HALOALKANES AND HALOARENES

chloramphenicol,-------- typhoid fever.

iodine containing hormone, *thyroxine*,------ - deficiency of which causes a disease called *goiter.*

Chloroquine ----malaria

halothane is used as an anaesthetic during surgery.

1

CLASSIFICATION

- These may be classified as mono, di, or polyhalogen (tri-,tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,
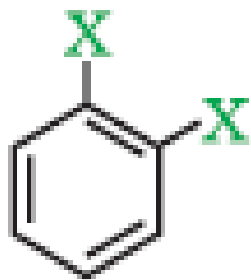
C_2H_5X

Monohaloalkane

CH_2X
|
CH_2X

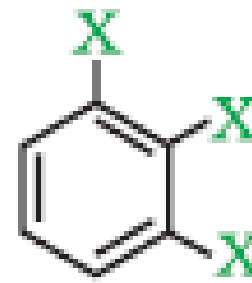Dihaloalkane

CH_2X
|
CHX
|
CH_2X

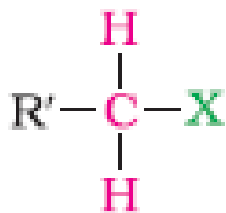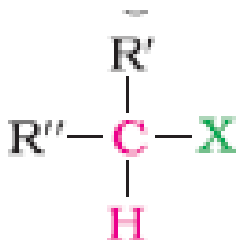Trihaloalkane

Monohaloarene   Dihaloarene   Trihaloarene

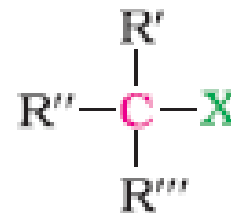*(a) Alkyl halides or haloalkanes (R—X)*

In alkyl halides, the halogen atom is bonded to an alkyl group (R). They form a homologous series represented by $C_nH_{2n+1}X$. They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached.
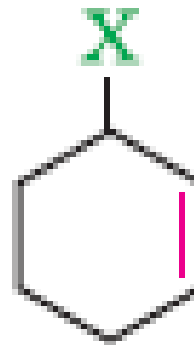

Primary (1°)   Secondary (2°)   Tertiary (3°)

(B) ALLYLIC HALIDES
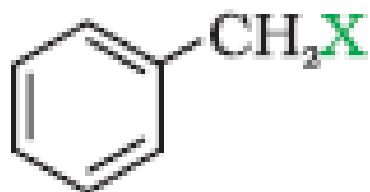
- These are the compounds in which the halogen atom is bonded to an *sp3-hybridised carbon atom next to carbon-carbon double bond (C=C) i.e. to an allylic carbon.*

(C) BENZYLIC HALIDES

- These are the compounds in which the halogen atom is bonded to an *sp3-hybridised carbon atom next to an aromatic ring.*

CH_2X

(1°)

R' X R''

$R' = CH_3, R'' = H (2°)$

$R' = R'' = CH_3 (3°)$

COMPOUNDS CONTAINING *SP²* C—X BOND

(a) **Vinylic halides**

- These are the compounds in which the halogen atom is bonded to an *sp2-hybridised carbon atom of a carbon-carbon double bond*(C = C).

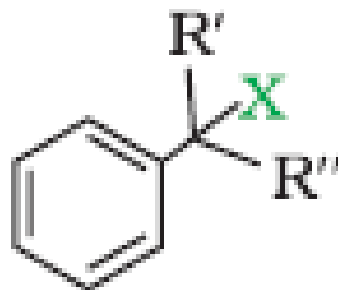# (B) ARYL HALIDES

- These are the compounds in which the halogen atom is bonded to the *sp2-hybridised carbon atom of an aromatic ring.*

NOMENCLATURE
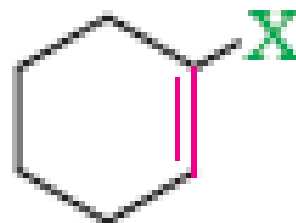
$CH_3CH_2CH_2Br$
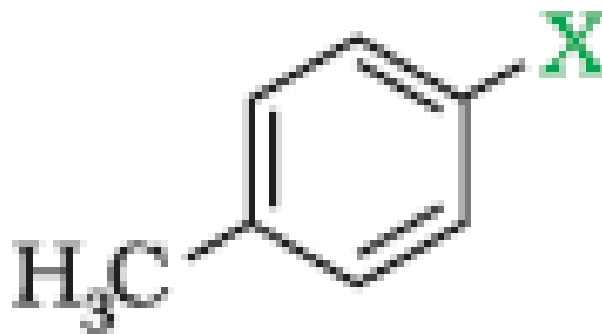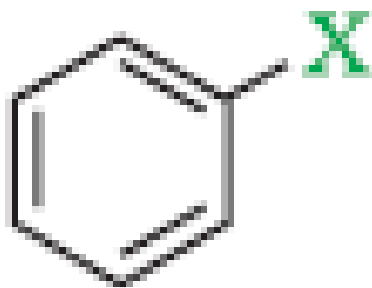
: n-Propyl bromide

: 1-Bromopropane

$H_3C-CH-CH_3$
|
Cl
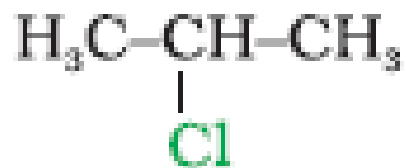
Isopropyl chloride

2-Chloropropane

CH_3
|
$H_3C-CH-CH_2Cl$
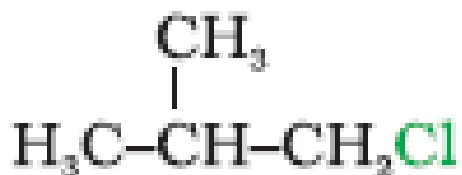
Isobutyl chloride

1-Chloro-2-methylpropane
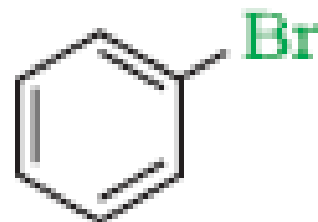
Bromobenzene

Bromobenzene

8
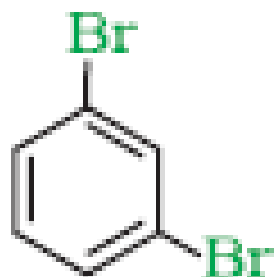
m-Dibromobenzene
1,3-Dibromobenzene
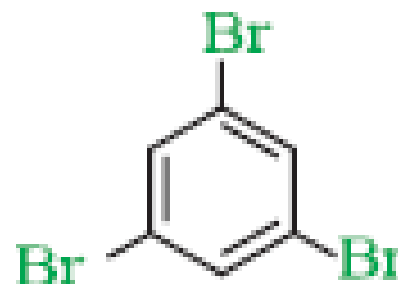
sym-Tribromobenzene
1,3,5-Tribromobenzene
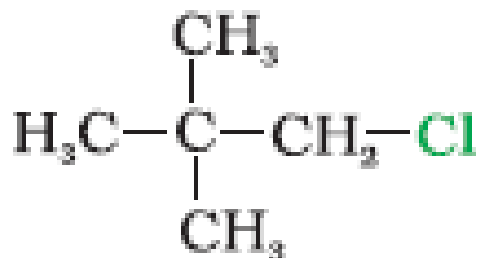
1-Chloro-2,2-dimethylpropane
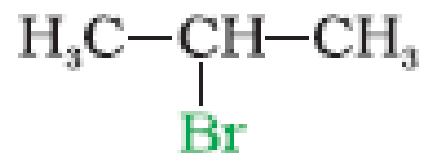
2-Bromopropane

THE DIHALO-COMPOUNDS

$H_3C-CHCl_2$

H_2C-CH_2
| |
Cl   Cl
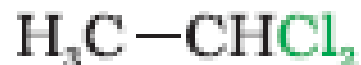
Common name: Ethylidene chloride (*gem-dihalide*)

Ethylene dichloride (*vic-dihalide*)
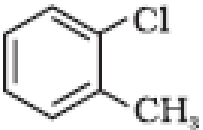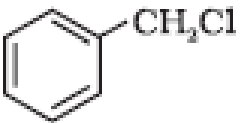
IUPAC name: 1, 1-Dichloroethane

1, 2-Dichloroethane

10

Table 10.1: Common and IUPAC names of some Halides

Structure	Common name	IUPAC name
$CH_3CH_2CH(Cl)CH_3$	sec-Butyl chloride	2-Chlorobutane
$(CH_3)_3CCH_2Br$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(CH_3)_3CBr$	tert-Butyl bromide	2-Bromo-2-methylpropane
$CH_2 = CHCl$	Vinyl chloride	Chloroethene
$CH_2 = CHCH_2Br$	Allyl bromide	3-Bromopropene
(o-chlorotoluene structure)	o-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
(benzyl chloride structure)	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CH_3CH_2CH_2F$	n-Propyl fluoride	1-Fluoropropane

- Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

Write IUPAC names of the following:

(i)

(ii)

(iii)

(iv)

(v)

(vi)
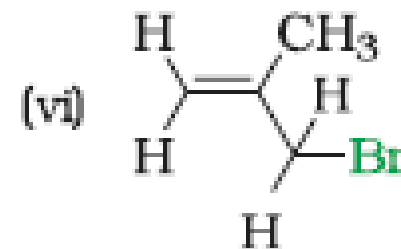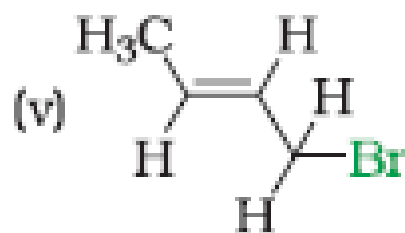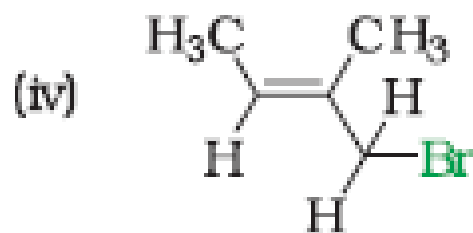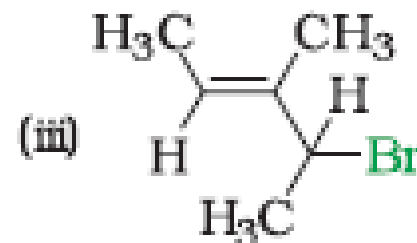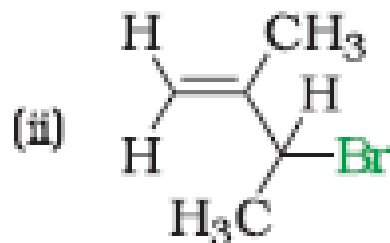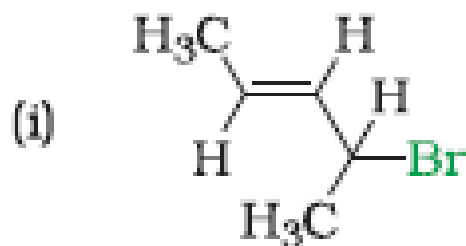
(i) 4-Bromopent-2-ene

(ii) 3-Bromo-2-methylbut-1-ene

(iii) 4-Bromo-3-methylpent-2-ene

(iv) 1-Bromo-2-methylbut-2-ene

(v) 1-Bromobut-2-ene

(vi) 3-Bromo-2-methylpropene

HOMEWORK

10.1 Write structures of the following compounds:
- (i) 2-Chloro-3-methylpentane
- (ii) 1-Chloro-4-ethylcyclohexane
- (iii) 4-tert. Butyl-3-iodoheptane
- (iv) 1,4-Dibromobut-2-ene
- (v) 1-Bromo-4-sec. butyl-2-methylbenzene.

NATURE OF C-X BOND

- Since halogen atoms are more electronegative than carbon, the carbonhalogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.

METHODS OF PREPARATION

○ From Alcohols

$$R{-}OH \ + \ HX \ \xrightarrow{\ ZnCl_2\ } \ R{-}X \ + \ H_2O$$

$$R{-}OH \ + \ NaBr \ + \ H_2SO_4 \longrightarrow \ R{-}Br \ + \ NaHSO_4 \ + \ H_2O$$

$$3R{-}OH \ + \ PX_3 \longrightarrow \ 3R{-}X \ + \ H_3PO_3 \qquad (X = Cl, \ Br)$$

$$R{-}OH \ + \ PCl_5 \longrightarrow \ R{-}Cl \ + \ POCl_3 \ + \ HCl$$

$$R{-}OH \ \xrightarrow[\ X_2 = Br_2, I_2\ ]{\ red\ P/X_2\ } \ R{-}X$$

$$R{-}OH \ + \ SOCl_2 \longrightarrow \ R{-}Cl \ + \ SO_2 \ + \ HCl$$

16
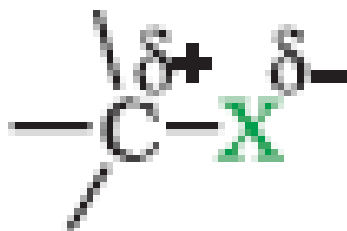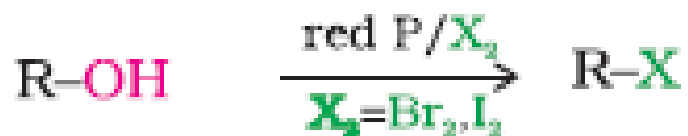
- The order of reactivity of alcohols with a given **haloacid** is **3°>2°>1°.**

- The above method is not applicable for the preparation of aryl halides because the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond

FROM HYDROCARBONS

○ *(a) By free radical halogenation*

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

(B) BY ELECTROPHILIC SUBSTITUTION

- Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride.

o-Halotoluene   p-Halotoluene

19
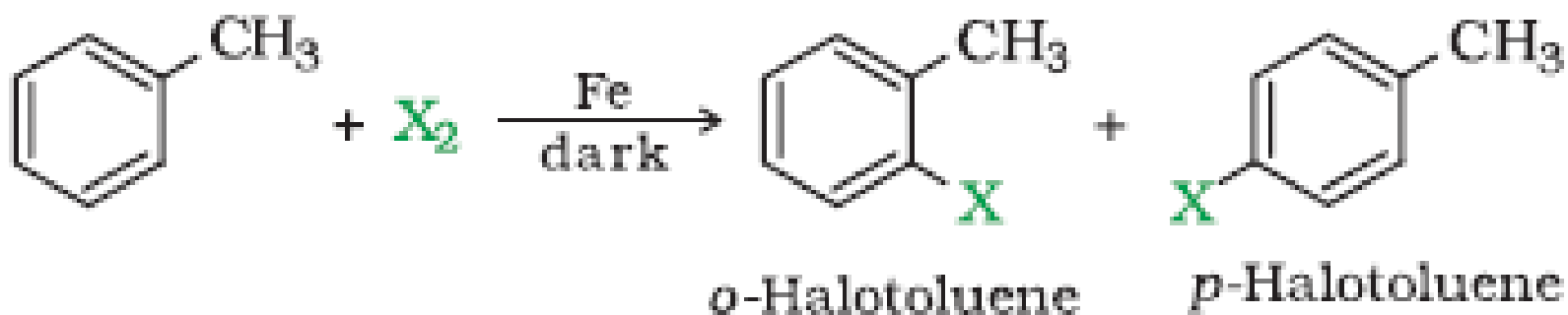
➤ The *ortho and para isomers can be easily separated due to large* difference in their melting points.

