Haloalkanes and Haloarenes

Alkanes $\xrightarrow[+X]{-H}$ Halo Alkanes
where X = F, Cl, Br, I

$R-H \xrightarrow[+X]{-H} R-X$

Monohaloalkanes :→ Alkyl Halides $C_nH_{2n+1}X$

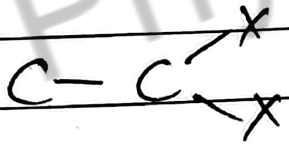
$R-\underset{1^\circ}{CH_2}-X$ Primary

R_2CH-X (2°) Secondary

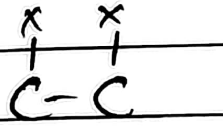
R_3C-X (3°) Tertiary

Dihaloalkanes:

Geminal



Vicinal



Trihalo Alkanes :– Haloforms

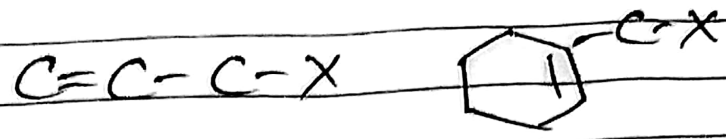
$CHCl_3$	$CHBr_3$	CHI_3
Chloroform	Bromoform	Iodoform

Tetrahalo alkane

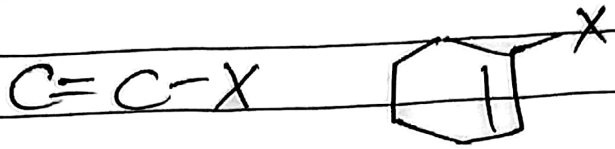
CCl_4	CBr_4
Carbon Tetrachloride	Carbon Tetrabromide

Physicswallah

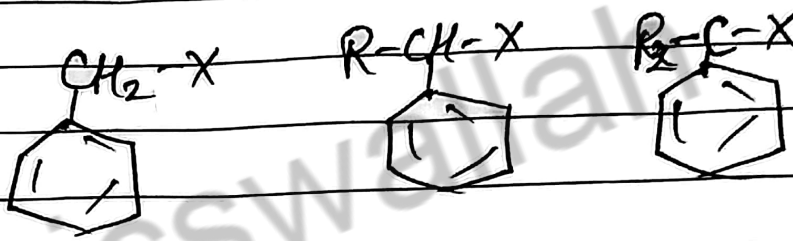
Allylic Halides



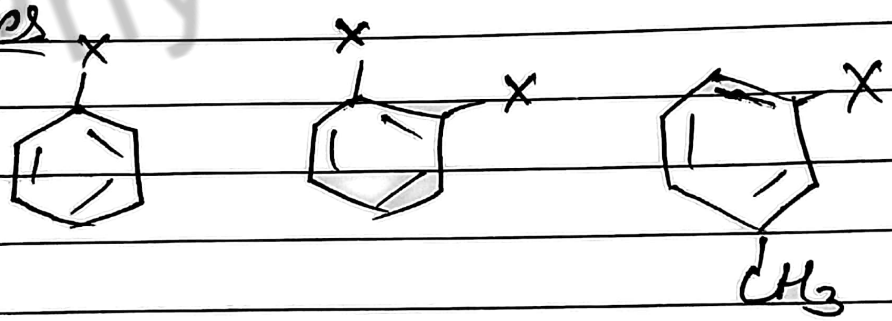
Vinylic Halides



Benzylic Halides



Aryl Halides



In this chapter we will discuss mostly Alkyl Halides & Aryl Halides

Physicswallah

Methods of Preparation of Haloalkanes

1) From Alkanes :- Halogenation of Alkane

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

Chlorination

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3-Cl + HCl$$

Problem: It gives mixed products

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

$$CH_3Cl \xrightarrow[-HCl]{Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{Cl_2} CHCl_3 \xrightarrow[-HCl]{Cl_2} CCl_4$$

Hence not used in laboratory preparation

It proceeds through Free Radical Mechanism

$$CH_3-CH_2-CH_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{(Major)}}{CH_3-\underset{Cl}{CH}-CH_3} + \underset{\text{(Minor)}}{CH_2-CH_2-CH_2-Cl}$$

as $3^\circ > 2^\circ > 1^\circ$ (Free Radical Stability)

For detail mechanism see Hydrocarbons → Halogenation of Alkane & Selectivity

Physicswallah

Bromination Proceeds through same way

In case of Iodination → It is reversible as HI formed is a strong reducing agent & reduces the alkyl halide to alkane

$$R-H + I_2 \rightleftharpoons R-I + HI$$

To prevent Backward reaction, strong oxidising agent such as Conc HNO_3 or HIO_3 are used

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Complete Mechanism & More Questions on Halogenation of Alkane → "Halogenation of Alkanes - Physicswallah & Selectivity Physicswallah" under class 11th Hydrocarbons.

Physicswallah

② From Alkenes

$$R-CH=CH_2 + HX \longrightarrow R-\underset{\displaystyle X}{CH}-CH_3$$

Markovnikov's Addition

$$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{\displaystyle Br}{CH}-CH_3$$

Actual Mechanism is $E^{\oplus}$ Addition

$\Longrightarrow$

$CH_3-CH=CH_2 + HBr \longrightarrow$

$\downarrow H^+$

$CH_3-\overset{\oplus}{C}H-CH_3 \xrightarrow{Br^\ominus} CH_3-CH(Br)-CH_3$

Carbocation Intermediate

(Can undergo Rearrangement as well then Markovnikov's Rule has no meaning)

$\longrightarrow$ Racemic mixture is obtained in case of chiral

($sp^2 \longrightarrow$ attack can occur from both sides)

