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12th Class Chemistry
Haloalkanes and Haloarenes

By Palnivel ahir

Haloalkanes and Haloarenes.

The replacement of hydrogen atom in hydrocarbon, aliphatic or aromatic, by halogen atom results in the formation of alkyl halide (Haloalkane) and aryl halide (haloarene), respectively.

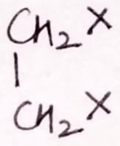
• Classification of Haloalkanes and Haloarenes.

On the Basis of Number of Halogen atoms.

These are the compounds may be classified as mono, di, tri or tetra halogen compounds according as they contain one, two, three or four halogens atoms. For Example:-

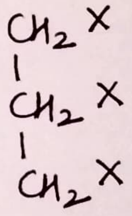
C_2H_5X

Monohaloalkane



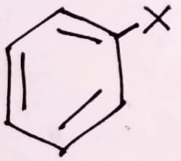
$$\begin{array}{c} CH_2X \\ | \\ CH_2X \end{array}$$

Dihaloalkane

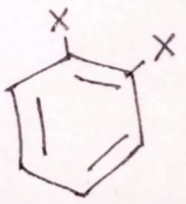


$$\begin{array}{c} CH_2X \\ | \\ CH_2X \\ | \\ CH_2X \end{array}$$

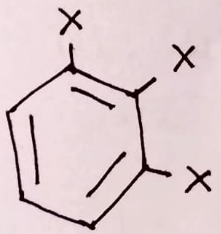
Trihaloalkane



Monohaloarene



Dihaloarene



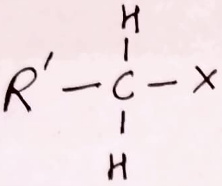
Trihaloarene

Note:- Where x is halogen.

[X = F, cl, Br, I].

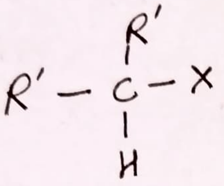
on the basis of the Nature of the Carbon to which halogen atom is attached, halogen derivatives are classified as 1°, 2°, 3°,.

Example :-



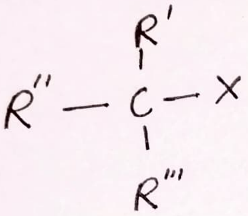
$$R'-\overset{H}{\underset{H}{C}}-X$$

Primary (1°)



$$R'-\overset{R'}{\underset{H}{C}}-X$$

Secondary (2°)



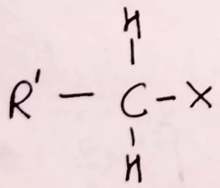
$$R''-\overset{R'}{\underset{R'''}{C}}-X$$

Tertiary (3°).

- Classification on the basis of type of hyberidization of carbon bonded to the halogen atom [C-X Bond].

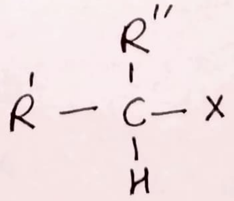
1) Compounds containing Sp^3 hybridised carbon :-

(a) In alkyl halides, The halogen atom is bonded to an alkyl group. They can be further classified as Primary, Secondary or tertiary.



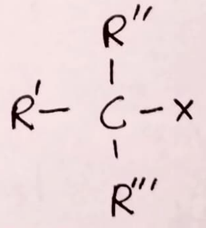
$$R'-\overset{H}{\underset{H}{C}}-X$$

Primary (1°)



$$R'-\overset{R''}{\underset{H}{C}}-X$$

(Secondary (2°)



$$R'-\overset{R''}{\underset{R'''}{C}}-X$$

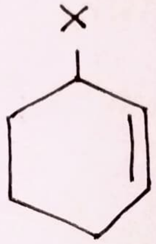
Tertiary (3°).

(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.

Example :-

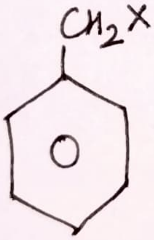
$H_2C = CH - CH_2 - X$



(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.

Example :-



2> Compounds containing Sp² C-X bond.

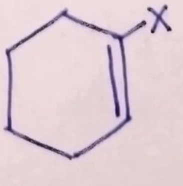
These are the

(a) Vinylic halides :-

These are the compounds in which halogen atom is bonded to an Sp² hybridised carbon atom.

Example :-

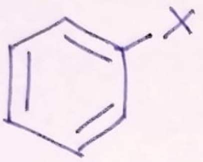
$H_2C = CH - X$

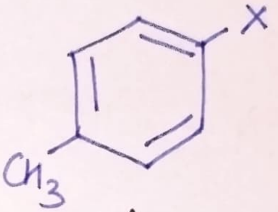


(b) Aryl halides :-

These are the compounds in which the halogen atom is bonded to the Sp^2- hybridised carbon atom of an aromatic ring.

Example :-





- ## Nomenclature of Haloalkanes and Haloarenes.

⇒ The common names of alkyl halides are derived by naming the alkyl group followed by the halide. Alkyl halides are named as halo substituted hydrocarbon in the IUPAC system of nomenclature.

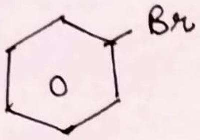
Example :-

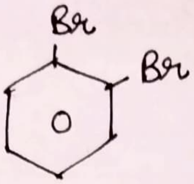
	$CH_3CH_2CH_2Br$	$H_3C-\underset{Cl}{\underset{\mid}{CH}}-CH_3$	$H_3C-\overset{CH_3}{\overset{\mid}{CH}}-CH_2Cl$
Common name :	n- propyl bromide	Isopropyl chloride	Isobutyl chloride.
IUPAC NAME :	1- Bromopropane	2- Chloropropane	1- Chloro -2- methyl propane.

