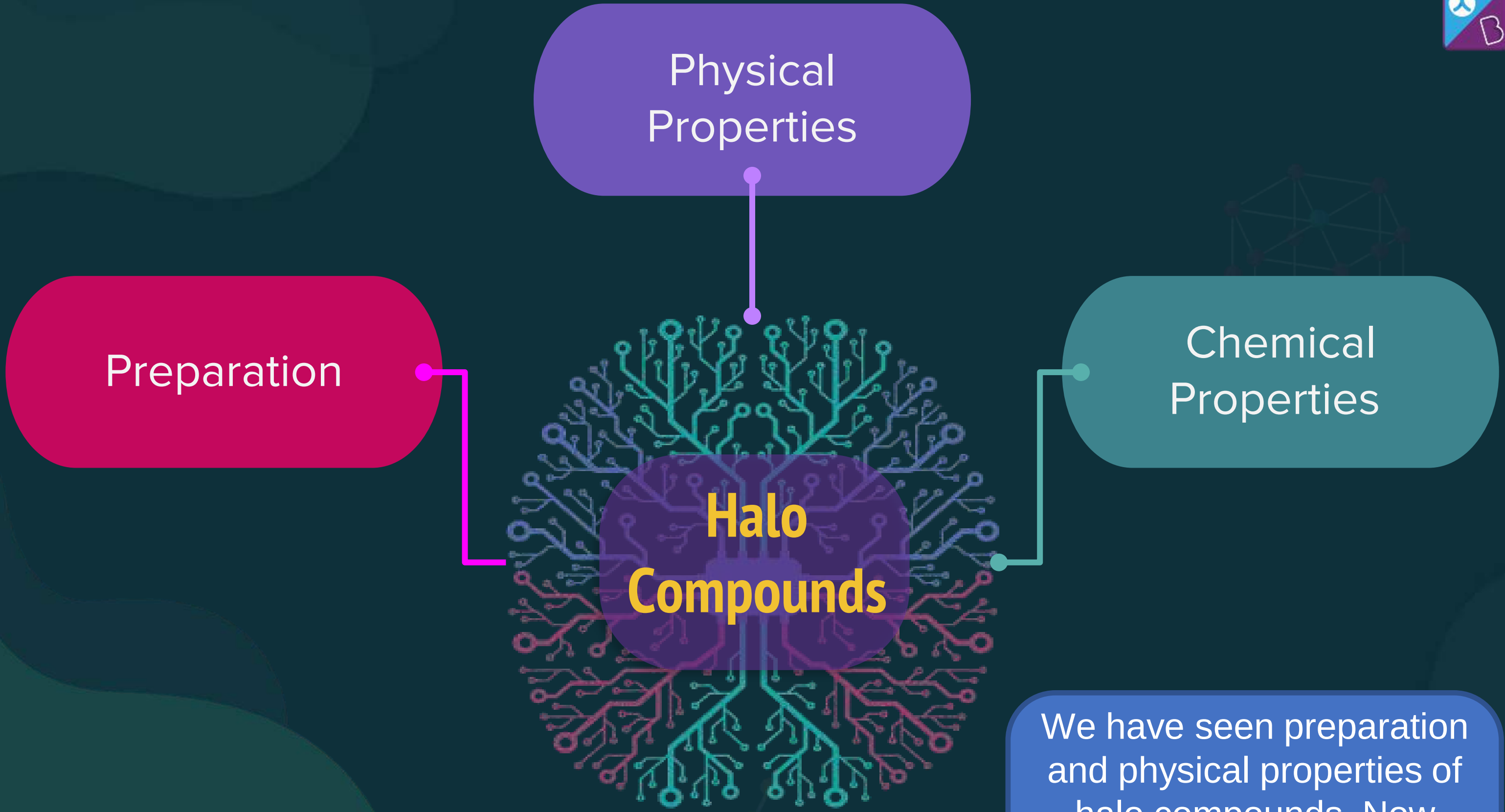
Density ↑

For same hydrocarbon chain, as the size of halogen increase, density increases.