$CH_3-\overset{CH_3}{\underset{|}{C}}H-CH=CH_2 + HCl \longrightarrow CH_3-\overset{CH_3}{\underset{|}{C}}H-\underset{Cl}{\underset{|}{C}}H-CH_3$

Markovnikov's Rule

(Wrong) ✗

Mechanism

$CH_3-\overset{CH_3}{\underset{|}{C}}H-CH=CH_2 \xrightarrow{H^+} CH_3-\overset{CH_3}{\underset{|}{\overset{\oplus}{C}}}H-CH-CH_3$

$\downarrow H^\ominus$ shift

$CH_3-\overset{CH_3}{\underset{|}{\overset{\oplus}{C}}}-CH_2-CH_3$

$\downarrow Cl^\ominus$

$CH_3-\overset{CH_3}{\underset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_2-CH_3$

(Correct)

Physicswallah

Only with HBr

In case we use peroxide (Kharasch effect/Peroxide effect is observed) → Anti Markovnikov's Rule is followed. → Free Radical Mechanism.

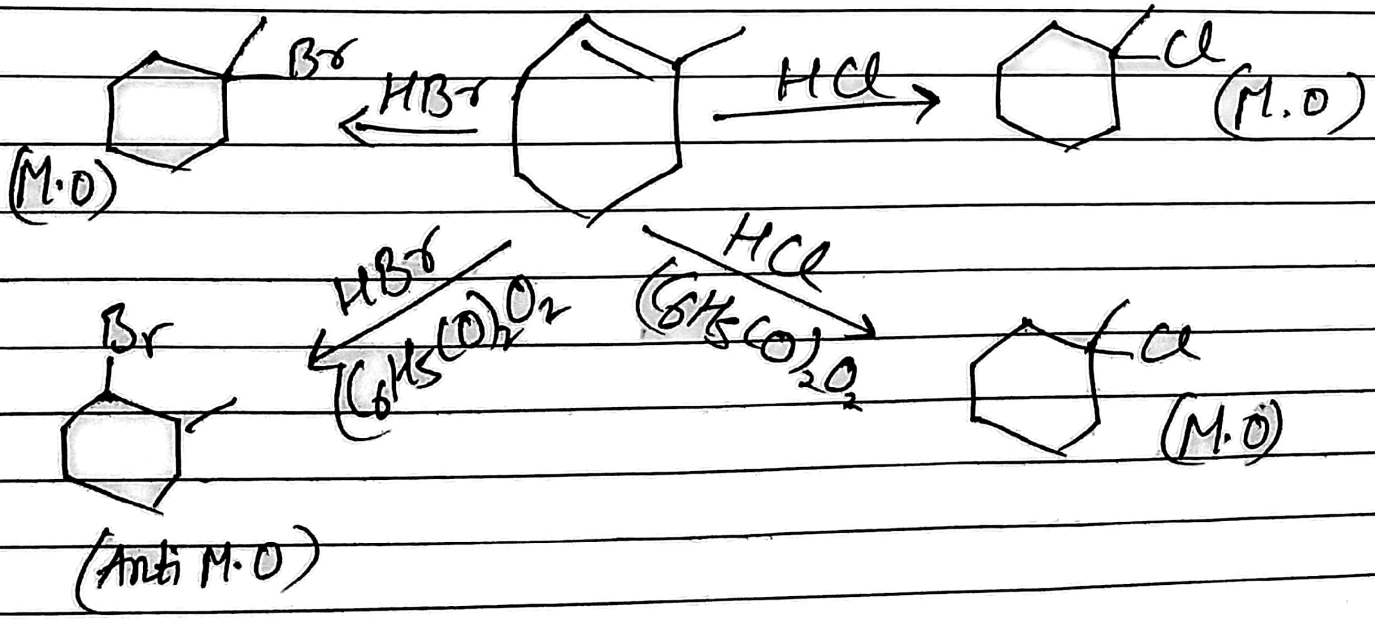
$R-CH=CH_2 + HBr \xrightarrow{Peroxide} R-CH_2-CH_2-Br$

Anti M.O. Rule

$CH_3-CH=CH_2 + HBr \xrightarrow{Peroxide} CH_3-CH_2-CH_2-Br$ (M.O)

$CH_3-CH=CH_2 + HCl \xrightarrow{Peroxide} CH_3-\underset{Cl}{CH}-CH_3$ (Anti M.O)

(Peroxide effect Observed only in HBr)



Physicswallah

Allylic Substitution

$$CH_3-CH=CH_2 + X_2 \xrightarrow{\text{Reagent}} \underset{\displaystyle X}{CH_2-CH=CH_2}$$

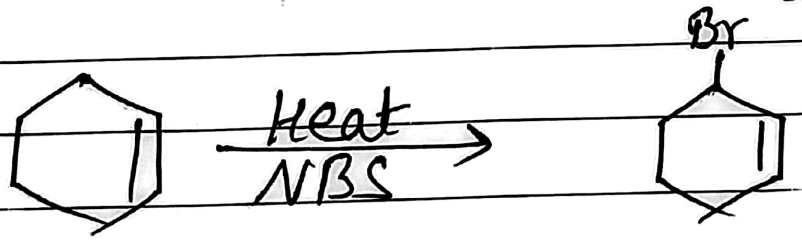
Reagents :- i) Halogens at high Temperature (400–600°C)

ii) NBS / hν High Temp/Heat

iii) SO_2Cl_2

$$CH_3-CH=CH_2 \xrightarrow[Cl_2]{500^\circ C} \underset{\displaystyle Cl}{CH_2-CH=CH_2}$$

$$CH_3-CH=CH_2 \xrightarrow[NBS]{\text{Heat}} \underset{\displaystyle Br}{CH_2-CH=CH_2}$$



For detail Mechanism → watch Allylic Substitution physicswallah.

Physicswallah