➤ Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO_3, HIO_4) to oxidise the HI formed during iodination.

➤ Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

(C) SANDMEYER'S REACTION

When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by –Cl or –Br.

Benzene diazonium halide

21

$X = Cl, Br$
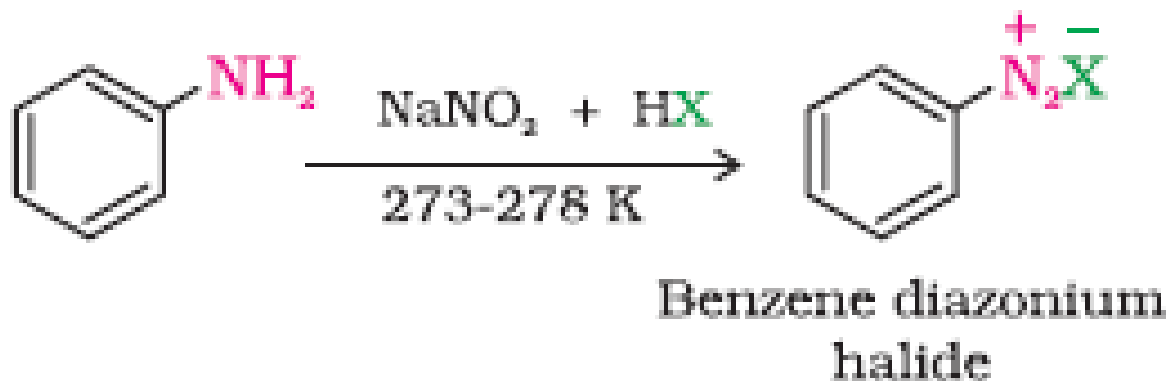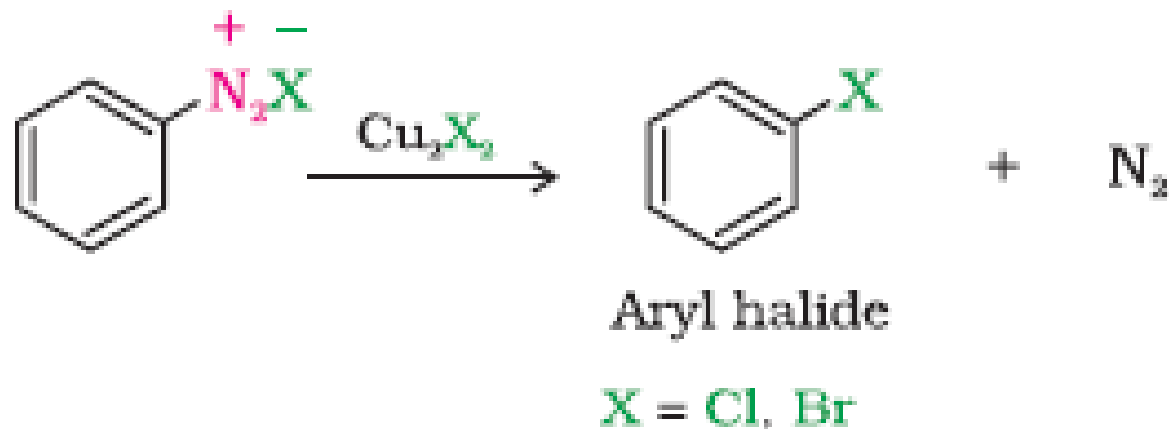
Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.
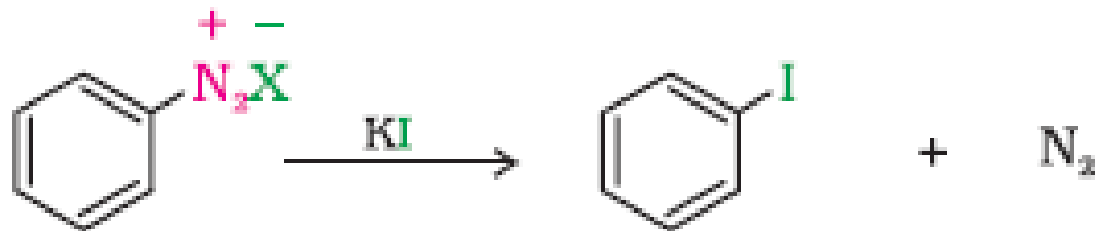
(D) FROM ALKENES

(i) ***Addition of hydrogen halides****: An alkene is converted to* corresponding alkyl halide by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.

Propene yields two products, however only one predominates as per **Markovnikov's rule**.

23
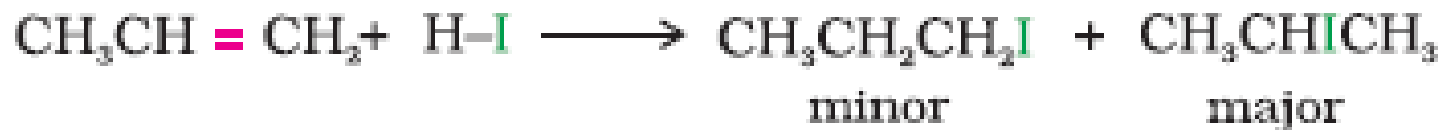
MARKOVNIKOV'S RULE.

The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses **lesser number of hydrogen atoms**.

ANTI-MARKOVNIKOV'S RULE.

In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule.
This happens only with HBr but not with HCl and Hl.
This addition reaction was observed by M.S. Kharash and F.R. Mayo in 1933 at the University of Chicago.
This reaction is known as *peroxide or Kharash effect* or addition reaction anti to Markovnikov rule.

- Write the products of the following reactions:

(i) + HBr $\longrightarrow$

(ii) $CH_3-CH_2-CH=CH_2$ + HCl $\longrightarrow$ $CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3$

(iii) $CH_2-\underset{\underset{H}{|}}{C}=CH_2$ + HBr $\xrightarrow{\text{Peroxide}}$ $CH_2-CH_2-CH_2-Br$

(II) ADDITION OF HALOGENS:

In the laboratory, addition of bromine in CCl_4 *to an alkene resulting in discharge of reddish brown colour of bromine constitutes an important method for the detection of double bond in a molecule. The addition results in the synthesis of vic-dibromides, which are colourless*
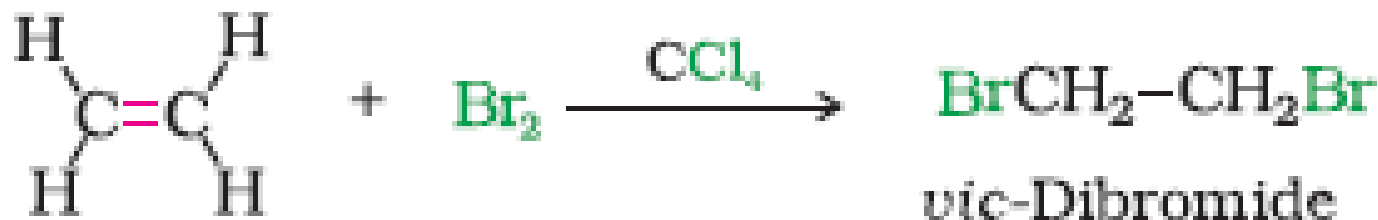
FINKELSTEIN REACTION.

Alkyl iodides are often prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone.
This reaction is known as **Finkelstein** reaction.

$$R–X \ + \ NaI \longrightarrow R–I \ + \ NaX$$

$$X = Cl, Br$$

NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.

SWARTS REACTION.

The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3.

The reaction is termed as **Swarts reaction.**

$$H_3C-Br + AgF \longrightarrow H_3C-F + AgBr$$

PHYSICAL PROPERTIES

- Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light.

- Many volatile halogen compounds have sweet smell.

- The boiling points of isomeric haloalkanes decrease with increase in branching

- For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.

$CH_3CH_2CH_2CH_2Br$ $CH_3CH_2CHCH_3$ $H_3C-\underset{Br}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$

Br

b.p./K   375   364   346
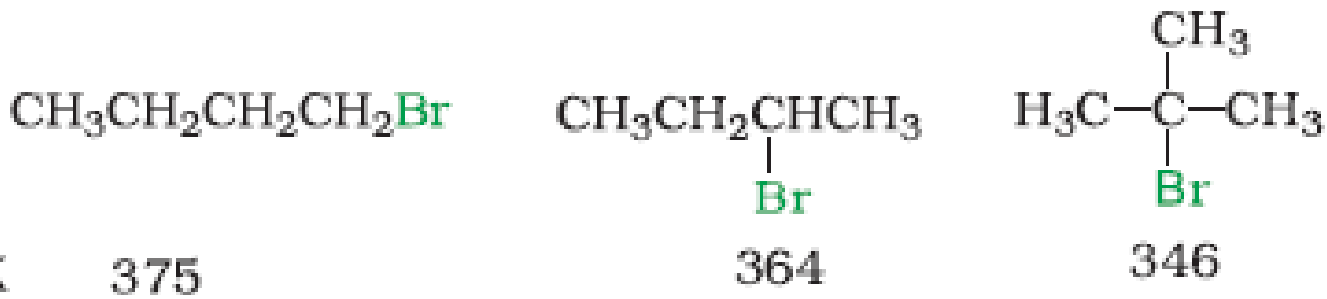
- Boiling points of isomeric dihalobenzenes are very nearly the same.
- However, the *para-isomers are high melting as compared to their ortho and meta-isomers. It is due to symmetry of para-isomers that fits in* crystal lattice better as compared to *ortho- and meta-isomers.*
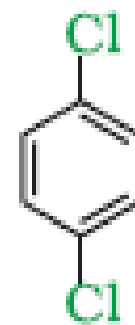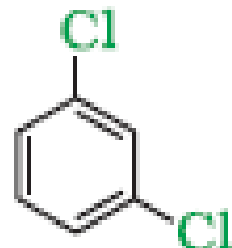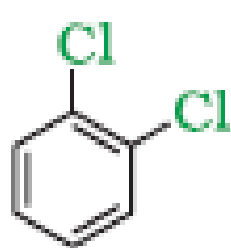
	ortho	meta	para
b.p / K	453	446	448
m.p / K	256	249	323

Density

- Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water.

- The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms

Solubility

- *The haloalkanes are only very slightly soluble in water. In order for a* haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules.

- Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water.

- As a result, the solubility of haloalkanes in water is low.

- However, haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

Reactions of Haloalkanes

The reactions of haloalkanes may be divided into the following categories:

- (i) Nucleophilic substitution
- (ii) Elimination reactions
- (iii) Reaction with metals.