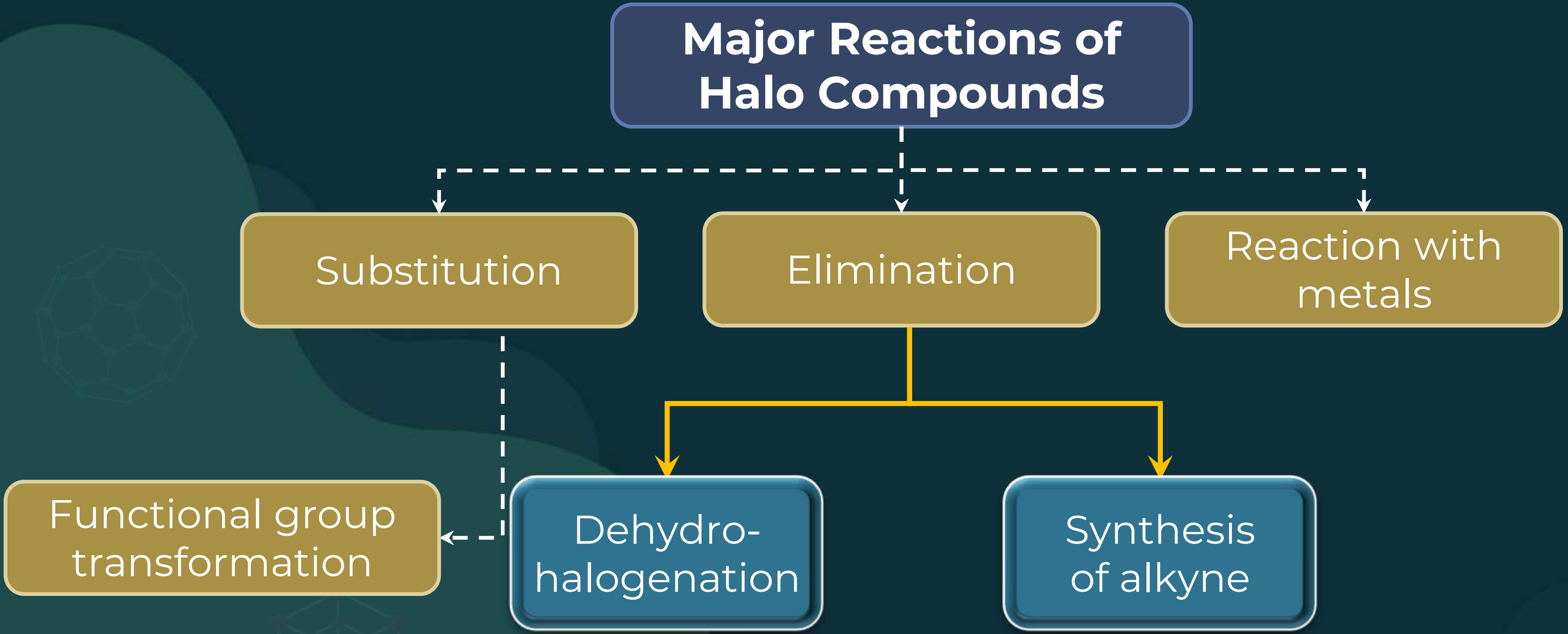


Density increases with number of halogens.

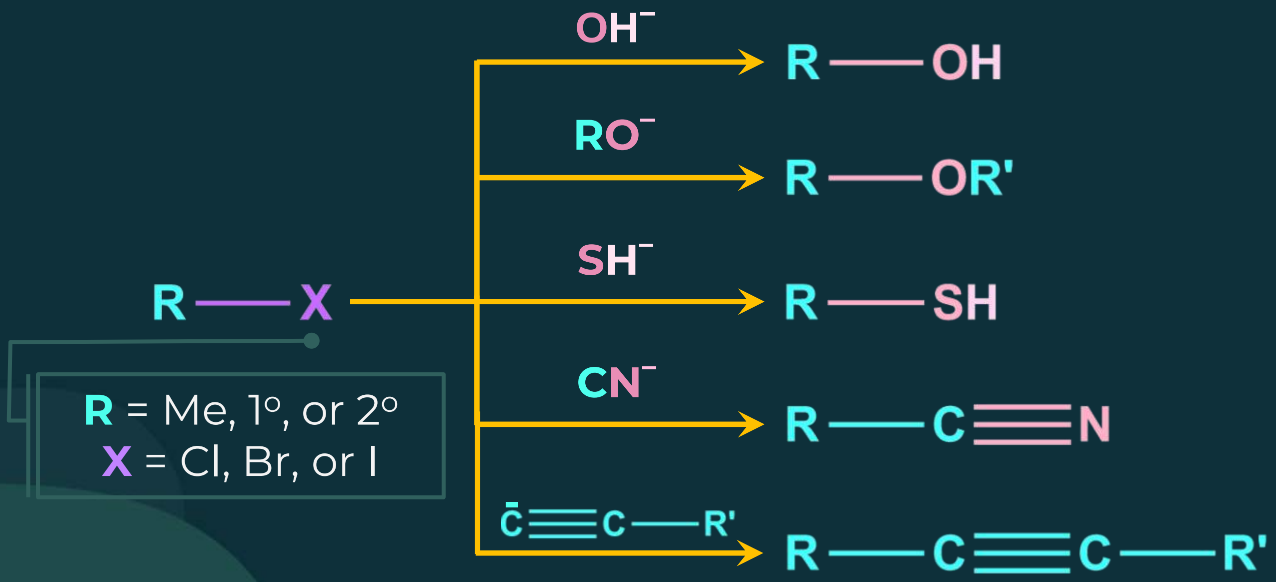




We have seen preparation and physical properties of halo compounds. Now let's discuss chemical properties of these compounds.

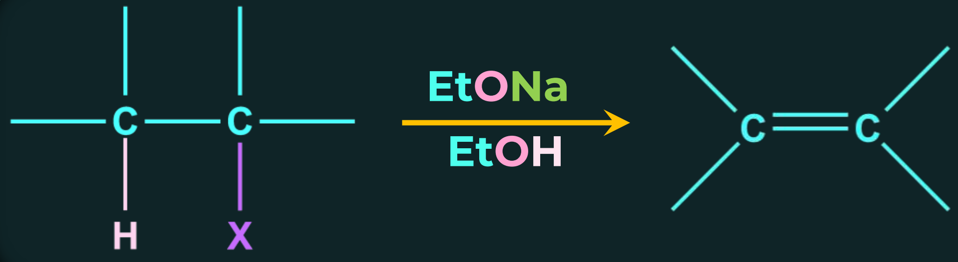

Major Reactions of Halo Compounds
Substitution
Elimination
Reaction with metals
Functional group transformation
Dehydro-halogenation
Synthesis of alkyne