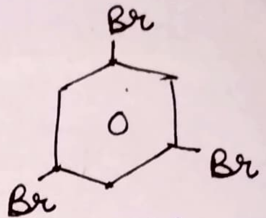
NOTE :-

⇒ Haloarenes are the same for Common name and IUPAC name. For dihalogen aromatic compounds, the Prefixes o,- m-.. and p- are used in common system but in IUPAC System 1,2; 1,3; and 1,4 are used For Example :-

Example :-





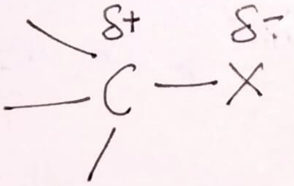


Common name :	Bromobenzene	m-Dibromo benzene	Sym- Tribromo benzene.
IUPAC Name :	Bromobenzene	1,3- Dibromo benzene	1,3,5- Tribromo benzene.

- **Preparation of Haloalkanes :-**

- **Nature of C-X bond :-**

⇒ As halogen is more electeronegative than carbon, the C-X bond is polarised, carbon atom bears a partial positive charged and X (Halogen) bears a partial negative charge.



⇒ C-X bond length increases as we move from C-F to C-I. for this reason bond energy decreases from C-F to C-I.

Bond energy ↓ decreases

C-F

C-Cl

C-Br

C-I

Bond length. ↓ increases.

• Preperation of Haloalkanes :-

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

$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3.$$

$$R-OH + PX_5 \longrightarrow R-X + POX_3 + HX.$$

$$R-OH \xrightarrow{Red\ P/X_2} RX$$

$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl.$$

• From Hydrocarbons

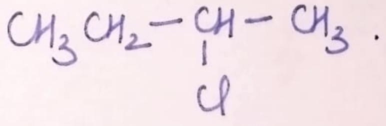
(a) By Free radical halogenation :- (From alkanes)

$$R-H + X_2 \xrightarrow{h\nu} R-X + HX$$

[where, X = Cl, Br, I].

Example :-

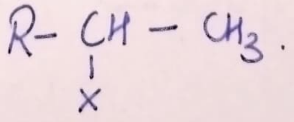
$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2\ /\ UV\ light} CH_3CH_2CH_2CH_2Cl + CH_3Cl_2$$



$$CH_3CH_2-\underset{Cl}{CH}-CH_3.$$

(b) From alkenes :-

(i) Addition of hydrogen halide :-



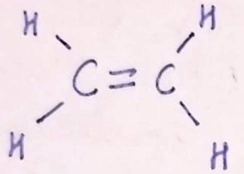
$$\Rightarrow RCH=CH_2 + HX \longrightarrow R-\underset{X}{CH}-CH_3.$$

(Markownikoff's addition).

$\Rightarrow$ $RCH{=}CH_2 + HX \xrightarrow{\text{Peroxide}} R{-}CH_2{-}CH_2{-}X$.

(Anti- Markownikoff's Addition).

(ii) Addition of halogen :-



$+ Br_2 \xrightarrow{CCl_4} BrCH_2{-}CH_2Br$.

Vic- dibromide

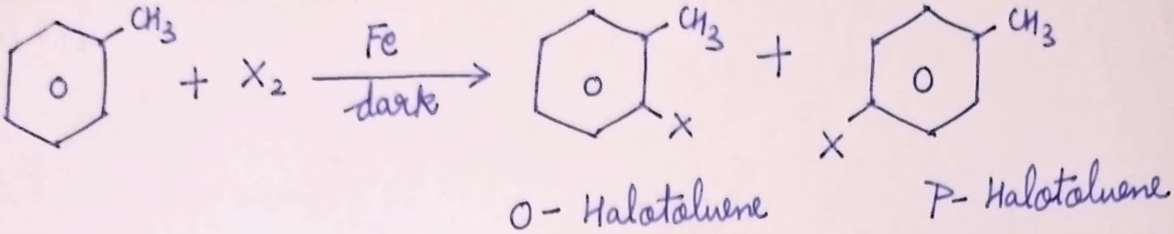
Note :- Vic- dibromide (Vicinal) => Compounds that have bromides on adjacent Carbons.

Vic- dihalides → Compounds that have halogens on adjacent Carbons.

Markownikoff's Addition → From hydrogen halide [H-X] the +ve charged hydrogen attached to the carbon atom which have ~~less~~ more number of Hydrogen atoms. and -ve charged Halogen attached to the Carbon atom which have ~~more~~ less number of Hydrogen atoms.

Anti - Markownikoff 's Addition → This is opposite of Markownikoff's Addition.

• Electrophilic Substitution :-



Note :- (i) Aryl chlorides and bromides can be easily prepared by electrophilic Substitution of arenes with chlorine and bromine respectively.

(ii) Iodination can be carried out in the presence of HIO_4 or HNO_3 to oxidise HI produced in the reaction. otherwise the reaction becomes reversible.

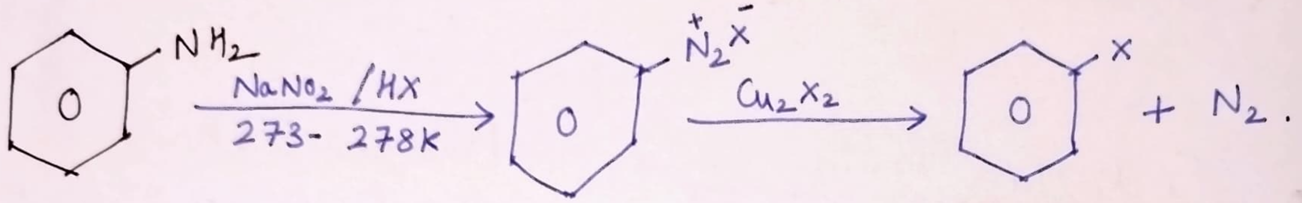
(iii) Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

• Swarts Reaction :-

Fluoroalkanes are prepared by treating alkyl chloride/ bromide in the presence of a metallic fluoride Such as AgF, Hg_2F_2, CoF_2, or SbF_3. This reaction is known as Swarts reaction.

$$\underset{\text{Methyl bromide}}{CH_3Br} + \underset{\text{Silver fluoride}}{AgF} \longrightarrow \underset{\text{Fluoromethane}}{CH_3F} + \underset{\text{Silver Bromide.}}{AgBr}$$

- **Sandmeyer's Reaction :-** Primary aromatic amine, dissolved in dil., HCl, on treatment with Sodium nitrite, produces diazonium salt which on treatment with Copper halide (Say Cu_2Cl_2) gives halogen compound.