(I) *NUCLEOPHILIC SUBSTITUTION REACTIONS*

$$\text{N}\bar{\text{u}} \;+\; \overset{\delta^+}{-}\overset{|}{\underset{|}{\text{C}}}\overset{\delta^-}{-}\text{X} \;\longrightarrow\; \overset{|}{\underset{|}{\text{C}}}\text{-Nu} \;+\; \bar{\text{X}}$$

Mechanism:
This reaction has been found to proceed by two different mechanims which are described below:

(a) Substitution nucleophilic bimolecular (SN²)

(b) Substitution nucleophilic unimolecular (SN¹)

(a) Substitution nucleophilic bimolecular (SN²)

- The reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants.
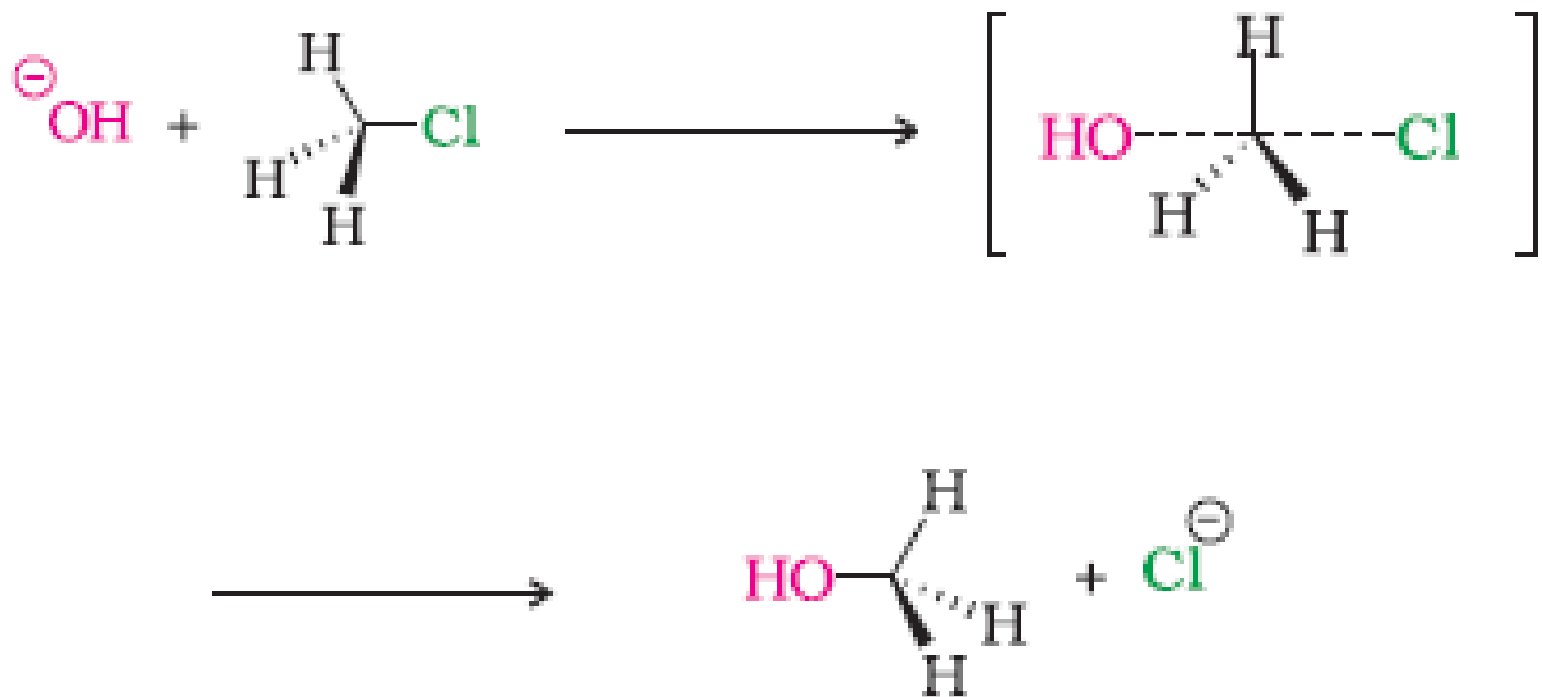
INVERSION OF CONFIGURATION.

- The incoming nucleophile interacts with alkyl halide causing the carbonhalide bond to break while forming a new carbon-OH bond.

- These two processes take place simultaneously in a single step and no intermediate is formed.

- As the reaction progresses and the bond between the nucleophile and the carbon atom starts forming, the bond between carbon atom and leaving group weakens.

- As this happens, the configuration of carbon atom under attack inverts in much the same way as an umbrella is turned inside out when caught in a strong wind, while the leaving group is pushed away.

- This process is called as **inversion of configuration.**

- Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles.
- Thus the order of reactivity followed is:

Primary halide > Secondary halide > Tertiary halide.

Methyl
(30)

Ethyl 1°
(1)
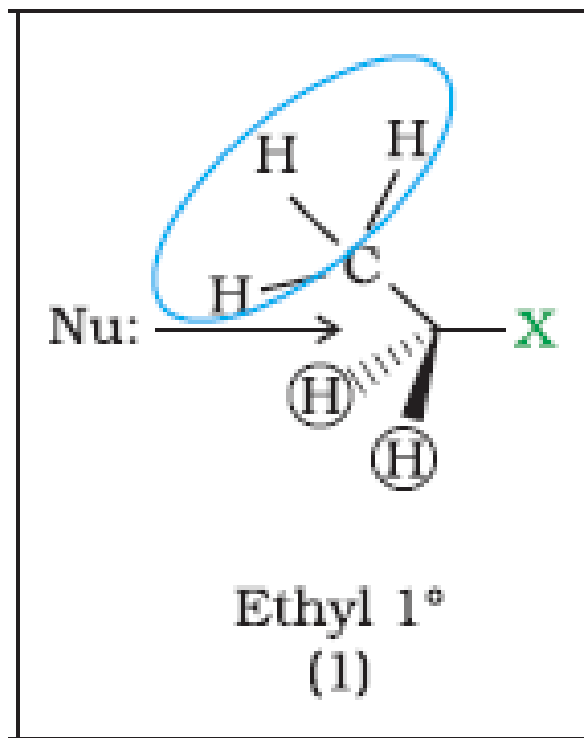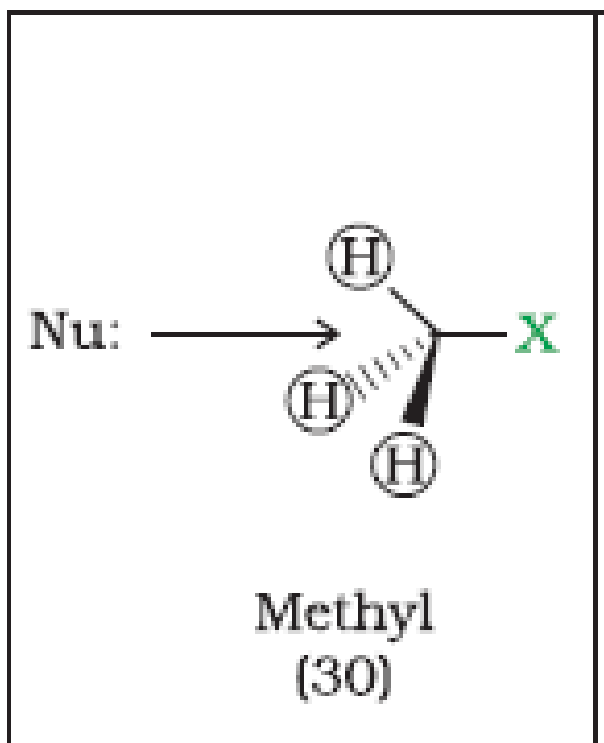
Steric effects in S$_N$2 reaction. The relative rate of S$_N$2 reaction is given in parenthesis

Isopropyl 2°
(0.02)
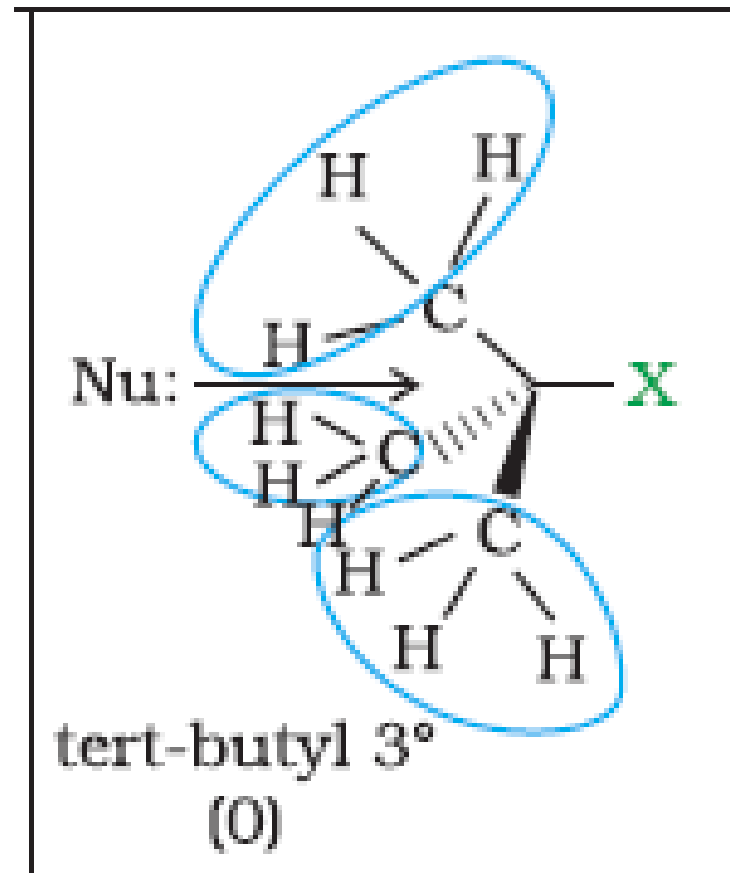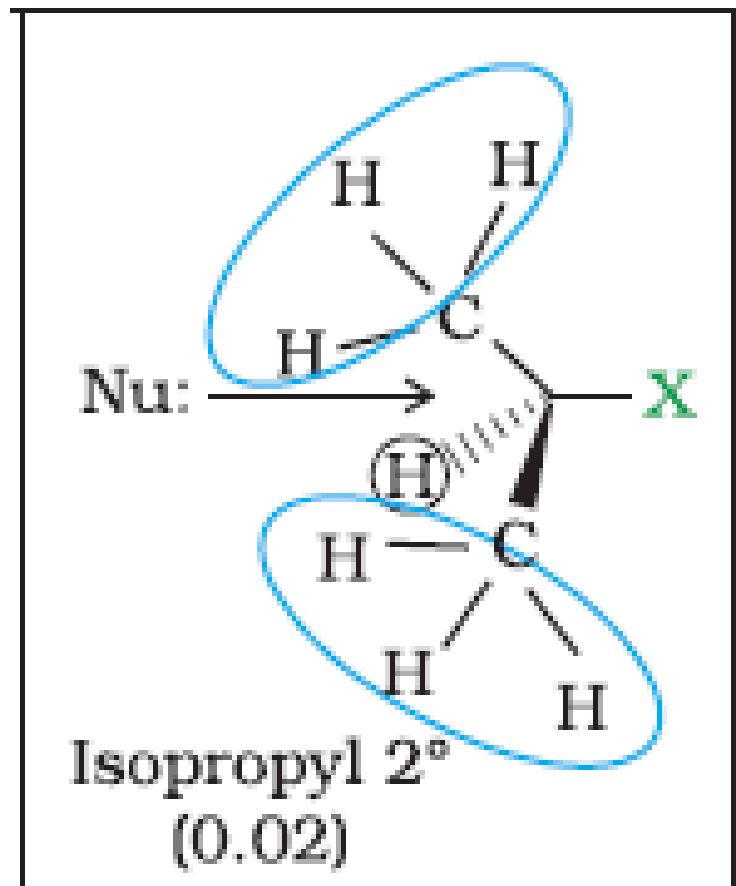
tert-butyl 3°
(0)

(b) Substitution nucleophilic unimolecular (SN¹)

- **SN¹** reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.).

- The reaction between *tert-butyl* bromide and hydroxide ion yields *tert-butyl alcohol and follows* the first order kinetics, *i.e., the rate of reaction depends upon the* concentration of only one reactant, which is *tert- butyl bromide.*

$(CH_3)_3CBr$ + ^-OH $\longrightarrow$ $(CH_3)_3COH$ + Br^-

2-Bromo-2-methylpropane   2-Methylpropan-2-ol

- It occurs in two steps. In step I, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion.
- The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction.

$(CH_3)_3CBr$ $\xrightleftharpoons{\text{step I}}$

CH$_3$—C$^{\oplus}$ (with H$_3$C and CH$_3$) + $Br^{\ominus}$

CH$_3$—C$^{\oplus}$ (with H$_3$C and CH$_3$) + ^-OH $\xrightarrow{\text{step II}}$ $(CH_3)_3COH$
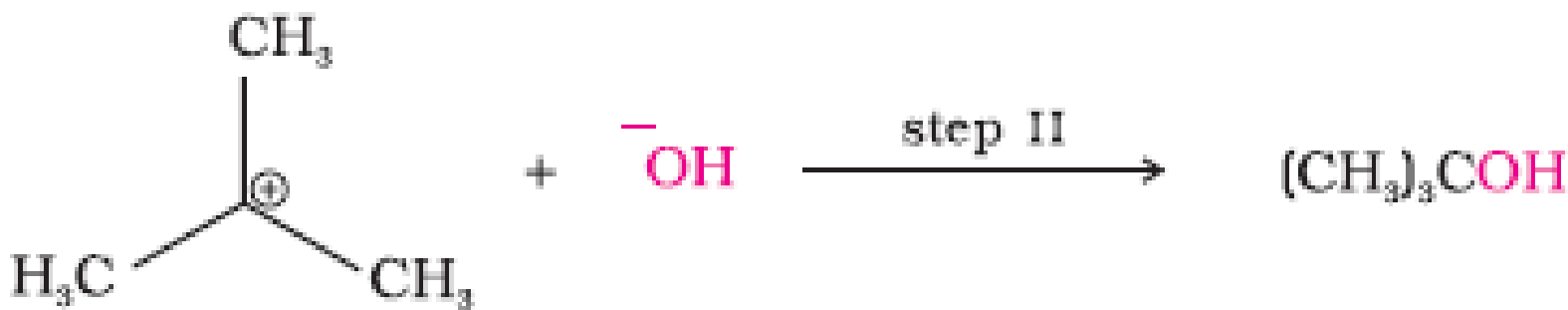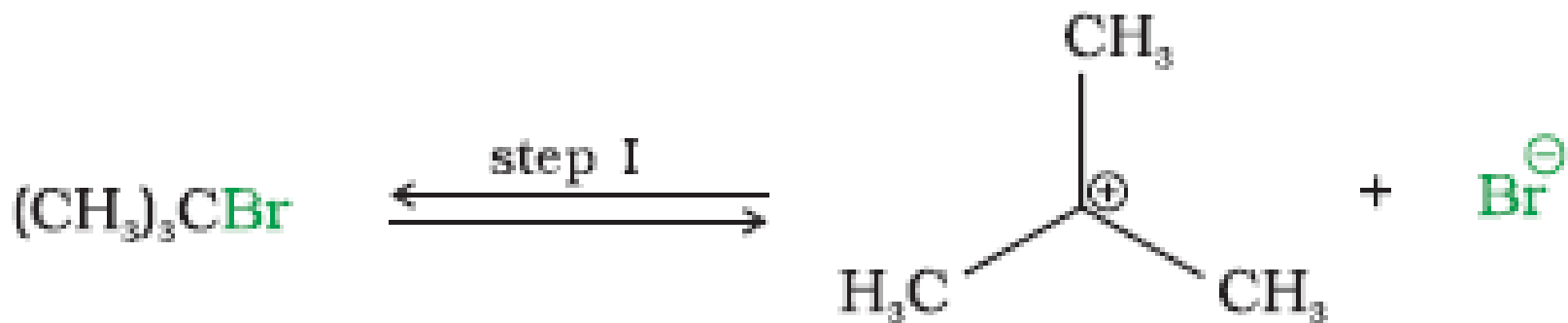
- Step I is the slowest and reversible. It involves the C–Br bond breaking for which the energy is obtained through solvation of halide ion with the proton of protic solvent.

