

HALOALKANES & HALOARENES

By- Dr. Achla Rani

For- class B.Sc. 1

OBJECTIVES

After studying this unit, **STUDENTS** will be able to

- **Name** haloalkanes and haloarenes according to the IUPAC system of nomenclature from their given structures;
- **Describe** the reactions involved in the preparation of haloalkanes and haloarenes and understand the various reactions that they undergo;
- **Correlate** the structures of haloalkanes and haloarenes with various types of reactions;
- **Use** stereochemistry as a tool for understanding the reaction mechanism;

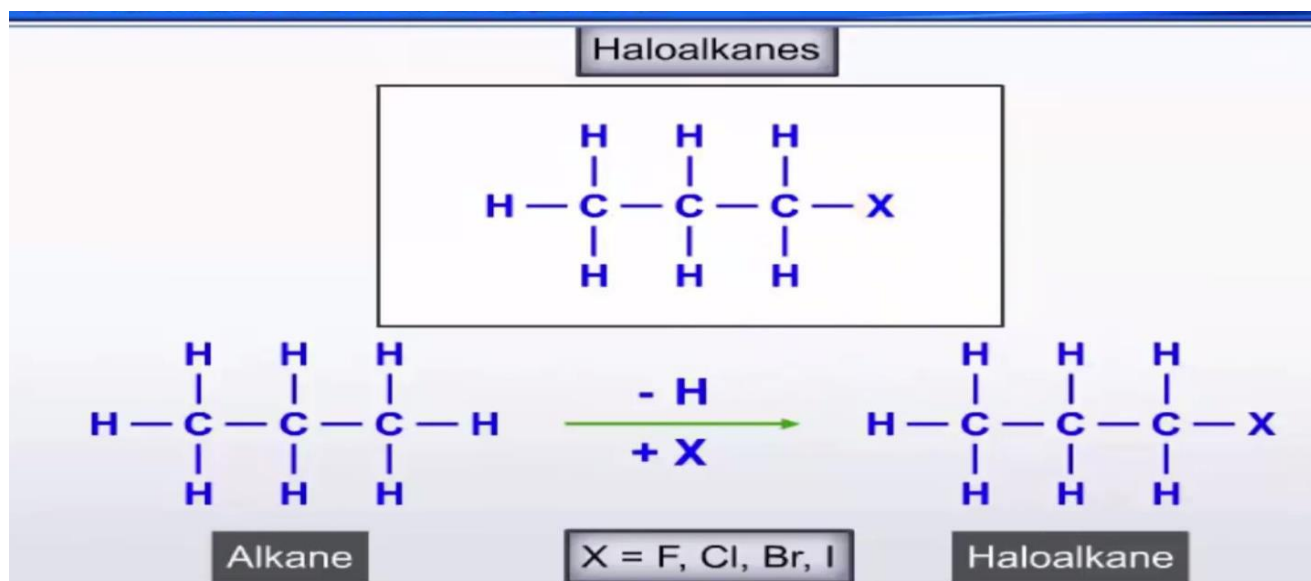
OUTLINE

- 1. INTRODUCTION, CLASSIFICATION, NOMENCLATURE**
- 2. PHYSICAL PROPERTIES OF HALO ALKANES & HALO ARENES**
- 3. METHODS OF PREPARATION**
- 4. CHEMICAL PROPERTIES**
- 5. OPTICAL ISOMERISM**
- 6. SN1 & SN2 REACTIONS**
- 7. POLY HALOGEN COMPOUNDS**

What is meaning of haloalkane?

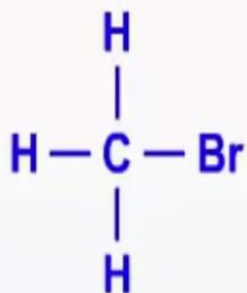
Organic compounds formed by replacement of one or more hydrogen atom/s by halogen atom/s. from Hydrocarbon

Ex: chloromethane, Dichloromethane etc.

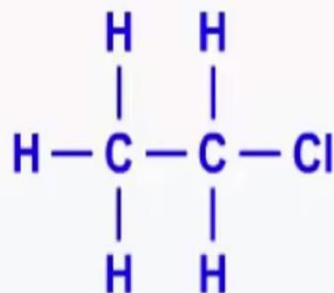


Examples for haloalkanes

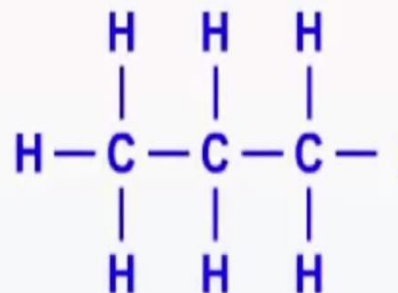
Haloalkanes



Bromomethane



Chloroethane

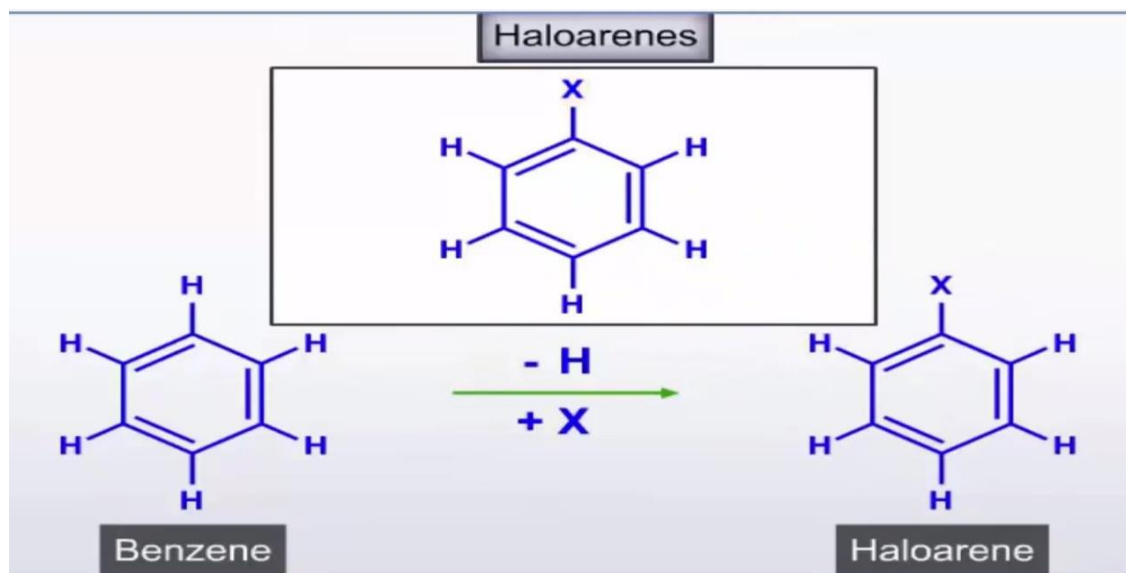


Iodopropane

Alkylhalides

What is meaning of haloarene?

If one or more hydrogen is displaced by halogen atom/s in aromatic ring , product is called as Haloarenes



Importance of Halogen derivative.

Haloderivative Organic compounds have many important for Mankind:

1. As solvents for non-polar compounds.

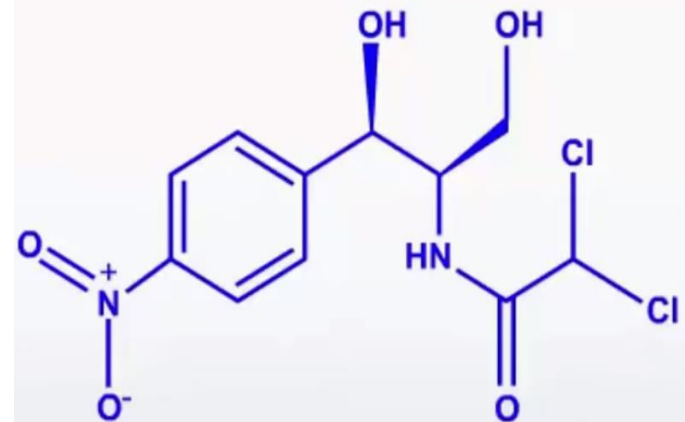


Medicine



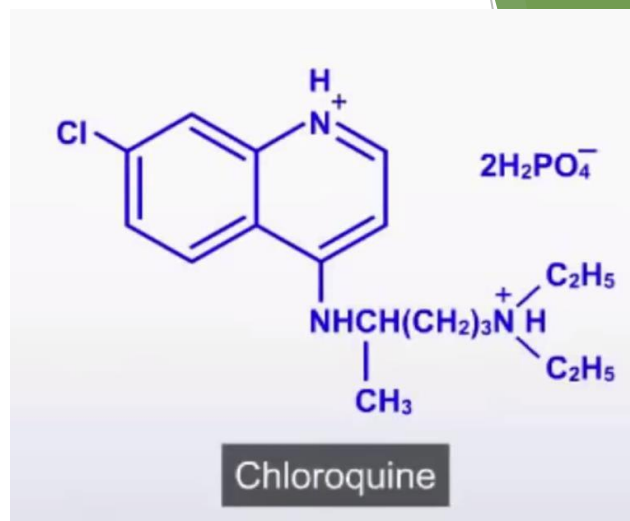
Research

2. Chloramphenicol
(medicine) to treat typhoid
fever.



Chloramphenicol

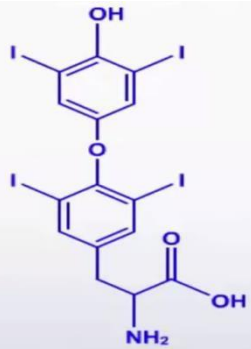
3. Chloroquine
(medicine) used
to treat malaria.



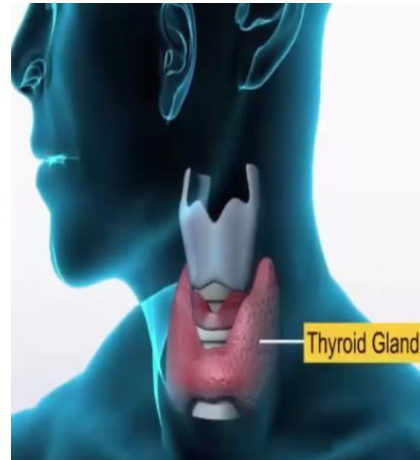
**4. Some fluorinated
compounds are being
developed as blood substitute
in surgery.**



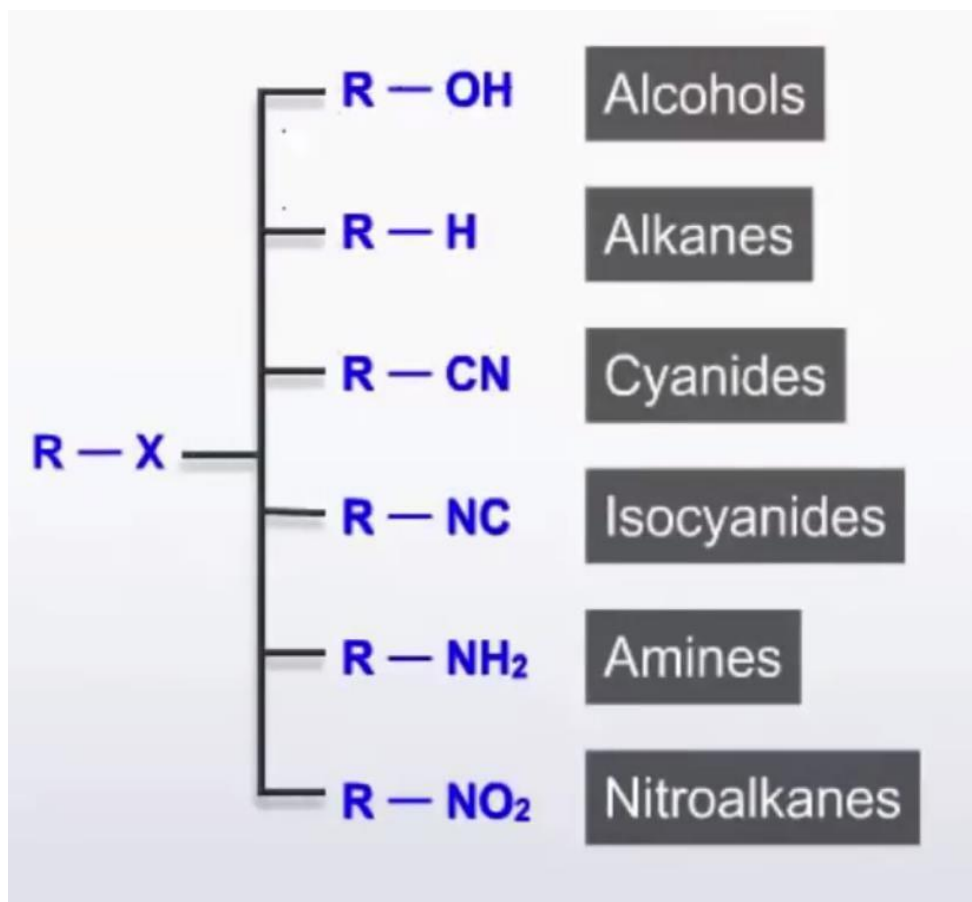
5. THYROXINE is used in the treatment of Goitre disease



Thyroxine



6. As starting materials for synthesis of many compounds.



Classification of Haloderivatives

Based on
Number of
Halogen atoms

Monohalogen

Dihalogen

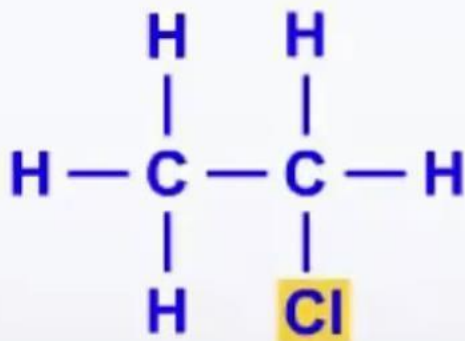
Polyhalogen

Based on the hybridisation of C-atom
of C-X bond of monohalocompounds

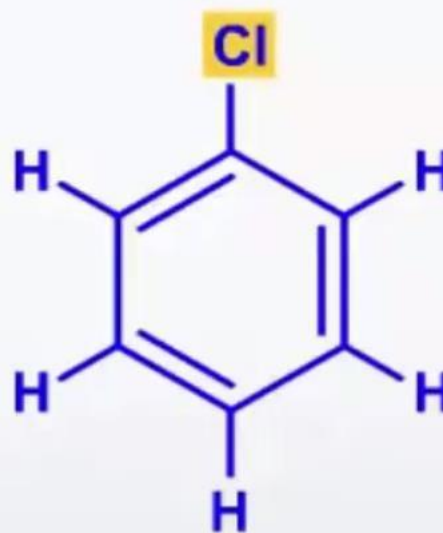
Compounds
containing sp^3 C-X
bond (X = F, Cl, Br, I).

Compounds containing
 sp^2 C-X bond

Monohalo derivatives



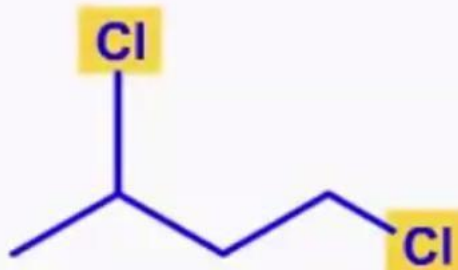
Chloroethane



Chlorobenzene

Dihalo derivatives

Dihaloalkane



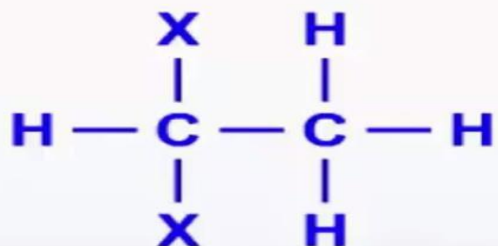
1,3-dichlorobutane

Dihaloarene



1,3-dibromobenzene

Dihalo derivatives

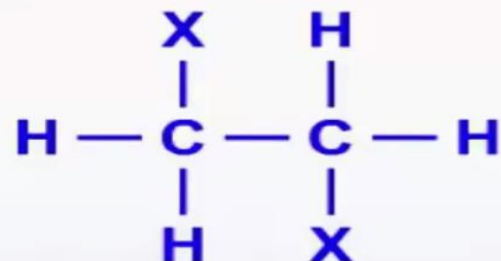


Common name:

Alkylidene halide

IUPAC name:

1,1-dihaloalkane

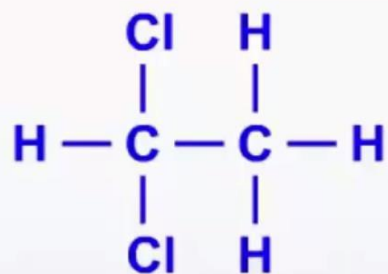


Common name:

Alkylene dihalide

IUPAC name:

1,2-dihaloalkane

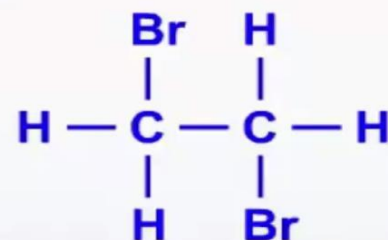


Common name:

Ethylidene chloride
(gem-dihalide)

IUPAC name:

1,1-dichloroethane



Common name:

Ethylene dibromide
(vic-dibromide)

IUPAC name:

1,2-dibromoethane

Trihalo derivatives

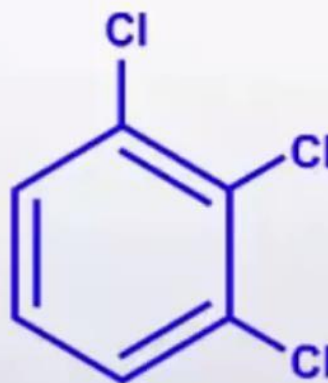
Classification of Haloalkanes and Haloarenes

Trihaloalkane



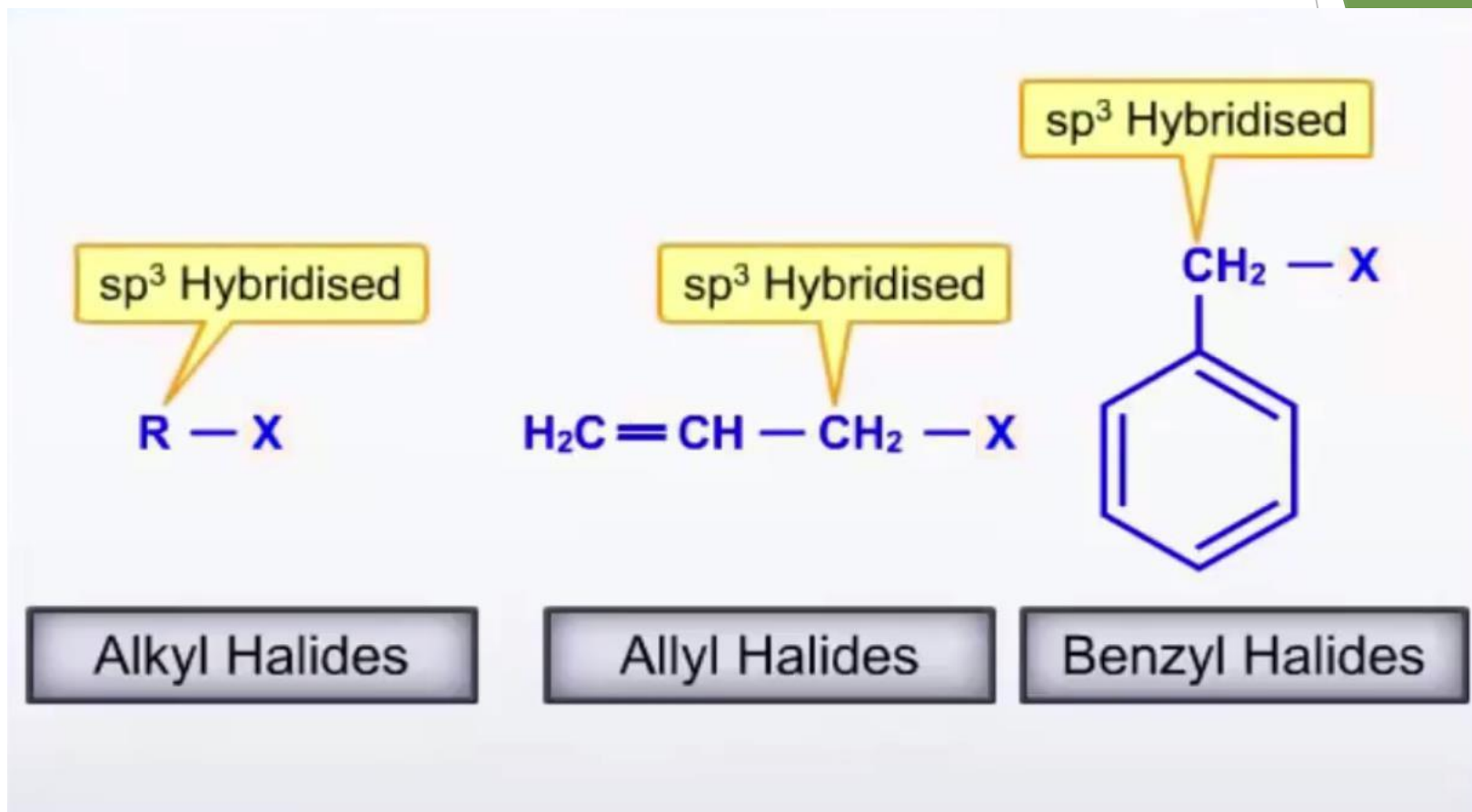
2,3,4-trichloropentane

Trihaloarene



2,3,4-trichlorobenzene

Compounds containing sp^3 C-X bond (X = F, Cl, Br, I).

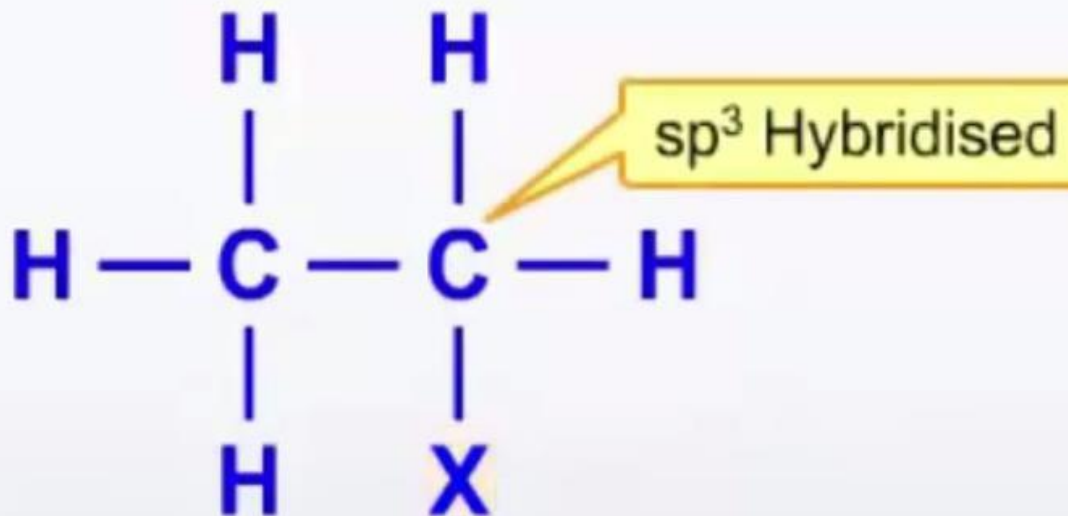


Alkyl Halides (Haloalkanes)

An Alkyl Group



A Halogen Atom



Homologous series of alkyl halides

n	$C_nH_{2n+1}X$
1	CH_3X
2	C_2H_5X
3	C_3H_7X
4	C_4H_9X

Based on the nature of $C - X$ bond

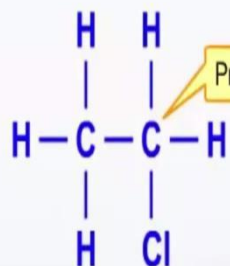
Primary (1°)



Secondary (2°)



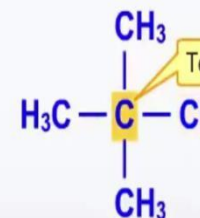
Tertiary (3°)



Primary Carbon (1°)

Ethyl Chloride

Secondary Carbon (2°)



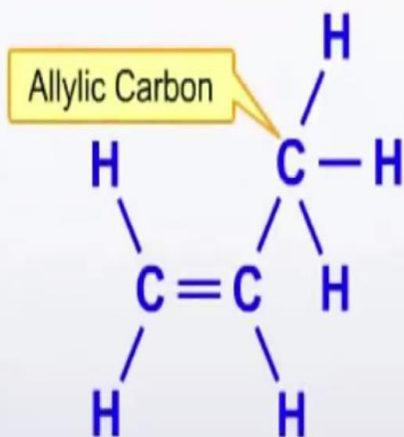
Tertiary Carbon (3°)

Tertiary Butyl Chloride

Allylic halides

Allylic Carbons

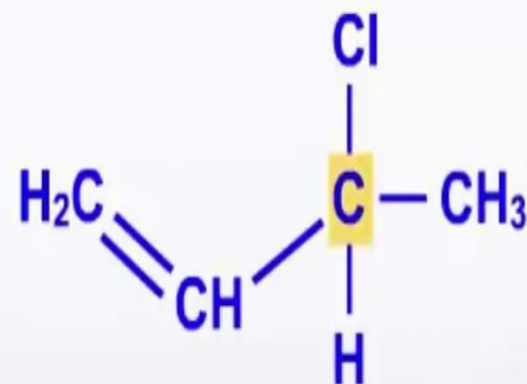
Allylic carbons are carbon atoms bonded to a carbon atom that is doubly bonded to another carbon atom.