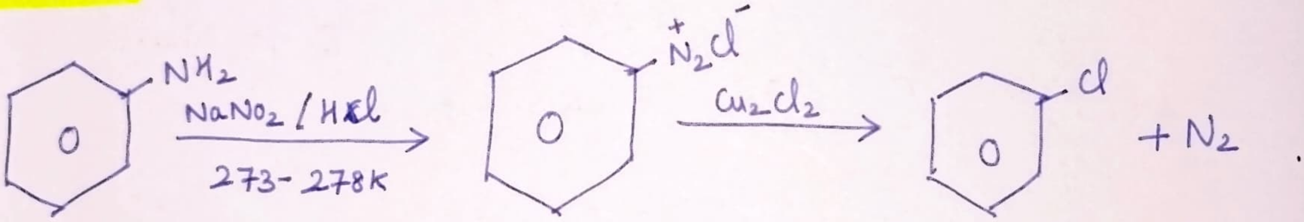
(Aromatic amine)
(Aniline)

(Diazonium Salt)

(Haloarene).

[X = Cl, Br].

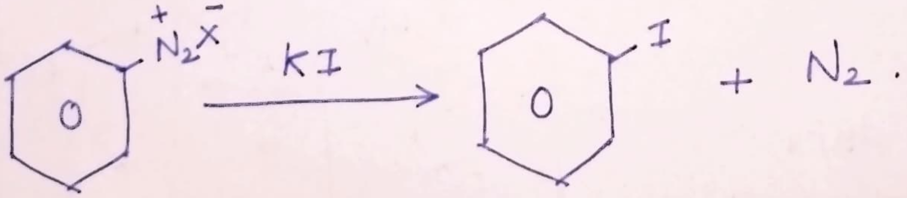
Example :-



Aniline

(Chloro benzene)

Note :-
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.



- ## Borodine-Hundsdiecker reaction :-

=> Generally, bromoalkanes are prepared by the reaction known as Borodine - Hundsdiecker reaction.

$$CH_3COO^-Ag^+ + Br_2 \xrightarrow{CCl_4} CH_3Br + CO_2 + AgBr.$$

- ## Finkelstein Reaction :- [Halogen Exchange].

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

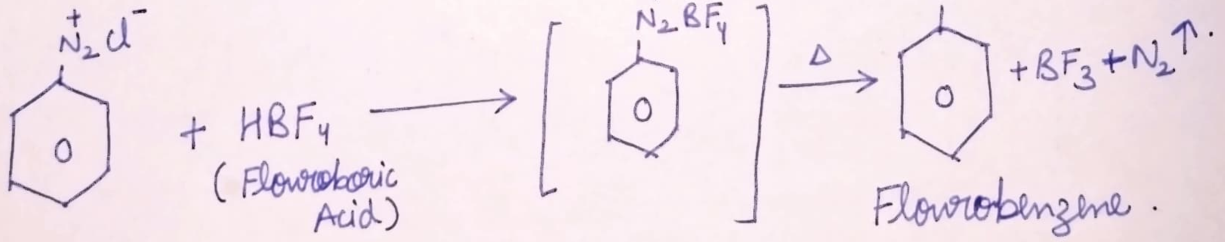
$$R-X + NaI \xrightarrow[(Reflux)]{Acetone} R-I + NaX.$$

[where X = Cl, Br].

- ## Balz - Schiemann reaction.

=> The fluoroarenes are not easily prepared due to high reactivity of flourine. the flouroarenes are prepared. by addition of fluoroboric Acid [HBF_4] . and this reaction is called Balz - Schiemann reaction.

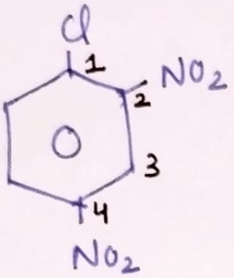
=>



Questions [Some Previous years]

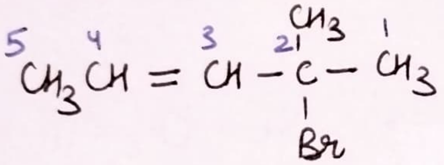
Ques 1) = Write the Structure of 2, 4- dinitrochlorobenzene

[C.BSE- 2017]



Ques 2) = Write the IUPAC name of .

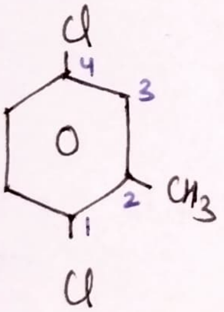
(a) [CBSE - 2008, 2009]



$$\overset{5}{CH_3}\overset{4}{CH} = \overset{3}{CH} - \overset{2}{\underset{Br}{\overset{CH_3}{C}}} - \overset{1}{CH_3}$$

2- Bromo - 2- methyl pent-3-ene .

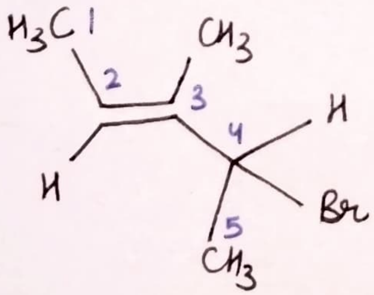
(b) [CBSE - 2013] .



1, 4- dichloro -2- methyl benzene .

[CBSE- 2008, 2009, 2010].