Functional Group Transformation

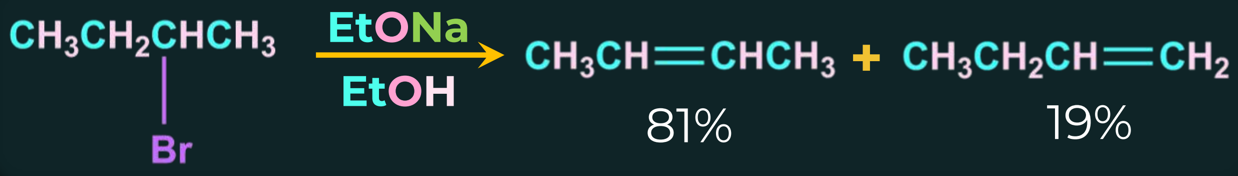


Dehydrohalogenation

General reaction

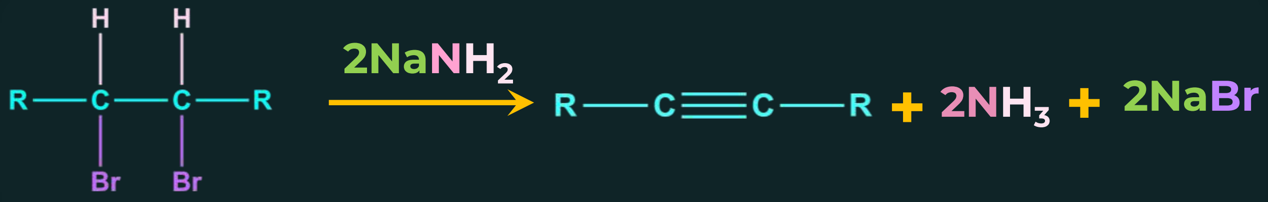


Example



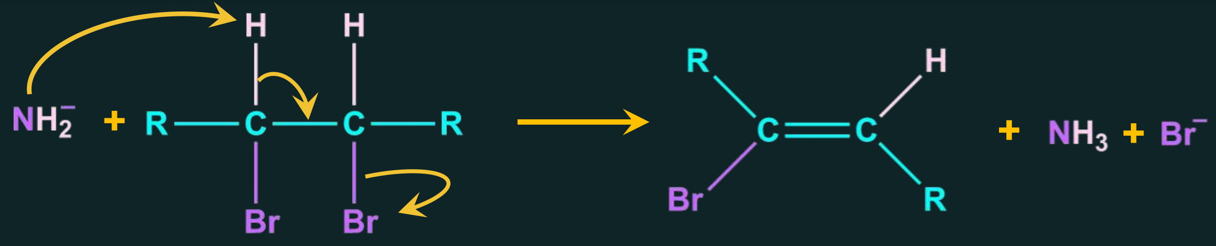
Synthesis of Alkynes

Alkynes can be synthesised from alkenes via **vicinal dihalides**

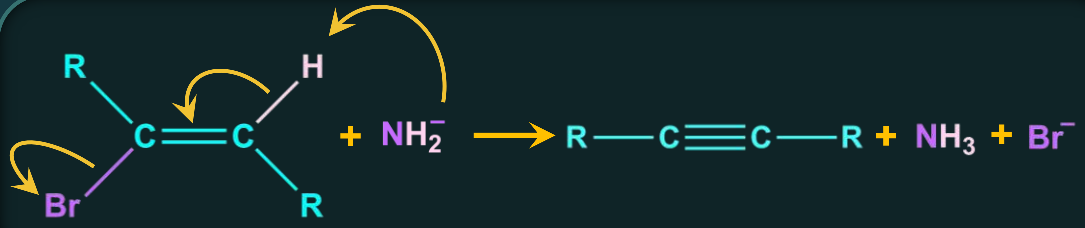


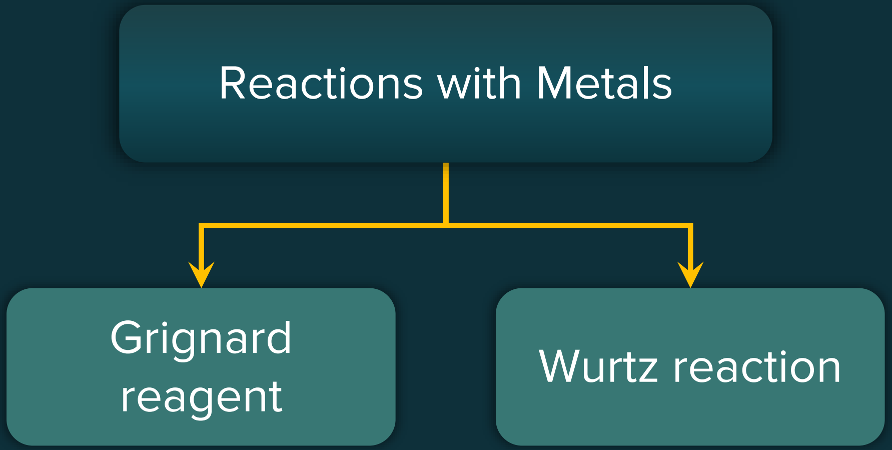
Mechanism

Step 1



Step 2




Reactions with Metals
Grignard reagent
Wurtz reaction

Preparation of Grignard Reagent

Compounds that contain **carbon–metal** bonds

Grignard reagents are prepared by the reaction of an **organic halide with magnesium metal** in an anhydrous ether solvent.