- Since the rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion.

- Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction.

- In case of alkyl halides, 3^0 alkyl halides undergo SN^1 reaction very fast because of the high stability of 3^0 carbocations.

- We can sum up the order of reactivity of alkyl halides towards SN^1 and SN^2 reactions as follows:

For S_N2 reaction
→

Tertiary halide; Secondary halide; Primary halide; CH_3X

←
For S_N1 reaction
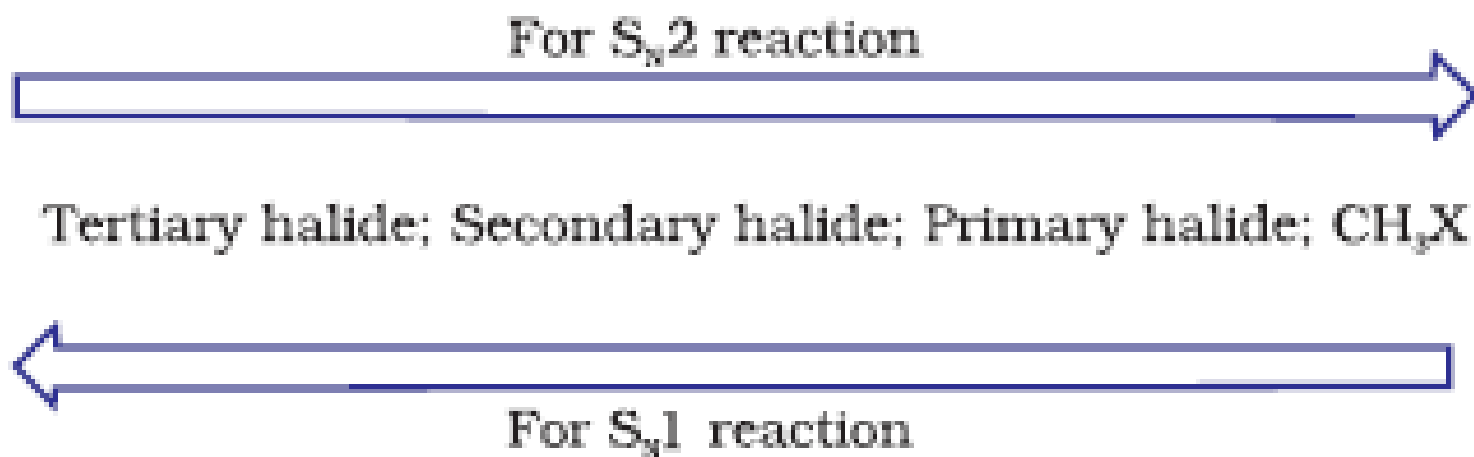
- Allylic and benzylic halides show high reactivity towards the SN^1 reaction.
- The carbocation thus formed gets stabilised through resonance
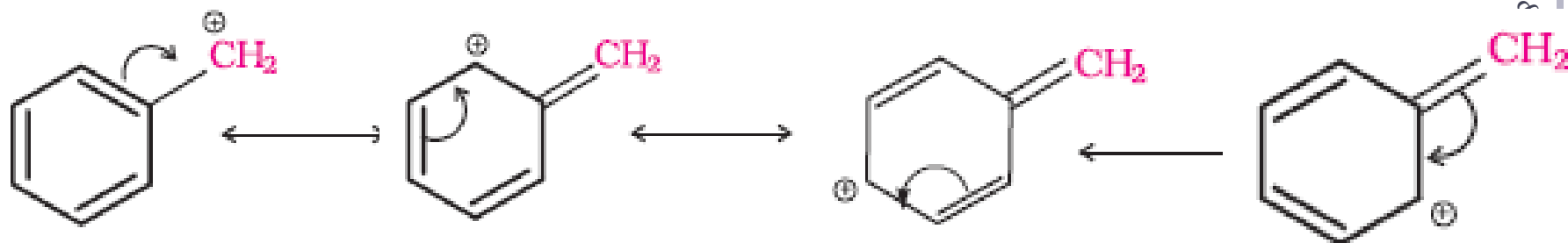
For a given alkyl group, the reactivity of the halide, R-X, follows the same order in both the mechanisms R–I> R–Br>R–Cl>>R–F.

- In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?

(c) Stereochemical aspects of nucleophilic substitution reactions

- A S_N2 reaction proceeds with complete stereochemical **inversion** while a S_N1 reaction proceeds with **racemisation.**

- (i) *Plane polarised light and optical activity*:

Such (+) and (–) isomers of a compound are called **optical isomers and the phenomenon is termed as optical isomerism.**

- (ii) *Molecular asymmetry, chirality and enantiomers*

- The spatial arrangement of four groups (valencies) around a central carbon is tetrahedral and if all the substituents attached to that carbon are different, such a carbon is called **asymmetric carbon or stereocentre.**

- The resulting molecule would lack symmetry and is referred to as asymmetric molecule. The asymmetry of the molecule is responsible for the optical activity in such organic compounds.

CHIRALITY

An object that cannot be superimposed
on its mirror image is called chiral

Mirror	Mirror

Chiral objects
Nonsuperimposable
mirror images
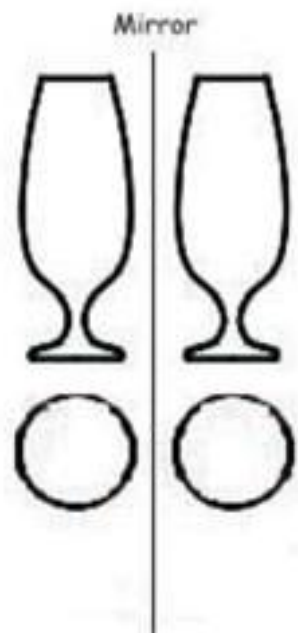
Nonchiral objects
Superimposable
mirror images

propan-2-ol
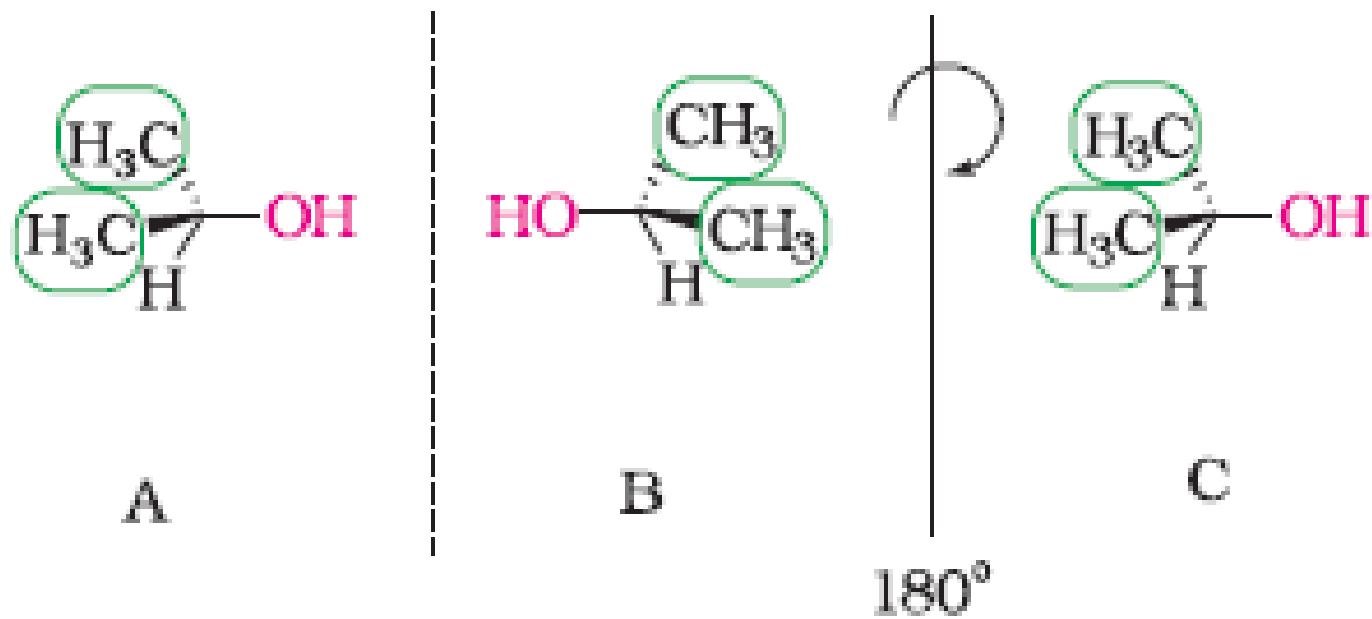
C obtained by rotating B by 180°
C is superimposable on its mirror image A

Butan-2-ol

H_3C C_2H_5 OH H

D

CH_3 HO C_2H_5 H

E

$180°$

C_2H_5 H_3C OH H

F
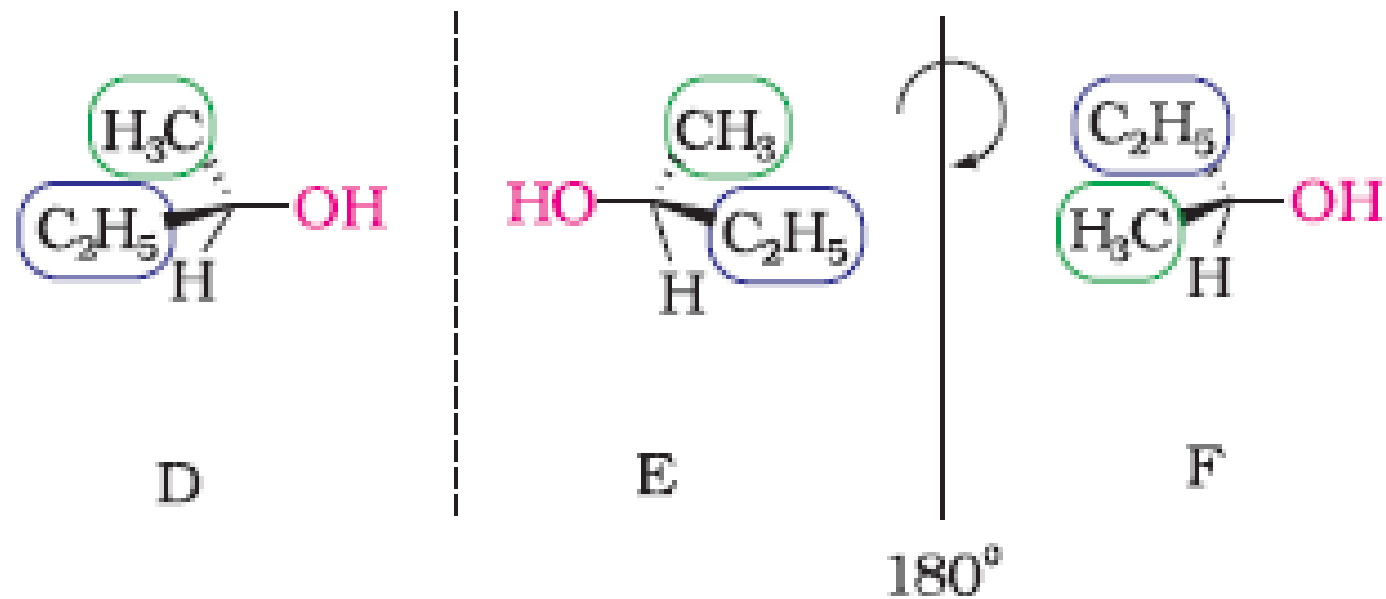
F obtained by rotating E by 180°
F is non superimposable on its mirror image D

- The stereoisomers related to each other as nonsuperimposable mirror images are called **enantiomers**
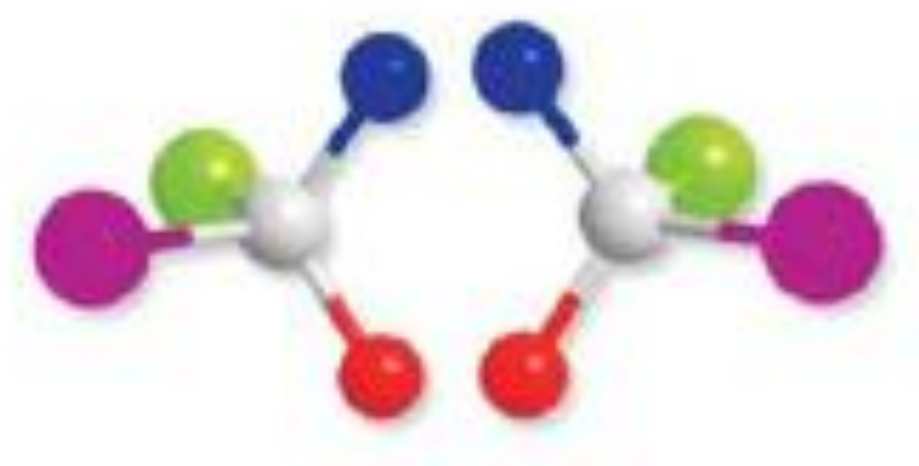
Fig. 10.5: *A chiral molecule and its mirror image*

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- Enantiomers possess identical physical properties namely, melting point, boiling point, solubility, refractive index, etc.
- They only differ with respect to the rotation of plane polarised light.
- If one of the enantiomer is *dextro rotatory, the other will be laevo rotatory.*
- A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as **racemic mixture or racemic modification.**
- The process of conversion of enantiomer into a racemic mixture is known as **racemisation.**

Identify chiral and achiral molecules in each of the following pair of compounds.