(c)



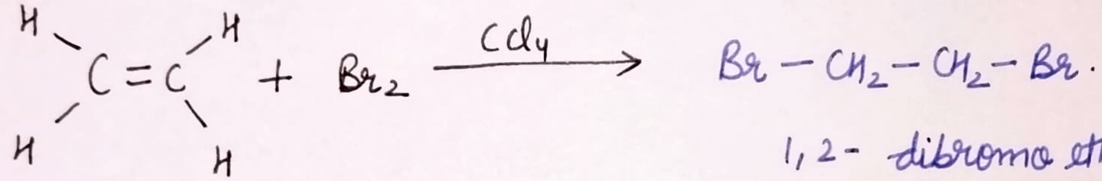
4- Bromo -3- methyl pent-2-ene .

Ques 3> Complete the following reax:-

(i) $CH_3CH_2CH=CH_2 + HBr \longrightarrow CH_3-CH_2-\underset{|\atop Br}{CH}-CH_3$.

[CBSE - 2011]

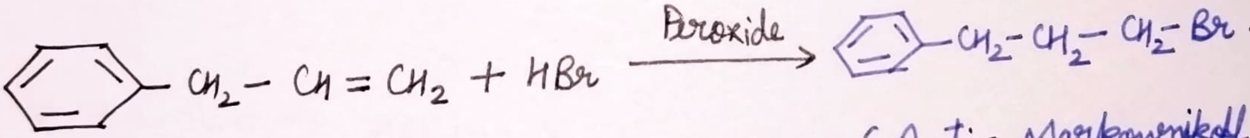
(Markownikoff's rule applied).

(ii) 

[CBSE- 2008]

1,2- dibromo ethane .

(vic - dibromide).

(iii) 

[CBSE- 2014]

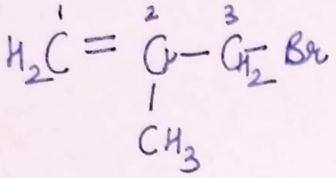
(Anti - Markownikoff rule applied).

(iv) $C_6H_5N_2Cl + KI \longrightarrow C_6H_5I + KCl$.

PREVIOUS YEARS EXAMINATION QUESTIONS

1. Write the structure of 3-bromo-2-methyl prop-1-ene [CBSE-2017]

=>



$$H_2\overset{1}{C}=\underset{\displaystyle CH_3}{\underset{|}{\overset{2}{C}}}-\overset{3}{CH_2}-Br$$

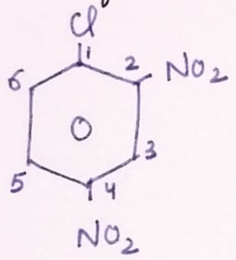
2. Write the structure of 1-bromo-4-chlorobut-2-ene [CBSE-2017].

=>

$$Br-\overset{1}{CH_2}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_2}-Cl$$

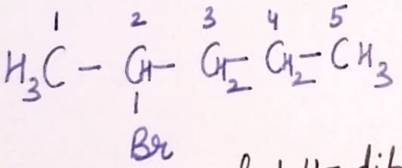
3. Write the Structure of 2,4-dinitrochlorobenzene [CBSE-2017].

=>



4. Draw the Structure of 2-bromopentane [CBSE-2014].

=>



$$H_3\overset{1}{C}-\underset{\displaystyle Br}{\underset{|}{\overset{2}{CH}}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

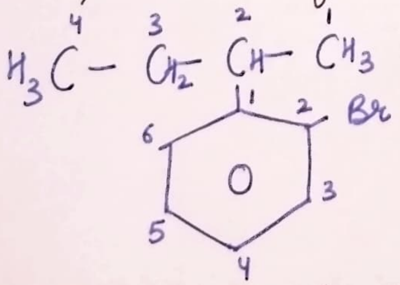
5> Draw the Structure of 1,4-dibromobut-2-ene [CBSE-2010, 2011].

=>

$$Br-\overset{1}{CH_2}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_2}-Br$$

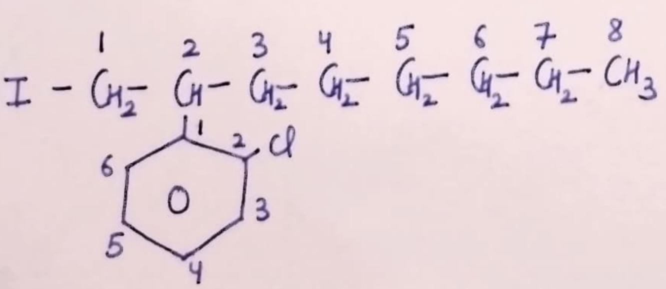
6> Draw the structure of 2-(2-bromophenyl) butane [CBSE-2011]

=>

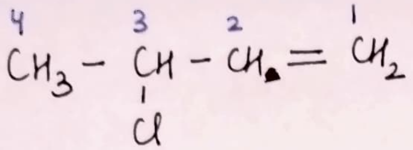


7> Draw the structure of 2-(2-chlorophenyl)-1-iodooctane. [CBSE-2011].

=>



8. Write the IUPAC name of [CBSE - 2013].



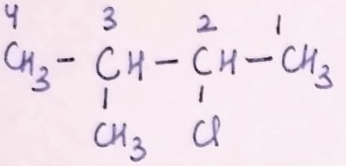
$\overset{4}{CH_3}-\underset{Cl}{\overset{3}{CH}}-\overset{2}{CH}=\overset{1}{CH_2}$

=> 3- Chloro - but-1- ene

9. Write the IUPAC name of [CBSE - 2013].

$(CH_3)_2CH\cdot CH(Cl)CH_3$

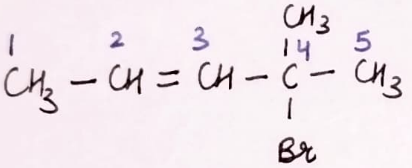
=>



$\overset{4}{CH_3}-\underset{CH_3}{\overset{3}{CH}}-\underset{Cl}{\overset{2}{CH}}-\overset{1}{CH_3}$

2- Chloro - 3 - methyl butane.