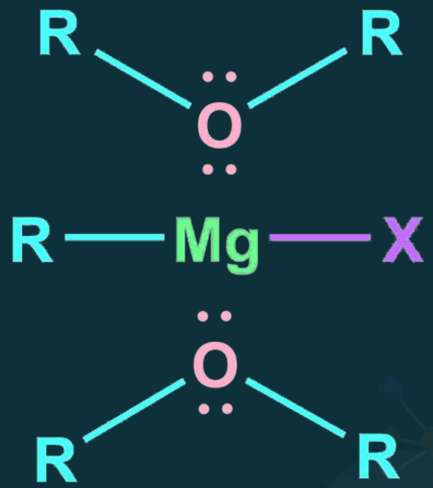
Grignard reagent → **RMgX**

Preparation and Properties

$$RX + Mg \xrightarrow{Et_2O} RMgX$$

$$ArX + Mg \xrightarrow{Et_2O} ArMgX$$

A Grignard reagent **forms a complex** with its ether solvent.



Structure and Reaction of Grignard Reagent

The **C-Mg bond** in Grignard reagents is **covalent** and not ionic.

$$\overset{\delta-}{R} - \overset{\delta+}{MgX}$$

Grignard reagents are **very strong bases**.

They react with any compound that has a **hydrogen atom** attached to an electronegative atom such as oxygen, nitrogen, or sulphur.

Reaction of Grignard Reagent

The reactions of Grignard reagents with water and alcohols are **acid–base reactions**.

Reaction of Grignard Reagent with H_2O

Reaction of Grignard Reagent with Alcohol

Wurtz Reaction

In this method **two moles** of alkyl halides are treated with '**Na**' metal in dry ether for preparation of higher alkanes from **1° or 2° alkyl halides**.

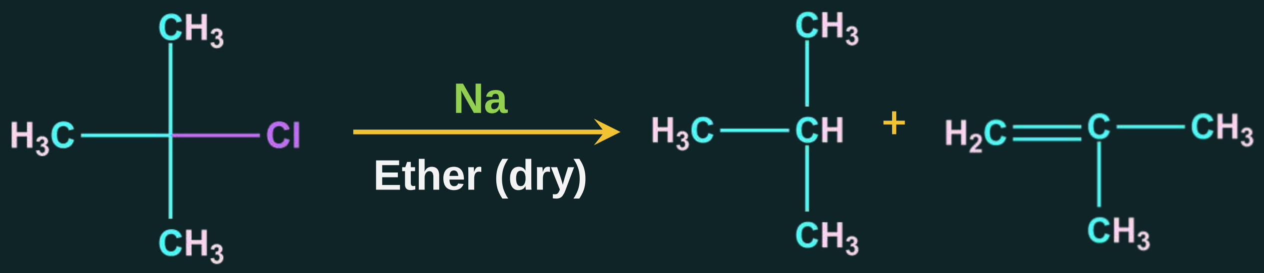
$$R{-}X + 2Na + X{-}R \xrightarrow[\text{Ether (dry)}]{\text{Na}} R{-}R + 2NaX$$

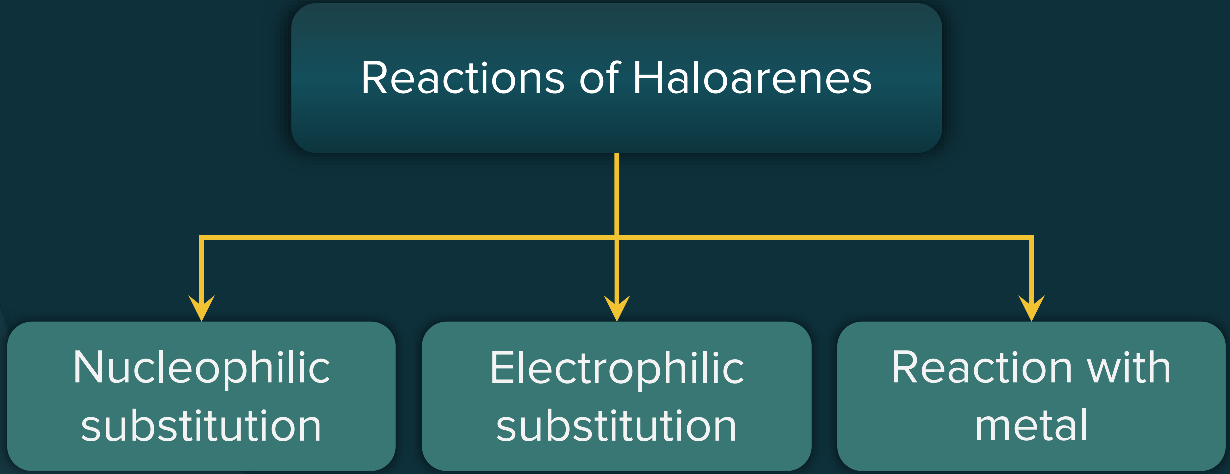
Wurtz Reaction

1° or 2° alkyl halides can give Wurtz reaction, but in case of **3° alkyl halides**, coupling reaction and S_N2 reaction are not possible.