Allylic Carbon

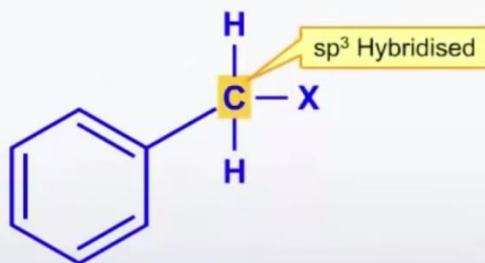


Allylic Carbons

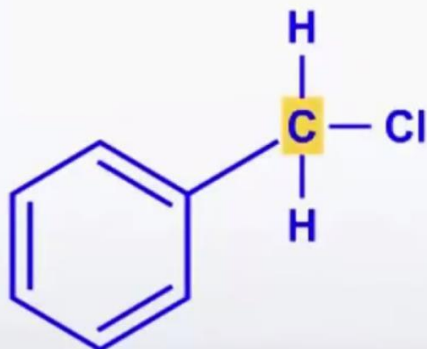


Benzylic halides

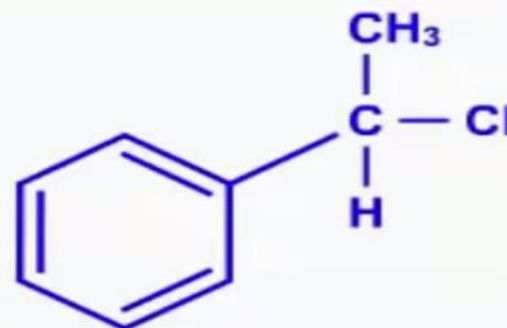
Benzylic Halides



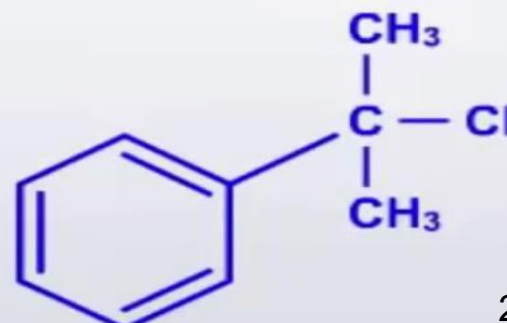
Primary Benzylic Halide



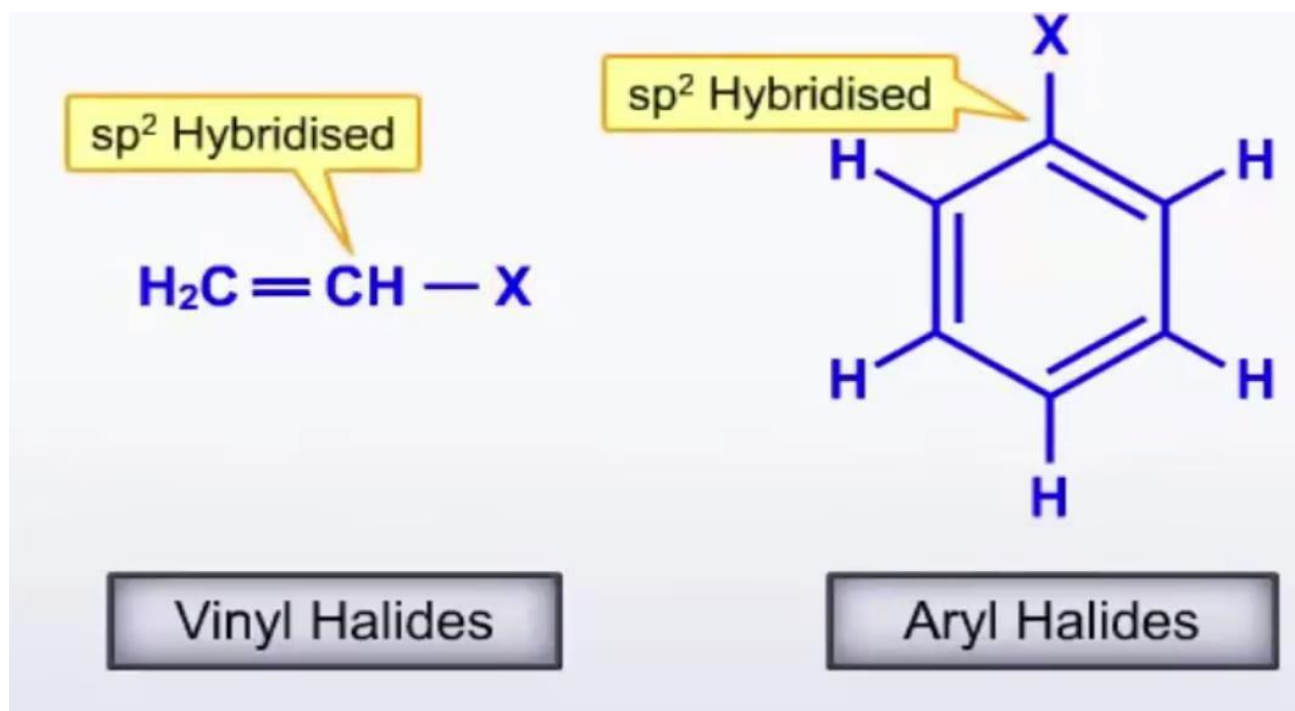
Secondary Benzylic Halide



Tertiary Benzylic Halide

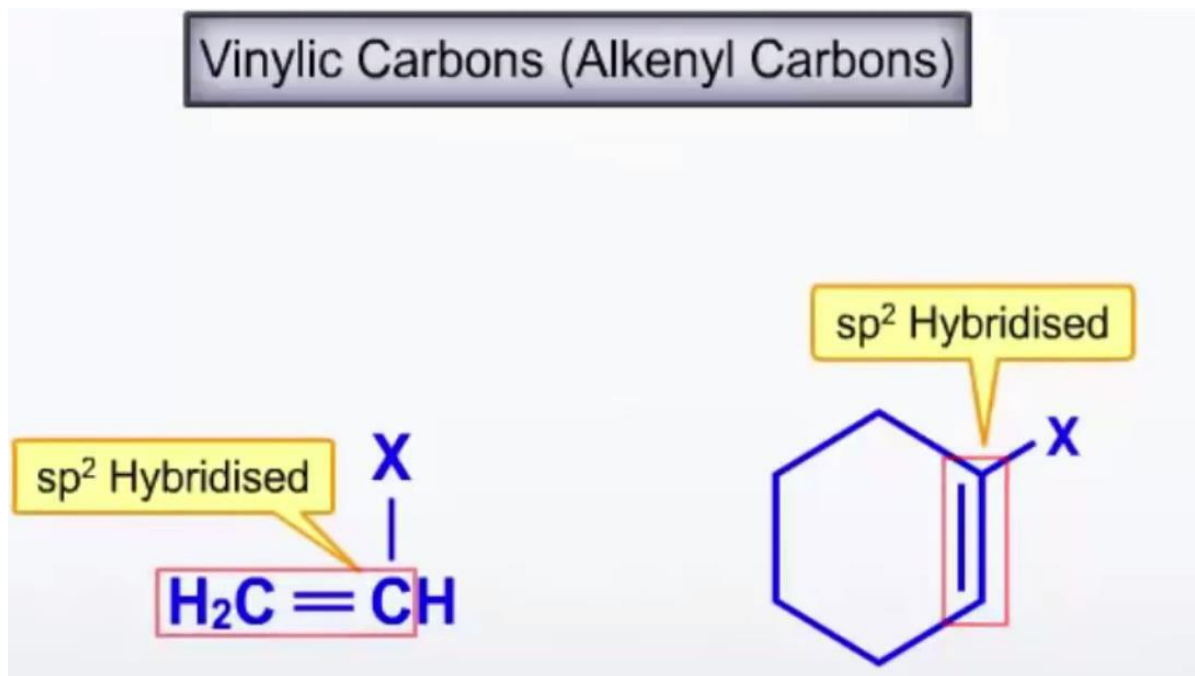


Compounds containing sp^2 C-X bond (X = F, Cl, Br, I).



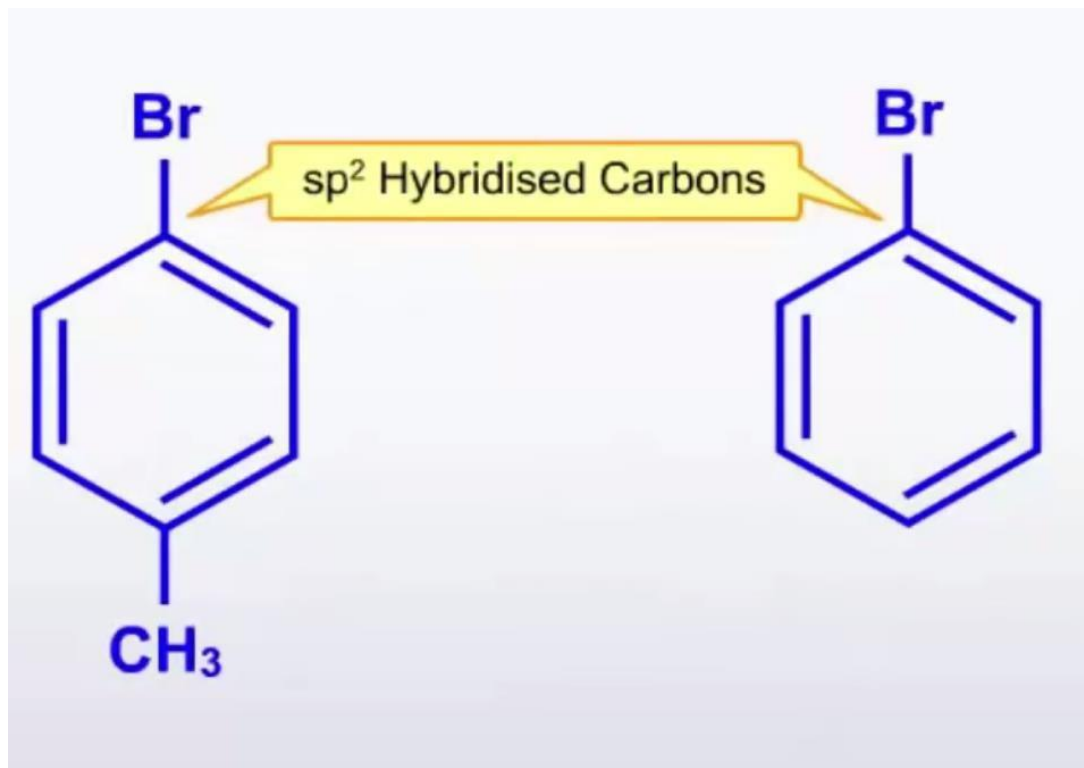
Vinylic halides

halogen atom is bonded to a sp^2 hybridised carbon atom of a carbon-carbon double bond (C = C).

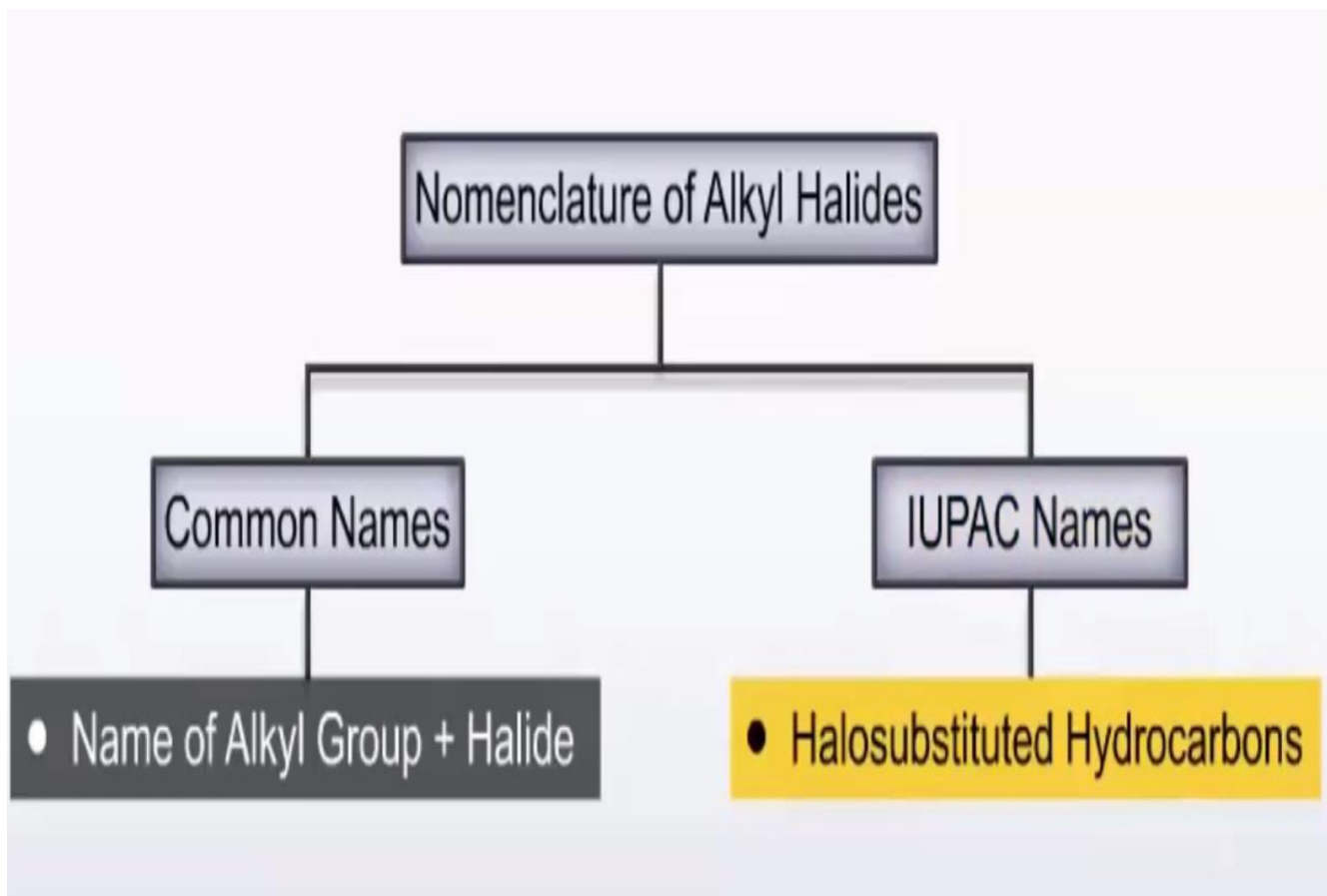


Aryl halides

halogen atom is directly bonded to the sp^2 hybridised carbon atom of an aromatic ring.



NOMENCLATURE



NOMENCLATURE

ORDER OF NAMING Halogen compounds

PREFIXES

- F Floro
- Cl Chloro
- Br Bromo
- I Iodo

WORD ROOT

- 1C meth
- 2C eth
- 3C Prop

PRIMARY SUFIXES

- ane
- ene
- yne

Example-1

3 2 1



1-Bromo +

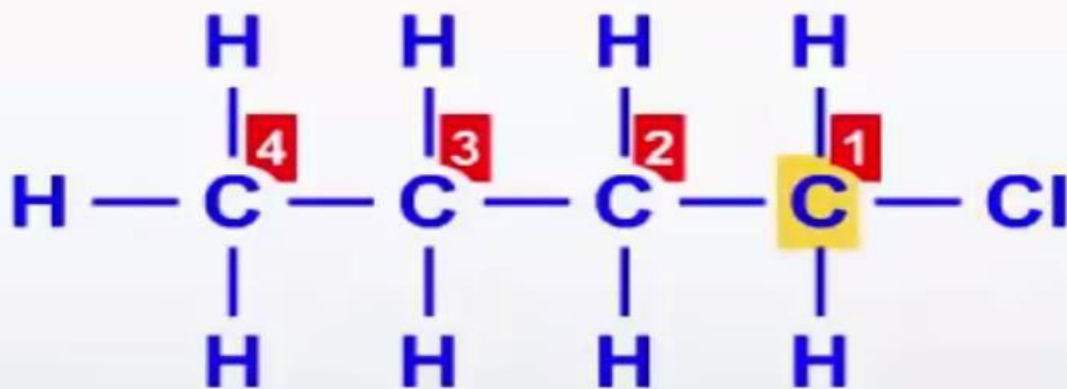
prop

+ane

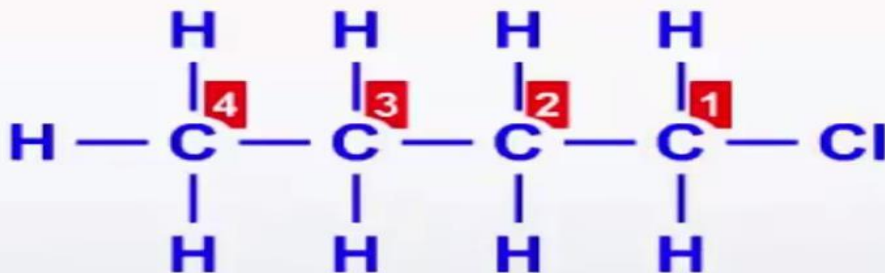


1-Bromopropane

Example-2



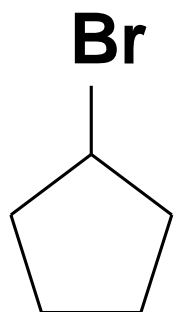
IUPAC Name



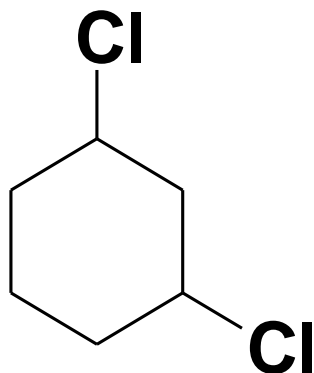
1-chlorobutane

Example 3

Name the following:



bromocyclopentane

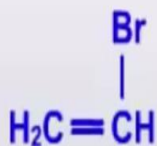


1,3-dichlorocyclohexane

Q-1



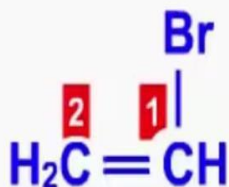
Give the IUPAC names of the following compounds?



Vinylbromide



Allylchloride



Common name:

Vinylbromide

Solution:

IUPAC name:

Bromoethene



Common name:

Allylchloride

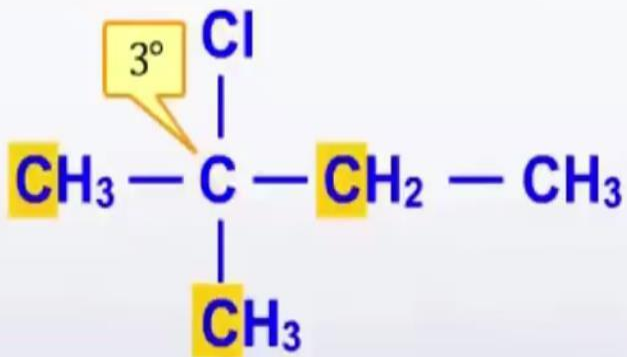
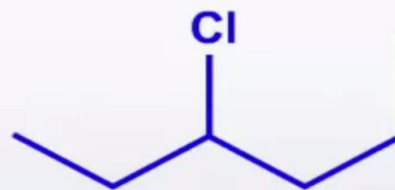
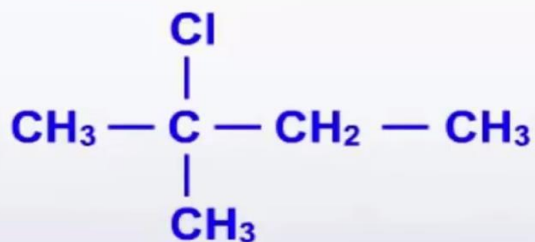
IUPAC name:

3-chloropropene

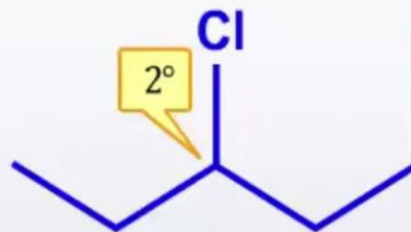
Q-2



Give the IUPAC names for the following molecules.
Are they primary, secondary or tertiary haloalkanes?



2-Chloro-2-methylbutane
(3° haloalkane)



3-Chlorohexane
(2° haloalkane)

Q-3



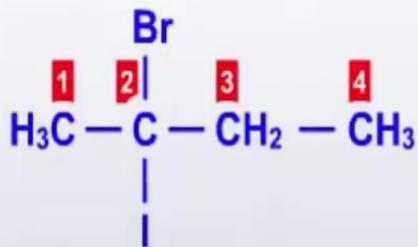
Draw structural formulas for the following molecules

2-bromo-2-iodobutane

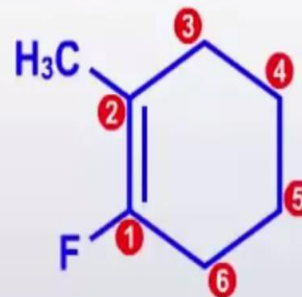
1-fluoro-2-methylcyclohexene

2-bromo-2-iodobutane

Answers:



1-fluoro-2-methylcyclohexene



Q-4

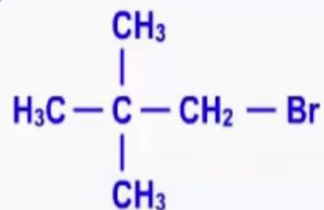


What are the common and IUPAC names of following compounds?

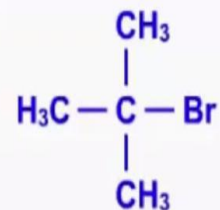
(A)



(B)



(C)



(A)



Solution:

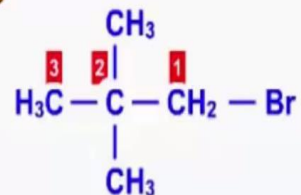
Common name:

Secondary butylbromide

IUPAC name:

2-bromobutane

(B)



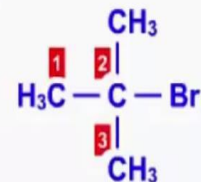
Common name:

Neopentylbromide

IUPAC name:

1-Bromo-2,2-dimethylpropane

(C)



Common name:

Tertiary butylbromide

IUPAC name:

2-bromo-2-methylpropane

Q-5



Naming dihaloalkanes:
Give the IUPAC names of the following compounds

(A)



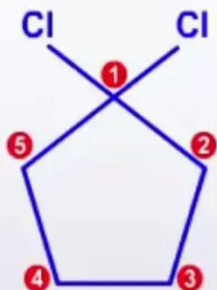
(B)



(C)

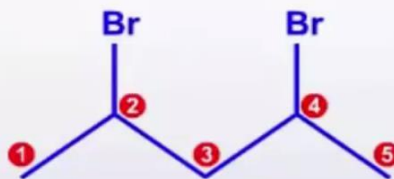


(A)

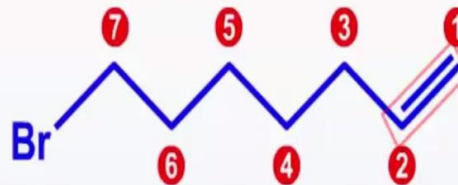


1,1-dichlorocyclopentane

(B)



2,4-dibromopentane



7-bromohept-1-ene
(7-bromo-1-heptene)

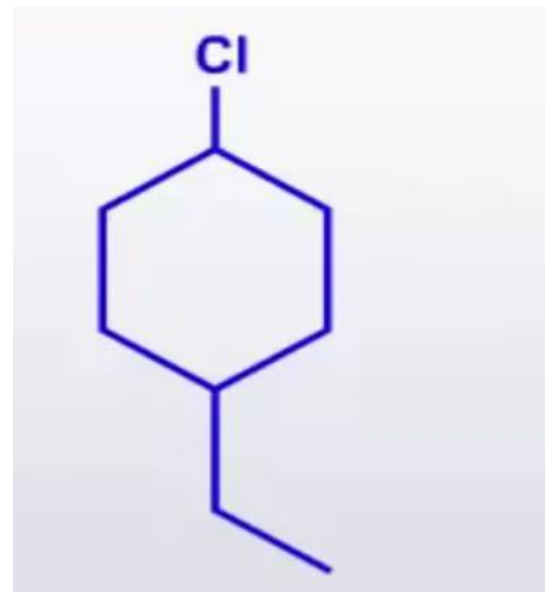
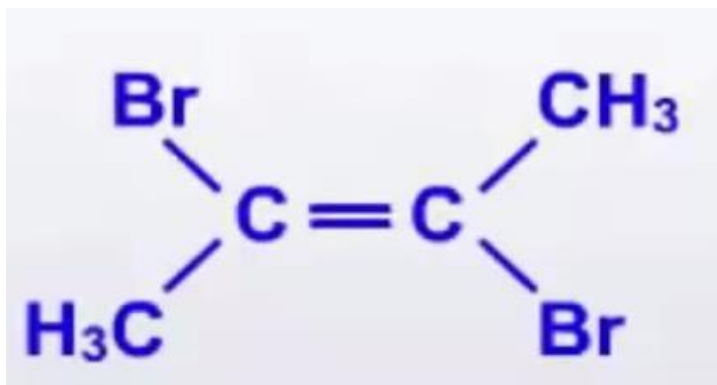
Q-6



Draw formulas for the following compounds

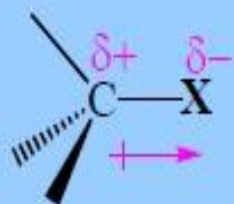
2,3-Dibromobut-2-ene

1-Chloro-4-ethylcyclohexane



Nature of C-X bond

The carbon center is sp^3 hybridized in alkyl halides and the C-X bond is polarized as shown because of the greater electronegativity of the halogen.



Now THINK why **of the following:**

1. The C-X bond in haloalkanes is polar in nature.
2. C-X bond length increases as $C-F < C-Cl < C-Br < C-I$.
3. C-F bond is less reactive as compared to C-I bond.
4. Order of Dipole moment is $CH_3-Cl > CH_3-F > CH_3Br > CH_3I$
5. The dipole moment of chlorobenzene is lower than that of cyclohexylchloride.

Physical properties of haloalkanes & haloarenes

Solubility

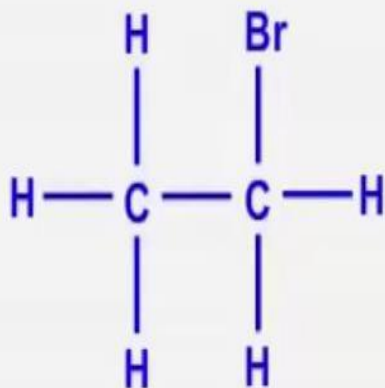
Halo alkanes are not able to form hydrogen bonds with water and, even though they are polar in nature, they are practically insoluble in water. However, they are soluble in organic solvents like alcohol, ether, benzene, etc.



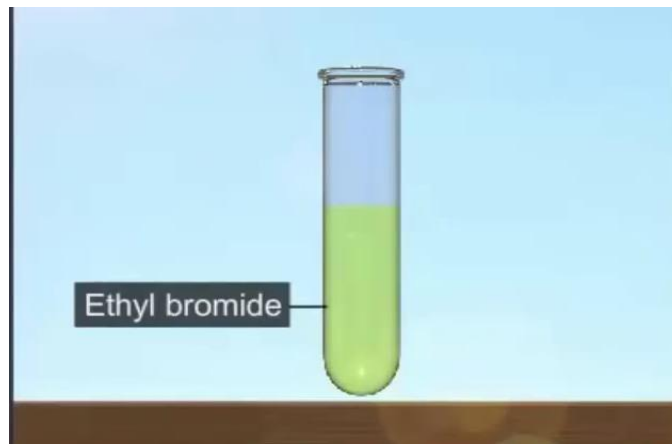
PHYSICAL STATE

Compound	Physical state
Methyl chloride (CH_3Cl)	Gas
Methyl bromide (CH_3Br)	Gas
Ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$)	Gas
Chlorofluoromethane (CH_2ClF)	Gas
Higher alkyl halides up to C_{18}	Liquids
Higher alkyl halides more than C_{18}	Solids

Ethyl bromide



Turns yellow when exposed to light and air

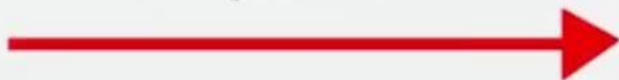


BOILING POINT

Boiling point increases with increase in number of carbon atoms in the chain.

Van der waals forces increase with increase in size of the carbon chain.

Boiling Point



X = F, Cl, Br, I

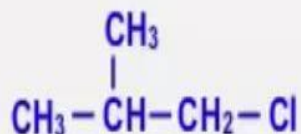
BOILING POINT

Effect of branching on boiling point



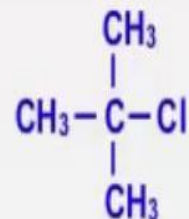
n-butyl chloride

Boiling point 78.5 °C



iso-butyl chloride

Boiling point 69 °C



tert-butyl chloride

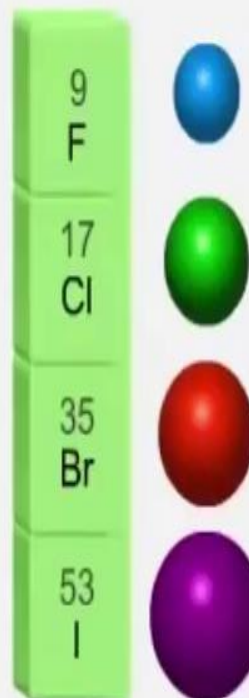
Boiling point 51 °C

BOILING POINT



Halogen

Order of B.P	R - F < R - Cl < R - Br < R - I			
At.Wt of Halogen	F 19	Cl 35.5	Br 80	I 127



R - X

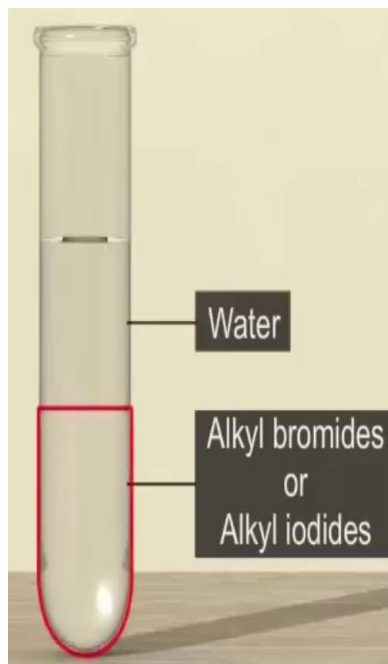
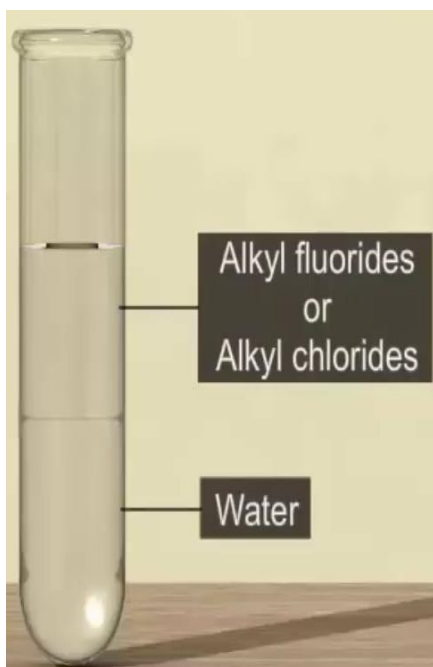
R = Alkyl group





X = Halogen (F, Cl, Br, I)

DENSITY

Polychloro alkanes	Density (gmL^{-1})
CH_2Cl_2	1.336
CHCl_3	1.487
CCl_4	1.595

DENSITY



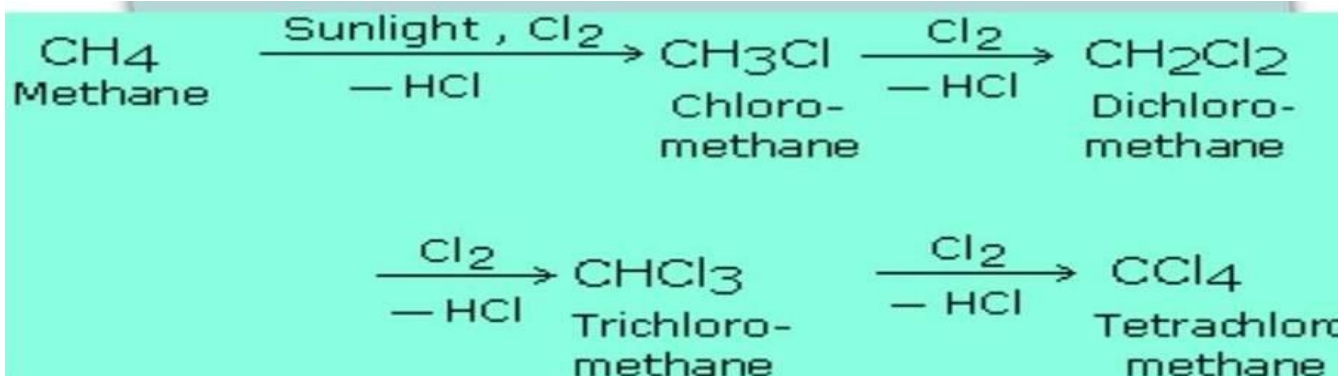
Halogen	
9 F	
17 Cl	
35 Br	
53 I	

METHODS OF PREPARATION OF ALKYL HALIDES

1. FROM ALKANE
2. FROM ALKENE
3. FROM ALCOHOL
4. BY HALOGEN EXCHANGE METHOD

1.FROM ALKANE

Haloalkanes can be prepared from alkanes and alkenes when the halogen atom replaces the hydrogen atom.