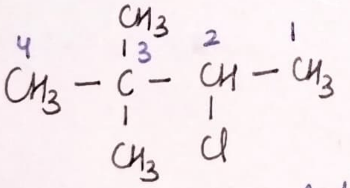
10. Write the IUPAC name of [CBSE-2012]



$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\underset{Br}{\overset{CH_3}{\overset{4}{C}}}-\overset{5}{CH_3}$

=> 4- Bromo - 4- methyl pent -2- ene.

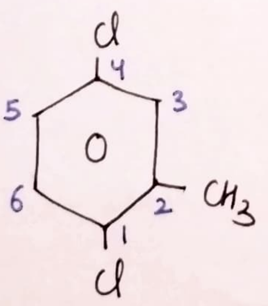
11. Write the IUPAC name of. [CBSE - 2014].



$\overset{4}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{3}{C}}}-\underset{Cl}{\overset{2}{CH}}-\overset{1}{CH_3}$

=> 2- Chloro - 3,3- dimethyl butane.

12. Write the IUPAC name of

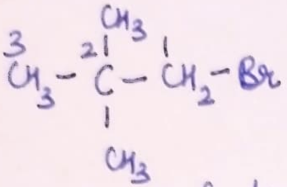


=> 1, 4- dichloro -2- methyl benzene

3. Write the IUPAC name of [CBSE - 2011].

$(CH_3)_3C\,CH_2Br$

=>



$$\overset{3}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\overset{1}{CH_2}-Br$$

1- Bromo - 2,2- dimethyl propane.

4> Write the IUPAC name of [CBSE - 2011].

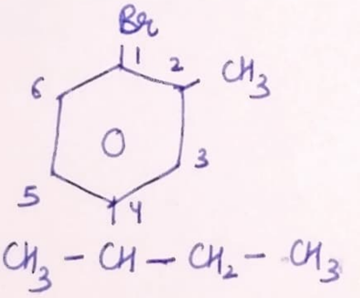
$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-Br$

=> 3 - Bromo prop -1- ene

15> Draw the structure of 1- Bromo -4- Sec - butyl -2- methyl benzene

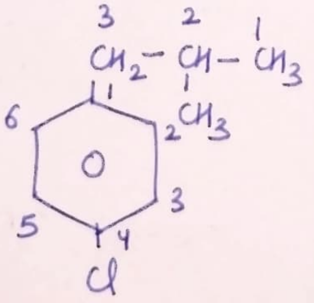
[CBSE-2010].

=>

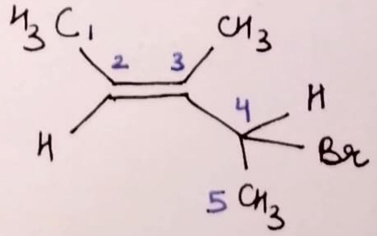


16 Draw the structure of 3-(4- Chlorophenyl) -2- methyl propane.

[CBSE- 2011C].

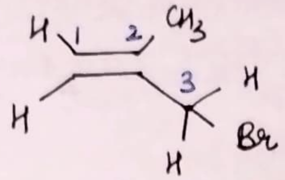


17. Write the IUPAC name of [CBSE- 2008].



4- Bromo -3- methyl pent-2-ene.

18. Write the IUPAC name of

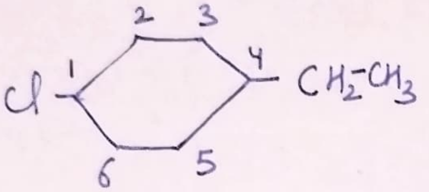


(CBSE-2008,
2009

=> 3- Bromo -2- methyl prop - 1- ene.

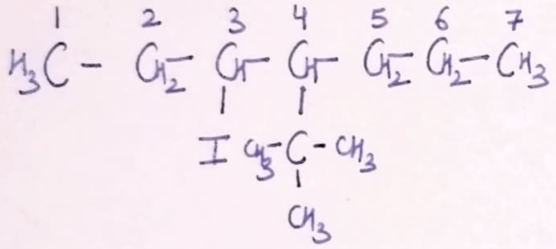
19. Draw the Structure of the Compound 1- chloro -4- ethyl cyclohexane [CBSE- 2010C].

=>



20. Draw the Structure of the Compound 4-tert - butyl -3- iodoheptane [CBSE- 2010].

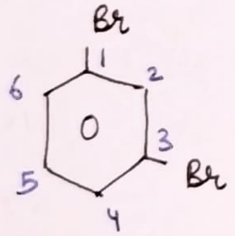
=>



$$\overset{1}{H_3C}-\overset{2}{CH_2}-\underset{\displaystyle I}{\overset{3}{CH}}-\underset{\displaystyle CH_3-\underset{\displaystyle CH_3}{C}-CH_3}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH_3}$$

21. Give the IUPAC names of the following compounds.

(a)



1, 3- dibromo benzene.

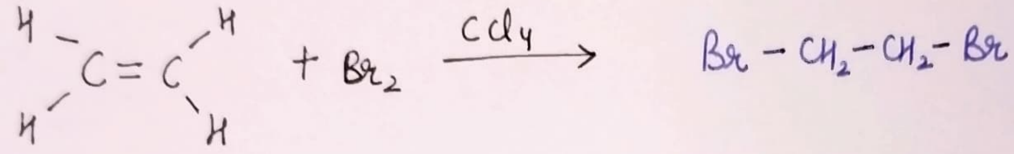
(b) $\overset{4}{Cl\,CH_2}\overset{3}{C}\equiv\overset{2}{C}\,\overset{1}{CH_2}\,Br$ 1- Bromo - 4- chloro but-2-yne.

(c) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-Cl$ 3- chloro prop -1- ene.

22. Complete the following reactions :-

(i) $C_6H_5N_2Cl + KI \longrightarrow C_6H_5I + KCl$.