(i)

H
H₃C══════ ⟍ OH
Br

(i)

H
H₃C══════ ⟍ Br
Br

(ii)

(ii)

HO   H
⟍ ╱
H₃C   ⟍ CH₃

(i)

H₃C ⟍   ╱ CH₃
⟍ ╱
H   OH

(ii)

(iii) CH₃CHCH₂CH₃   CH₃CH₂CH₂CH₂Br
        |
       Br   (i)   (ii)
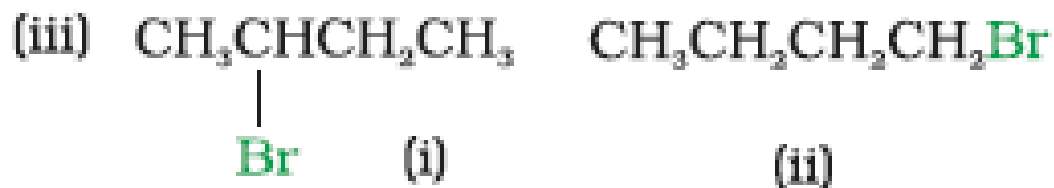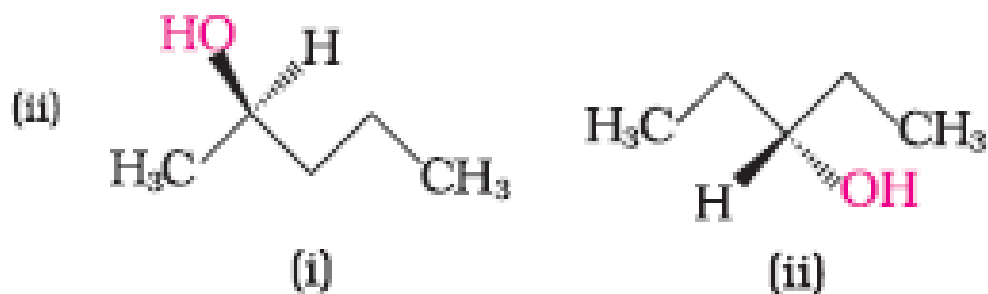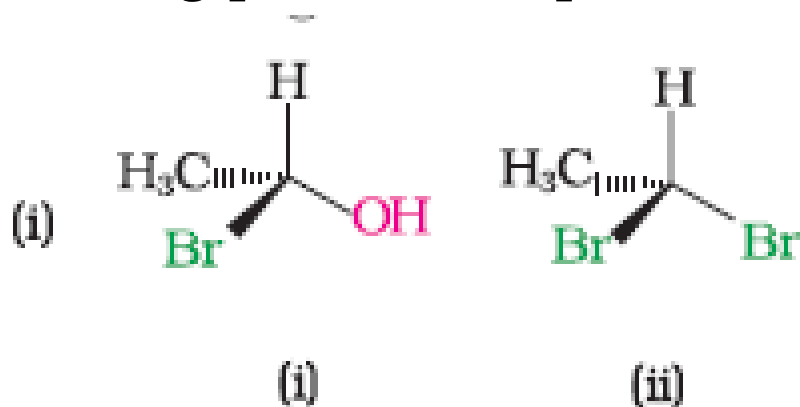
(iii) *Retention: Retention of configuration is the preservation of integrity* of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation.

- In general, if during a reaction, no bond to the stereocentre is broken, the product will have the same general configuration of groups around the stereocentre as that of reactant.

- Such a reaction is said to proceed with retention of the configuration.

CH_3

$H-\overset{CH_3}{\underset{CH_2}{\overset{|}{C}}}CH_2-\overset{|}{\overset{|}{C}}-OH$ + H-Cl $\xrightarrow{\text{heat}}$ $H-\overset{CH_3}{\underset{CH_2}{\overset{|}{C}}}CH_2-\overset{|}{\overset{|}{C}}-Cl$ + H-OH

CH_2

CH_3

(–)-2-Methylbutan-1-ol

CH_2

CH_3

(+)-1-Chloro-2-methylbutane

53
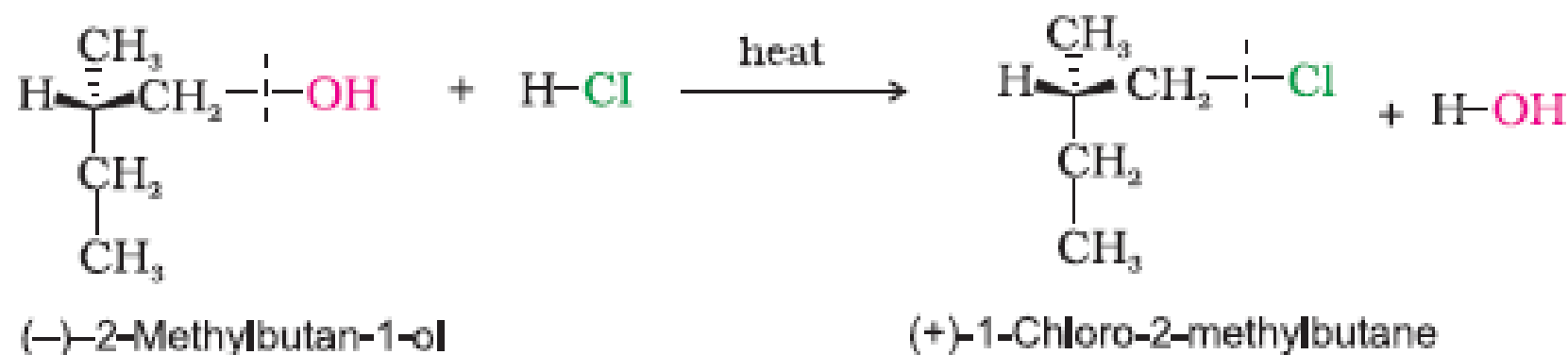
(iv) *Inversion, retention and racemisation:*

There are three outcomes for a reaction at an asymmetric carbon atom.

Consider the replacement of a group X by Y in the following reaction;
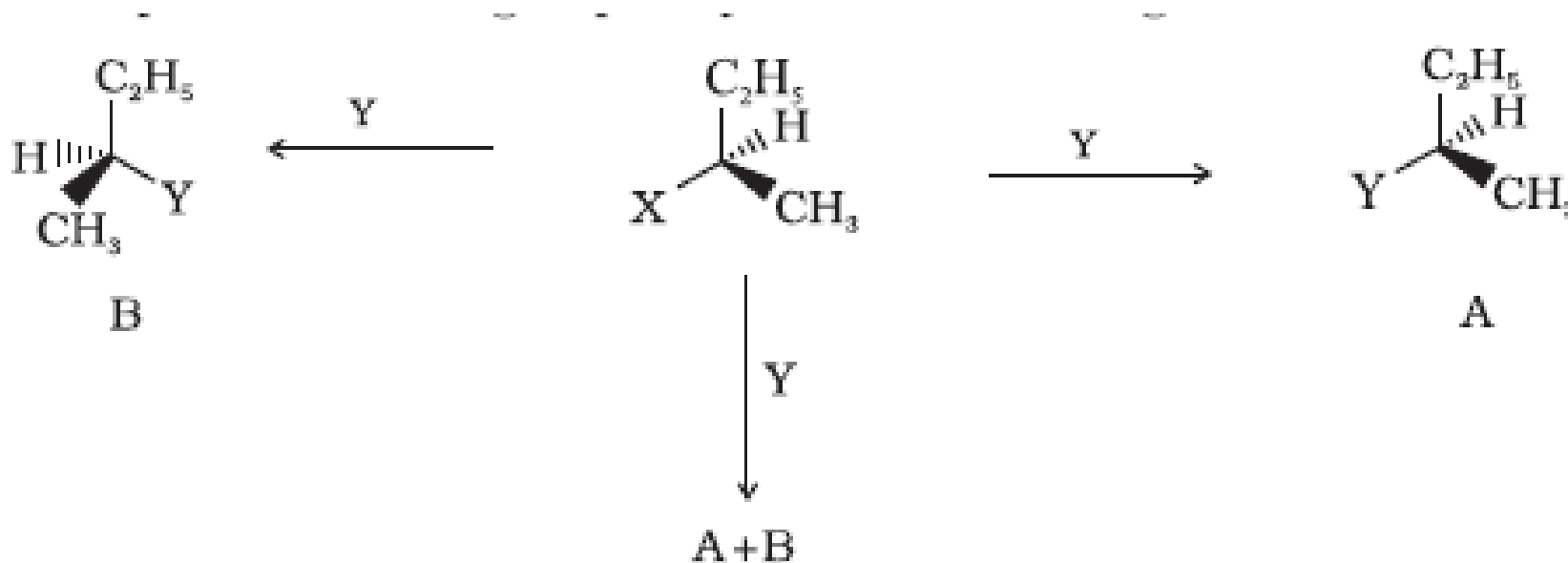
- If (A) is the only compound obtained, the process is called retention of configuration.
- If (B) is the only compound obtained, the process is called inversion of configuration.
- If a 50:50 mixture of the above two is obtained then the process is called racemisation and the product is optically inactive, as one isomer will rotate light in the direction opposite to another.

FRESH LOOK AT S_N1 AND S_N2

- In case of optically active alkyl halides, the product formed as a result of S_N2 mechanism has the inverted configuration as compared to the reactant.

- This is because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present.

- When (–)-2-bromooctane is allowed to react with sodium hydroxide, (+)-octan-2-ol is formed with the –OH group occupying the position opposite to what bromide had occupied.

$$H_3C \underset{C_6H_{13}}{\overset{H}{C}} \!\!-\!\! Br + {}^{\ominus}OH \longrightarrow HO \!\!-\!\! \underset{C_6H_{13}}{\overset{CH_3}{C}} H + Br^{\ominus}$$
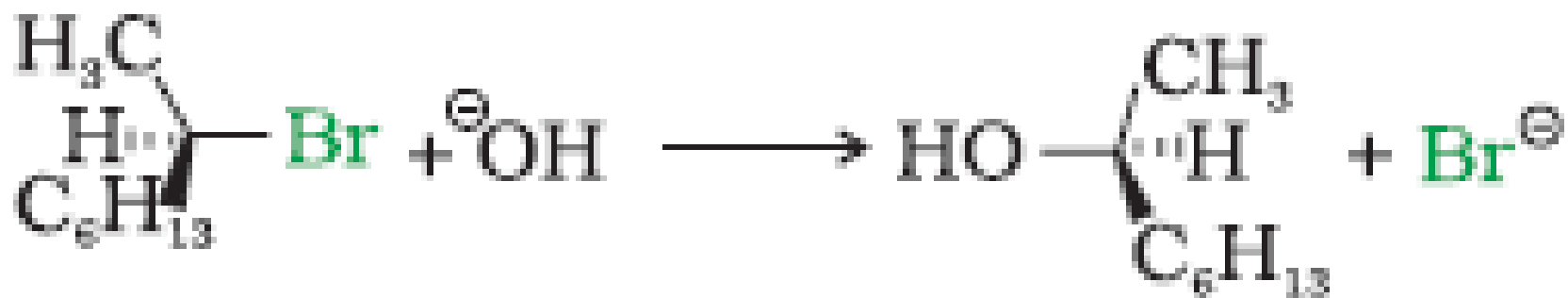
Thus, S_N2 reactions of optically active halides are accompanied by inversion of configuration.

S$_N$1 REACTIONS ARE ACCOMPANIED BY RACEMISATION

- In case of optically active alkyl halides, S$_N$1 reactions are accompanied by racemisation.

- Actually the carbocation formed in the slow step being *sp2* hybridised is planar (achiral).

- The attack of the nucleophile may be accomplished from either side resulting in a mixture of products, one having the same configuration (the –OH attaching on the same position as halide ion) and the other having opposite configuration (the –OH attaching on the side opposite to halide ion).

- This may be illustrated by hydrolysis of optically active 2-bromobutane, which results in the formation of (±)-butan-2-ol.

$$H_3C \overset{H_3C}{\underset{H_3CH_2C}{\diagdown}} \!\!\!\! \text{—Br} \quad \rightleftharpoons \quad \overset{CH_3}{\underset{H}{\oplus}}\!\!\!\diagdown CH_2CH_3 \quad + \quad \overset{\ominus}{Br}$$

(+)-Butan-2-ol

(–)Butan-2-ol
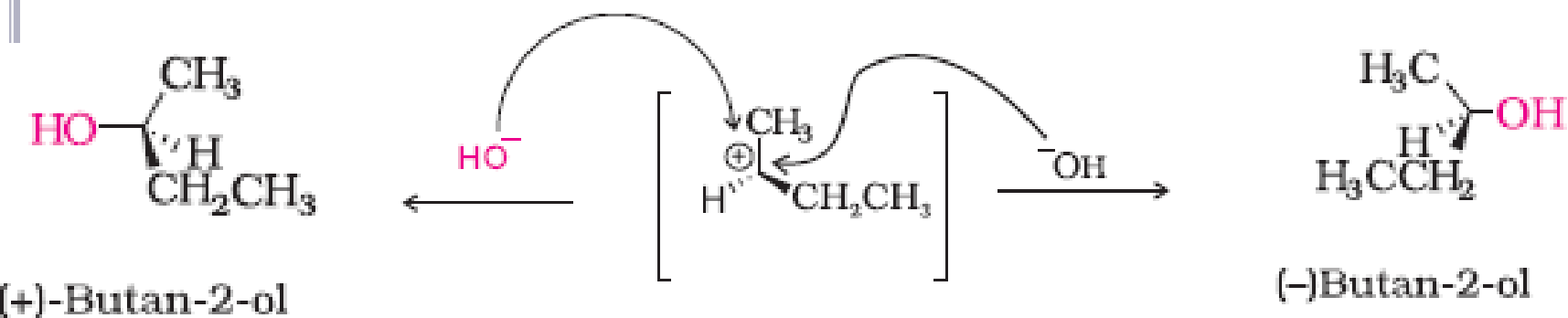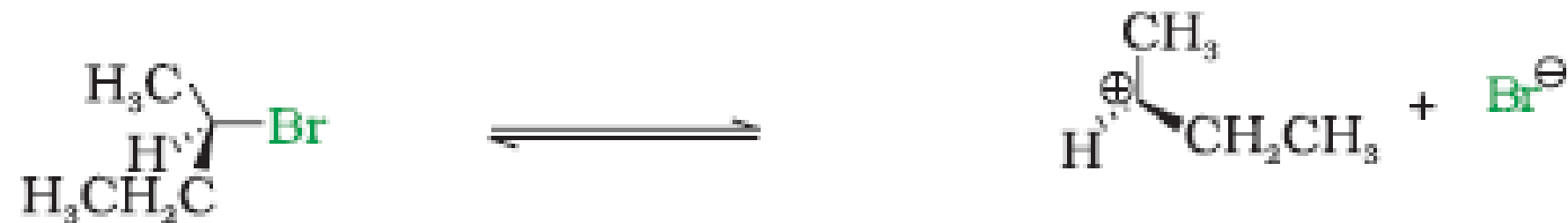
2. *Elimination reactions*

- When a haloalkane with β-hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β-carbon and a halogen atom from the α-carbon atom.