When pure components are needed, they can be obtained by fractional distillation.



Markownikoff's rule

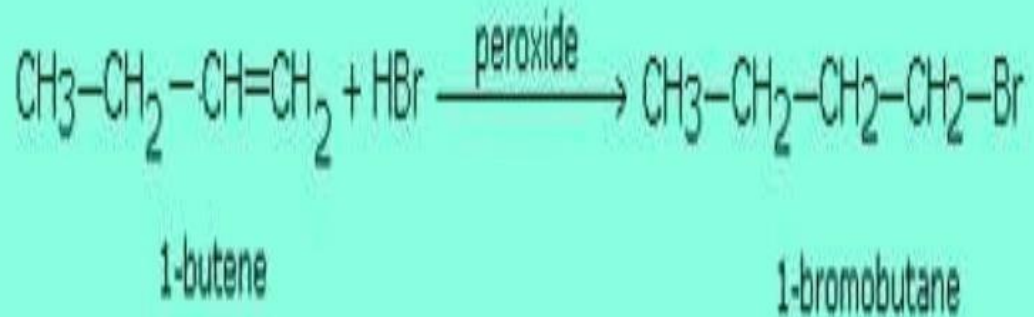
'the negative part of the attacking reagent attaches itself to the carbon atom carrying lesser number of hydrogen atoms while the positive part goes to the carbon atom with more number of hydrogen atoms'



Anti Markownikoff's rule

It has been observed that when HBr is added to an unsymmetrical double bond in the presence of organic peroxides such as benzoyl peroxide ($\text{C}_6\text{H}_5\text{CO-O-O-COC}_6\text{H}_5$), the reaction takes place against Markownikoff's rule.





Anti Markownikoff's rule or peroxide effect applies to the addition of HBr only and not to the addition of HI or HCl.



FROM ALCOHOL



3. FROM ALCOHOL

BY THE ACTION OF HALOGEN ACIDS

GROOVE'S PROCESS

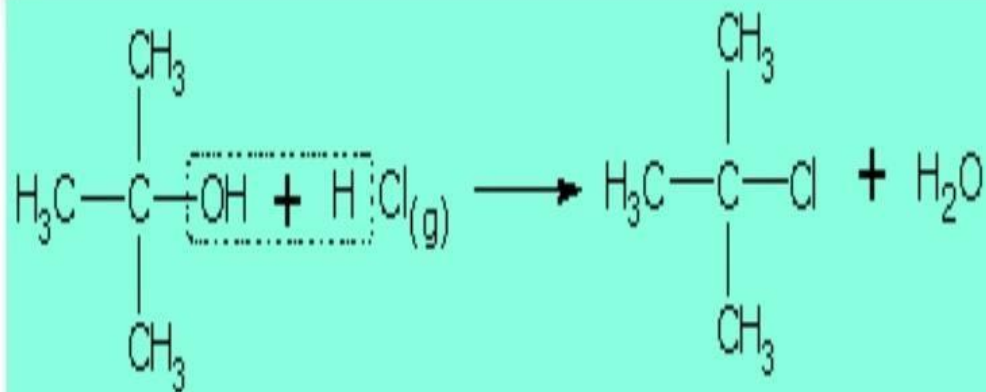


Ethanol
(Ethyl alcohol)

Chloroethane
(Ethyl chloride)



What is function of catalyst in above reaction?



2-Methyl -2-propanol

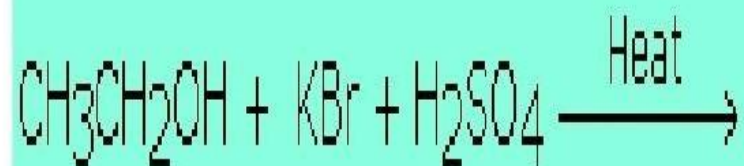
(tert-Butyl alcohol)

2-Chloro-2-methylpropane

(tert-Butyl chloride)

TERTIARY ALCOHOLS, ARE VERY REACTIVE AND THEREFORE, THEY REACT READILY WITH CONCENTRATED HCL EVEN IN THE ABSENCE OF THE CHLORIDE.

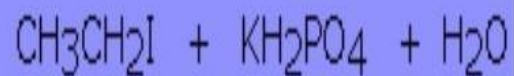
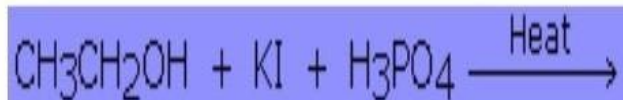




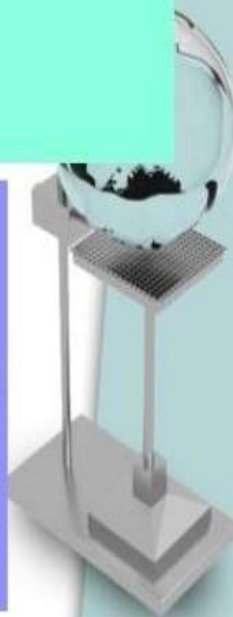
Ethanol



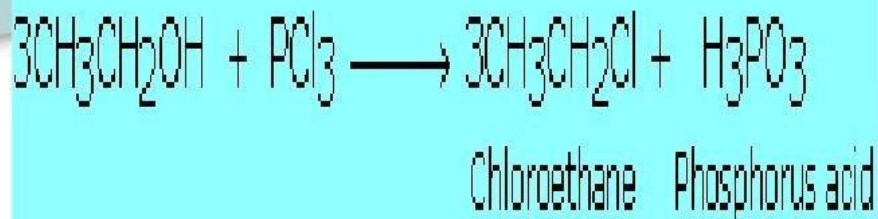
Bromoethane



Iodoethane Potassium dihydrogen
phosphate



2.By the action of phosphorus halides



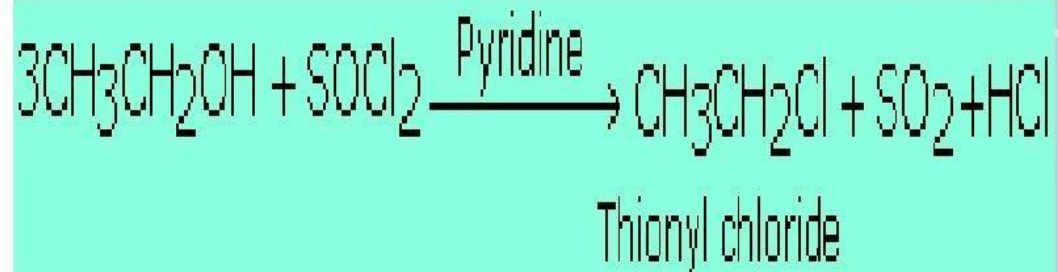
Bromoalkanes and iodoalkanes are prepared by the action of PBr_3 and PI_3 respectively on alcohols. As PBr_3 and PI_3 , are not very stable compounds, they are prepared in situ by the action of red phosphorus on Br_2 , or I_2 .



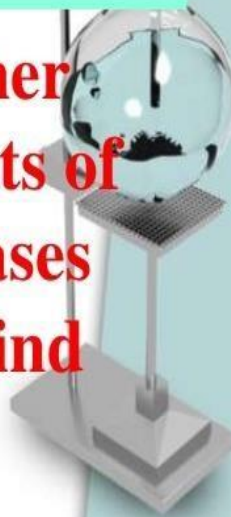
FROM ALCOHOL



3. with thionyl chloride:

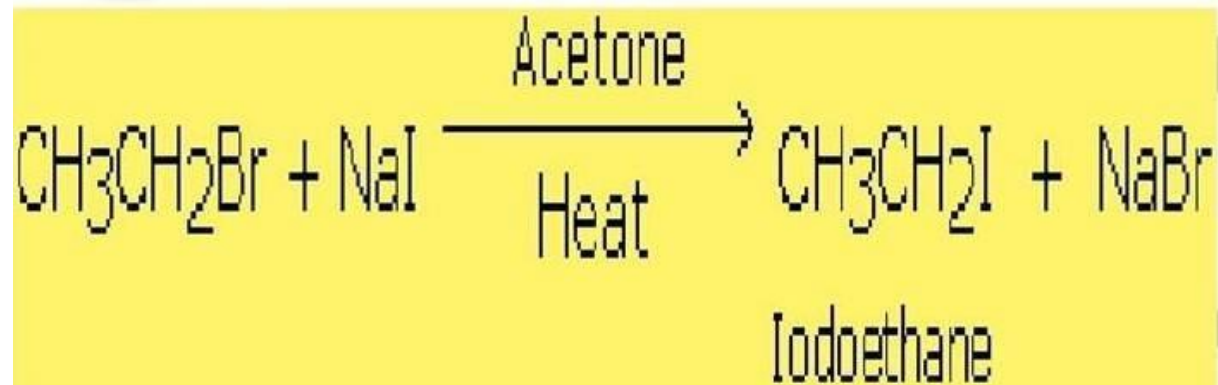


This method is preferred than other methods because both the products of the reaction (SO₂ and HCl) are gases and can easily escape leaving behind pure alkyl halide.



4. BY HALIDE EXCHANGE

Finkelstein reaction.



SWARTS REACTION



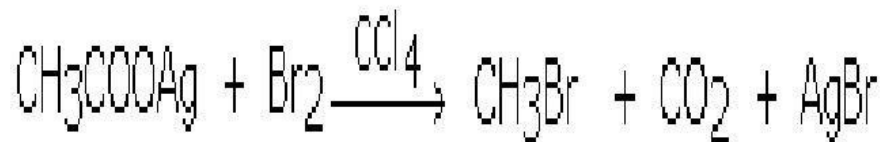
Mercurous
fluoride

Fluoroethane



From silver salts of acids

Borodine Hundsdiecker reaction



Silver acetate

Bromomethane

Chloroalkanes can also be obtained by this method by using Cl_2 instead of Br_2 , but, the yield of hloroalkanes is very poor.



CHEMICAL PROPERTIES

Types of Reactions of Haloalkanes

Nucleophilic Substitution Reactions

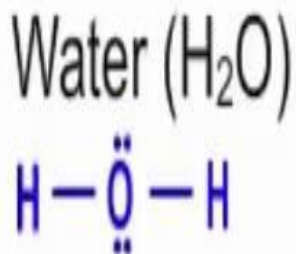
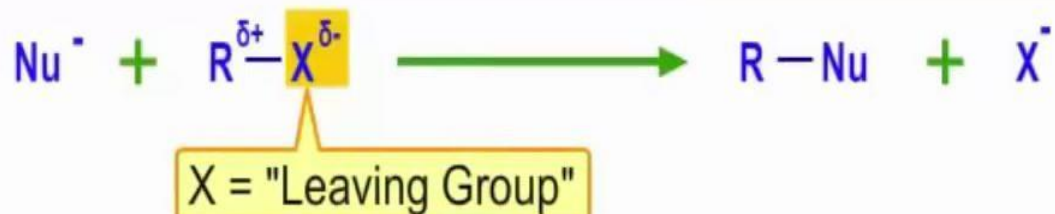
Elimination Reactions

Reaction with Metals

1. Nucleophilic substitution reactions

A nucleophile (Lewis base) substitutes for a halogen atom in an alkyl halide

General form of reaction:



Order of reactivity



Increasing reactivity in substitution reactions 

- Fluorides are the poorest leaving groups.
- Iodides are the best leaving groups.

Methyl
Halide

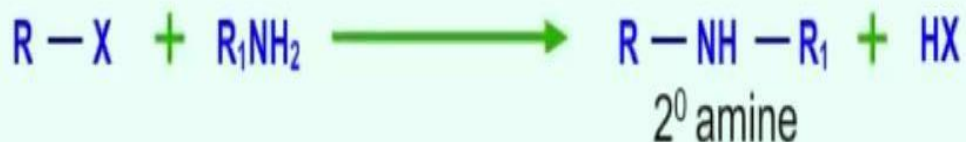
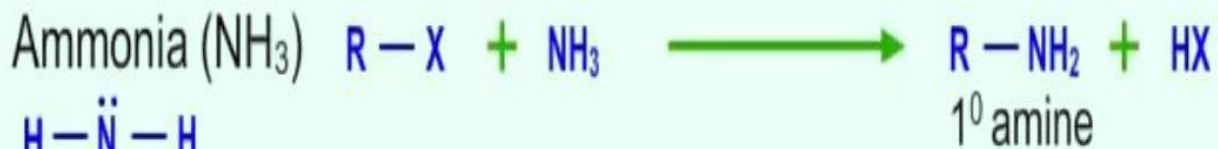
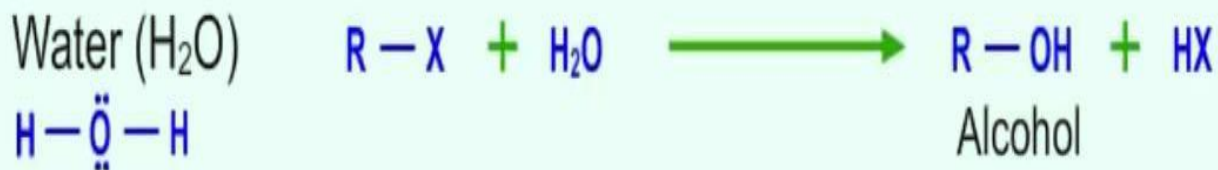
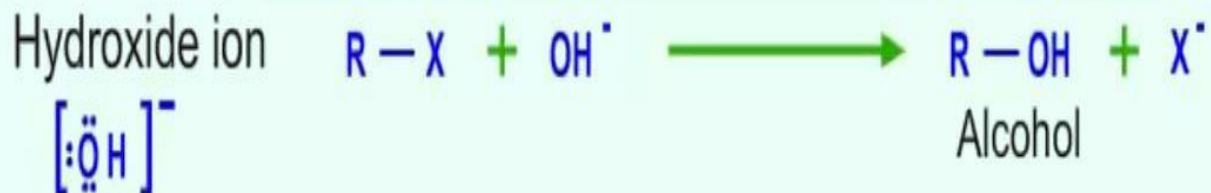
Primary
Alkyl Halide

Secondary
Alkyl Halide

Tertiary
Alkyl Halide



Nucleophilic Substitution Reaction



Reagent	Nucleophile (Nu ⁻)	Substitution product R-Nu	Class of main product
NaOH (KOH)	HO ⁻	ROH	Alcohol
H ₂ O	H ₂ O	ROH	Alcohol
NaOR'	R'O ⁻	ROR'	Ether
NaI	I ⁻	R-I	Alkyl iodide
NH ₃	NH ₃	RNH ₂	Primary amine
R'NH ₂	R'NH ₂	RNHR'	Sec. amine
R'R''NH	R'R''NH	RNR'R''	Tert. amine
KCN	$\bar{C}\equiv N:$	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitrile
KNO ₂	O=N-O	R-O-N=O	Alkyl nitrite
AgNO ₂	Ag- \ddot{O} -N=O	R-NO ₂	Nitroalkane
R'COOAg	R'COO ⁻	R'COOR	Ester
LiAlH ₄	H	RH	Hydrocarbon
R'-M ⁺	R ⁻	RR'	Alkane

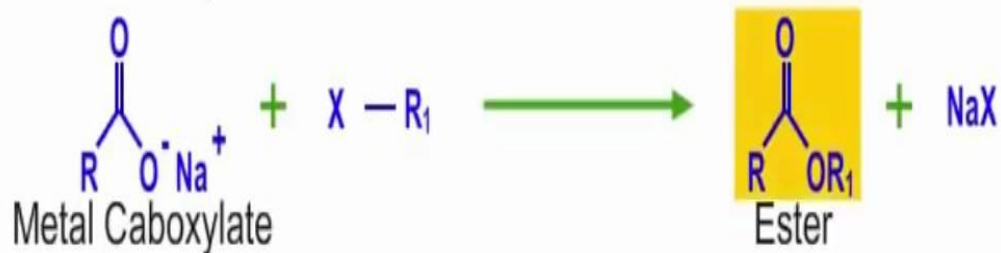
Williamsons synthesis

Sodium or potassium salts of:

- Alkoxide



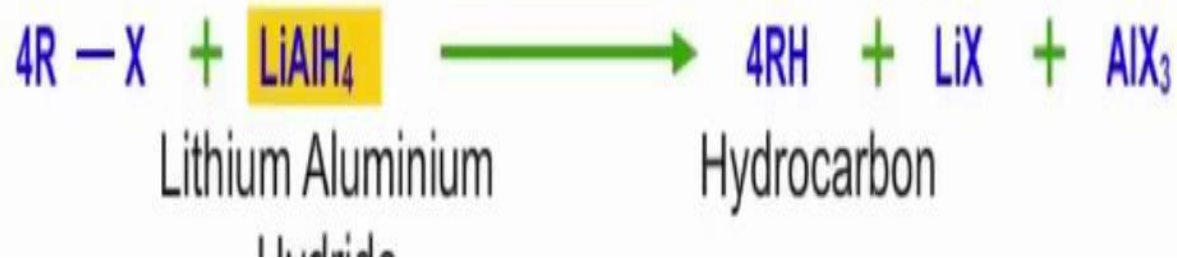
- Metal Carboxylate

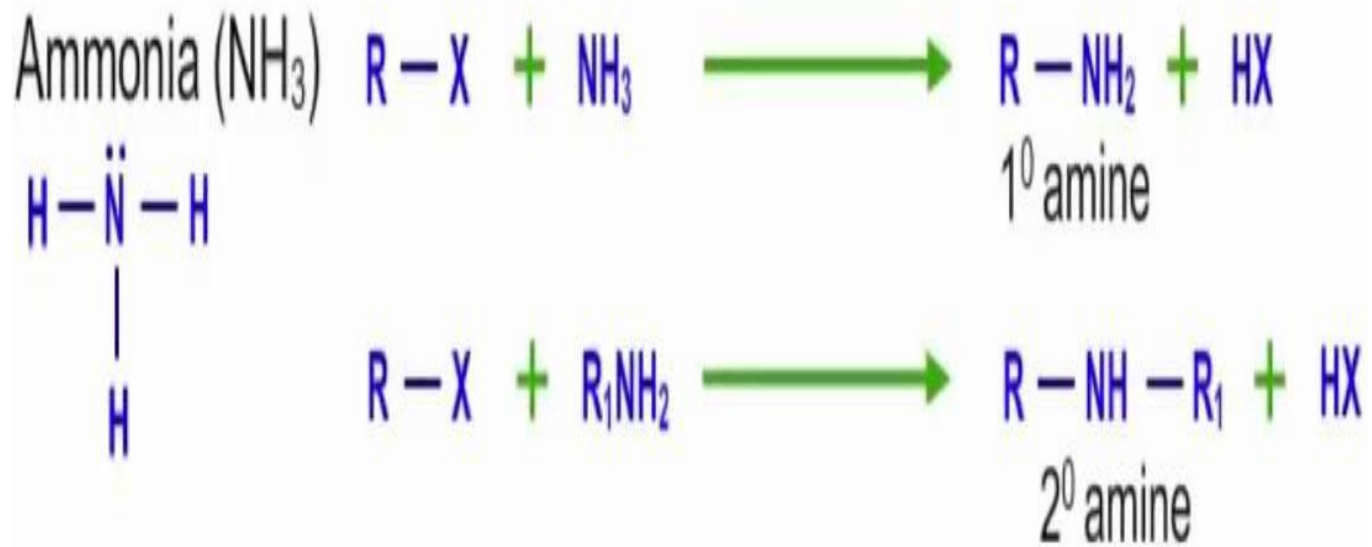


Iodide (I^-)



Hydride (H^-)





Ambident Nucleophiles

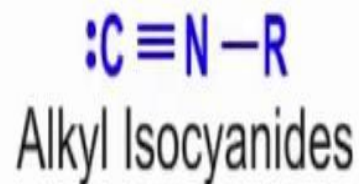


Cyanide ion $[\text{:C}\equiv\text{N:}]$

Link through Carbon:



Link through Nitrogen:



Ambident Nucleophiles

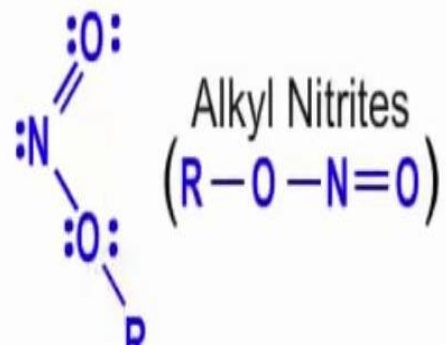


Nitrite $[NO_2]^-$

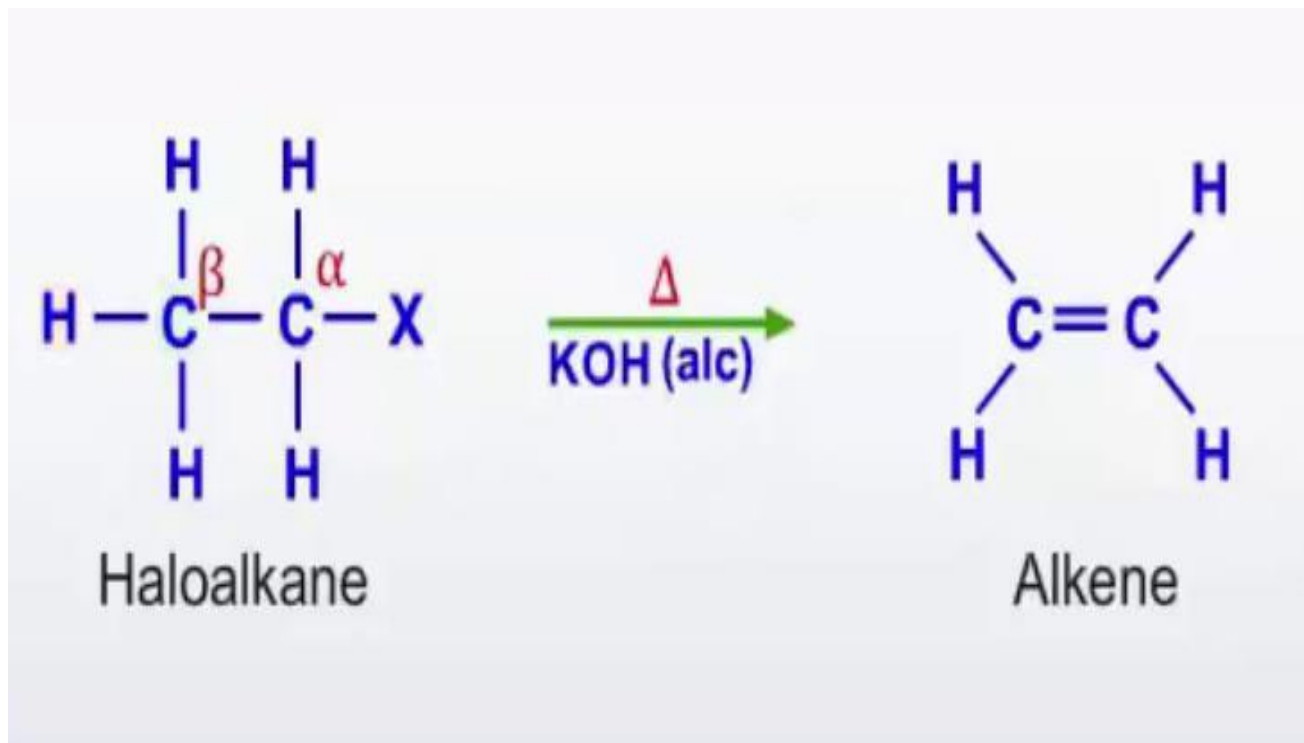
Link through Nitrogen:



Link through Oxygen:

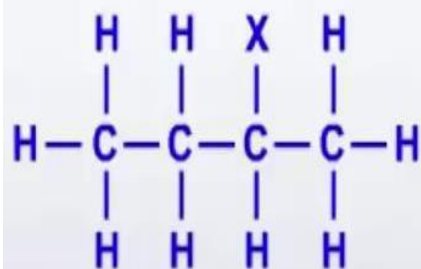


Elimination Reactions





What if there is more than one beta hydrogen in the molecule?