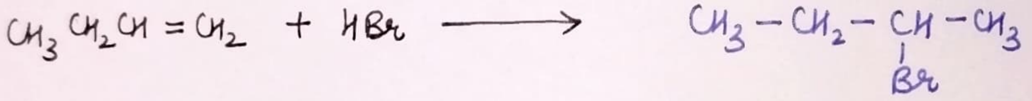
(ii)



(iii)

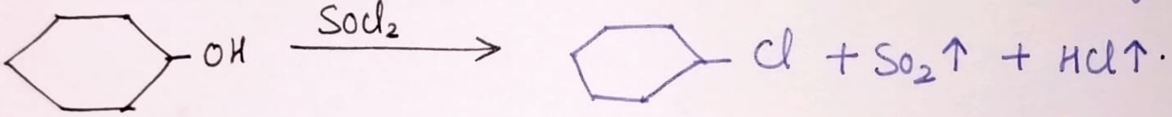
(Markownikoff's rule).

(iv)

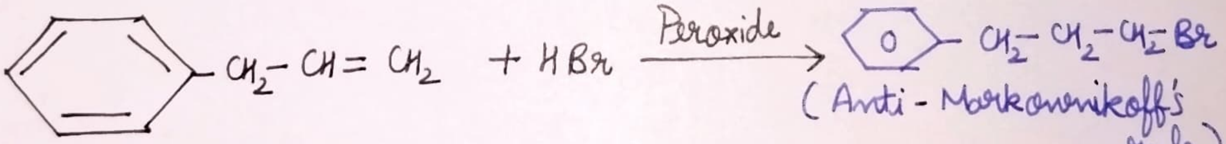


$CH_3CH_2CH=CH_2 + HBr \longrightarrow CH_3-CH_2-\underset{Br}{CH}-CH_3$ [Markownikoff's rule

(v)



(vi)

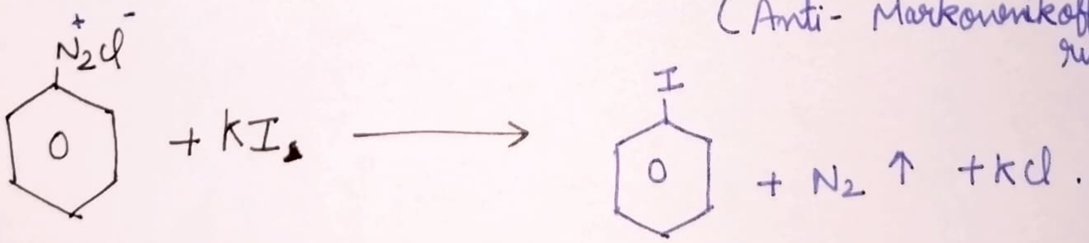


(Anti-Markownikoff's rule).

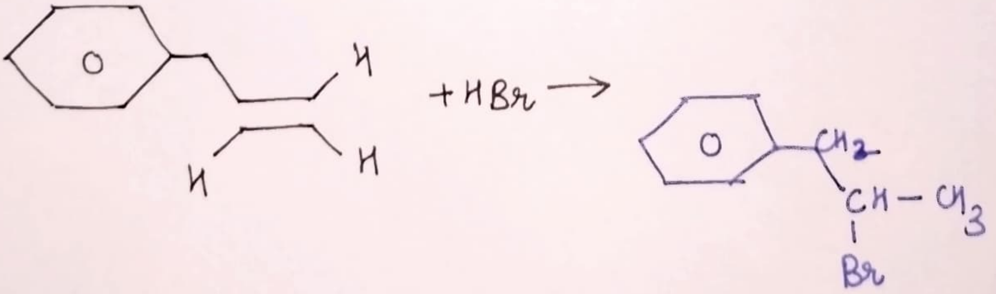
(vii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{Peroxide} CH_3CH_2CH_2-CH_2-Br$

(Anti-Markownikoff's rule).

(viii)



(ix)



(Markownikoff's rule)

- ## PHYSICAL PROPERTIES OF HALOALKANE AND HALOARENES.

1) The boiling and melting point of alkyl halides increases with increase in the size of alkyl group.

2) For the same alkyl group, the boiling point decrease in order RI > RBr > RCl > RF

3) For isomeric alkyl halides, boiling point decreases with branching.

4) Amongst any isomeric haloarene p- isomer has highest melting and boiling point due to symmetry.

5) The stability of haloalkane decreases down the group because the strength of C-X bond decreases, (RF > RBr > RCl > RI) due to increase in size of halogen atom down the group.

6) C-X bond in aryl halides is shorter (due to partial double bond character acquired by C-X bond due to resonance), stronger and less polar than in alkyl halides.

7) The haloalkanes are less soluble in water due to weak hydrogen bond formation.

8) The haloarenes are not soluble in water but they are soluble in organic solvent.

- ## Chemical Properties

Nucleophilic Substitution reactions

=> Those substitution reaction in which an atom or group of atoms are substituted by Nucleophile ($Nu^{\ominus}$).

↓

(nucleuse loving).

$$\overset{\delta+}{R}-\overset{\delta-}{X} + Nu^{\ominus} \longrightarrow R-Nu + X^{\ominus}.$$

Nucleophilic Substitution reactions are of two types :-

SN^1 Reaction

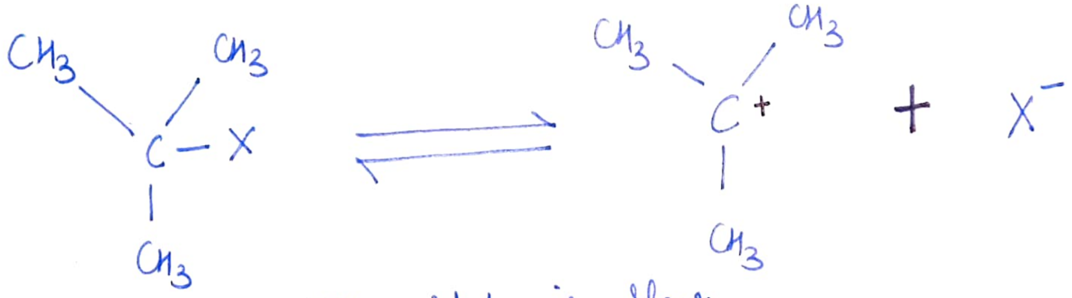
It is unimolecular nucleophilic Substitution Reaction.

$$R-X + Nu^{\ominus} \longrightarrow R-Nu + X^{\ominus}.$$

$$Rate = k[R-X].$$ [This is first order reaction].