- As a result, an alkene is formed as a product. Since β-hydrogen atom is involved in elimination, it is often called **β-elimination.**
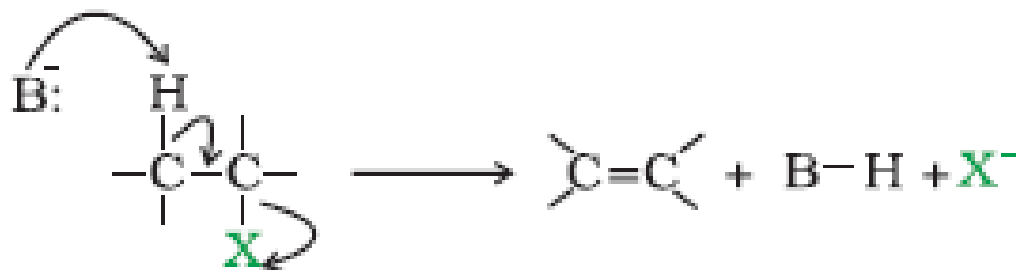
B=Base ; X=Leaving group

SAYTZEFF RULE

- If there is possibility of formation of more than one alkene due to the availability of more than one α-hydrogen atoms, usually one alkene is formed as the major product.

- These form part of a pattern first observed by Russian chemist, Alexander Zaitsev (also pronounced as Saytzeff) who in 1875 formulated a rule which can be summarised as

"*in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.*"

Thus, 2-bromopentane gives pent-2-ene as the major product.

$$H_3C-CH_2-CH_2-\underset{\underset{H}{|}}{\overset{\overset{Br}{|}}{CH}}-CH_2 \xrightarrow{\ ^-OH\ } H_3C-CH_2-CH_2-CH=CH_2$$

2-Bromopentane   Pent-1-ene   (19%)

$$H_3C-CH_2-CH_2-\underset{\underset{H}{|}}{\overset{\overset{Br}{|}}{CH}}-CH_2 \Longrightarrow H_3C-CH_2-CH=CH-CH_3$$

2-Bromopentane   Pent-2-ene   (81%)
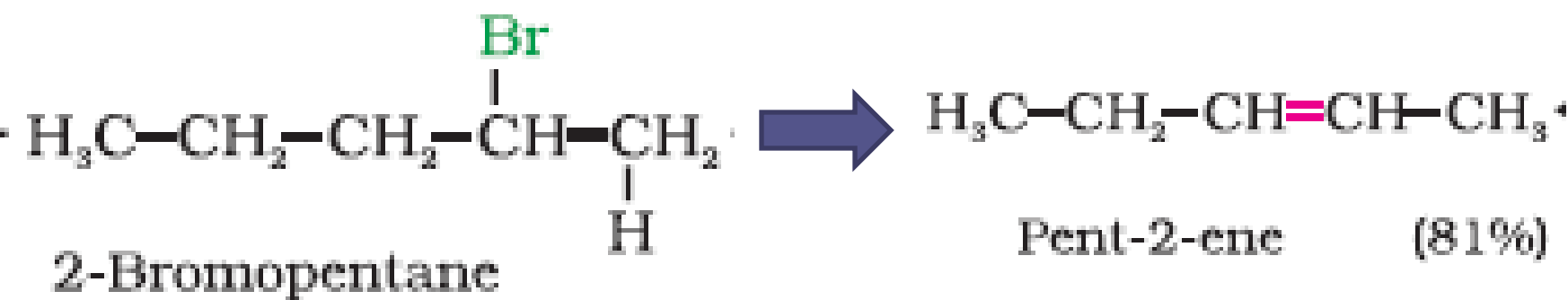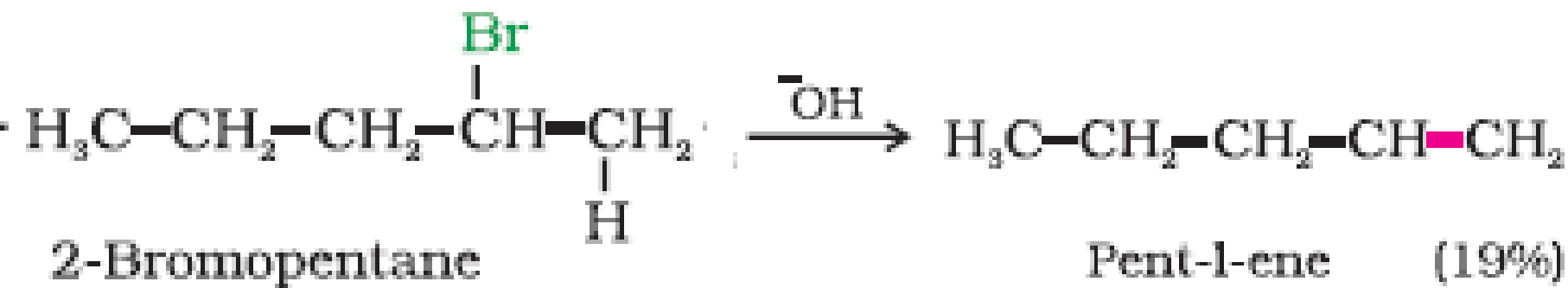
Elimination versus substitution

- Read for homework

3. REACTION WITH METALS

- Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds.

- Such compounds are known as **organo-metallic compounds.**

- **An** important class of organo-metallic compounds discovered by Victor Grignard in 1900 is alkyl magnesium halide, RMgX, referred as **Grignard Reagents.**

- **These reagents are obtained by the reaction of** haloalkanes with magnesium metal in dry ether.

$$CH_3CH_2Br \ + \ Mg \ \xrightarrow{\text{dry ether}} \ CH_3CH_2MgBr$$

Grignard reagent

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

$$\overset{\delta-}{R}-\overset{\delta+}{Mg}\,\overset{\delta-}{X}$$

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

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

It is therefore necessary to avoid even traces of moisture from a Grignard reagent.
On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

WURTZ REACTION

- Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide.

- This reaction is known as Wurtz reaction.

$$2RX + Na \longrightarrow RR + NaX$$

REACTIONS OF HALOARENES

○ *1. Nucleophilic substitution*

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

(i) *Resonance effect : In haloarenes, the electron pairs on halogen* atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.
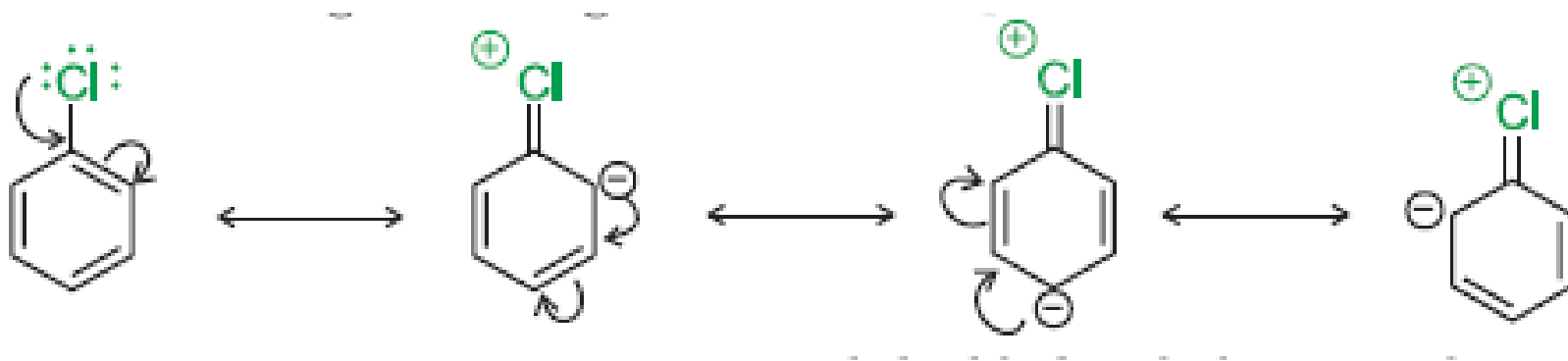
- C—Cl bond acquires a partial double bond character due to resonance.

- As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(ii) *Difference in hybridisation of carbon atom in C—X bond:*

- In haloalkane, the carbon atom attached to halogen is *sp3* hybridised while in case of haloarene, the carbon atom attached to halogen is *sp2-hybridised*.

Sp²-hybrid carbon
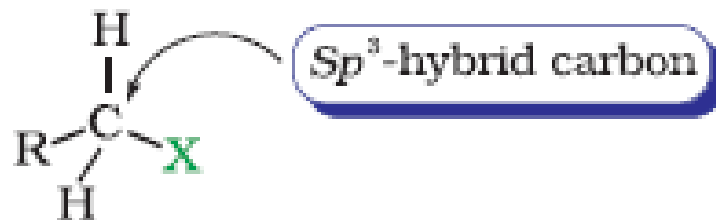
Sp³-hybrid carbon

- The *sp2 hybridised carbon with a greater s-character is more* electronegative and can hold the electron pair of C—X bond more tightly than *sp3-hybridised carbon in haloalkane with* less *s-chararcter.*

- *Thus, C—Cl bond length in haloalkane is* **177**pm while in haloarene is **169** pm.

- Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(iii) *Instability of phenyl cation:*

In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out.

**(iv) Because of the possible repulsion**, it is less likely for the electron rich nucleophile to approach electron rich arenes.
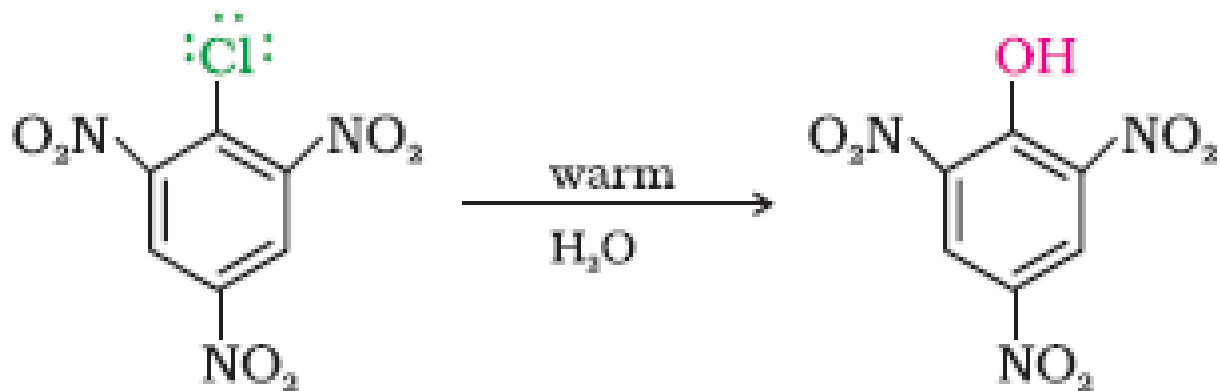
REPLACEMENT BY HYDROXYL GROUP

- Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres.
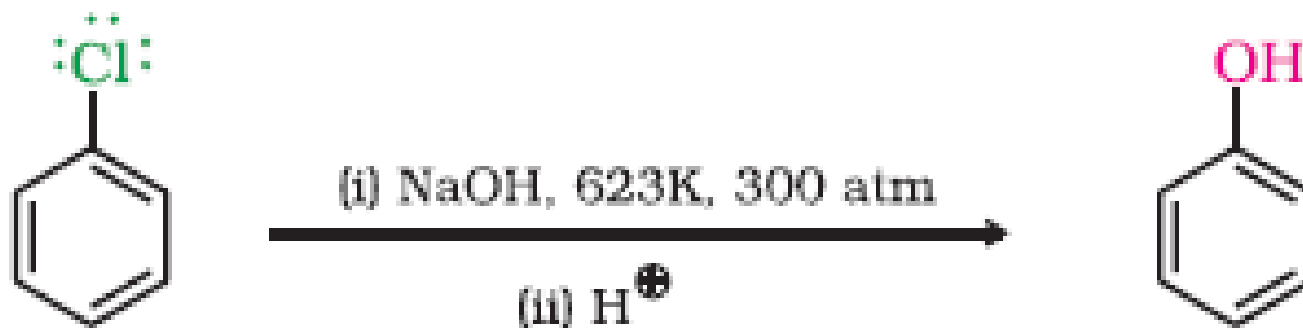
- The presence of an electron withdrawing group (-NO$_2$) at **ortho**- and **para**-positions increases the reactivity of haloarenes.
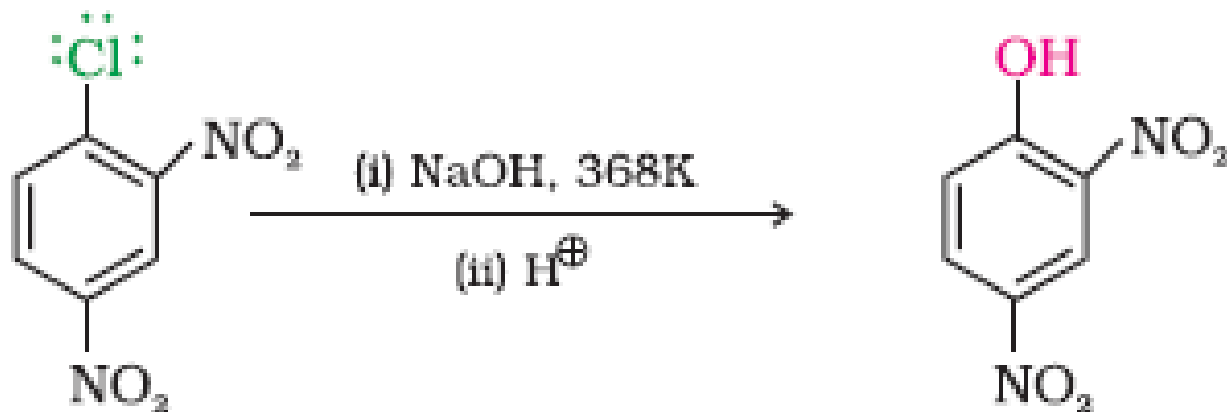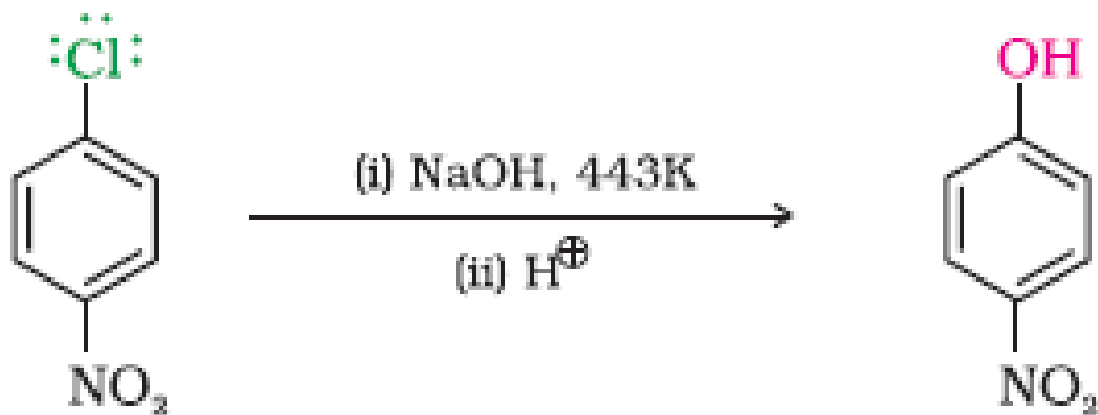
- The effect is pronounced when (-NO_2) group is introduced at *ortho and para- positions.*
- *However, no effect on reactivity of haloarenes is* observed by the presence of electron withdrawing group at *meta-position.*
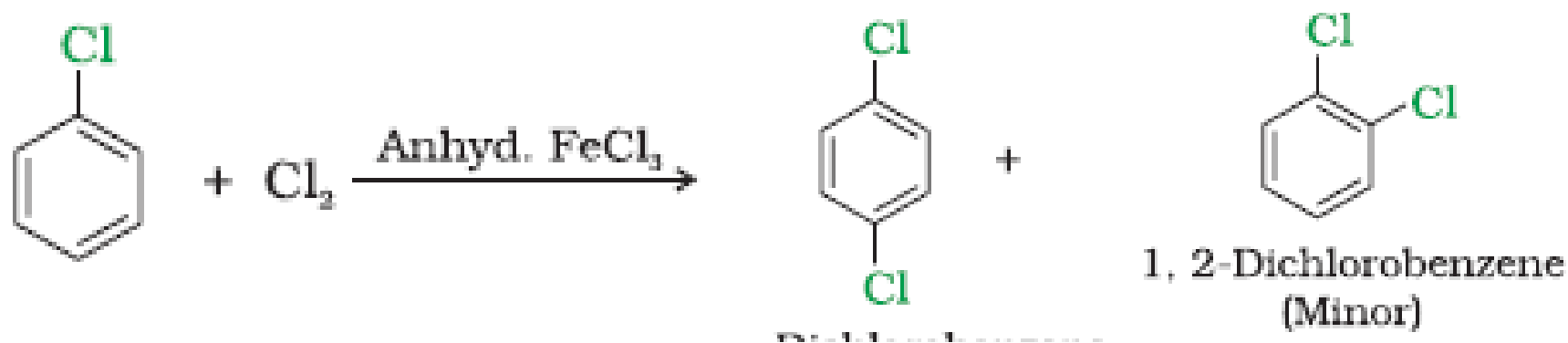
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2. ELECTROPHILIC SUBSTITUTION REACTIONS

- Haloarenes undergo the usual electrophilic reactions of the benzene ring such as **halogenation, nitration, sulphonation and Friedel-Crafts reactions.**

- Halogen atom besides being slightly deactivating is *o, pdirecting;* therefore, further substitution occurs at *ortho- and parapositions* with respect to the halogen atom.

- The *o, p-directing influence* of halogen atom can be easily understood if we consider the resonating structures of halobenzene as shown:
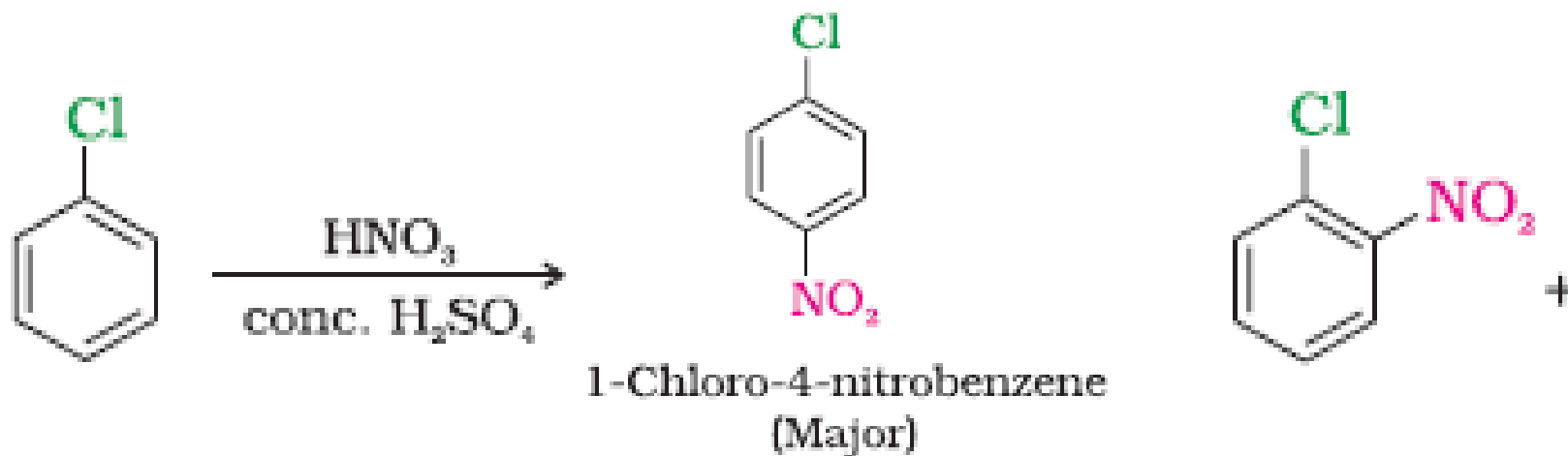
I   II   III   IV
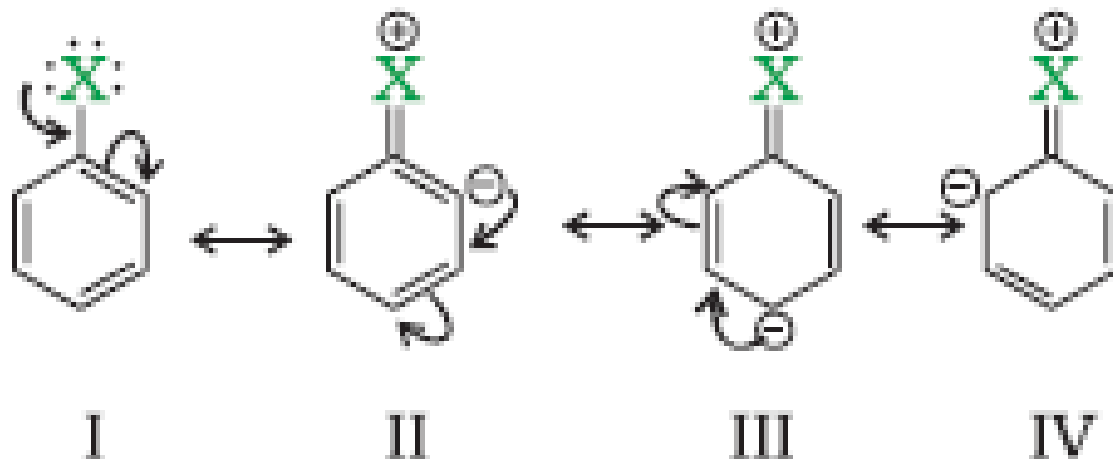
- Due to resonance, the electron density increases more at *ortho- and para-positions than at meta-positions.*

- *Further, the halogen atom* because of its –I effect has some tendency to withdraw electrons from the benzene ring.

- As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

(i) Halogenation

+ Cl_2 $\xrightarrow{\text{Anhyd. FeCl}_3}$

Dichlorobenzene

1, 2-Dichlorobenzene
(Minor)

(ii) Nitration

$\xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{HNO}_3}$

1-Chloro-4-nitrobenzene
(Major)

NO_2

+

(iii) Sulphonation

conc. H_2SO_4, Δ

SO_3H

+

4-Chlorobenzene sulfonic acid
(Major)

(iv) Friedel-Crafts reaction

1-Chloro-4-methylbenzene
(Major)

4-Chloroacetophenone
(Major)