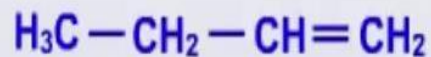


2-Halobutane

OH^-

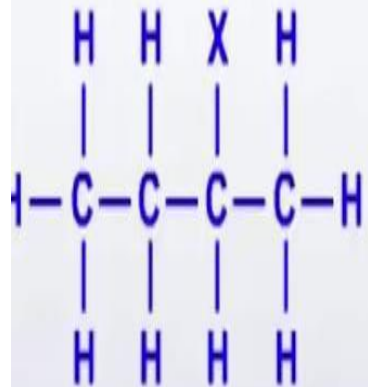


2-Butene



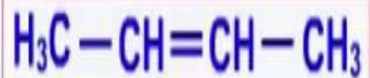
1-Butene

Zaitsev's Rule or Saytzeff's Rule



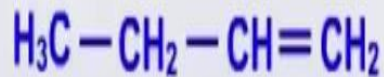
2-Halobutane

OH^-



2-Butene

Major Product



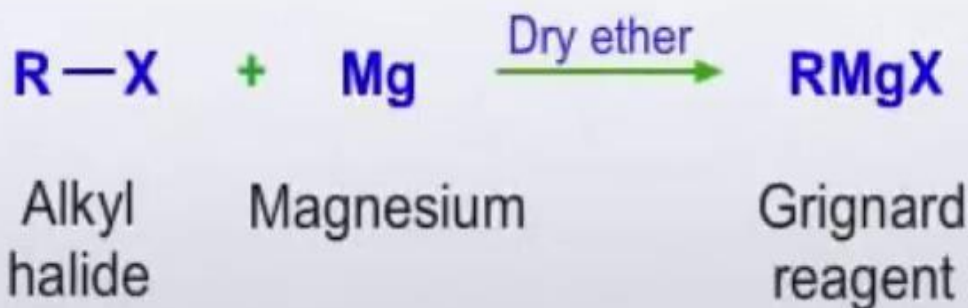
1-Butene

Minor Product

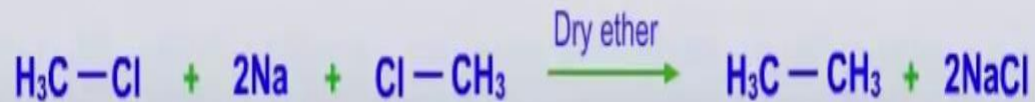
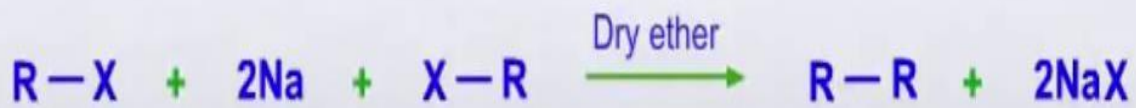
Reaction with Mg metal

Grignard Reagents

- Can be synthesised by combining the haloalkane with magnesium metal in dry ether
- General Equation

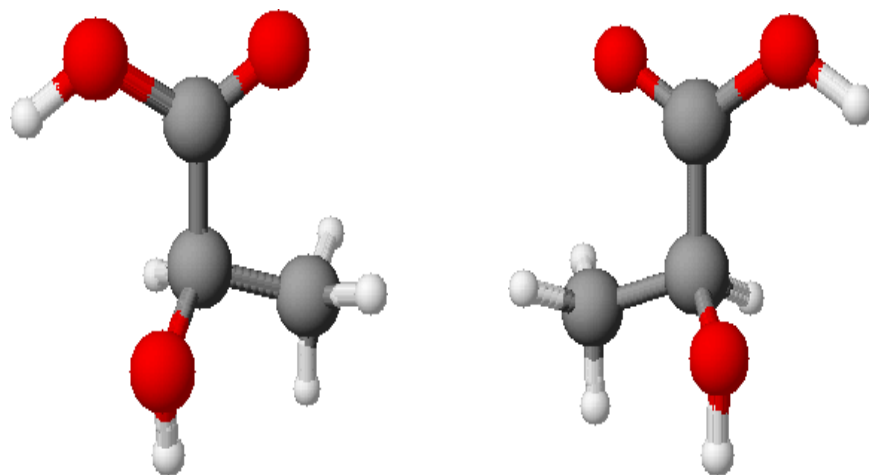


WURTZ REACTION



Stereochemistry-II

Optical Isomerism



Isomers

Same molecular formula

Constitutional

Differ in bond connectivity

Stereoisomers

Differ in three dimensional arrangement

Stereoisomers

Differ in three dimensional arrangement

Configurational

Differ in groups or atoms

Conformational

Due to free rotation

Configurational
Differ in groups or atoms

Geometrical
Due to restricted rotation

Optical
Due to Chirality

Carbon- carbon double bond

Carbon- nitrogen double bond

Nitrogen-nitrogen double bond

Ring Compounds

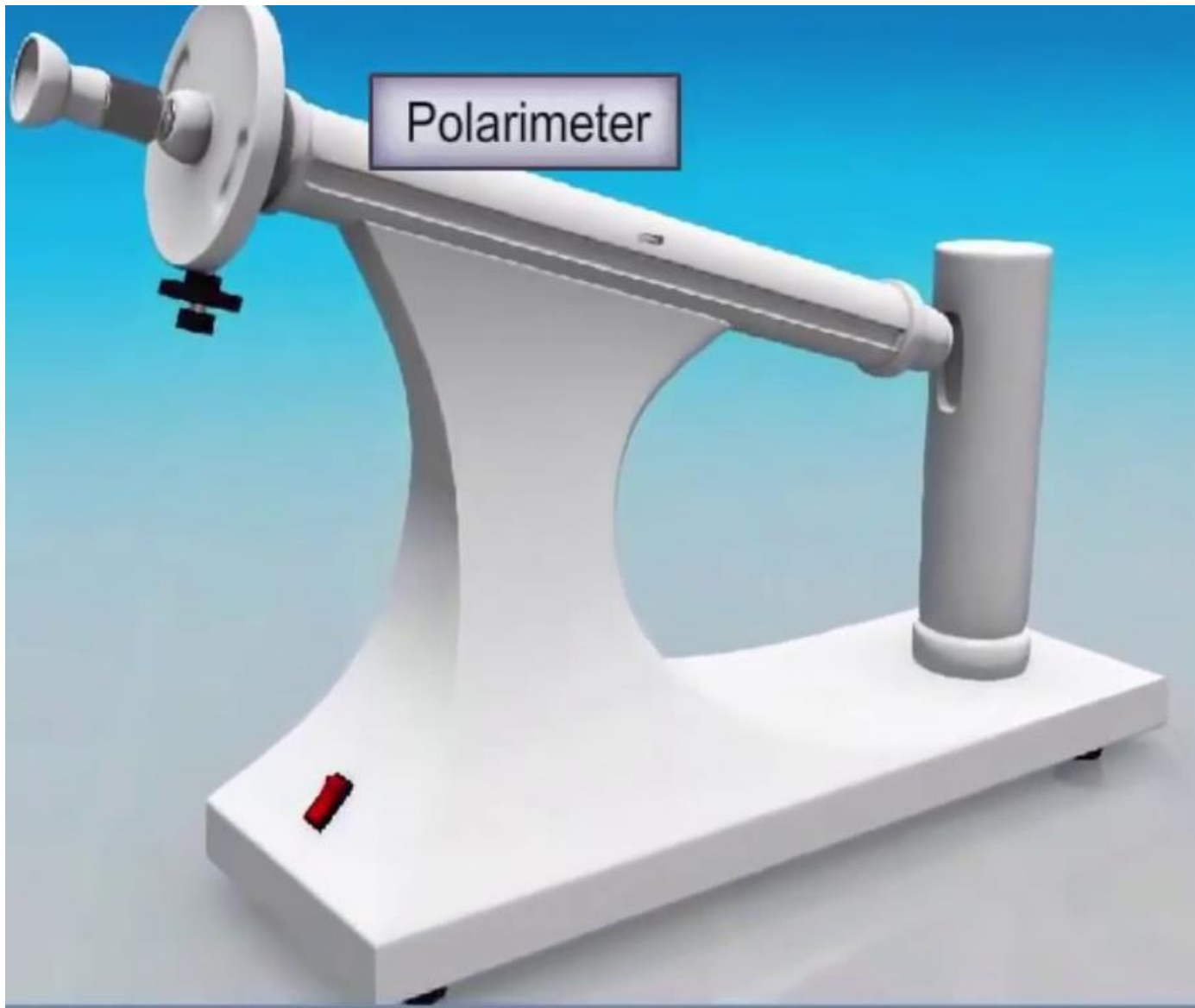
Optical Isomerism

Existence of two or more isomers of a substance that **differ** in their **optical activity**

Optical activity : the property of a molecule to rotate the plane of **plane-polarized light**.

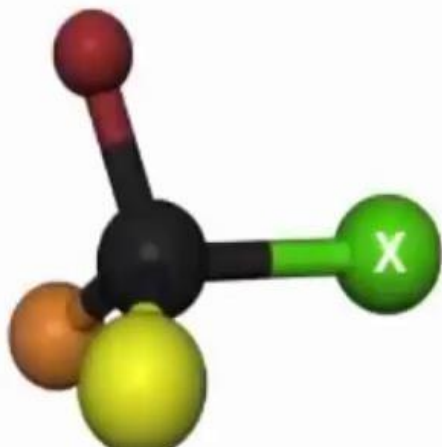
Elementary Concepts of Stereo Chemical Principles and Notations

- Plane Polarised Light
- Asymmetry
- Chirality
- Racemisation
- Inversion of Configuration
- Retention of Configuration

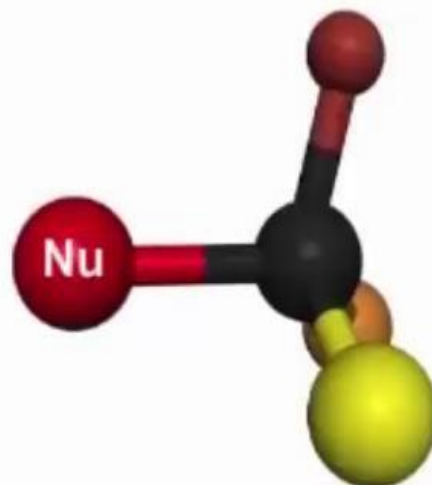




Initial Stage

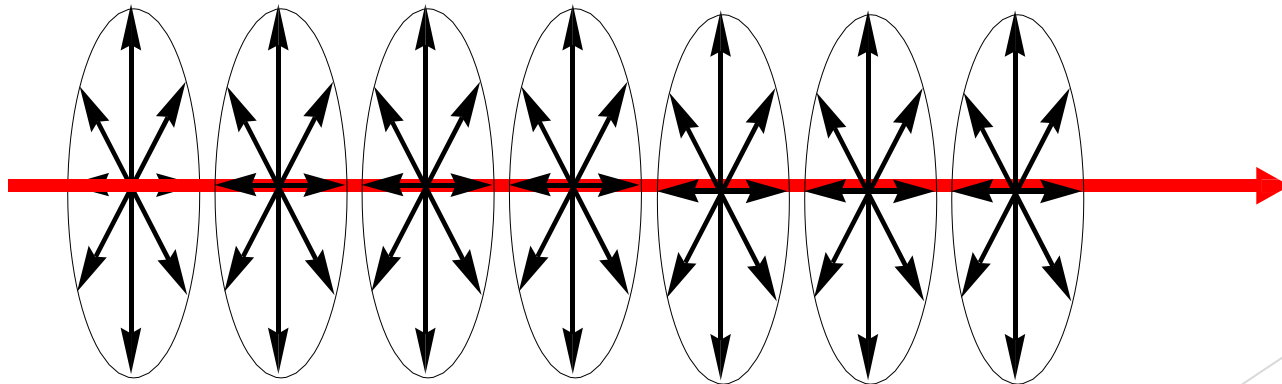


Final Stage

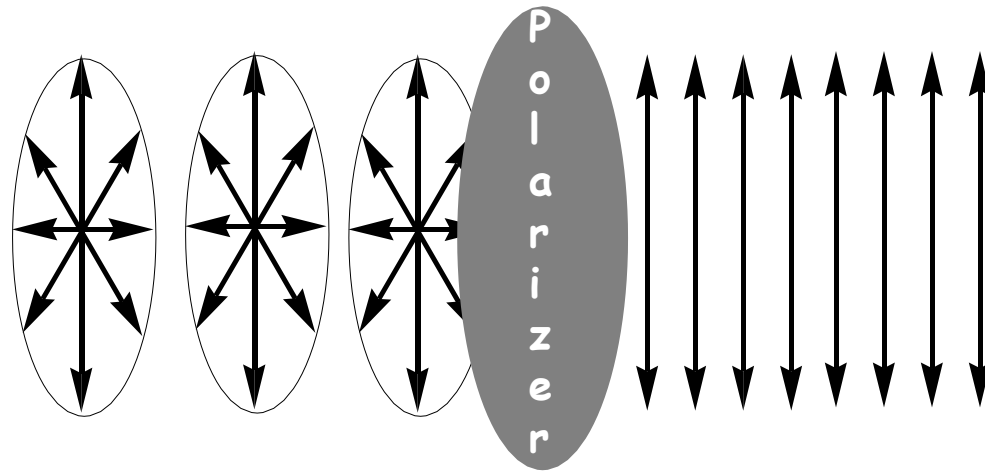


What is plane-polarized light ?

Ordinary light consists of oscillating electrical and magnetic fields or waves vibrating in all directions perpendicular to the direction the light beam

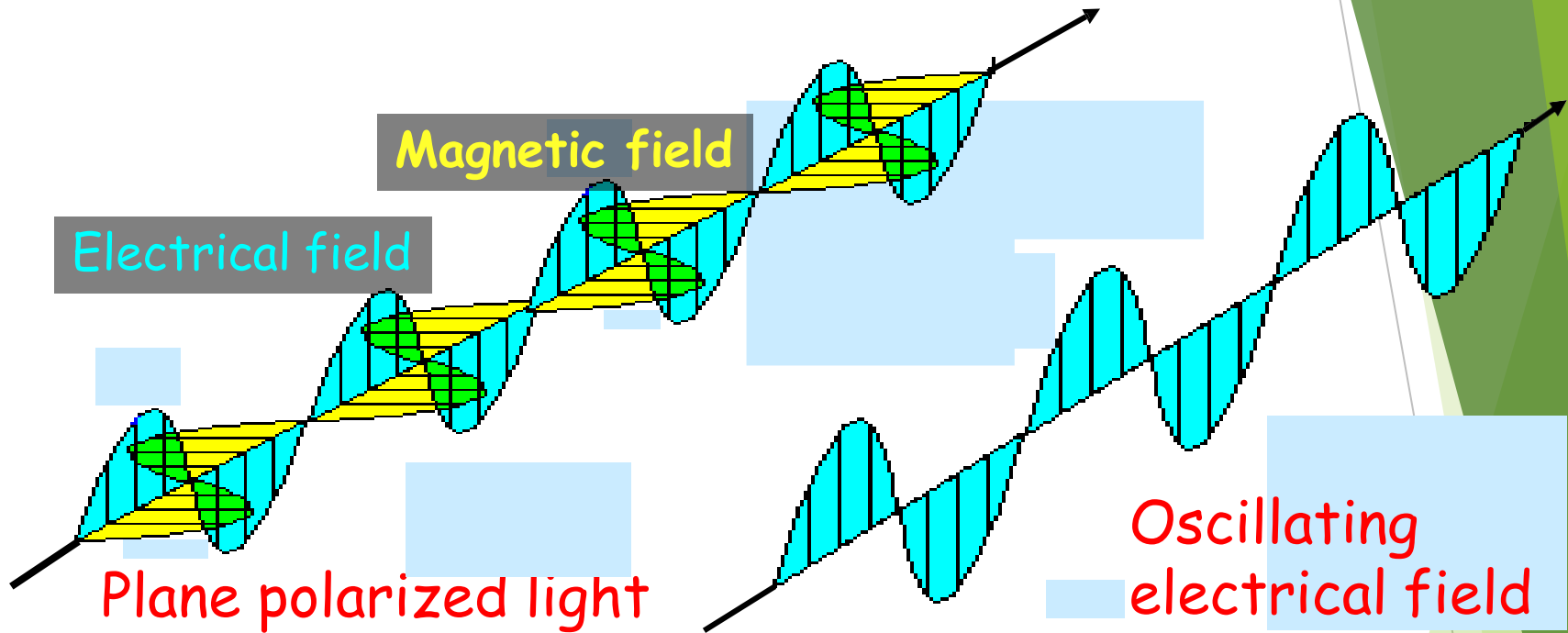


On passing the ordinary light through a device called **Polarizer**, its oscillations in *all but one* direction are blocked and the light emerging from the polarizer oscillates in only one plane

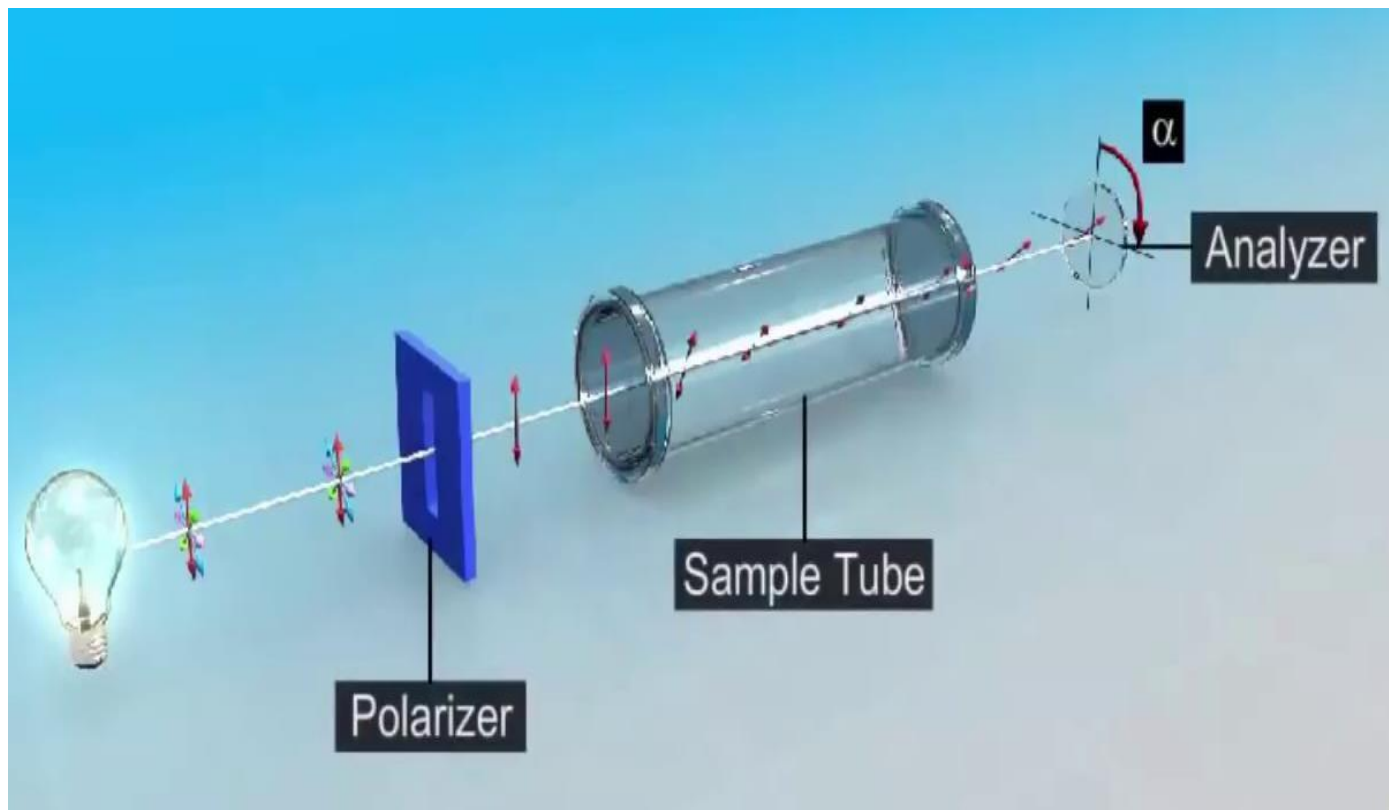


This is called plane polarized light

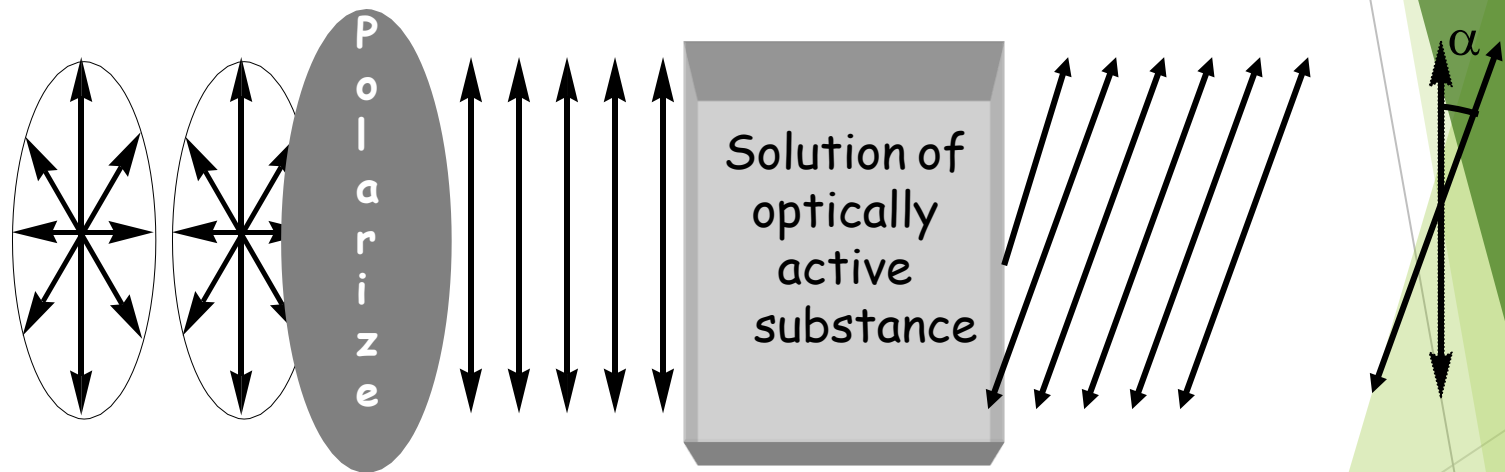
Plane-polarized light



The plane-polarized light has mutually perpendicular electric and magnetic fields. However, it is the electrical component that is more significant



An optically active substance interacts with the plane polarized light in such a way that the plane of light rotates.



The substance that rotates the plane of polarized light to the right is called **dextrorotatory** and the one that rotates it to the left is called **laevorotatory**

Dextrorotatory : rotation to right

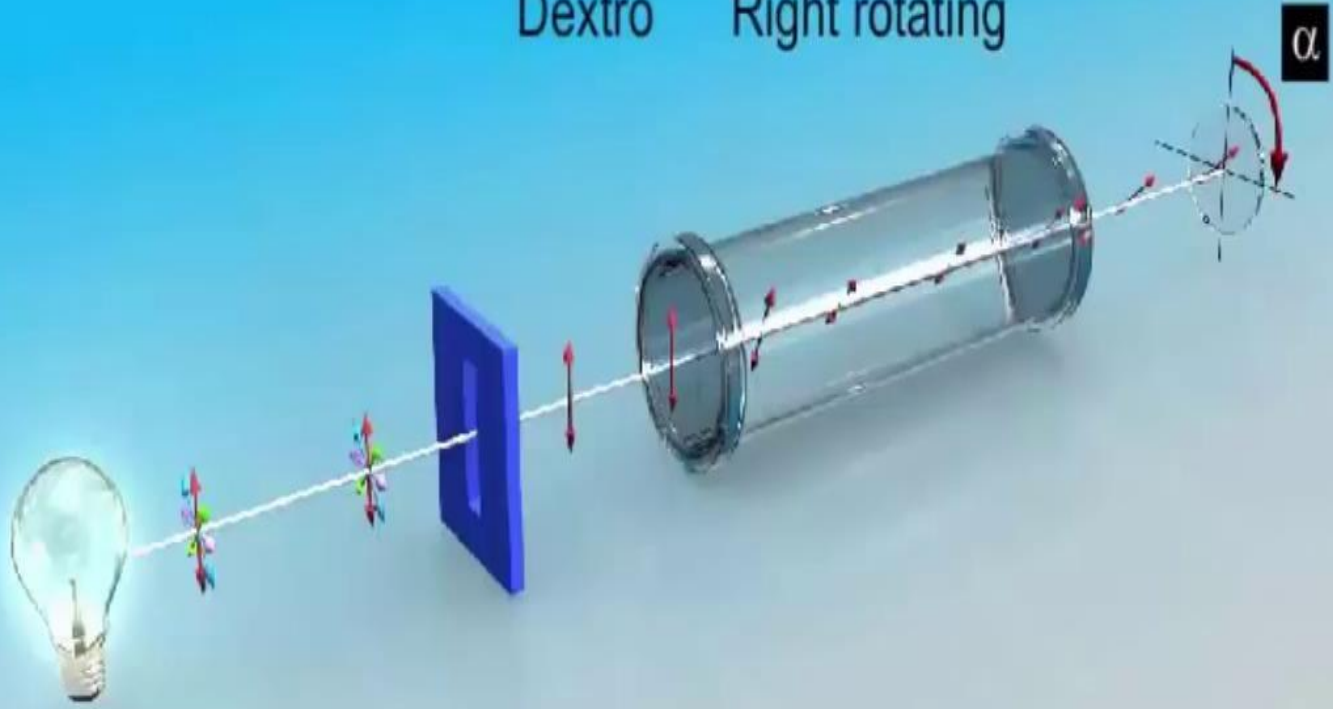
(The angle of rotation, α , is considered to be positive (+).)

Laevorotatory : rotation to left

(The angle of rotation, α , is considered to be negative (-).)

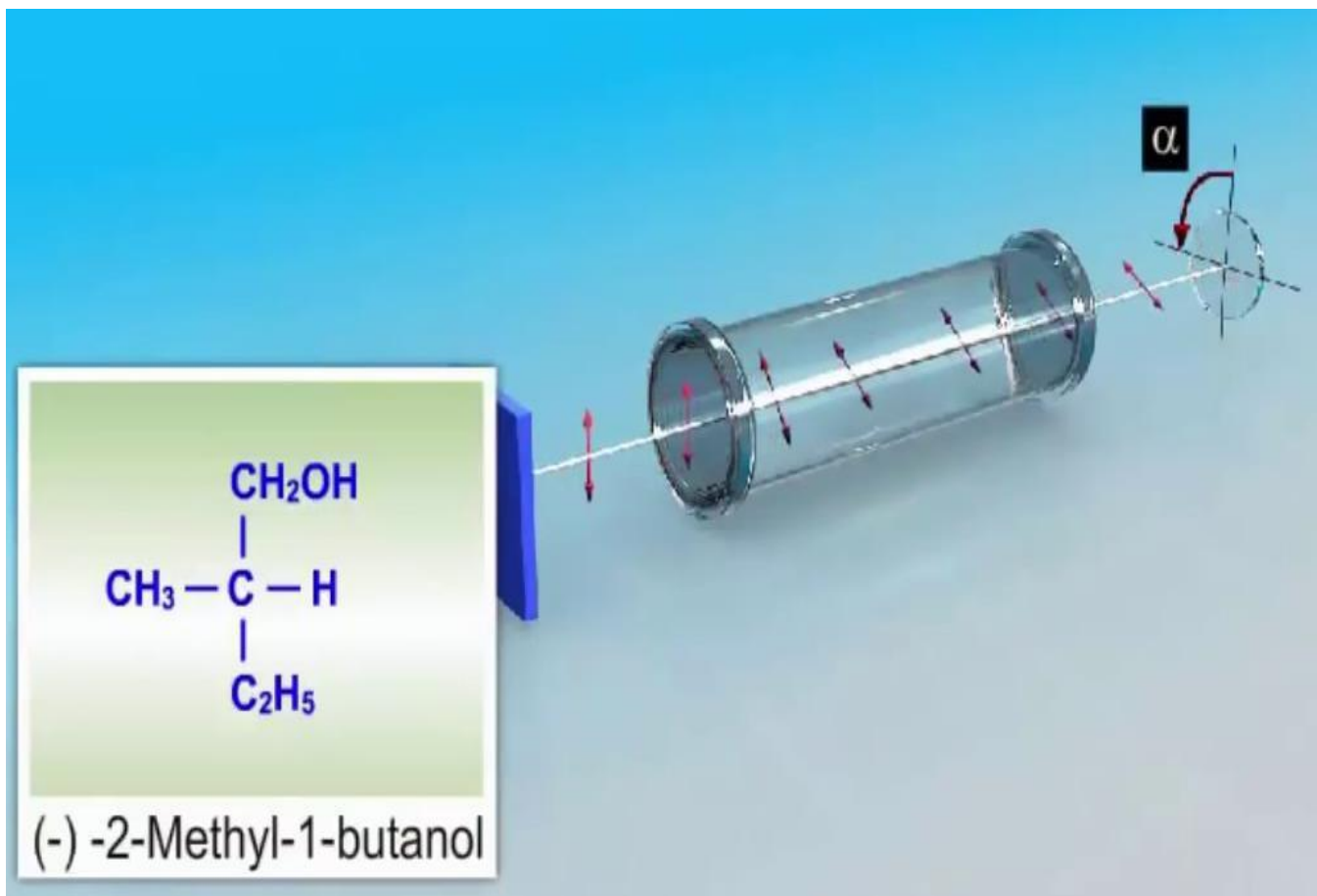
Dextrorotatory or d-form Substance

Dextro Right rotating



Example: $+52^\circ$

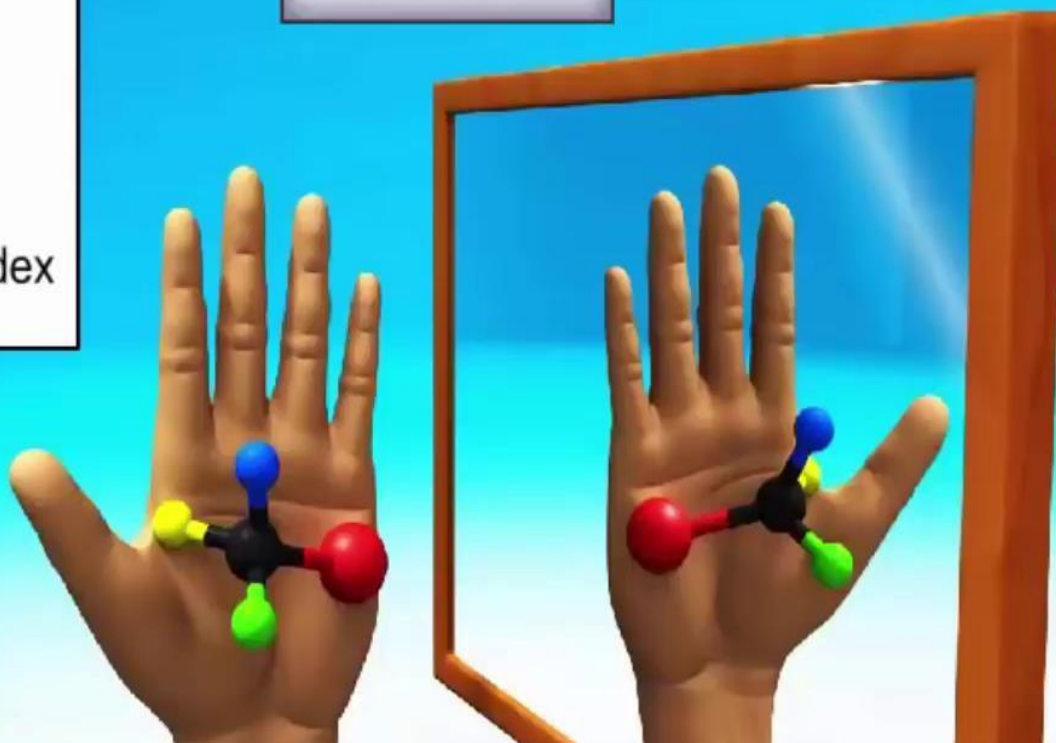
LEAVO ROTATORY COMPOUND



ENANTIOMERS

- Melting Point
- Boiling Point
- Solubility
- Refractive Index

Enantiomers



Cause of Optical Activity

Optical isomerism is due to
chirality in a molecule

Greek cheir : hand

Chiral objects have a "handedness"