↓

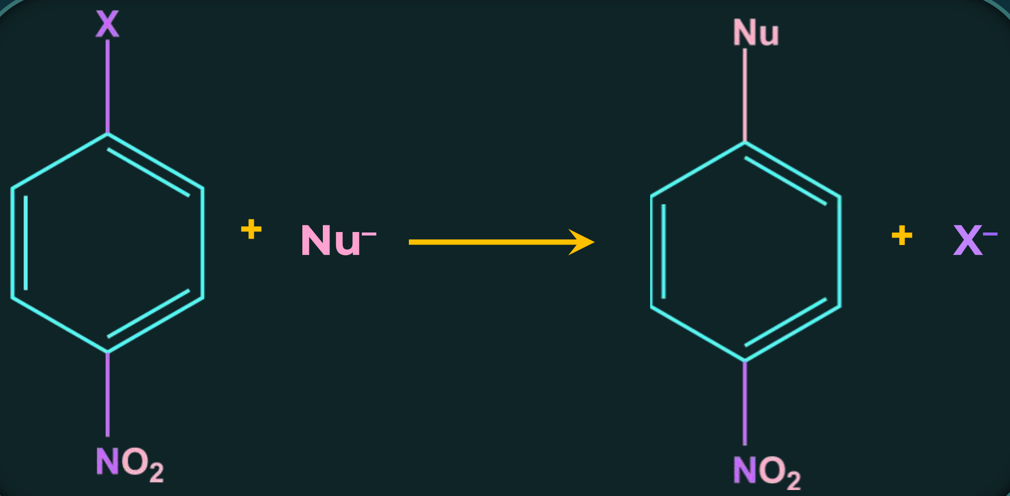
So, **disproportion** and **elimination** reactions take place.




Reactions of Haloarenes
Nucleophilic substitution
Electrophilic substitution
Reaction with metal

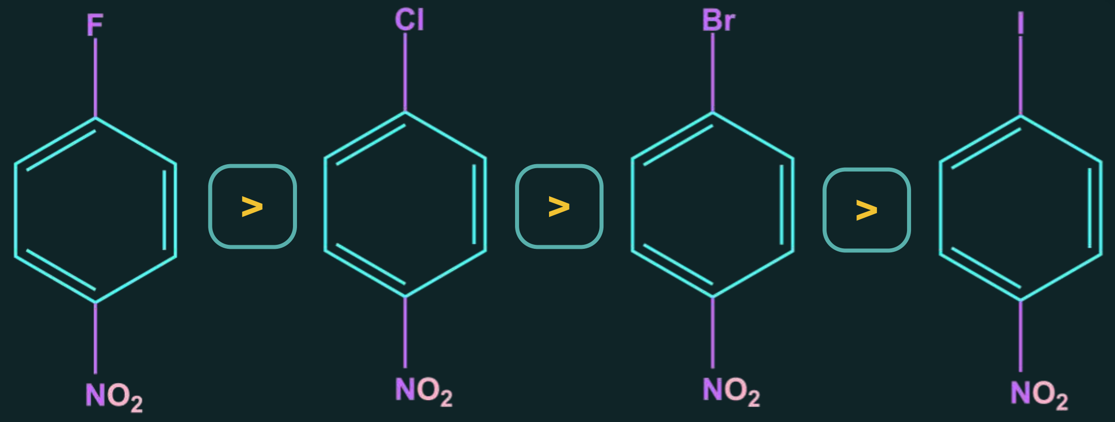
Nucleophilic Aromatic Substance (S_NAr)

General reaction



X = Halogen

Nucleophilic Aromatic Substance (S_NAr)



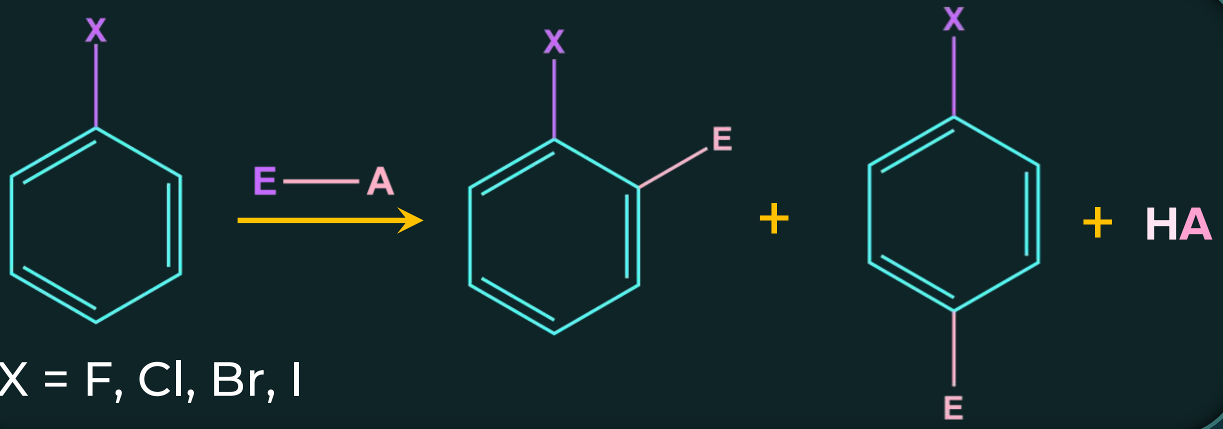
Rate of S_NAr increases

Electrophilic Substitution in Haloarenes

Rate of **electrophilic substitution** in **haloarenes (nitration)**

Recall

General reaction



X = F, Cl, Br, I

Halo groups are **ortho-para directors** and are **deactivating groups.**

Fittig Reaction

Aryl halides also give analogous compounds when treated with **sodium in dry ether**, in which two aryl groups are joined together.