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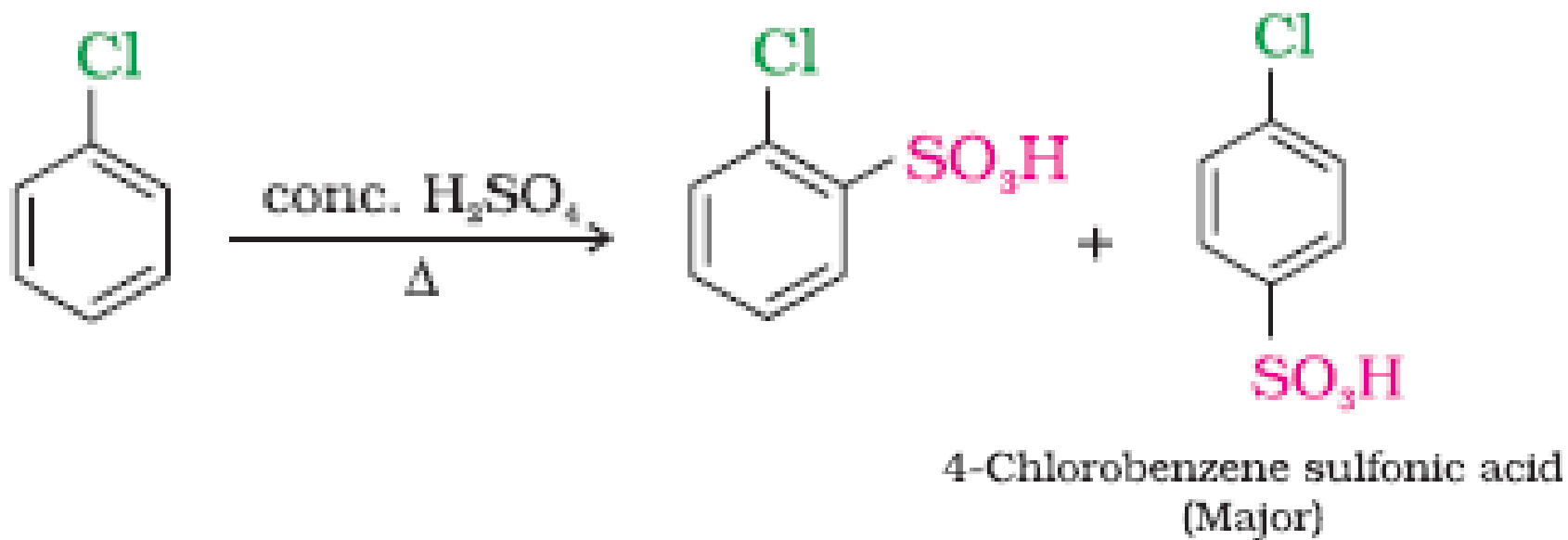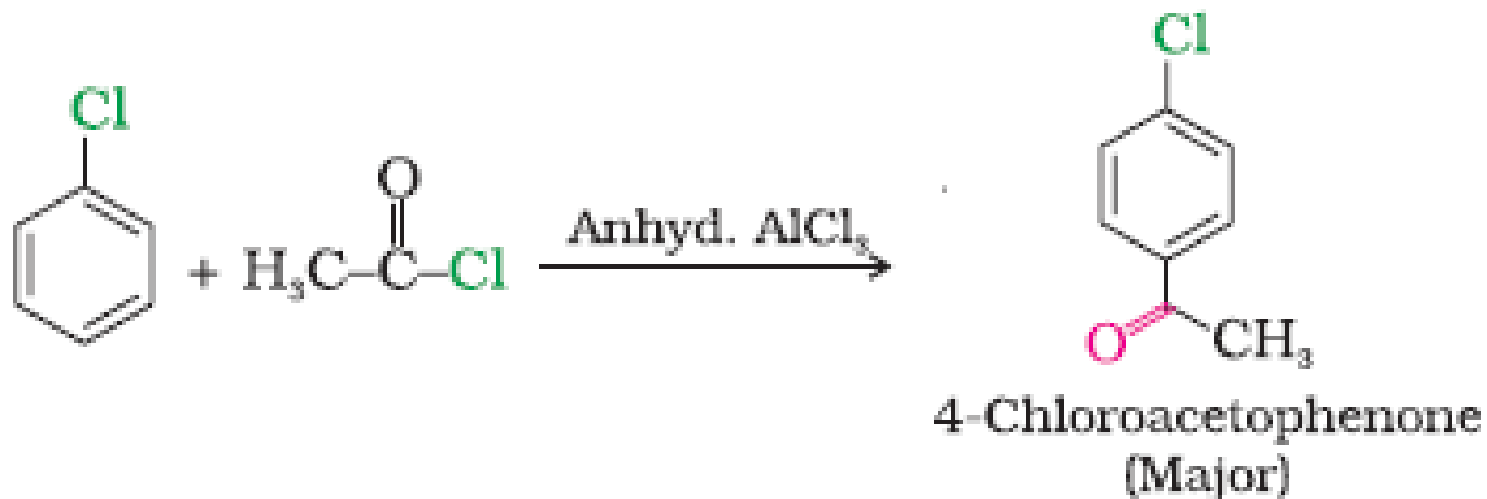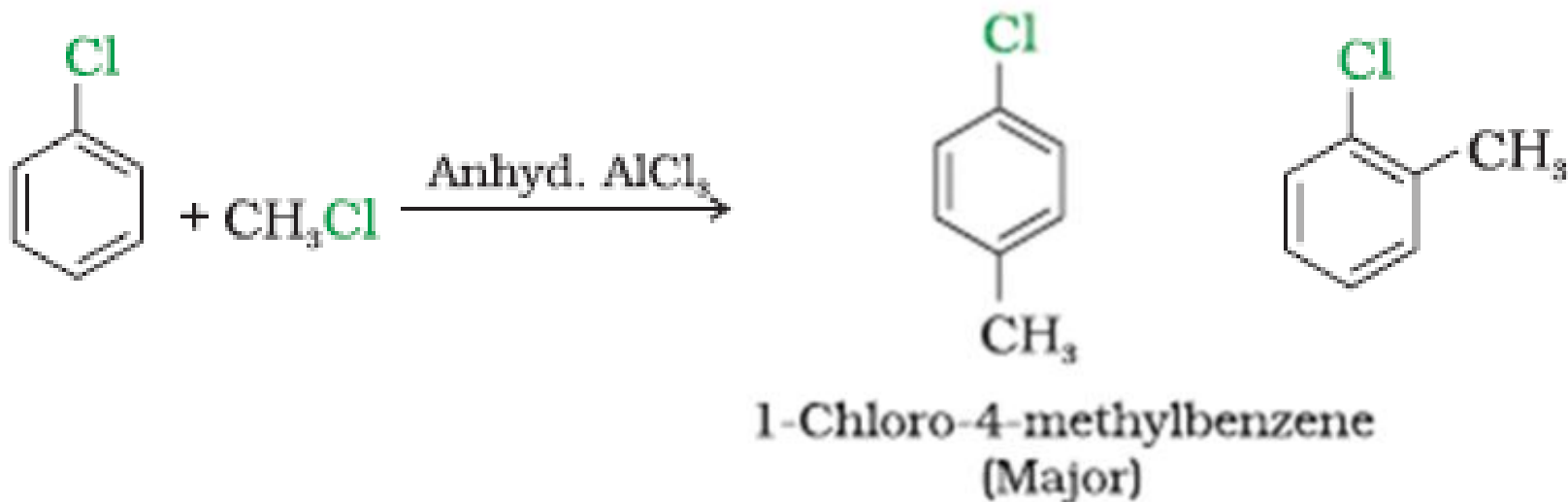
3. REACTION WITH METALS

○ *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.
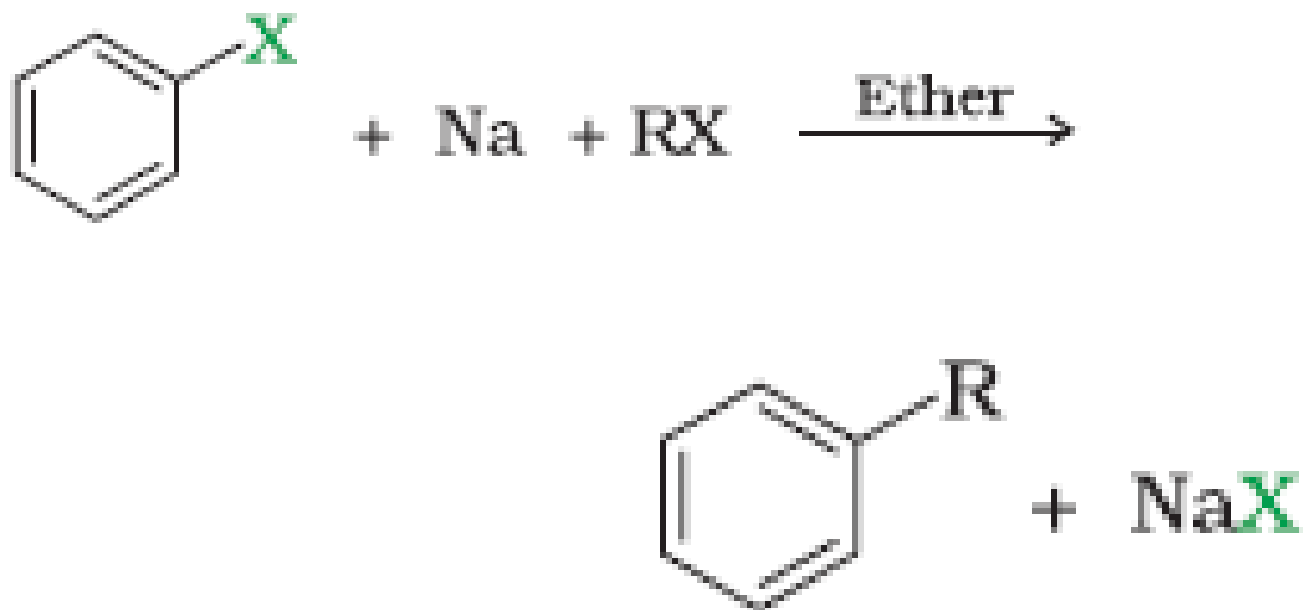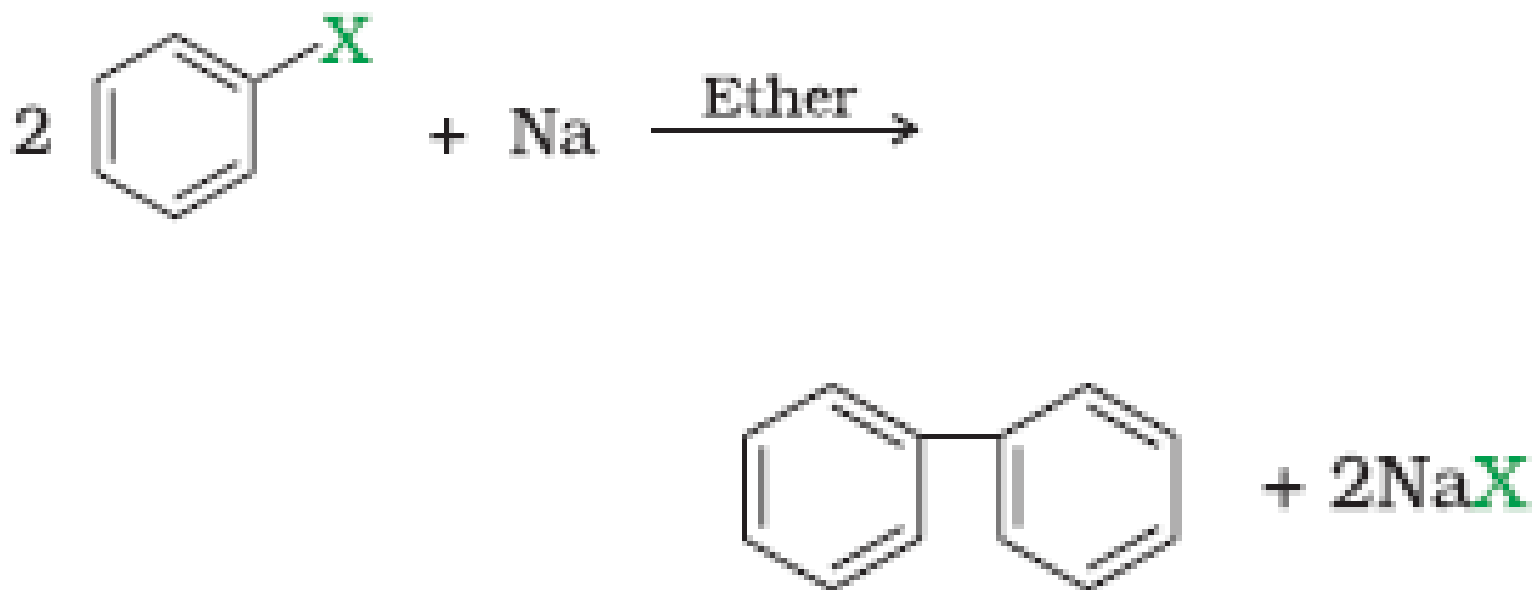
Fittig reaction

- 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.**

POLYHALOGEN COMPOUNDS

Triiodomethane (Iodoform)

- It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself.
- Due to its objectionable smell, it has been replaced by other formulations containing iodine.

Tetrachloromethane (Carbon tetrachloride)

- It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans.
- It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use.

- Until the mid 1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher.
- There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans.
- The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death.
- Exposure to CCl_4 can make the heart beat irregularly or stop.
- The chemical may irritate the eyes on contact.
- When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer.

Freons

- The chlorofluorocarbon compounds of methane and ethane are collectively known as freons.
- They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.
- Freon 12 (CCl_2F_2) is one of the most common freons in industrial use.
- It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.
- Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere.
- In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance
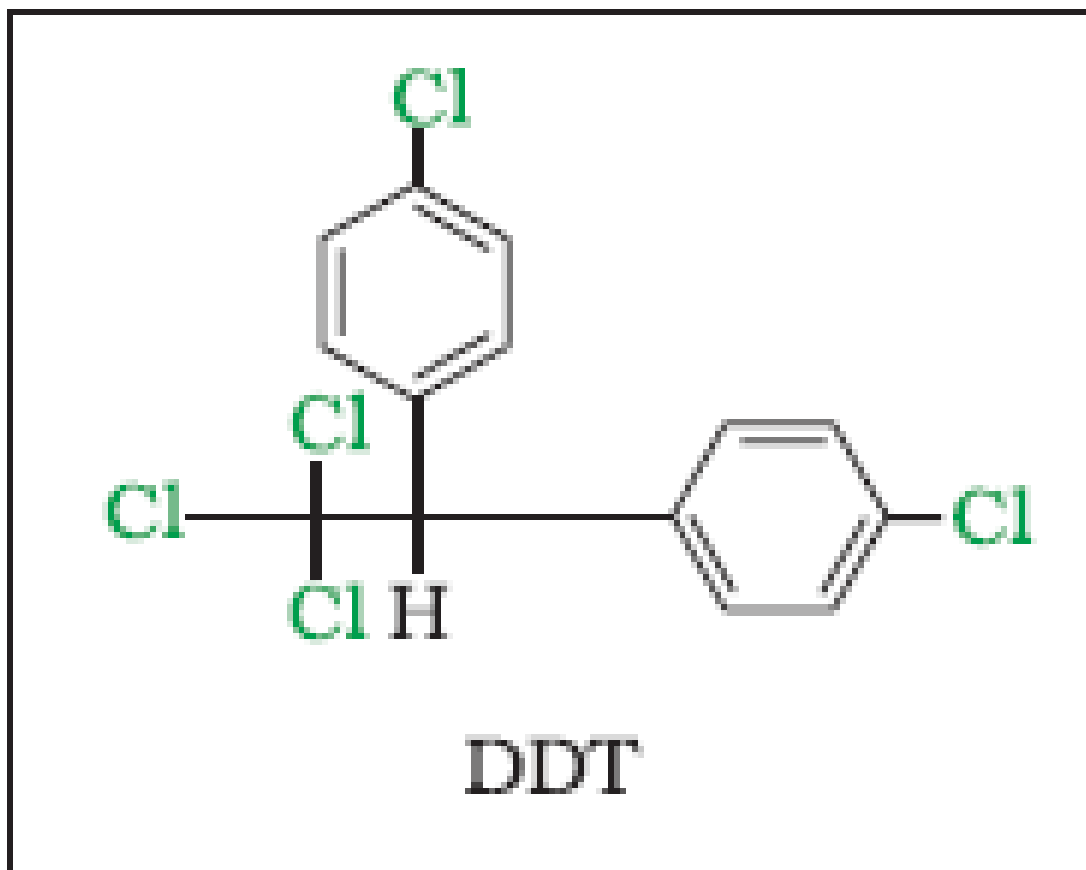
DDT

p,p'-Dichlorodiphenyltrichloroethane

- DDT, the first chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide.

- Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery.

- The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus.

- However, problems related to extensive use of DDT began to appear in the late 1940s.

- Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish.

- The chemical stability of DDT and its fat solubility compounded the problem.

- DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time.

- The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world.

DDT (STRUCTURE)

DDT

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THANK YOU