The SN^1 reaction mechanism occurs in two steps.

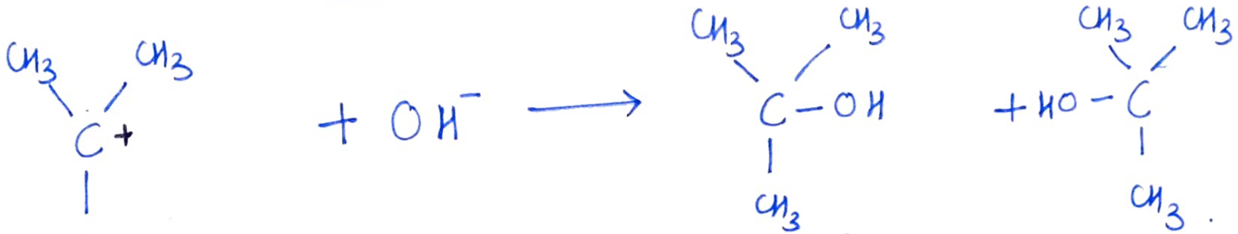
Step-1 Involving formation of Carbocation intermediates.



This step is slow
(Rate determining step).

Step-2 The Carbocation thus formed is attached by the Nucleophile.

[Attack of Nucleophile].



(50%) Retention (50%) Inversion

Here, OH^- attack the carbocation from both front and back side. and the backside attack chances is more.

→ when the nucleophile attack carbocation from front side is called Retention

→ when the nucleophile attack carbocation from back side is called Inversion.

(Racemisation)
[Retention + Inversion = Racemic Product formed]

→ In SN^1 reaction the racemic product formed.

→ Formation of stable Carbocation faster will be reaction.

→ The Reactivity order in SN^1 reaction.

$$3° > 2° > 1° > CH_3-X.$$

→ Weak Nucleophile is used.

→ Polar Protic Solvent is used. (Like water).

Note :-

Allyl and Benzyl halide show SN^1 mechanism Because they also form stable Carbocation due to resonance

SN^2 Reaction :-

It is Biomolecular Nucleophilic substitution reaction.

$$R-X + Nu^{\ominus} \longrightarrow R-Nu + X$$

$Rate = k[R-X][Nu^{\ominus}]$ [This is Second order reaction].

The SN^2 reaction mechanism occurs in one step.

Single Step :-

Transition State

(Inversion)

→ Less Steric hindrance faster will be reaction.
(Structural resistance).

$CH_3X > 1° > 2° > 3°$. [The Reactivity order in SN^2 reaction].

→ Strong Nucleophile is used (for single step).

→ Polar ~~Apoar~~ Aprotic Solvent (Like Acetone).

Note. ⇒ Strong bond in Alkyl halide.

(Difficult to Break). (easily Break).

$R-F > R-Cl > R-Br > \approx R-I$

SN^1 and SN^2 reaction fast →

← Slow.

[order of leaving group tendency is $I^- > Br^- > Cl^- > F^-$]

⇒ In case of optically active alkyl halide, SN^2 mechanism results in the inversion of Configuration while, SN^1 mechanism results in racemisation.

⇒ Alkyl halides are more reactive than aryl halides toward nucleophilic substitution reactions. It is due to the following reasons :-

1) In haloalkanes, there is single bond between R-X, which needs less bond dissociation energy, hence they are more reactive towards nucleophiles. In haloarenes there is double bond character between C-X bond due to resonance. therefore has more bond dissociation energy.

2> Carbon attached to halogen is sp^3 - hybridised in haloalkane and sp^2 hybridised in haloarene. sp^3 - hybridised carbon is less electronegative than sp^2 hybridised carbon. due to less s- character. Thus C-X bond length is shorter in haloarenes than in haloalkanes.

- **Basic Points About optical Isomerism :-**

1> **Chiral Carbon atom** (Asymmetric Carbon atom = The carbon atom which is attached to four different monovalent atoms.

2> **Enantiomers** are the mirror images of each other and are non - Superimposable.

3> Substances which rotate the plane polarised light towards right are called **dextrorotatory** (+) and those which rotate the plane polarised light towards left are called **Laevorotatory** (–).

4> If the product formed in a reaction has same stereochemistry as that of reactant, this process is called **retention of configuration**.

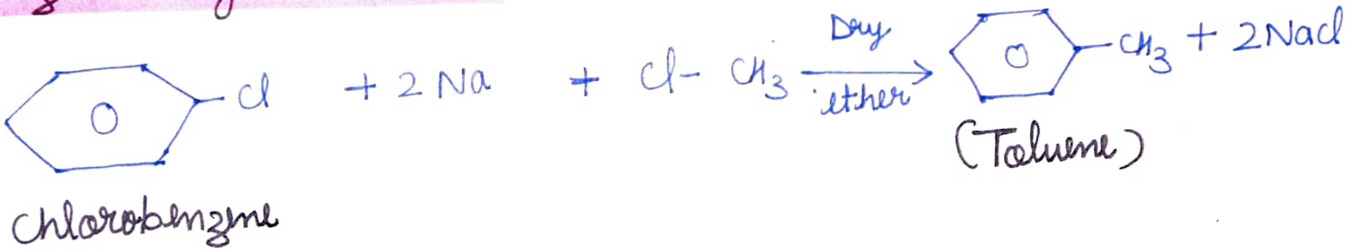
5> If the product formed in a reaction has a stereochemistry opposite to that of reactant, it leads to **inversion of configuration**. Many of the alkyl or aryl halide compounds can show optical isomerism.