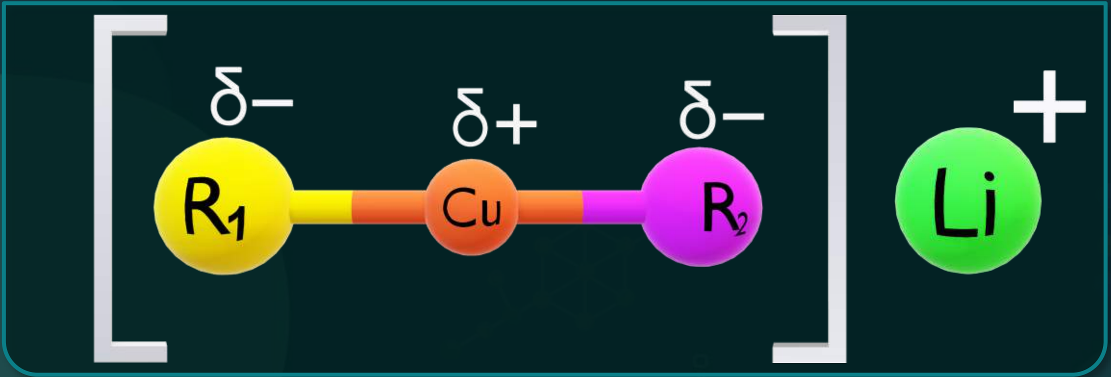
Corey-House Synthesis

Corey-House Synthesis

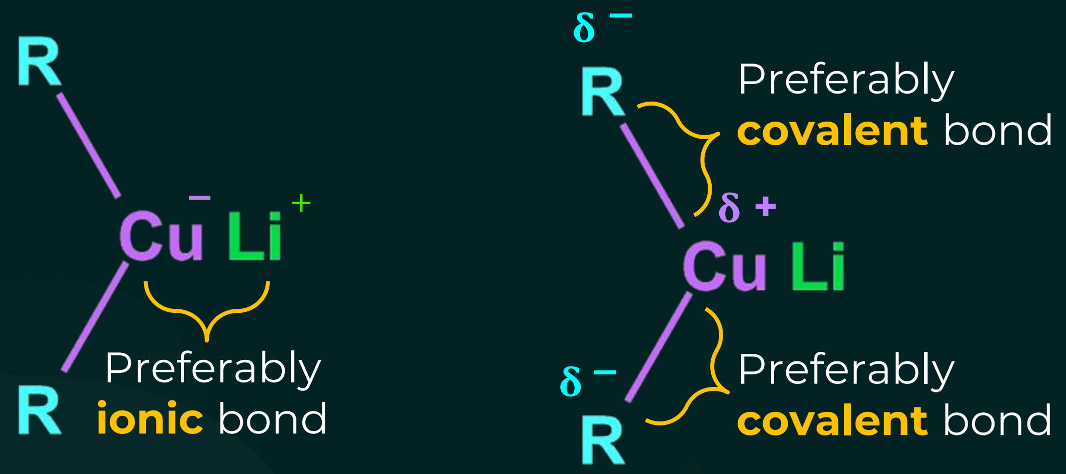
General Reaction

$$R'—X + R_2CuLi \longrightarrow R—R' + RCu + LiX$$

Gilman reagent

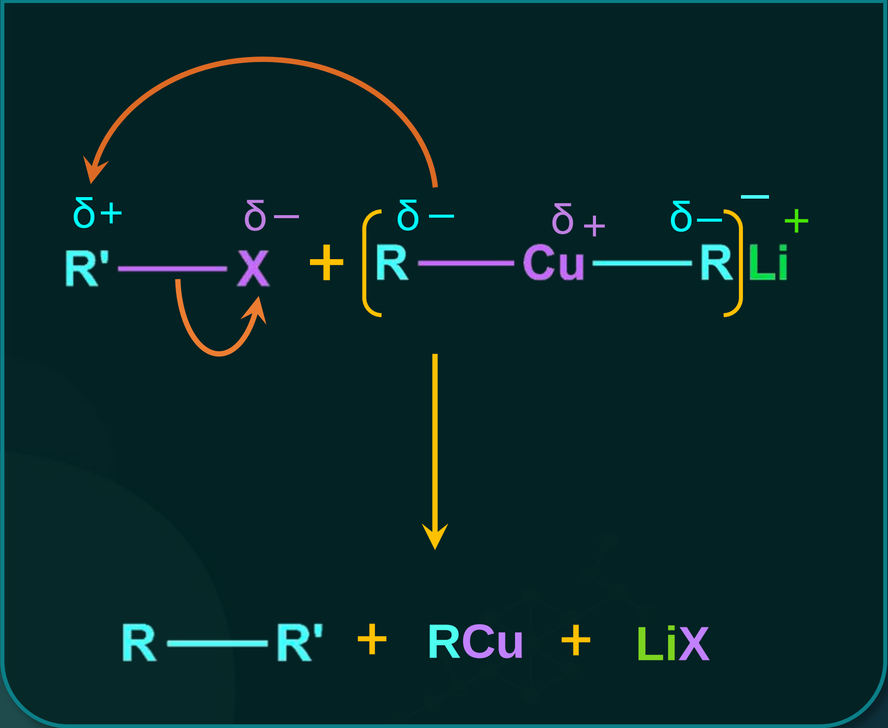


Structure of Gilman's Reagent



Corey House Synthesis

General Reaction



Corey House Synthesis

Example

$$CH_3CH_2CH_2CH_2Br + (CH_3)_2CuLi$$

$$\downarrow$$

$$CH_3CH_2CH_2CH_2CH_3 + CH_3Cu + LiBr$$

Alkane containing **odd** number of carbons

Corey House Synthesis

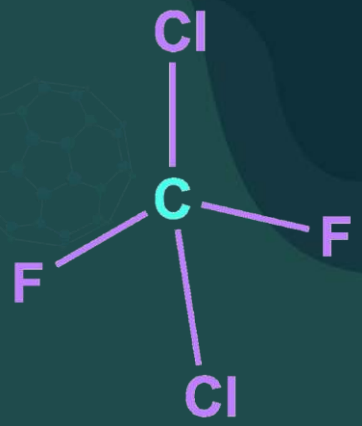
Example

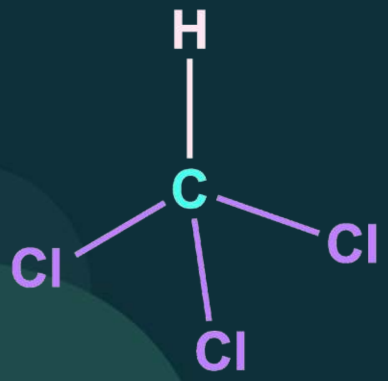
$$CH_3CH_2Br + (CH_3CH_2)_2CuLi \longrightarrow CH_3CH_2CH_2CH_3 + CH_3CH_2Cu + LiBr$$