The chirality of an object is
related to its symmetry rather
lack of it

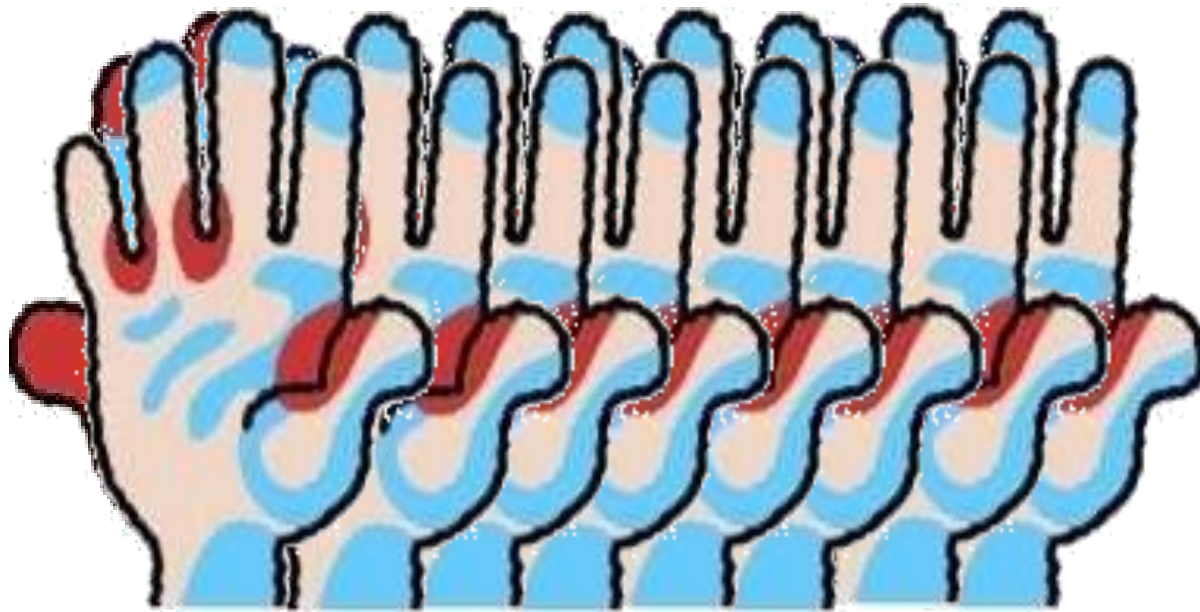
The objects with 'HANDEDNESS' cannot be superimposed on their mirror images.

e.g., hands or gloves



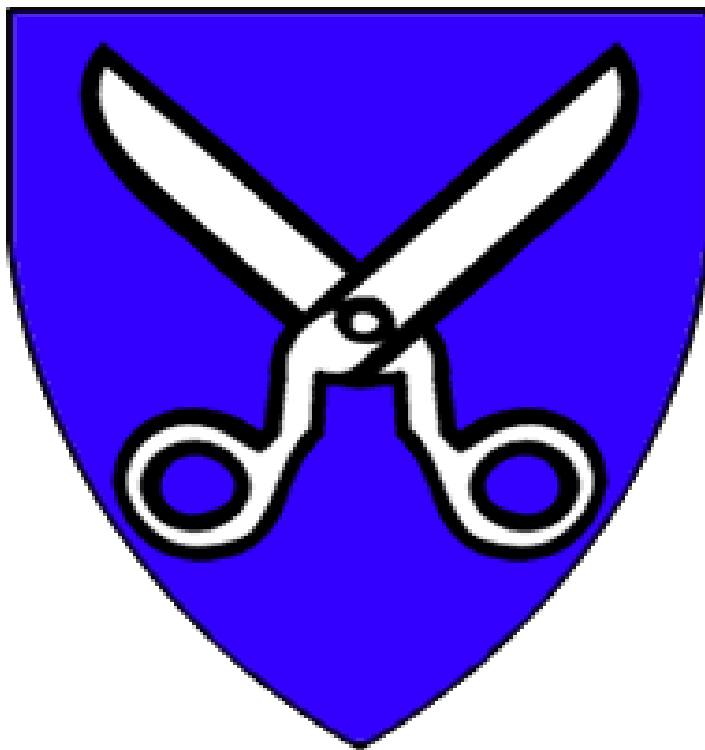
M
I
R
R
O
R





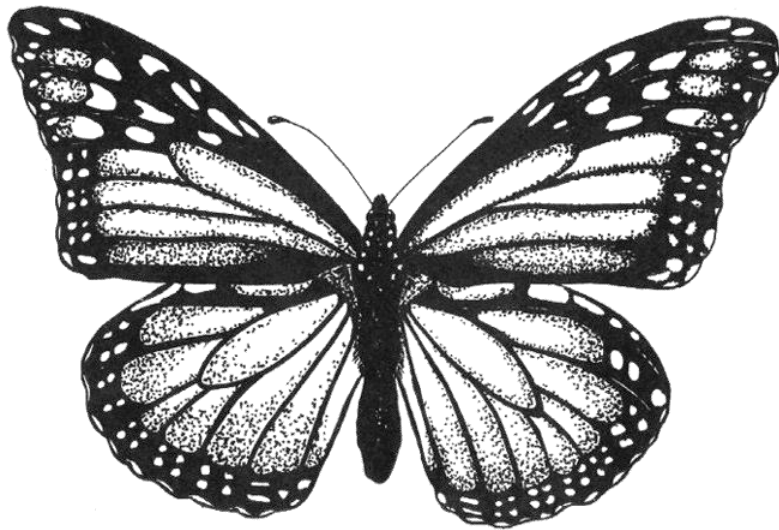
**A right hand cannot be
superimposed on a Left hand**

Is a scissor chiral ?



The objects that do not have a handedness can be superimposed on their mirror image.

e.g., a butterfly

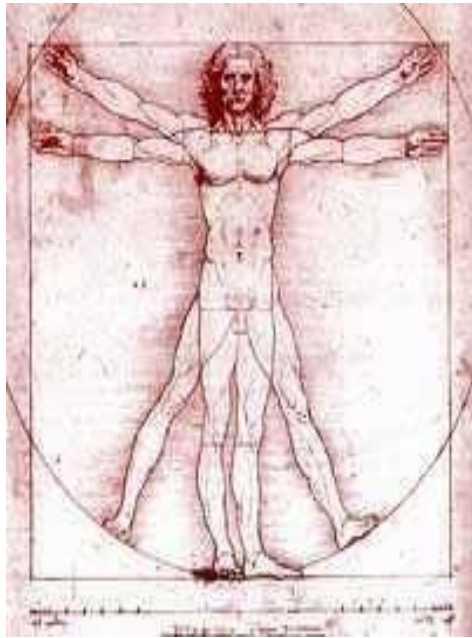


The objects that are superimposable on their mirror images are said to be **achiral**.

A butterfly is symmetric- one half of its body exactly overlaps its other half

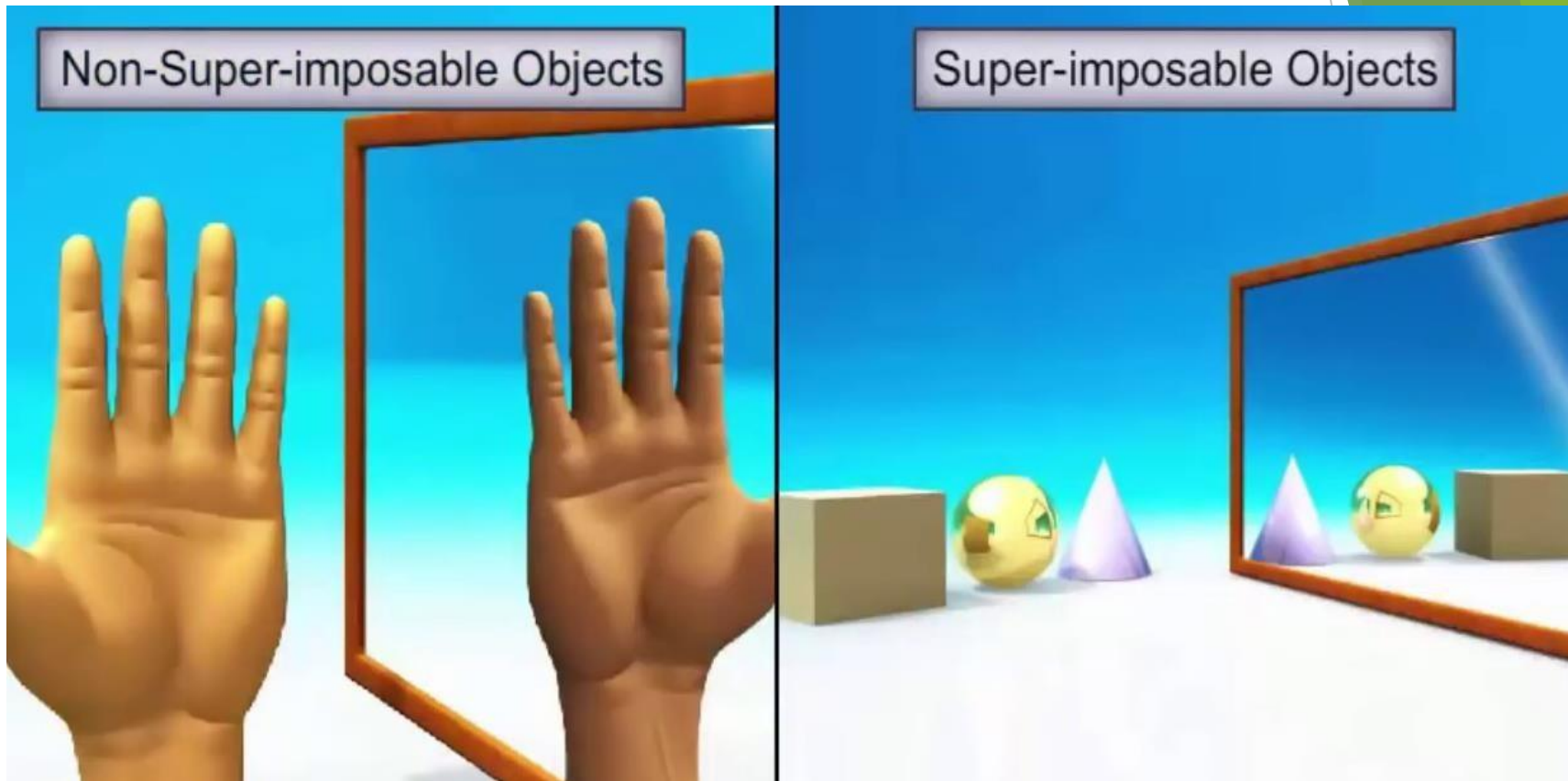


Some other examples are:



CHIRAL [ASYMMETRIC]

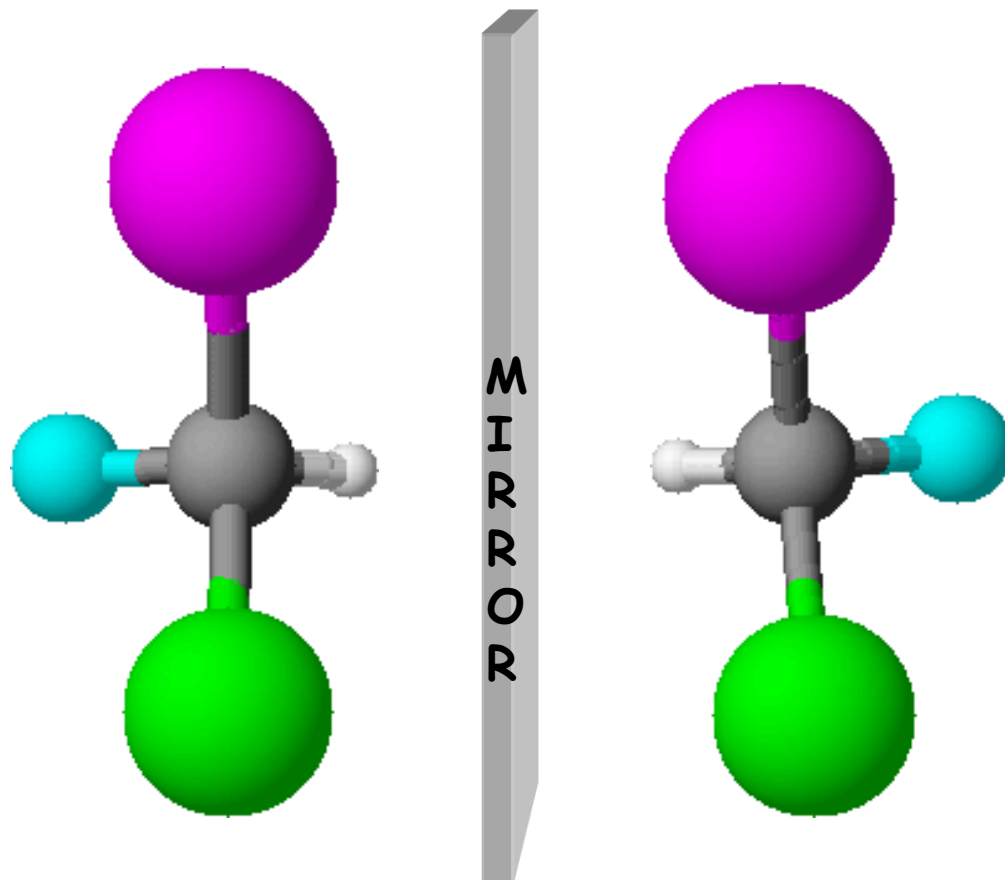
ACHIRAL [SYMMETRIC]

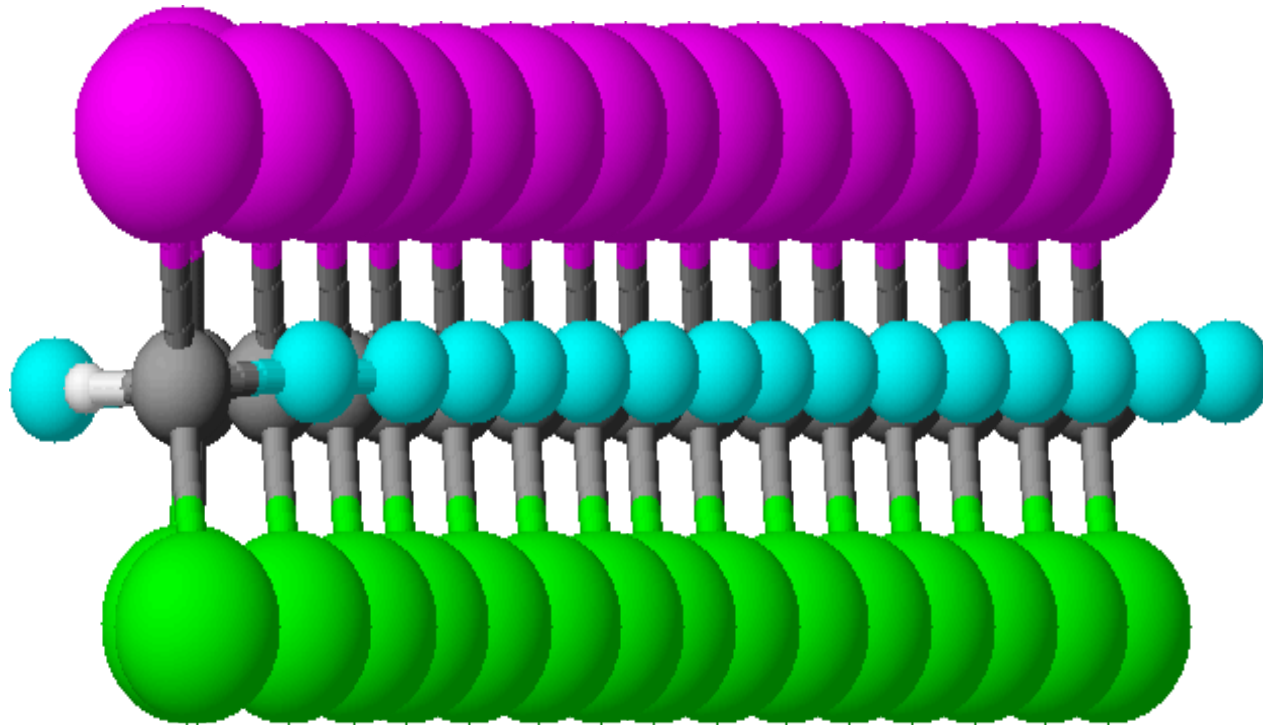


CHIRAL [ASYMMETRIC MOLECULES]

2-Chlorobutane	2, 3-Dihydroxypropanal
$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{H} - \text{C} - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CHO} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$
Lactic acid	Mandelic acid
$\begin{array}{c} \text{COOH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{COOH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{C}_6\text{H}_5 \end{array}$

Bromochlorofluoromethane

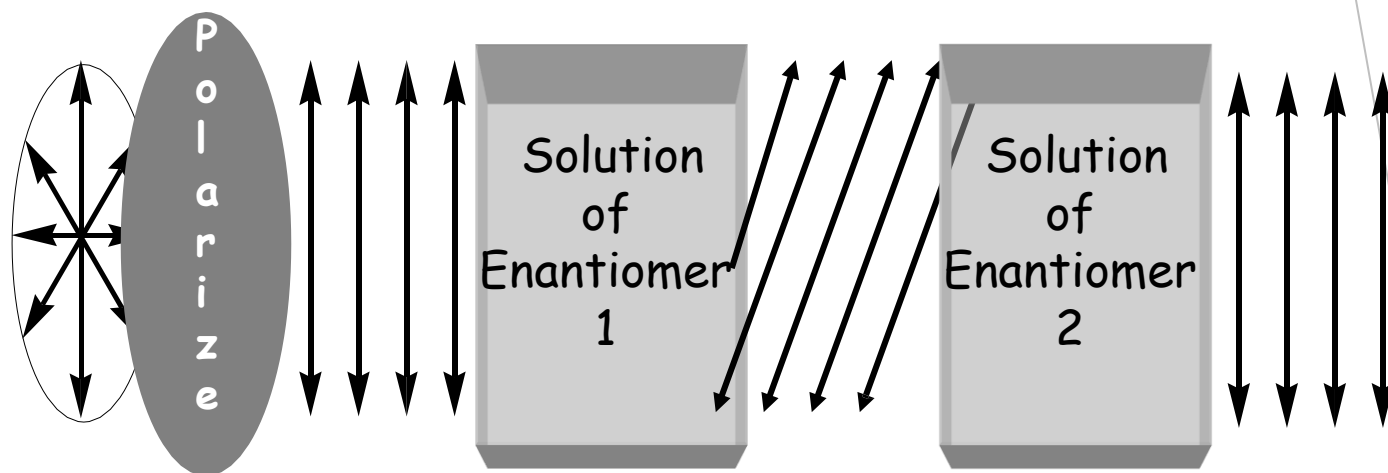




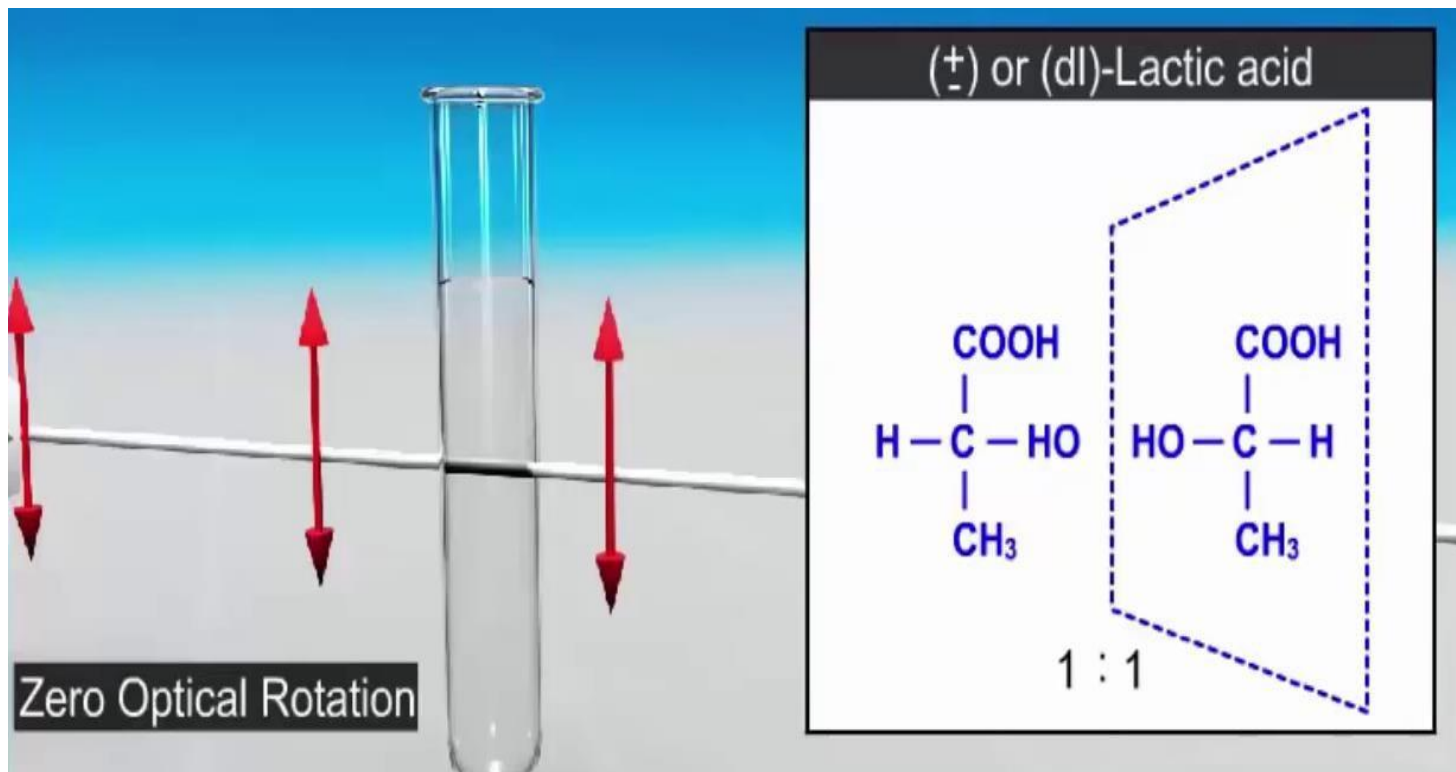
Non-superimposable hence chiral

- **Compounds that are not superimposable on their mirror images will show optical isomerism**
- **These isomers are called *enantiomers***
- **One of the isomers is *dextrorotatory* and the other is *laevorotatory***

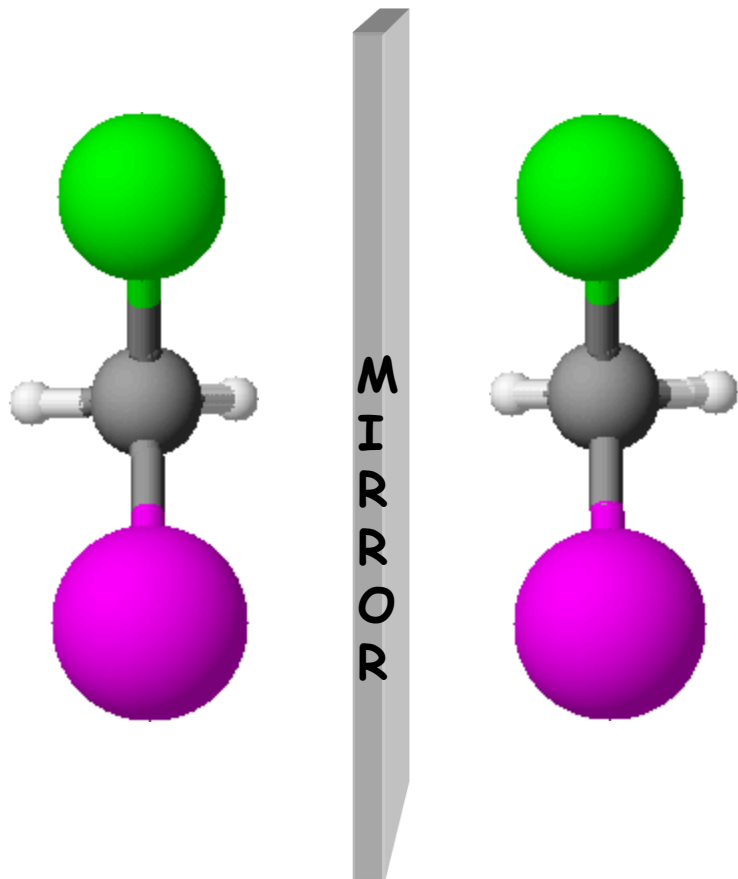
In a pair of optically active enantiomers, each enantiomer rotates the plane of polarized light in equal and opposite directions.