6> If in a reaction, 50% inversion and 50% retention occurs, the process is called Racemisation and the product is called **Racemic mixture**. A Racemic mixture is optically inactive as it is a mixture containing two enantiomers in equal proportion and have zero optical rotation.

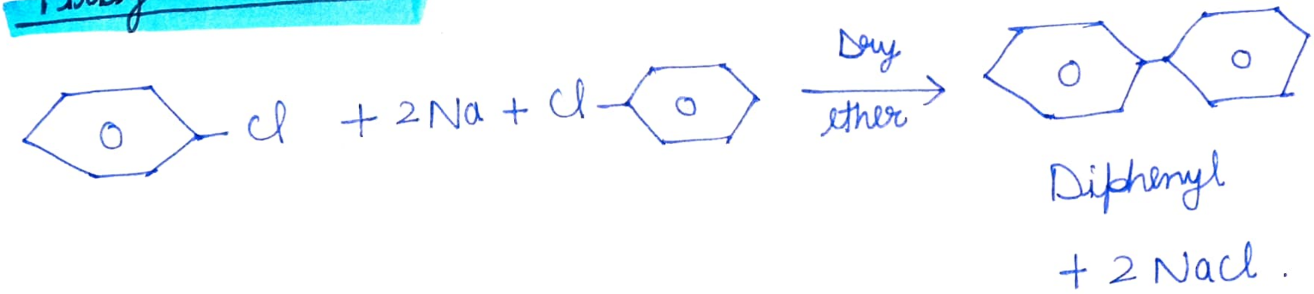
• Reaction with Metals :-

1) Wurtz - Fittig Reaction :-

When aryl halide is heated with alkyl halide in the presence of sodium in dry ether, halogen atom is replaced by alkyl group and alkyl arene is formed. This reaction is called **Wurtz - Fittig Reaction**.



2) Fittig Reaction :-



(When aryl halides react with sodium in the presence of dry ether, two aryl groups are joined together and diphenyl is formed. This reaction is called **Fittig Reaction**.)

Nucleophillic Substitution Reactions with Alkyl halide and Aryl halide.

(R–X)
Alkyl halide

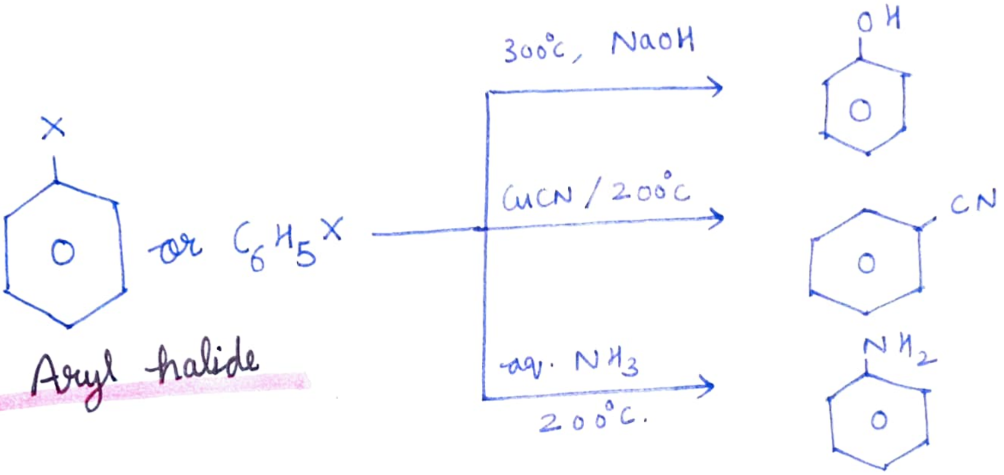
$R-X \xrightarrow{\text{with } KNO_2} R-O-N=O$.

$R-X \xrightarrow{\text{With } AgNO_2} R-NO_2$

$R-X \xrightarrow{\text{Aqueous } (KOH)} R-OH + KX$.

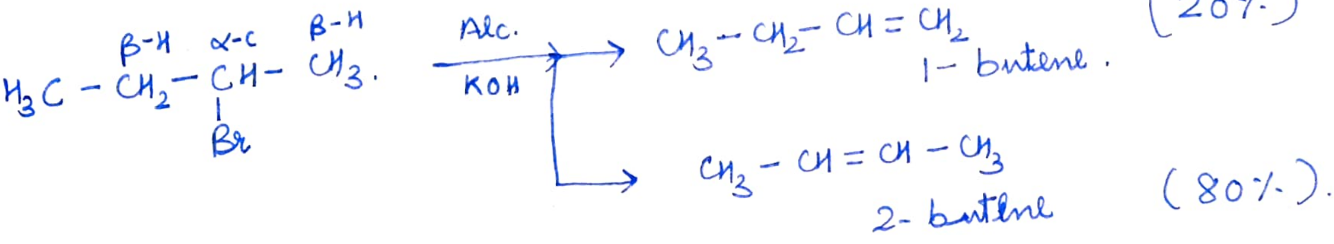
$R-X \xrightarrow{\text{with } NaCN} RCN$.

$R-X \xrightarrow{\text{With } AgCN} RN \equiv C$



Elimination Reactions :-

$R-X \xrightarrow{\text{Alc. KOH.}}$ unsaturated hydrocarbons.



$H_3C-CH_2-CH(Br)-CH_3 \xrightarrow[\text{KOH}]{\text{Alc.}} CH_3-CH_2-CH=CH_2$ 1- butene. (20%)

$\qquad\qquad\qquad\qquad \longrightarrow CH_3-CH=CH-CH_3$ 2- butene (80%).

- ## Electrophilic Substitution reaction :-