Alkane containing **even** number of carbons

Polyhalogen Compounds

Carbon compounds containing **more than** one halogen atom



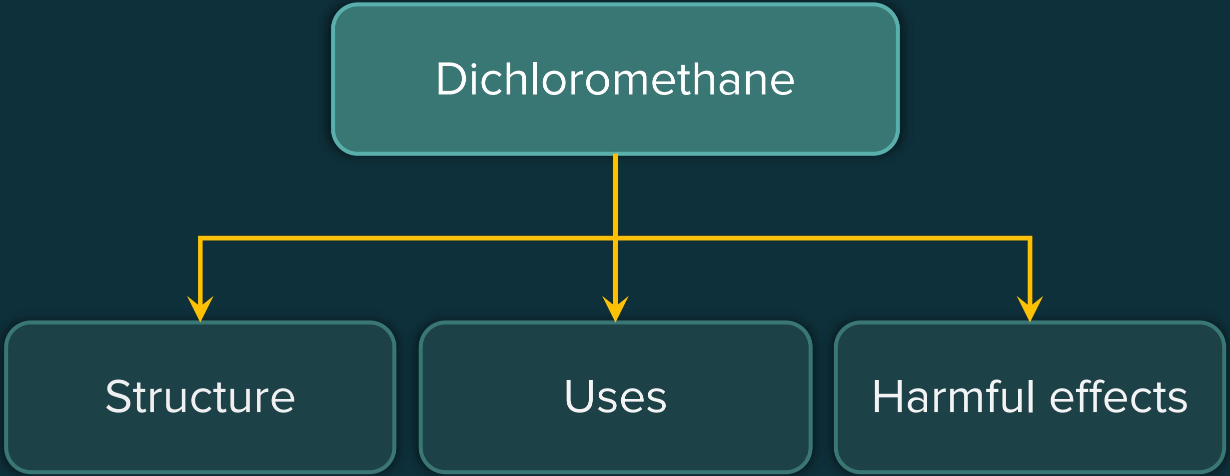


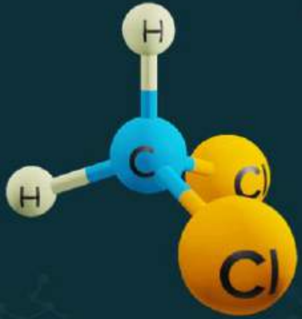
Useful in **industry** and **agriculture**

Polyhalogen Compounds

- Dichloromethane
- Trichloromethane
- Triiodomethane
- Tetrachloromethane
- Freons
- DDT

Dichloromethane (Methylene chloride)





Uses

Dichloromethane

- Paint remover
- Propellent in aerosol
- Metal cleansing
- As a solvent

Harmful Effects of Dichloromethane

Harmful Effects

- Slight hearing and vision impairment
- Harms the human central nervous system
- Tingling and numbness in the fingers and toes
- Nausea