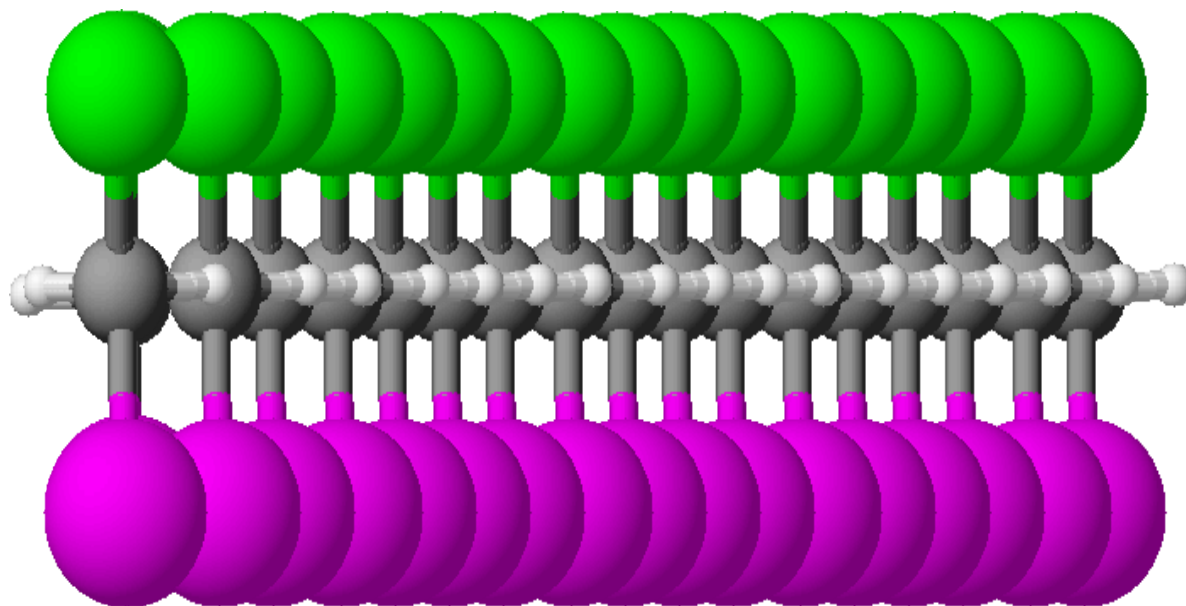


However, a mixture of two in equal proportions will be optically inactive and is called a **racemic mixture**



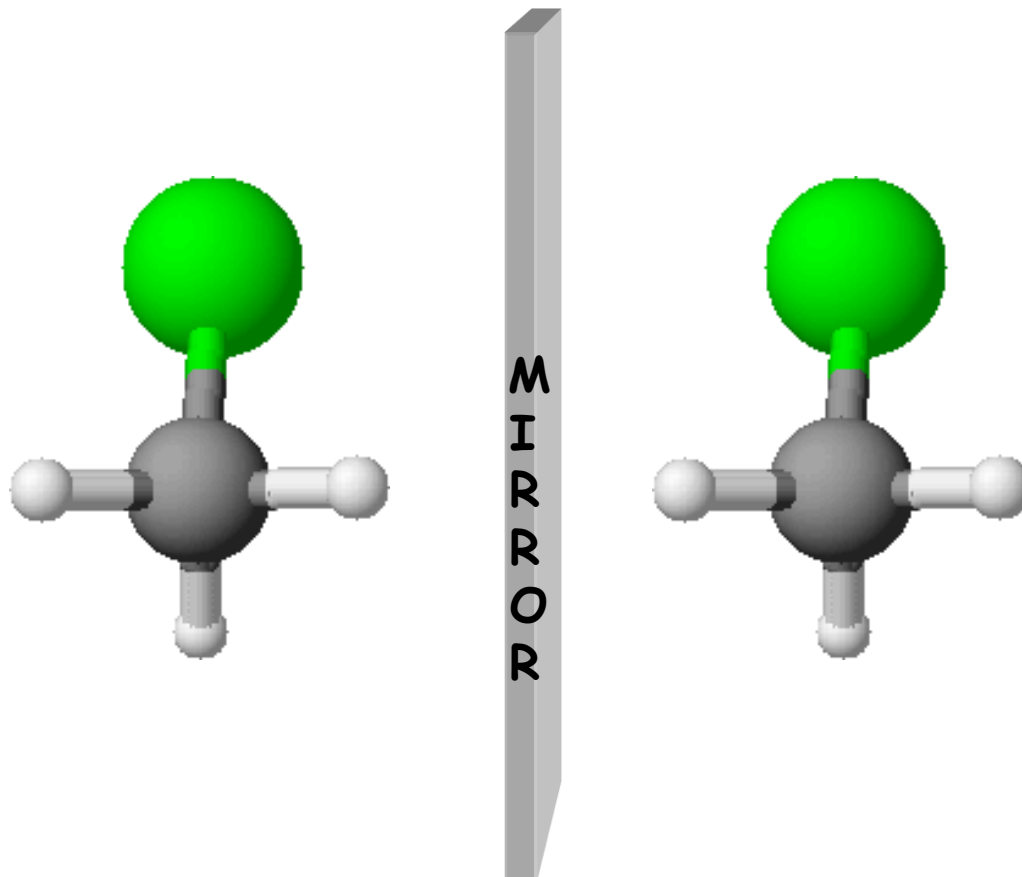
Bromochloromethane

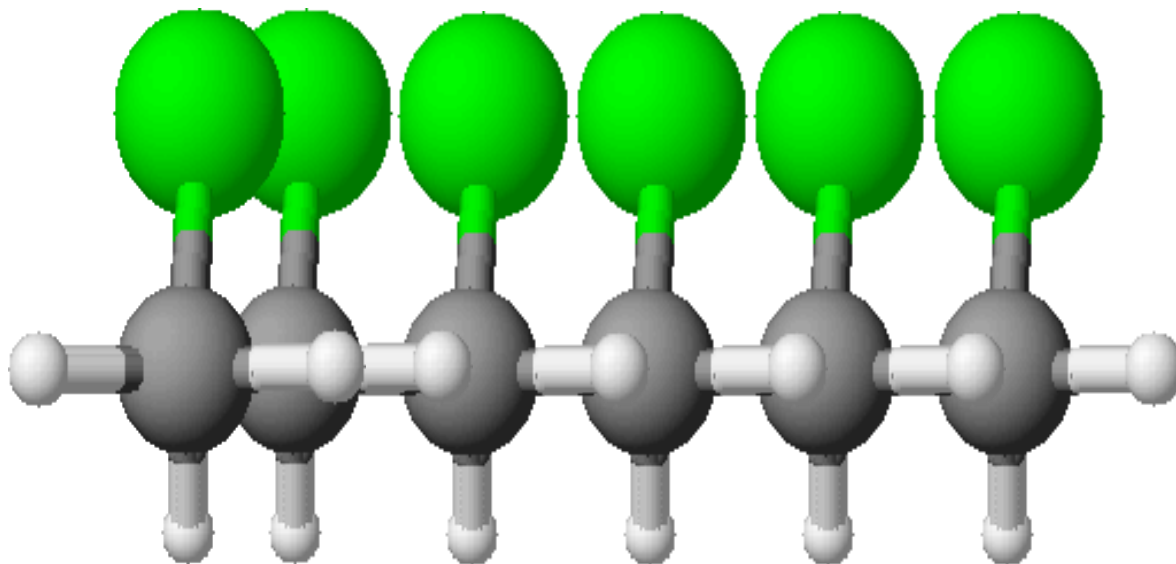




The mirror image is superimposable hence the molecule is **achiral** and does not show optical isomerism

Bromomethane





The mirror image is superimposable hence the molecule is achiral and does not show optical isomerism

Chirality (non-superimposability of mirror image) is a necessary and sufficient condition for a molecule to show optical activity

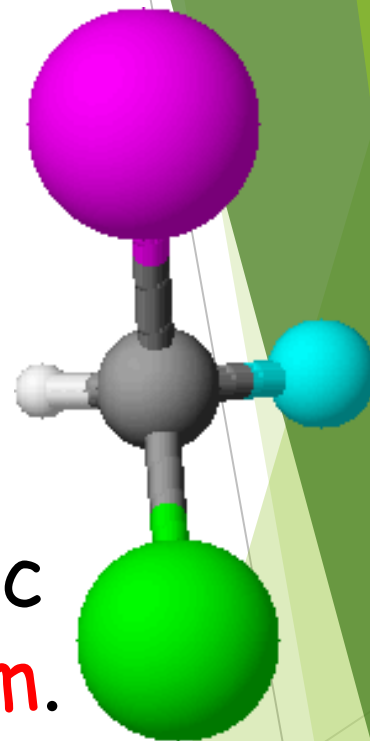
Recall the molecule of bromochlorofluoromethane

The carbon atom is attached to four different groups.

Such a carbon atom is known as **asymmetric** carbon atom.

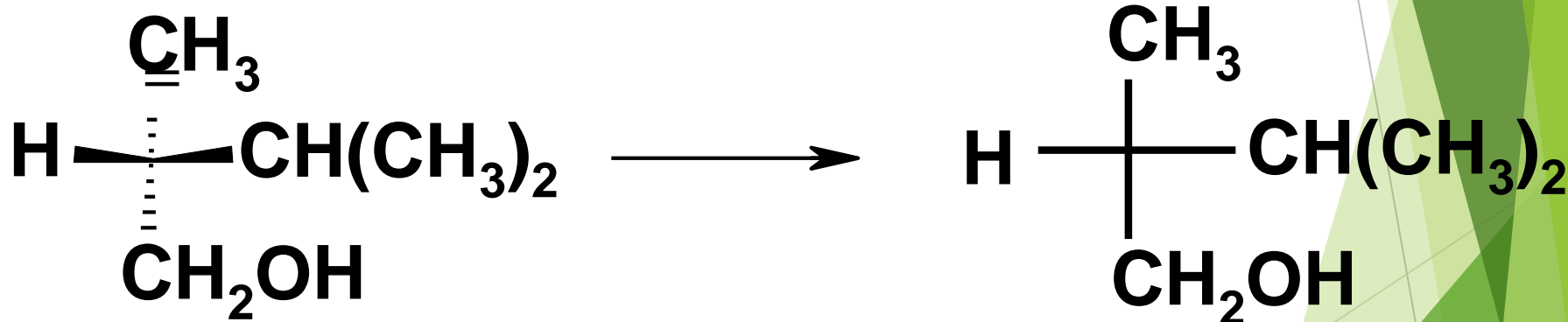
A molecule possessing asymmetric carbon atom shows **enantiomerism**.

Two optically active isomers (**one dextro- and other laevorotatory**) exist

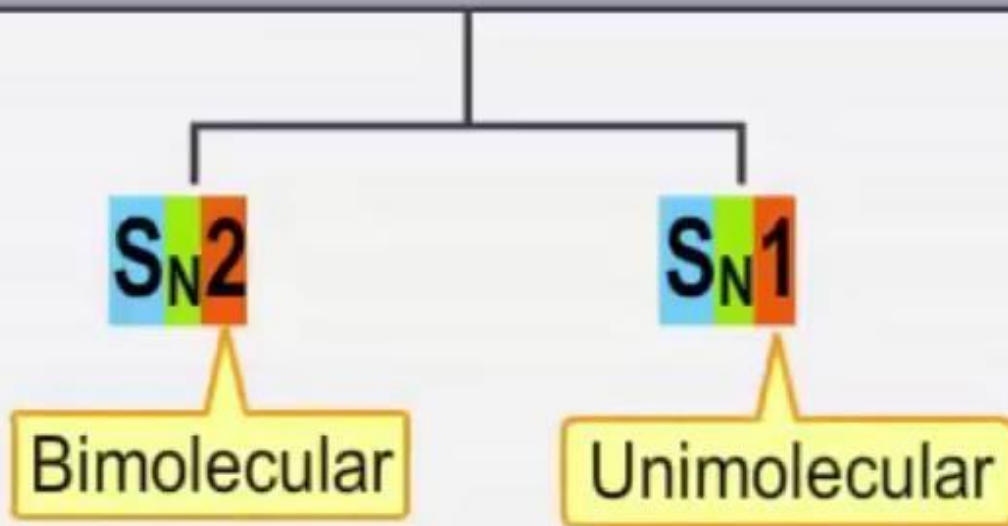


FISCHER PROJECTION

A two-dimensional representation of a three dimensional molecule



Nucleophilic Substitution Reaction



Substitution



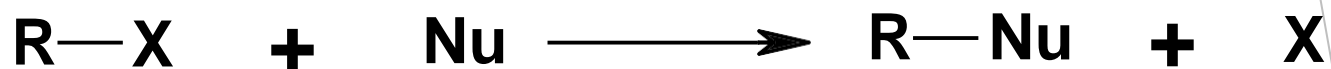
Nucleophilic



Reaction kinetics

Nucleophilic Substitution

- A substitution reaction where the reagent is a nucleophile
- A typical reaction of alkyl halides



- May follow S_N2 , S_N1 and S_Ni mechanisms
- *Depends on*



- ❖ Nature of substrate
- ❖ Reagent
- ❖ Reaction conditions

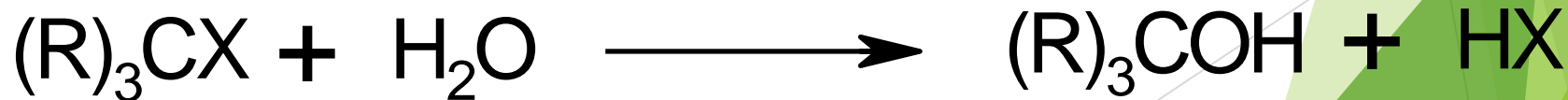
S_N1 Mechanism

S_N1 : Substitution Nucleophilic Unimolecular

Favoured

With neutral or weak Nucleophiles

(water, alcohols, amines)



S_N1 Mechanism

Unimolecular

Rate depends on conc. of **ONE** species

$$\text{Rate} = k[\text{RX}] \quad ; \quad \text{1st Order}$$

Depends on alkyl halide and NOT nucleophile

Two steps

The first step is slow or Rate-determining

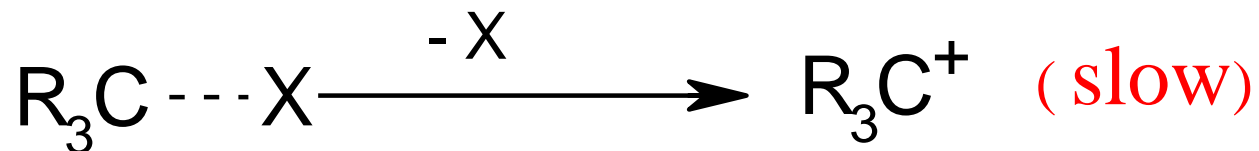
The second step is the fast step



The S_N1 Mechanism

Step 1

Cleavage of C-X bond (Formation of carbocation)



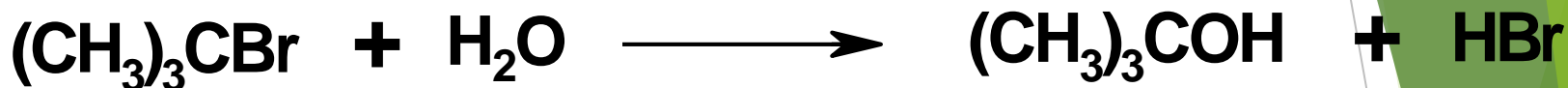
Step 2

Attack of nucleophile (Formation of product)



The S_N1 Mechanism

Example



Experimental facts

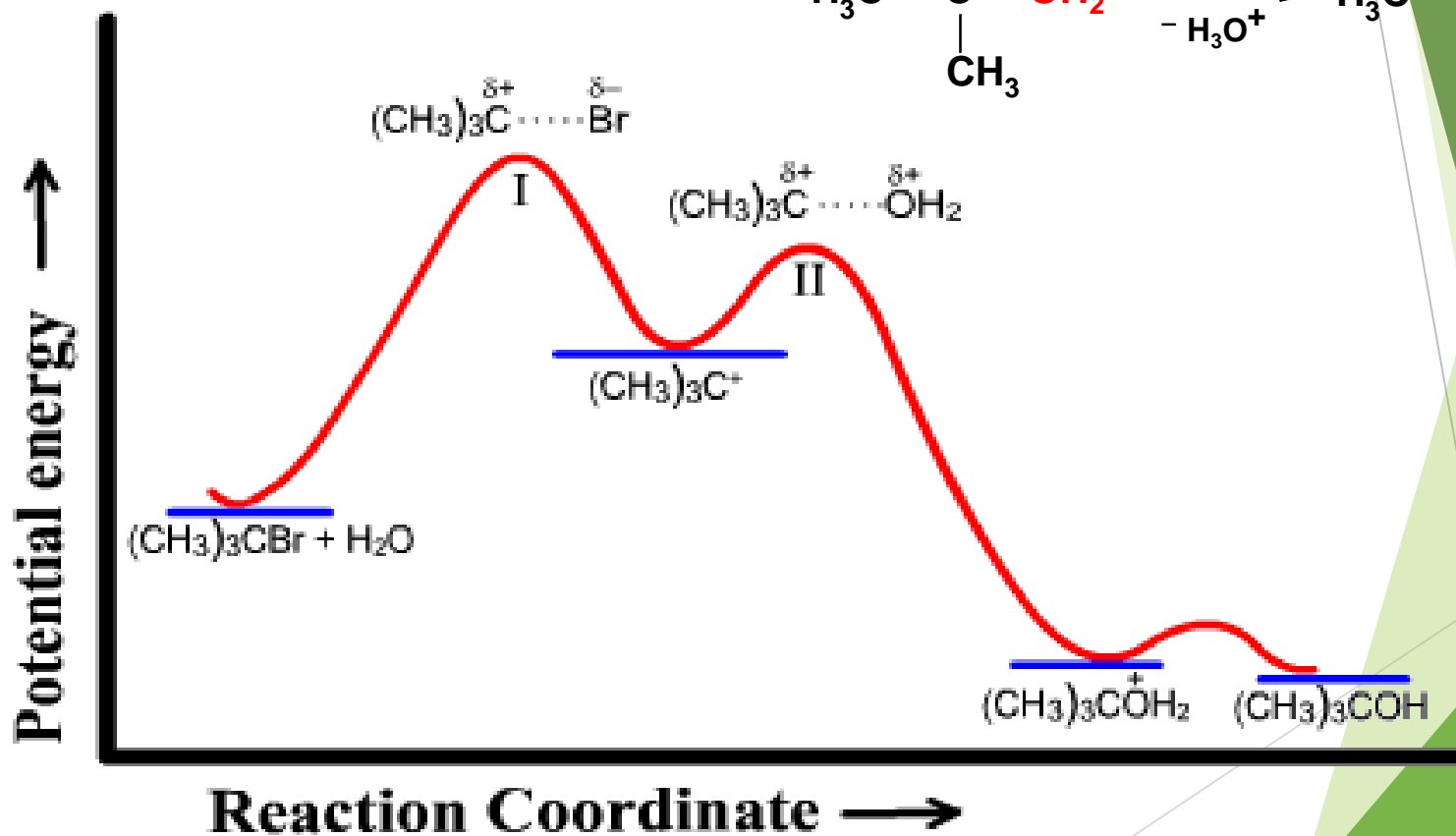
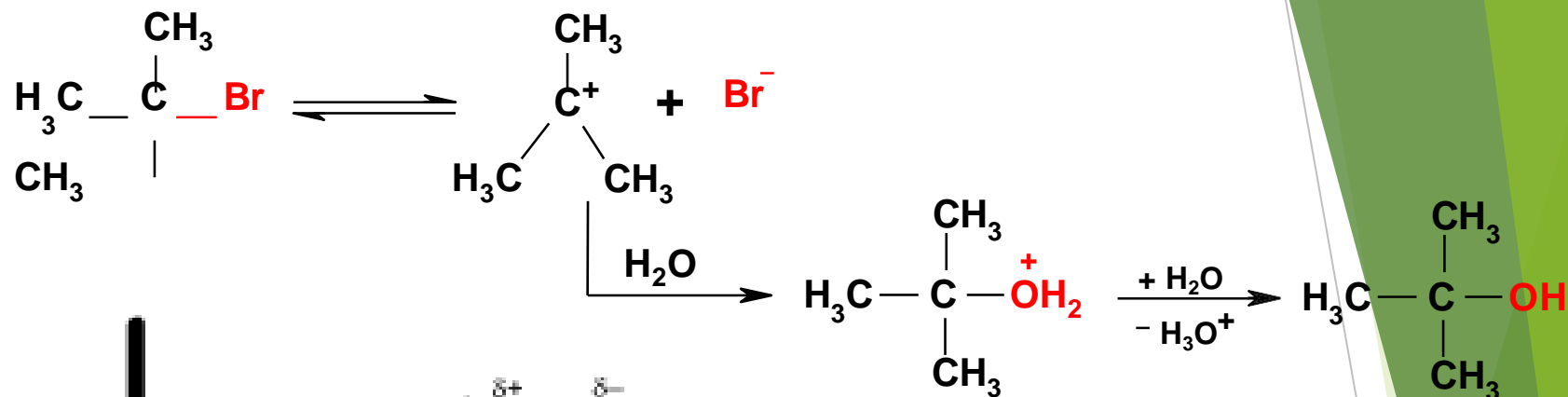
Doubling substrate conc. : **Rate doubled**

Doubling nucleophile conc. : **Rate unchanged**

Thus

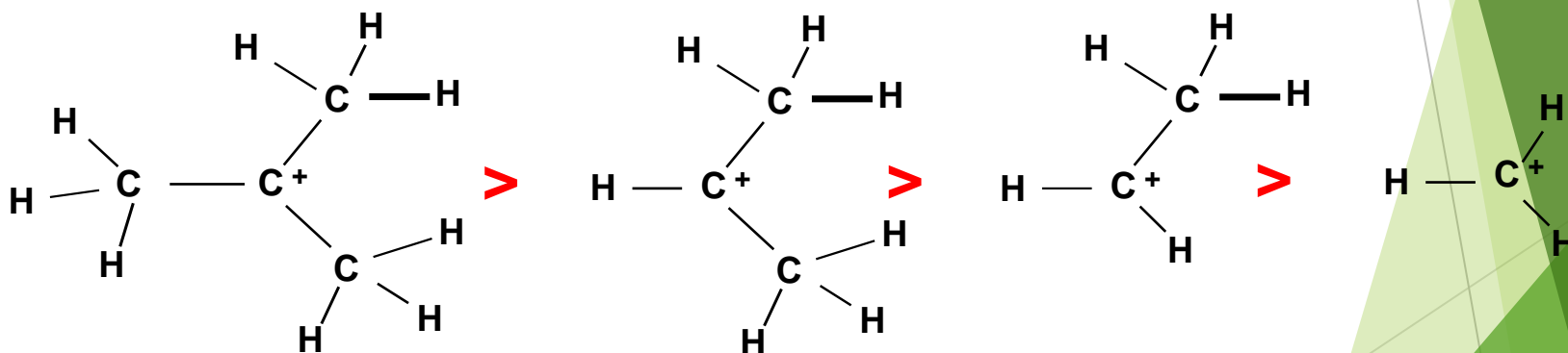
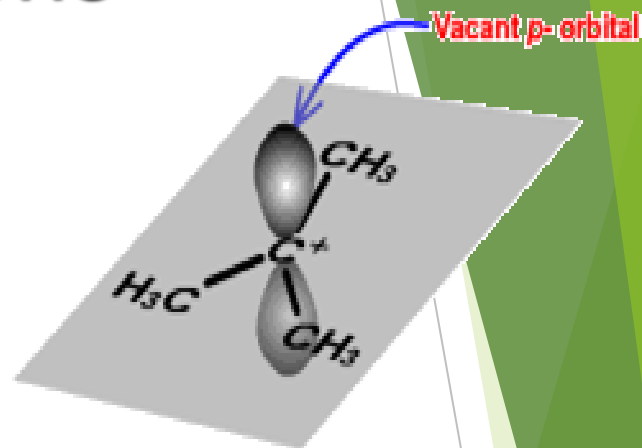
$$\text{Rate} \propto [(\text{CH}_3)_3\text{CBr}]$$

$$\text{Rate} = k [(\text{CH}_3)_3\text{CBr}]$$



Carbocations

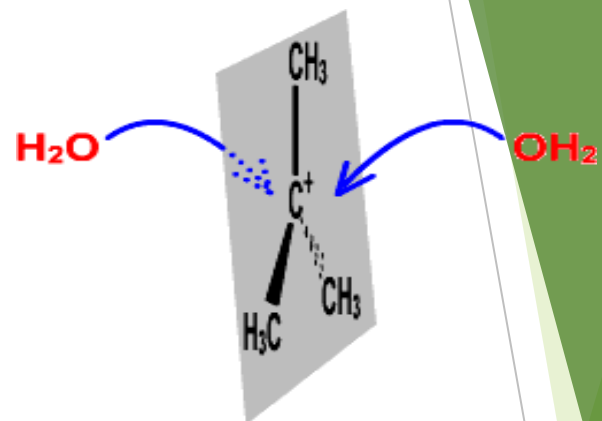
- Reactive intermediates
- Positively charged carbon
- Planar (sp^2 hybridised)



Hyperconjugation stabilises the positive charge

Carbocations are planar
Nucleophiles can
attack from both sides

Product is a racemic
mixture



Rate depends on stability of carbocation
Decrease in the order $3^\circ > 2^\circ > 1^\circ$

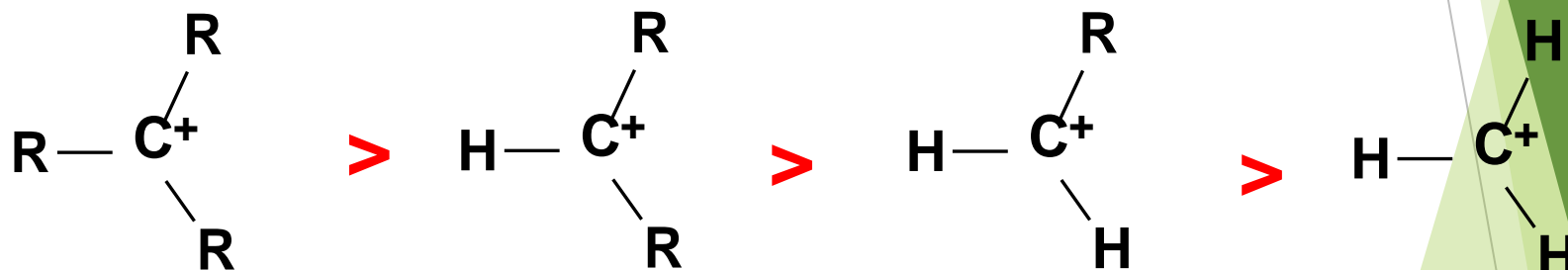
Resonance stabilised carbocations favoured

(allylic, benzylic)

Order of Reactivity in S_N1

Directly related to the stability of intermediate i.e. the **Carbonium ion** or the **Carbocation**

The order of reactivity is

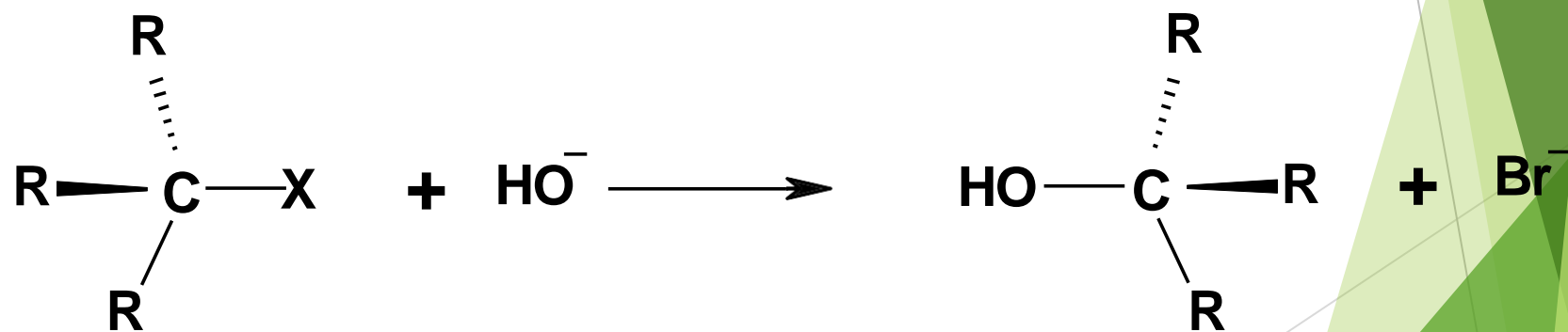


Tertiary > Secondary > Primary > Methyl

S_N2 Mechanism

S_N2 : **S**ubstitution **N**ucleophilic **B**imolecular

Favoured with strong nucleophiles

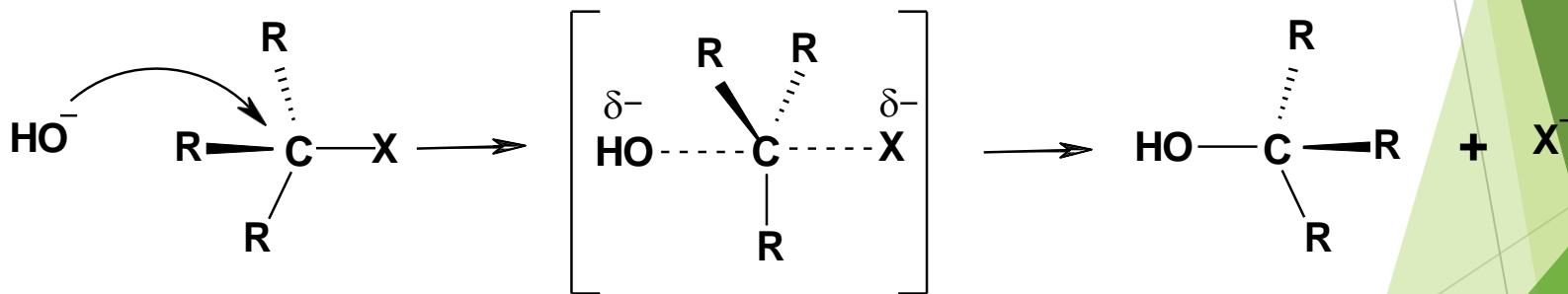


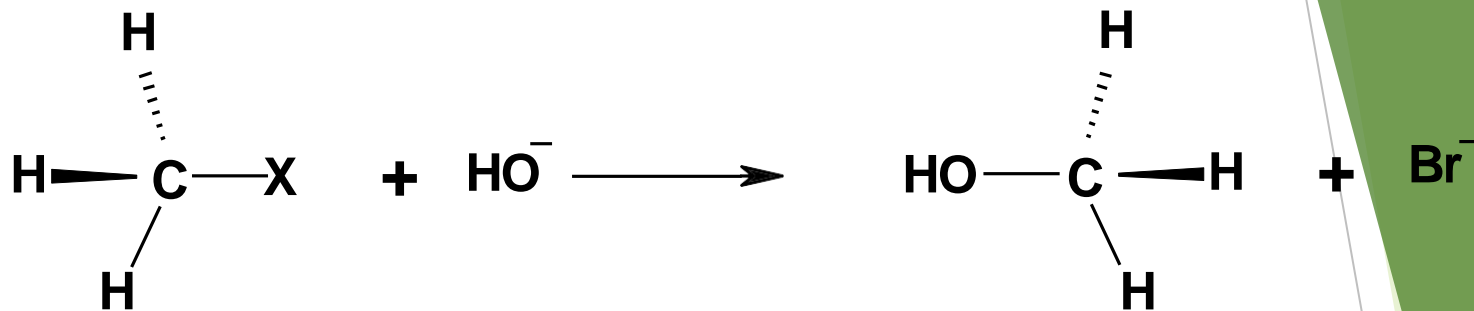
S_N2 Mechanism

Bimolecular

Rate depends on the conc. of **TWO** species

nucleophile and substrate





Experimental facts

Doubling nucleophile conc. : **Rate doubles**

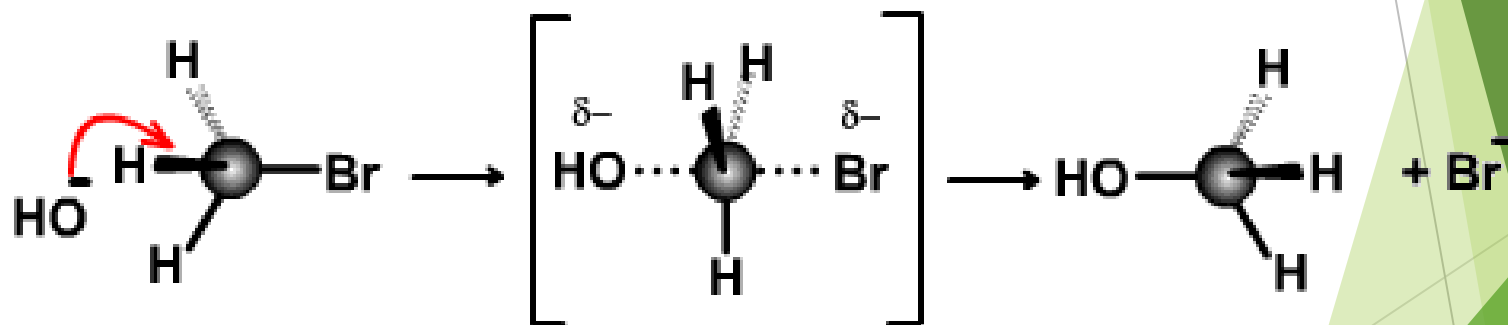
Doubling substrate conc. : **Rate doubles**