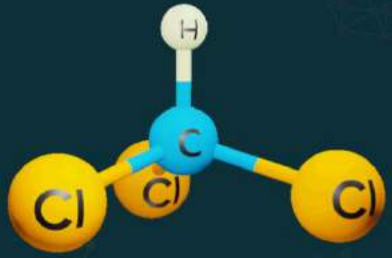
Direct contact can cause

- Burning and mild redness of skin
- Burning of cornea

Trichloromethane (Chloroform)

Trichloromethane

- Structure
- Uses
- Harmful effects



Uses

Trichloromethane

- Solvent for fats, alkaloids and iodine
- Production of freon refrigerants (R-22)
- Anesthetic in surgery

Harmful Effects of Trichloromethane

Chloroform exposure causes

- Dizziness, fatigue, and headache
- Damage to liver and kidneys

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

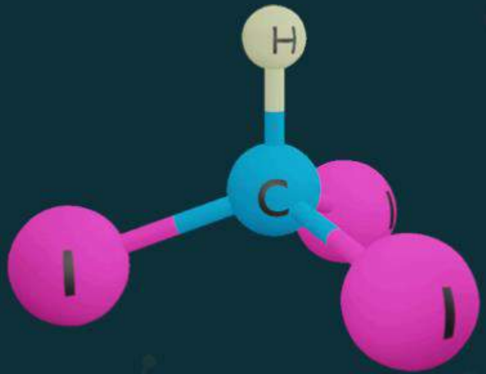
Phosgene → Highly poisonous gas

Triiodomethane (Iodoform)

Triiodomethane

Structure

Uses

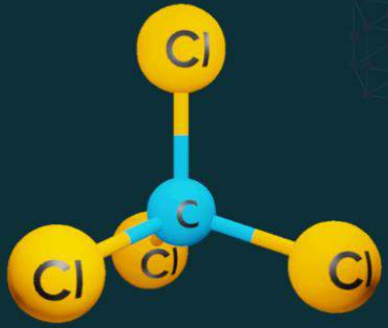


Has **antiseptic** properties due to the liberation of free iodine.

Tetrachloromethane (Carbon tetrachloride)

Tetrachloromethane

- Structure
- Uses
- Harmful Effects



Uses

Tetrachloromethane

- Manufacture of refrigerants and propellants for aerosol cans
- Feedstock in the synthesis of chlorofluorocarbons
- Pharmaceuticals manufacturing

Uses

Tetrachloromethane

- Cleaning fluid
- Degreasing agent
- Fire extinguisher

Harmful Effects of Tetrachloromethane

CCl_4 exposure causes

- Nerve cell damage
- Cardiac arrest
- Liver cancer

CCl_4 exposure causes

- Dizziness & light headedness
- Nausea and vomiting

Freons

Chlorofluorocarbon compounds of methane & ethane are collectively known as **freons**.

Freons

- Structure
- Uses and characteristics
- Harmful Effects

Uses

Uses of Freon-12

- Aerosol Propellants
- Refrigerators
- Air-conditioners

Characteristics of Freons

Freons are

- Stable
- Non-reactive
- Non-toxic
- Liquefiable gases

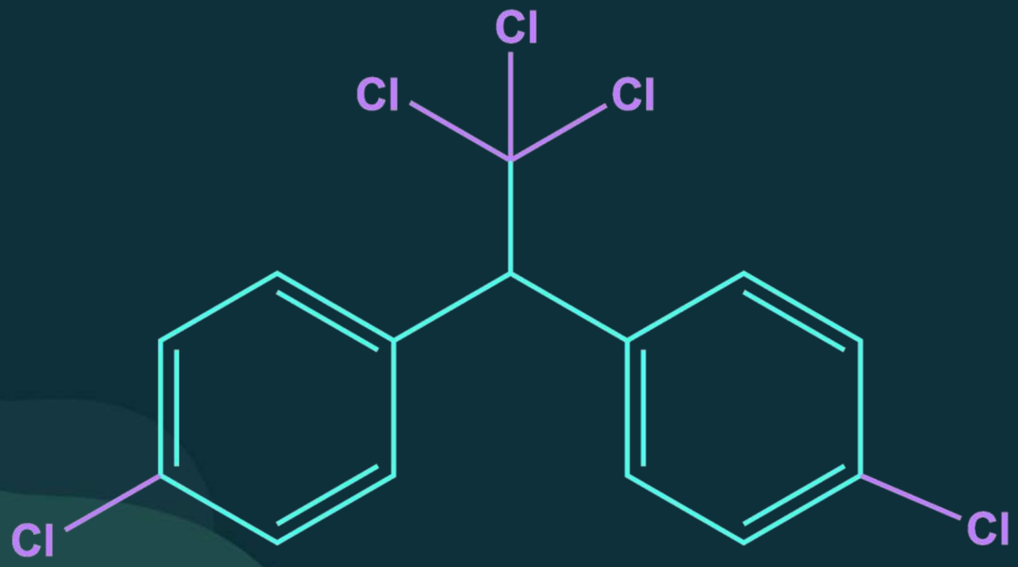
In **stratosphere**, freon is able to initiate radical chain reactions that can upset the natural **ozone balance.**

DDT

DDT

- Structure
- Uses
- Harmful Effects

Structure



Harmful Effect of DDT

DDT is not metabolised very rapidly by **animals**

↓

Deposited and stored in the **fatty tissues**.