Thus $\text{Rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$

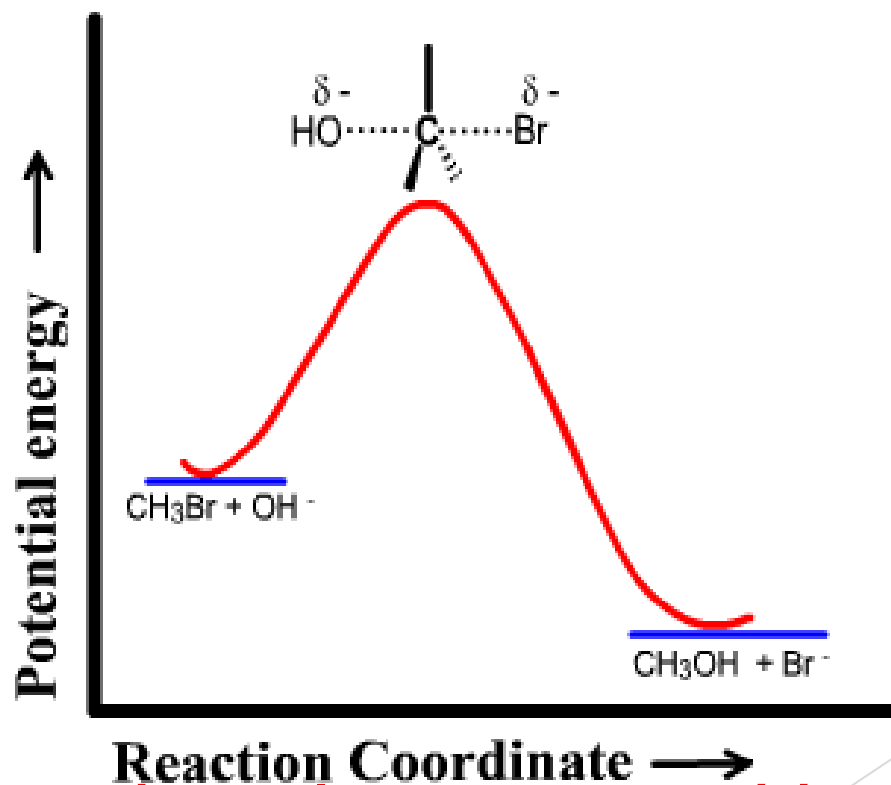
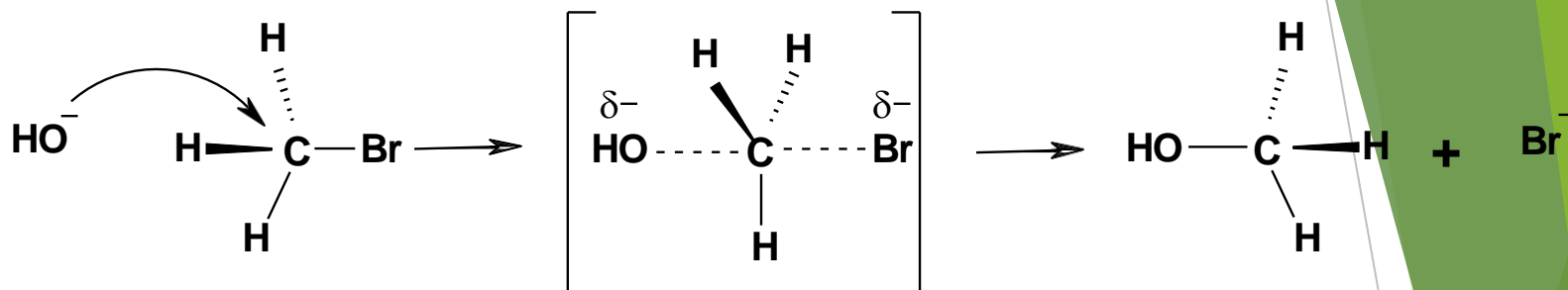
S_N2 Mechanism

One-step mechanism (Concerted)

Attack of nucleophile and removal of leaving group is simultaneous



Leaving group leaves **OPPOSITE** of the attacking nucleophile

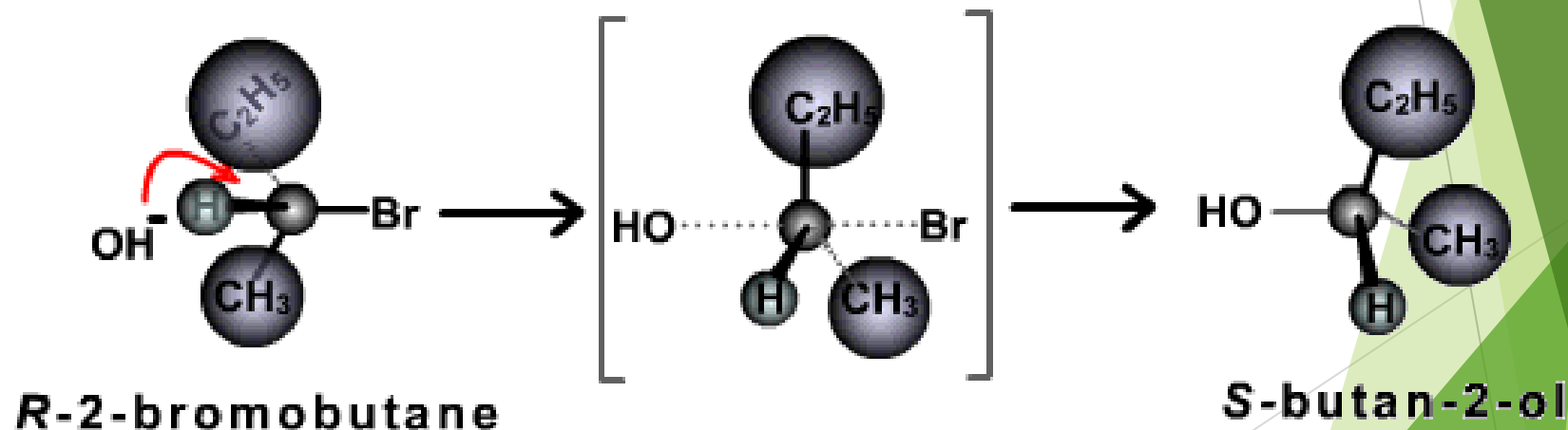


There is only one transition state

Stereochemistry of S_N2 Reaction

Attack from side opposite to the leaving group

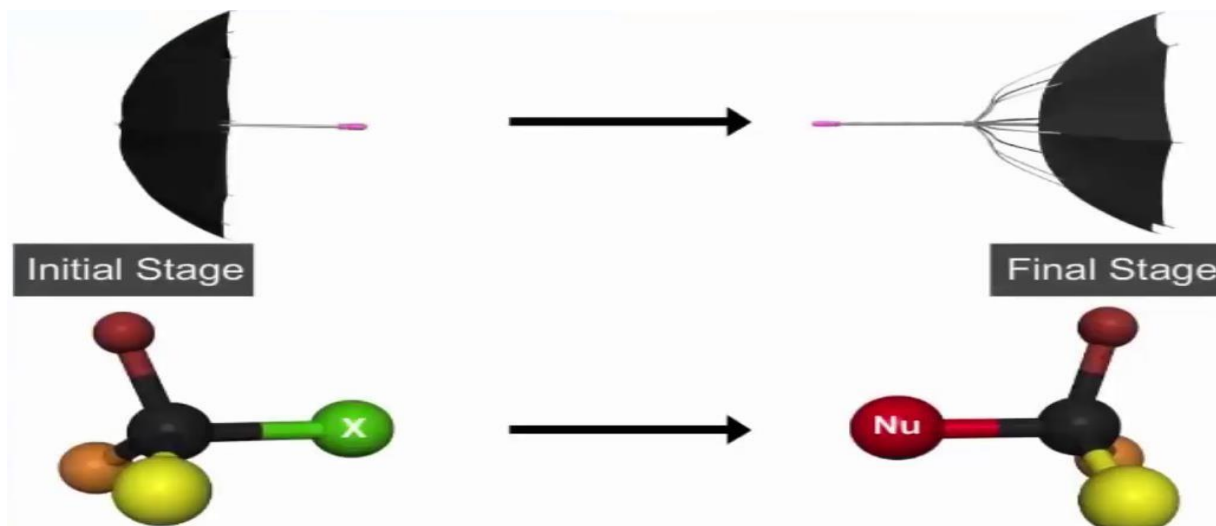
Inversion of Configuration (Walden inversion)



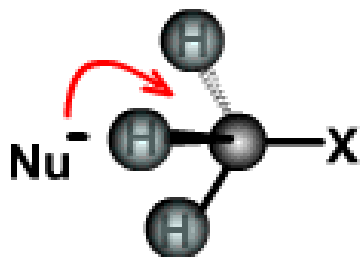
Stereochemistry of S_N2 Reaction

Attack from side opposite to the leaving group

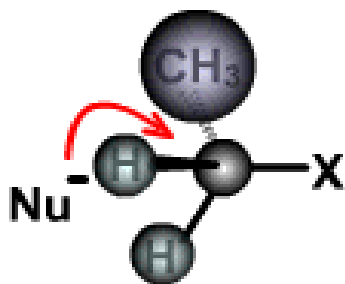
Inversion of Configuration (Walden inversion)



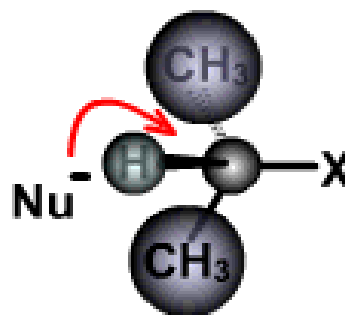
Steric Effect in S_N2 Reactions



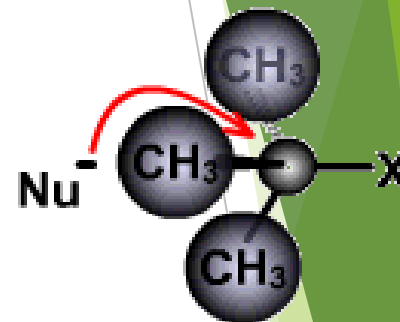
Methyl



Primary



Secondary



Tertiary

Reactivity

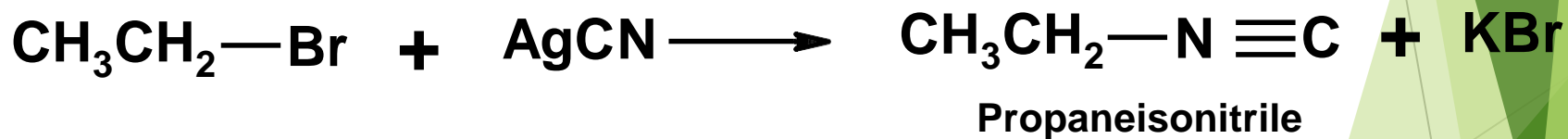
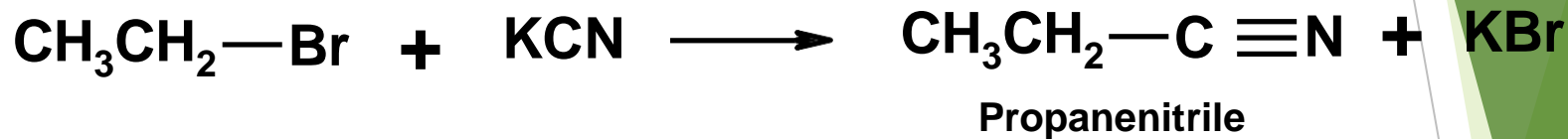
150

1

0.01

0.0001

Reaction with KCN and AgCN



S_N1 Vs S_N2

Mechanism

Unimolecular (two steps)

Bimolecular (one step)

Rate of Reaction

Depends only on the substrate

Depends on nucleophile and substrate

Nucleophiles

Favoured by neutral Nucleophiles

Favoured by strong Nucleophiles

S_N1 Vs S_N2

Solvents

Favoured by polar protic solvents

Favoured by polar aprotic solvents

Alkyl group

Favoured by Bulky alkyl groups

Favoured by less substituted alkyl groups

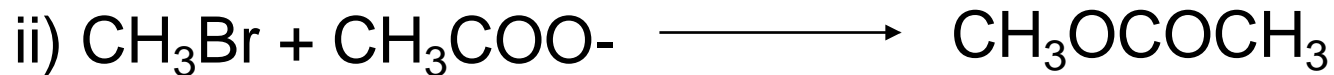
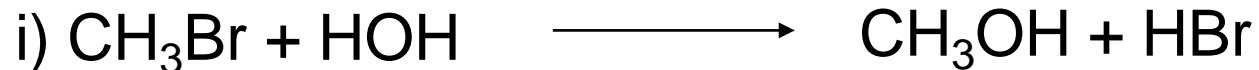
Stereochemistry

Racemic mixture

Inversion of configuration

Some Problems

1. Which one of the following will be faster and why?



2. Arrange the following in increasing order of reactivity towards S_N1 reactions:



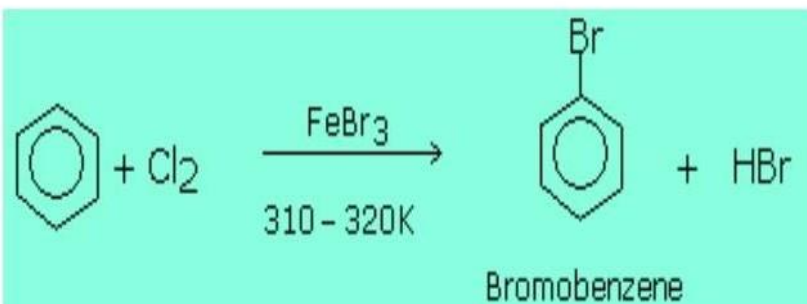
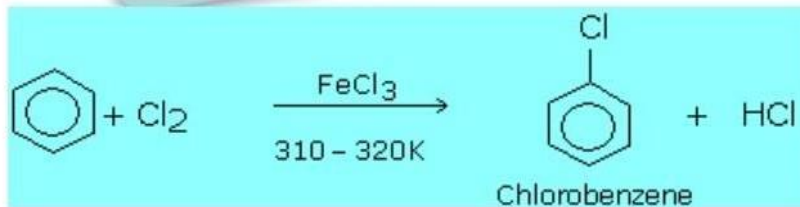
3. Arrange the following in increasing order of reactivity towards S_N2 reactions:

i) $(CH_3)_2CHBr$, $(CH_3)_3CBr$, CH_3CH_2Br

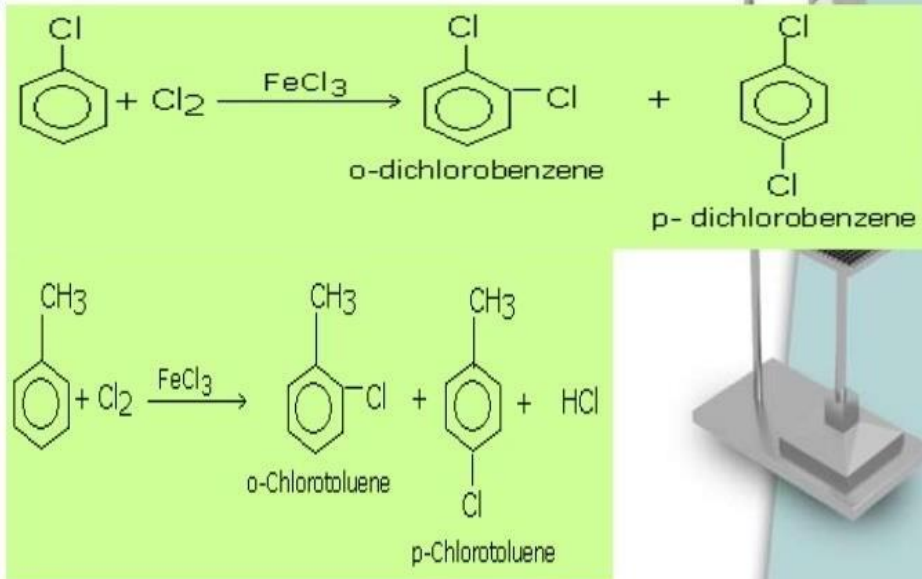
ii) CH_3CH_2Br , CH_3CH_2Cl , CH_3CH_2I

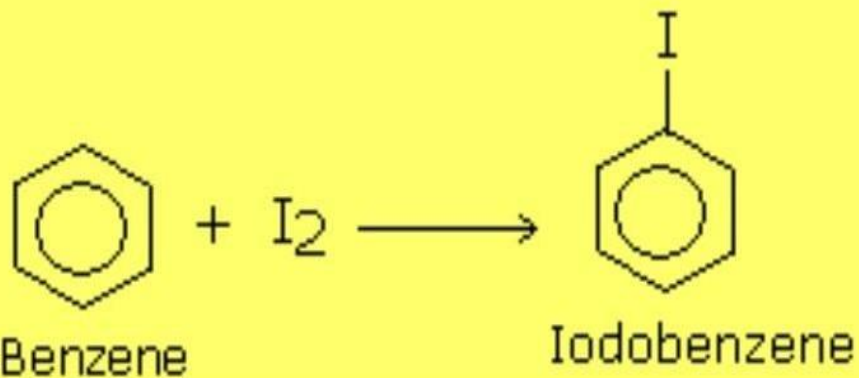
Preparative methods of haloarenes

1) Direct halogenation of aromatic ring

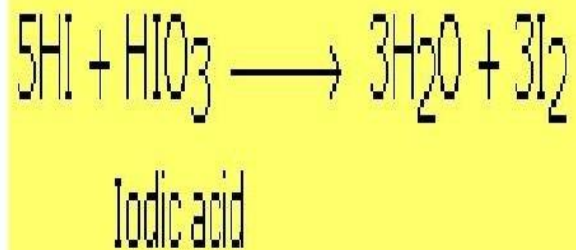


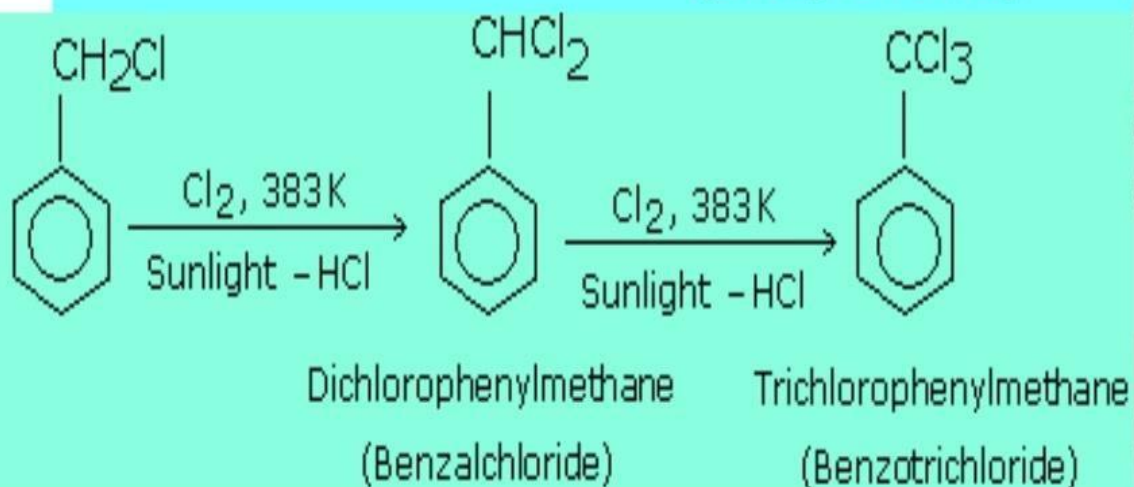
Halogenation of arenes is an electrophilic substitution reaction. The function of the halogen carrier is to generate 'electrophile' which attacks the benzene ring to form the product





Reversible process



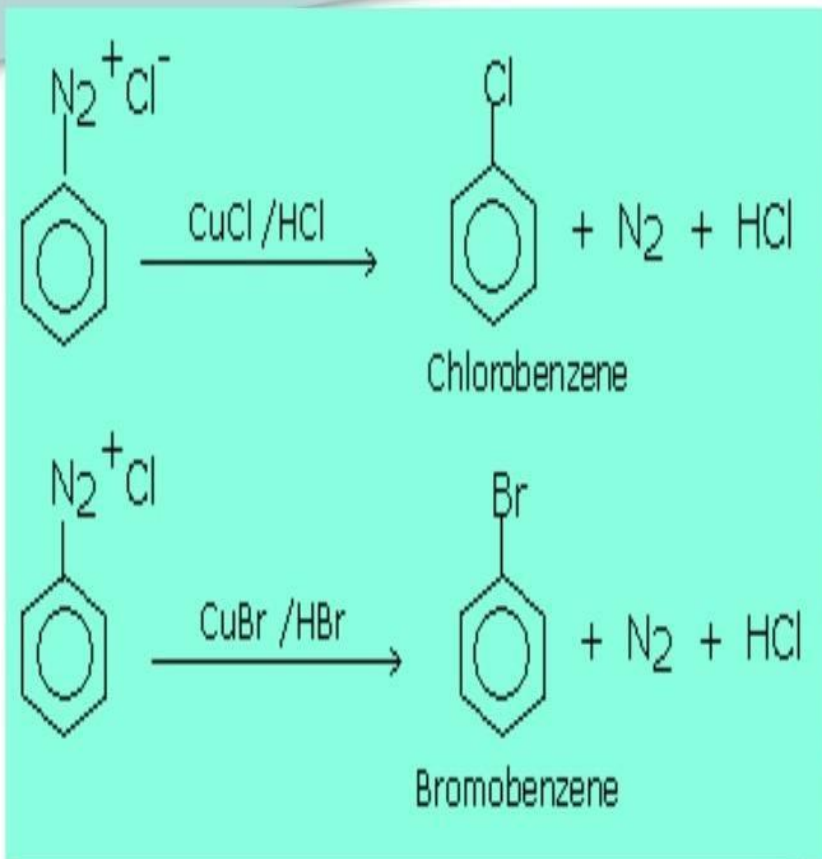


***Bromo compounds can be prepared in a similar way by reacting with Br_2 in the presence of FeBr_3 .**

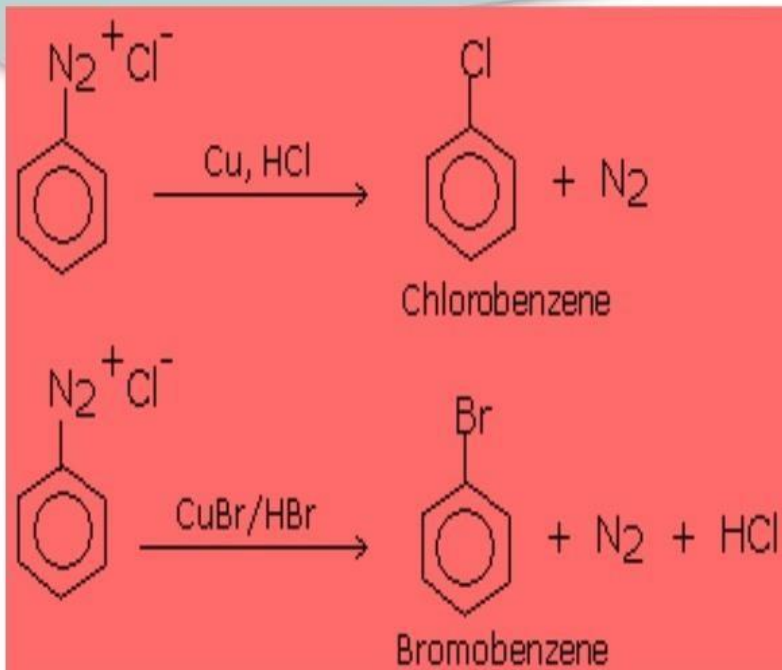
***The reaction with fluorine is violent and cannot be controlled. therefore, fluoroarene cannot be prepared by direct fluorination of aromatic hydrocarbon.**

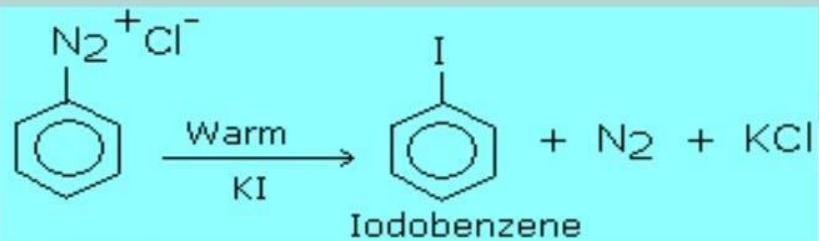


2.SANDMEYER'S REACTION

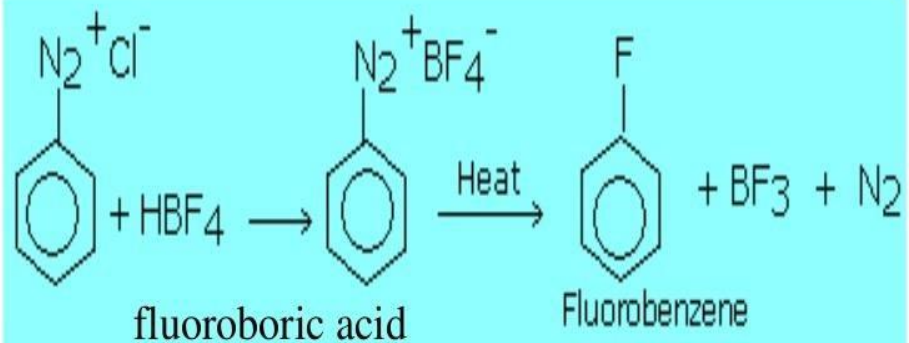


'GATTERMANN REACTION'





4. Balz-Schiemann reaction



CHEMICAL PROPERTIES OF HALO ARENES

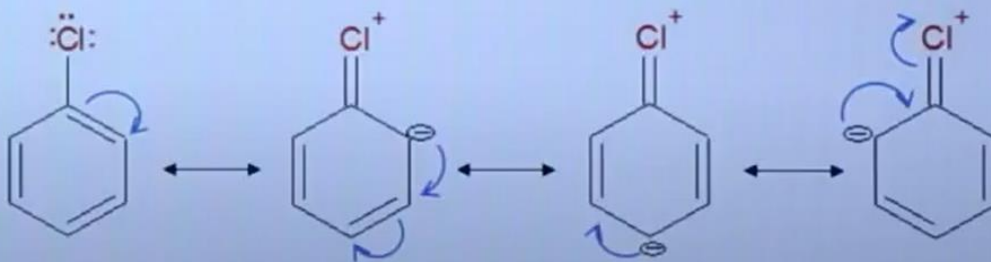
The reactions of haloarenes can also be divided into:

1. Nucleophilic Substitution Reactions
2. Electrophilic Substitution Reactions
3. Reaction with Metals

Reasons for the less reactivity of chlorobenzene

1. Resonance Effect

- Haloarenes are highly **unreactive** towards nucleophilic substitution reactions.
- The pair of electrons on halogen atom is in conjugation with the π –electrons of the benzene ring.
- Due to resonance, a partial double bond character of $C - X$ bond which is very difficult to be cleaved by nucleophile.



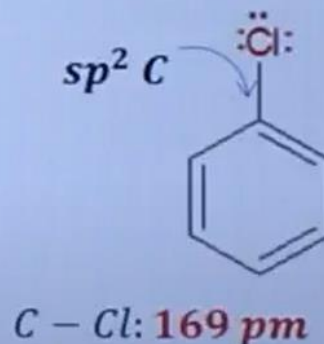
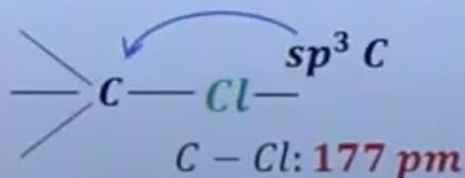
Reasons for the less reactivity of chlorobenzene

2. Hybridisation of C in C – X bond

- In haloarenes, X is attached to an sp^2 hybridized carbon atom.

$$sp^2 C > s - \text{character} > sp^3 C$$

- Since $sp^2 C$ has greater s – character and is more electronegative than $sp^3 C$, it withdraws the electrons of the C – X bond towards itself.
- Results in **decrease in bond length**.
- Shorter the bond length, **stronger** the bond.
- Greater difficulty in breaking a stronger C – X bond.



Reasons for the less reactivity of chlorobenzene

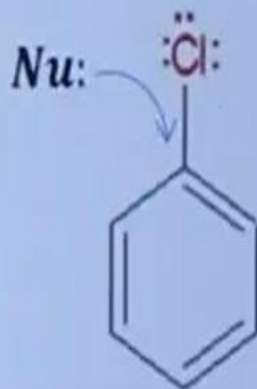
3. Instability of Phenyl Cation

- In haloarenes, when $C - X$ bond is broken, phenyl cation and X^- is formed.
- Phenyl cation is highly unstable as the positive charge resides on an electronegative sp^2 C atom.
- It is not stabilized by any electronic displacement effects like resonance.
- Due to unstable carbocation, it cannot undergo S_N1 reaction.

Reasons for the less reactivity of chlorobenzene

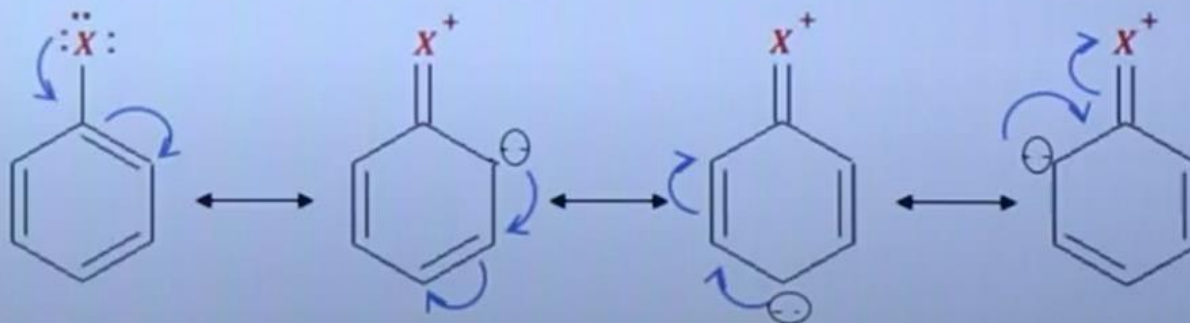
4. Electronic Repulsion

An incoming nucleophile experiences **repulsion** from the electron-rich phenyl ring in aryl halides.



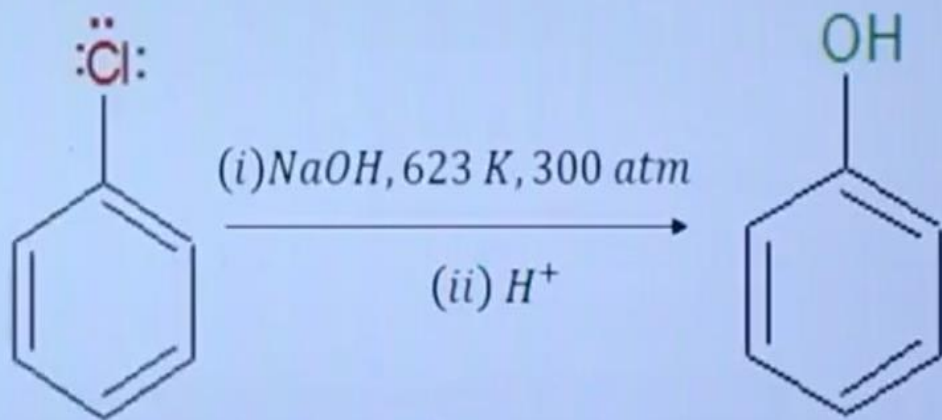
O- & p- directing

- Since haloarenes are electron-rich, these undergo electrophilic substitution reaction where the attacking species is an electrophile.
- Due to +M effect, electron density increases at *ortho* – and *para* – positions.
- **X** is deactivating due to $-I$ effect and withdraws electrons from benzene ring.
- Hence, these reactions are slow as compared to benzene.



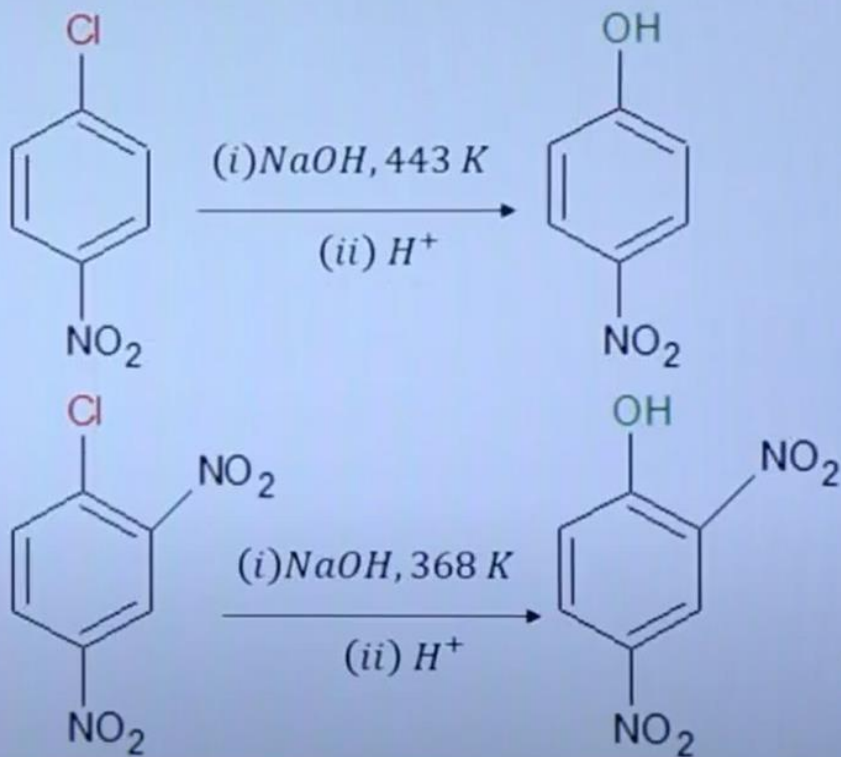
NUCLOPHILIC SUBSTITUTION REACTION

- Chlorobenzene can be converted into phenol under **drastic conditions**.
- *Temperature: 623 K and Pressure: 300 atm*



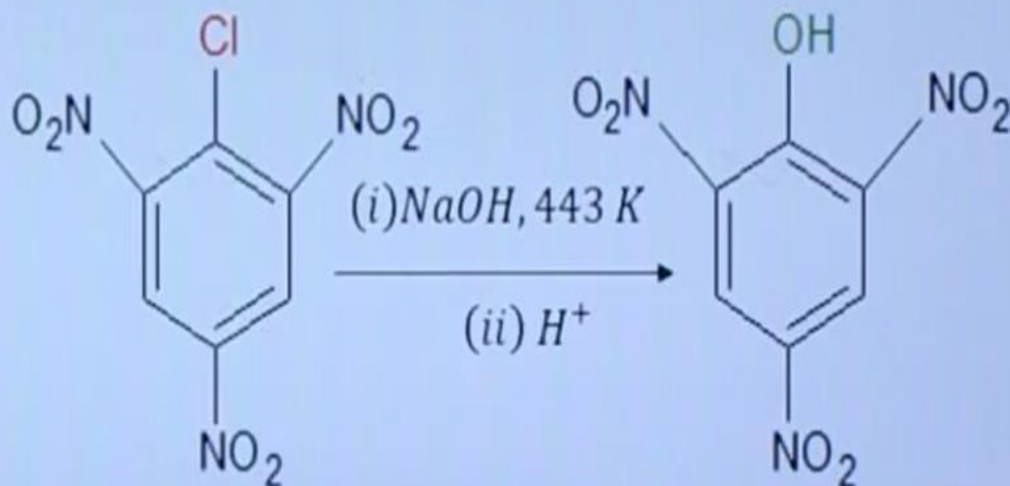
NUCLOPHILIC SUBSTITUTION REACTION

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



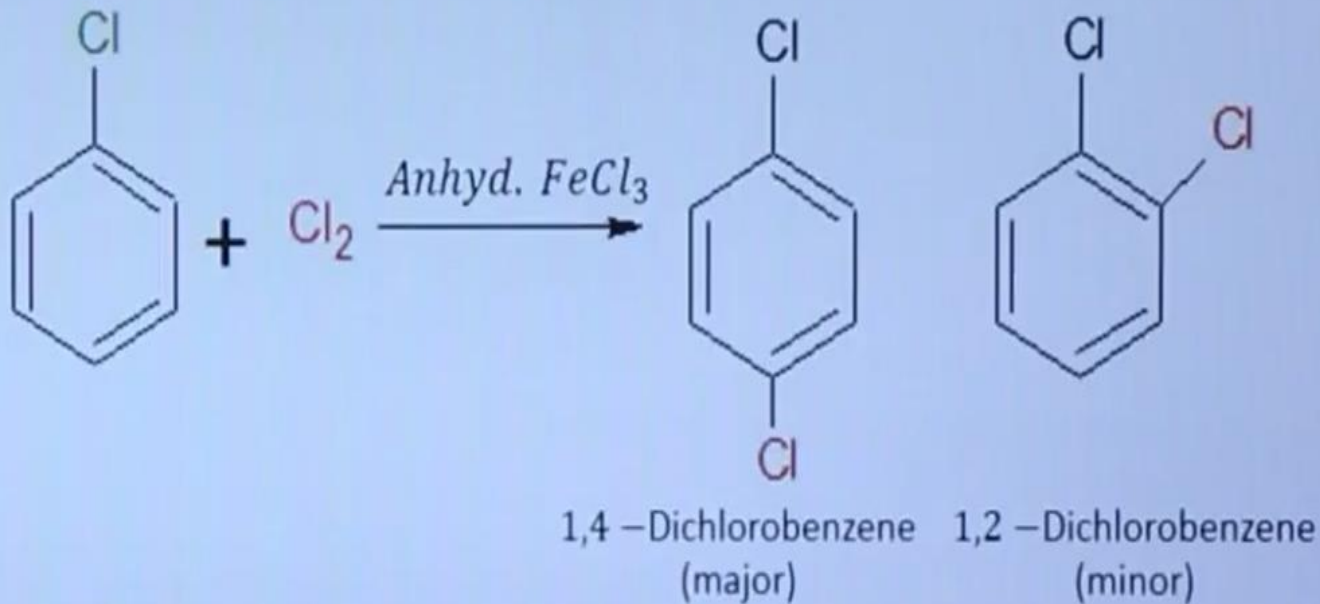
NUCLOPHILIC SUBSTITUTION REACTION

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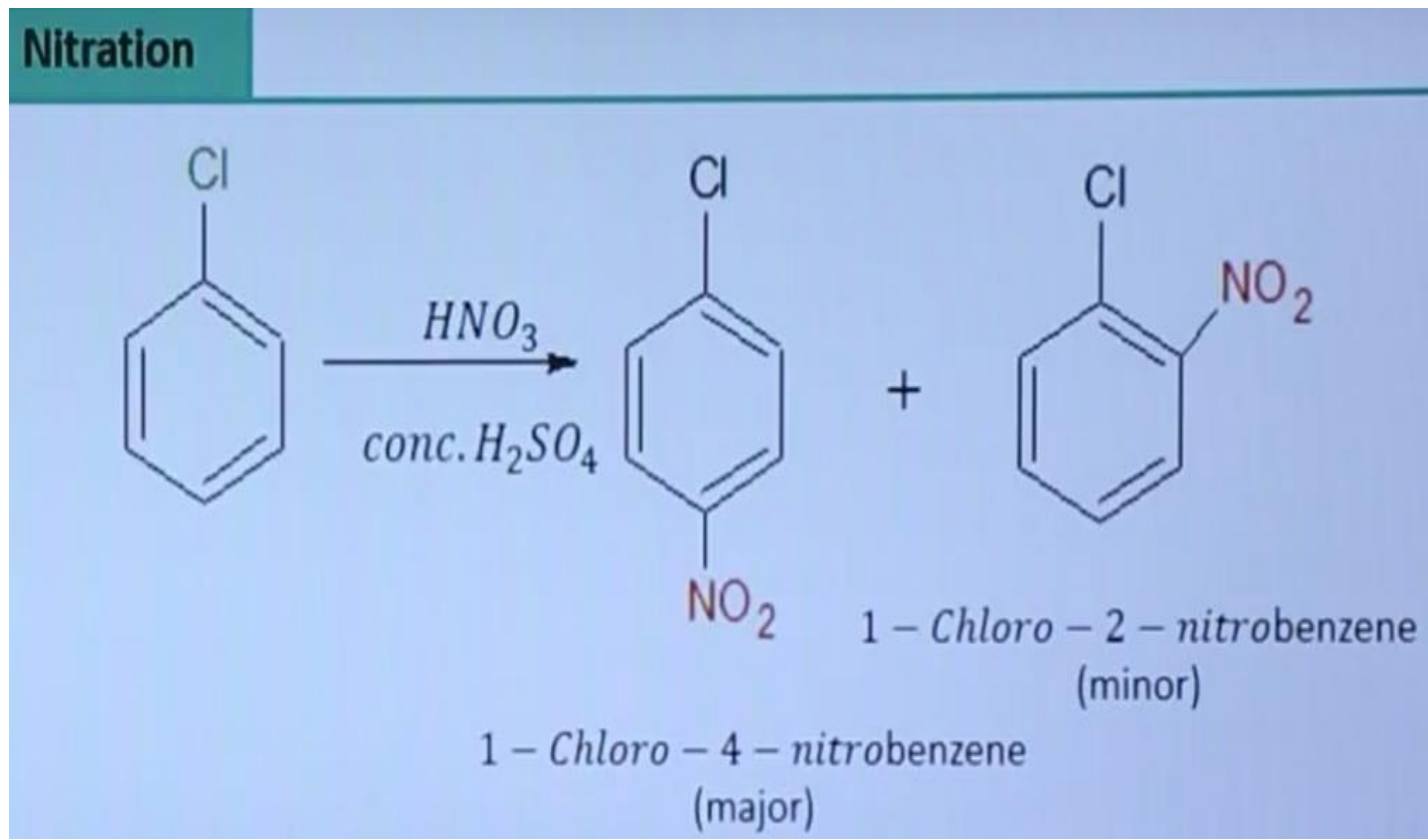


1. HALOGENATION

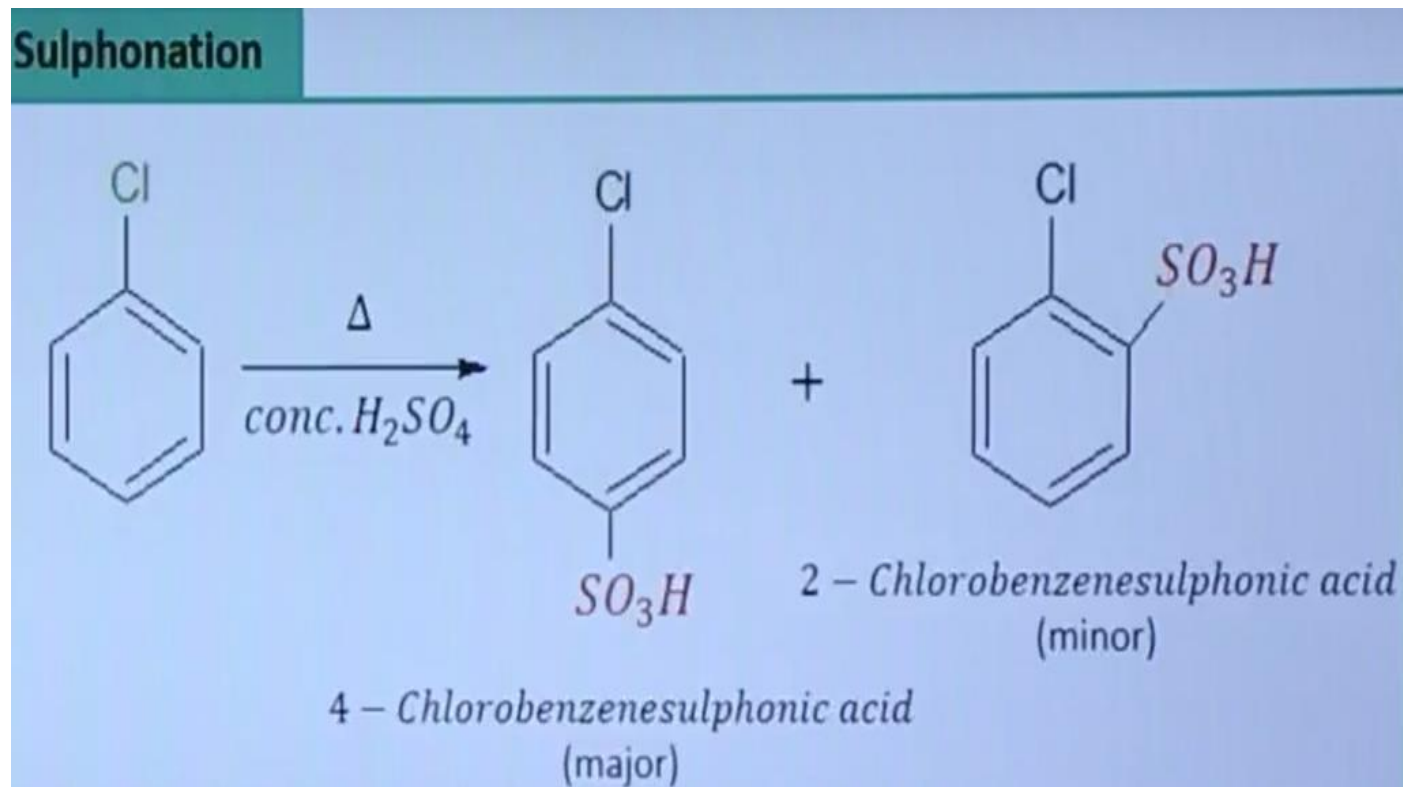
Halogenation



2. NITRATION

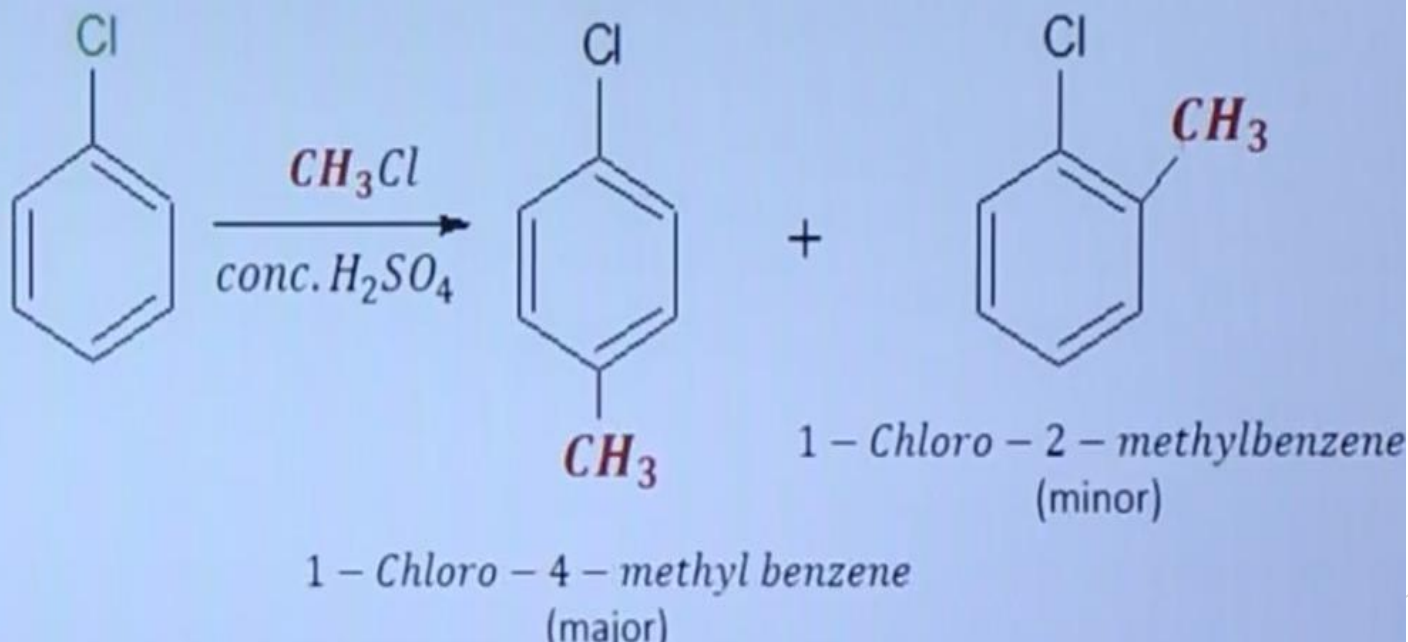


3.SULPHONATION



4. FRIEDEL-CRAFTS ALKYLATION

Friedel-Crafts Alkylation Reaction

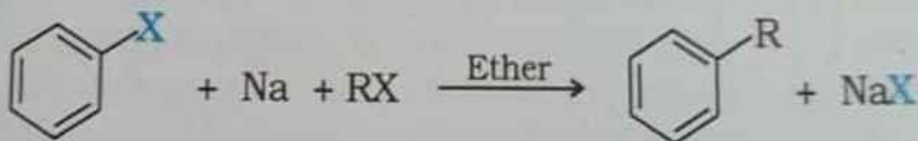


REACTION WITH METALS

3. Reaction with metals

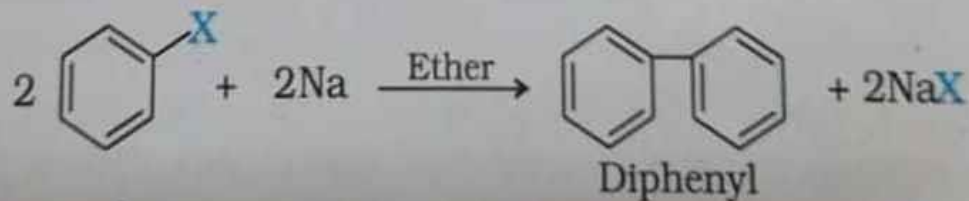
Wurtz-Fittig reaction

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.

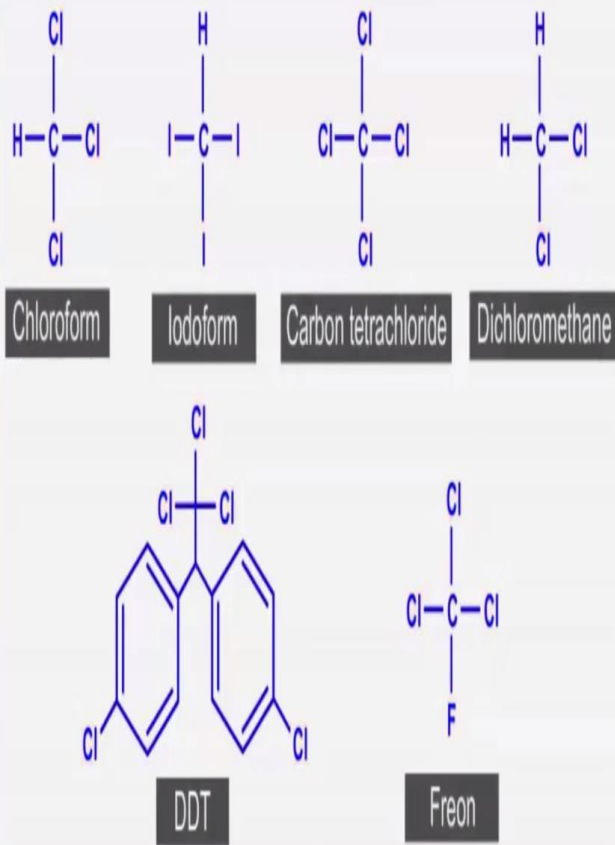


POLY HALOGEN COMPOUNDS

- Carbon compounds containing more than one halogen atom are referred to as *polyhalogen compounds*.

- Applications: Industry and Agriculture.

- Examples: Methylene chloride, Chloroform, Iodoform, Carbon tetrachloride, Freons and DDT



Dichloromethane

Dichloromethane CH_2Cl_2

Used as

- a solvent as a paint remover, propellant in aerosols
- Process solvent in manufacturing drugs.
- Metal cleaning and finishing solvent.

Harmful Effects

- Impairment in hearing and vision.
- Higher level causes dizziness, nausea, numbness in fingers.
- Direct contact with eyes burn the cornea.



Tetrachloromethane

Tetrachloromethane (Carbon tetrachloride), CCl_4

Used:

- As a solvent
- In the manufacture of refrigerants and propellants for aerosol cans.
- Feedstock in the synthesis of chlorofluorocarbons.
- Was used as cleaning fluid, degreasing agent, spot remover and as fire extinguisher.

Harmful Effects:

- Common: Dizziness, nausea, vomiting
- Severe: coma, unconsciousness or death.
- The chemical may irritate eyes on contact.
- In air, it depletes the ozone layer increasing human exposure to *UV*-rays, and consequently, eye diseases, skin cancer, decreased immunity etc.



Manufacture of refrigerants and aerosol propellants



Dry-cleaning fluid

Degreasing agent



Spot remover

Fire extinguisher

Triiodomethane

Triiodomethane (Iodoform), CHI_3

Used as

- Antiseptic previously.
- Due to the evolution of iodine.
- Due to its unpleasant smell, it is replaced by other formulations containing iodine.

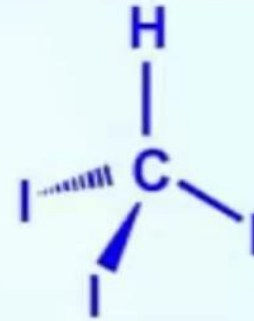
Characteristics of Triiodomethane (Iodoform)



Volatile and Pungent odour



Used as an antiseptic



Triiodomethane



Iodoform

Freons

Freons

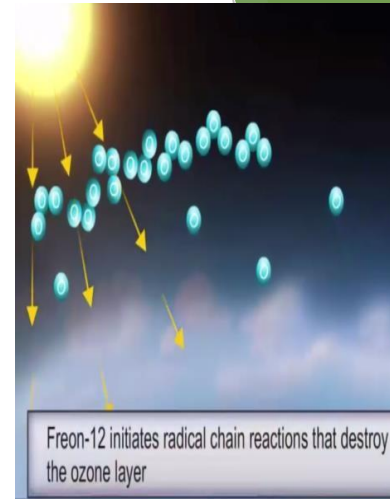
- The chlorofluorocarbon compounds of methane and ethane are collectively known as freons.
- Highly stable, non-toxic and non-corrosive.
- Easily liquefiable gases.
- Freon 12 CCl_2F_2 is the most common one used in industries.
- Manufactured by Swartz Reaction.

Used:

- In aerosol propellants, refrigeration and air conditioning.

Harmful Effects:

- In atmosphere, freons initiate radical chain reactions affecting the ozone layer.



DDT

p,p' – Dichlorodiphenyltrichloroethane (DDT)

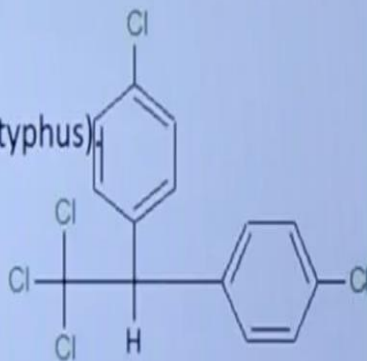
- The first chlorinated organic insecticides.
- Paul Muller, awarded Nobel Prize in Medicine and Physiology.

Used:

- Insecticide.
- Effective against mosquitos (malaria) and lice (typhus)

Harmful Effects:

- Many insects developed resistance to *DDT*.
- High toxicity towards fish.
- Not easily metabolized by animals due to high chemical stability and fat solubility.
- It is deposited and stored in the fatty tissues.



THANK
YOU