

Halogen Derivatives of Alkanes and Arenes [6 Marks for HSC]

When one or more hydrogen atoms of ~~aliphatic or~~ ~~aromatic~~ hydrocarbon are replaced by corresponding number of halogen atoms, the resulting compounds are called halogen derivatives of alkanes.

Halogen derivative of alkanes are classified as monohalogen derivative and polyhalogen derivative.

- 1) Monohalogen derivatives: When one hydrogen atom of alkane is substituted by one halogen atom, the compound formed are called monohalogen derivative of alkane. eg CH_3Cl (methyl chloride); $\text{CH}_3\text{CH}_2\text{Br}$ (Ethyl bromide)
- 2) Polyhalogen derivatives: When more than one hydrogen atoms of alkane are substituted by corresponding number of halogen atoms, the compounds formed are called polyhalogen derivatives of alkanes.

a) Dihalogen derivatives:

When two hydrogen atoms of alkanes are substituted by two halogen atoms, the compound formed are called dihalogen derivatives of alkanes.

eg CH_2Cl_2 (Methylene dichloride)

b) Trihalogen derivatives

When three hydrogen atoms of alkanes are substituted by three halogen atoms, the compounds formed are called trihalogen derivatives of alkanes.

eg CHCl_3 (Chloroform)

c) Tetrahalogen derivatives

When four hydrogen atoms of alkanes are substituted by four halogen atoms, the compounds formed are called tetrahalogen derivatives of alkanes.

eg CCl_4 (Carbon tetrachloride)

Monohalogen Derivatives

Monohalogen derivatives of alkanes are called alkyl halides. They are represented by general formula $C_nH_{2n+1}X$ or $R-X$

Alkyl halides are further classified as,

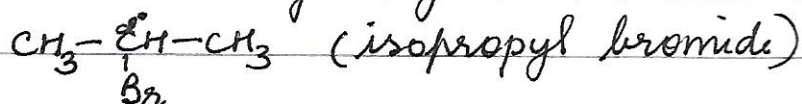
i) Primary alkyl halides

Alkyl halides in which a halogen atom is bonded to a primary carbon atom are called primary alkyl halide (1° Carbon atom is the carbon which is attached to only one or no other carbon atom)

eg $CH_3CH_2CH_2Cl$ (n-propyl chloride)

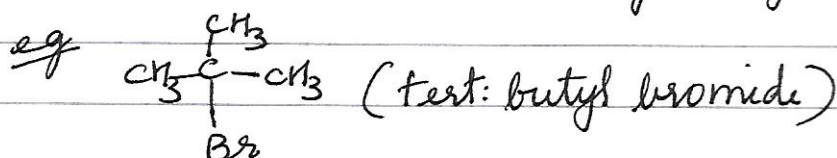
ii) Secondary alkyl halides

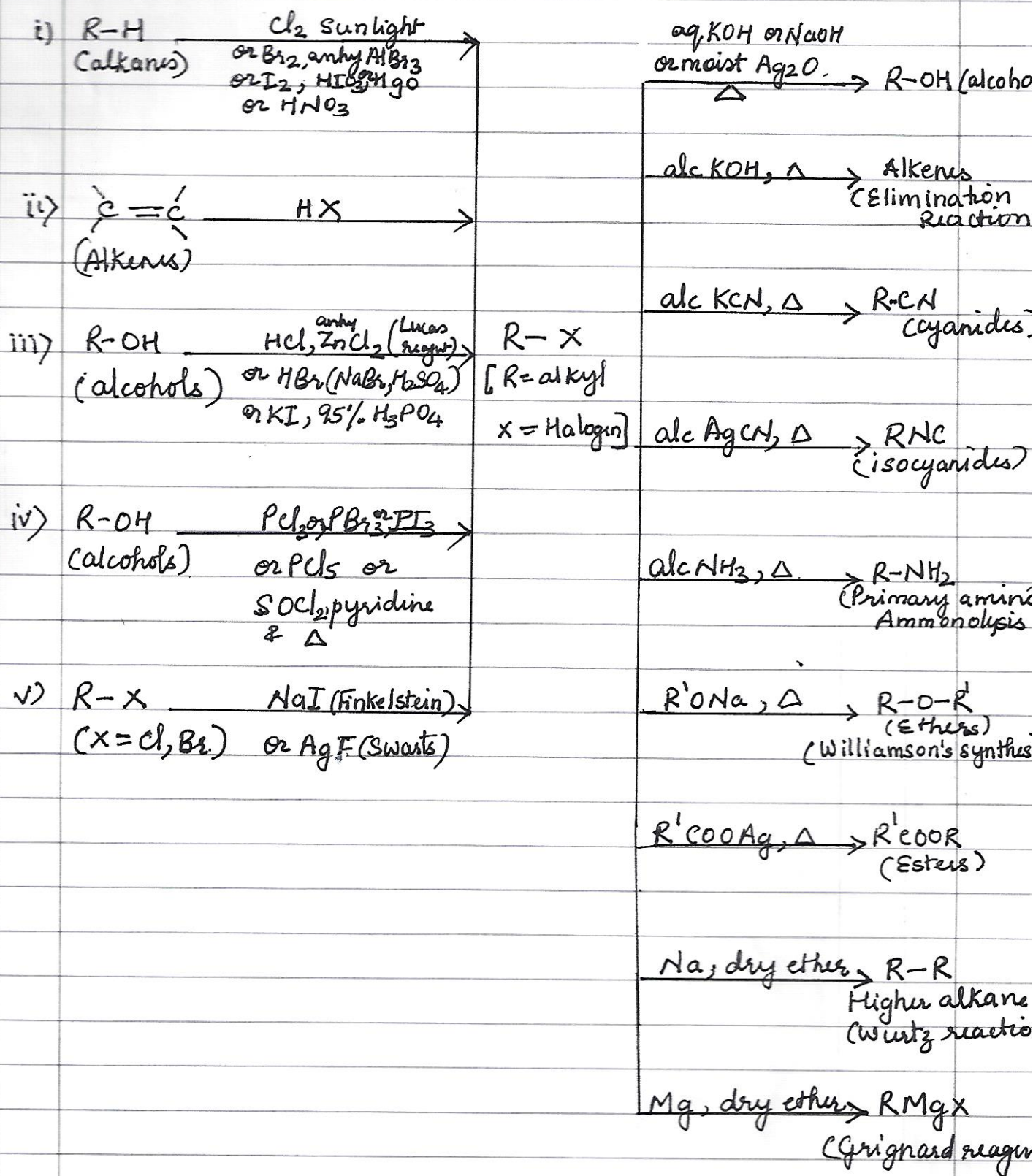
Alkyl halides in which halogen atom is bonded to secondary carbon atom (2° carbon is the carbon which is attached to two other carbon atoms) are called secondary alkyl halides.



iii) Tertiary alkyl halides

Alkyl halides in which halogen atom is bonded to tertiary carbon atom (3° Carbon is the carbon which is attached to three other carbon atoms) are called tertiary alkyl halides



Preparation of alkyl halidesProperties

Stereochemistry

Ordinary light → It consists of rays of light of different wavelength vibrating in different plane perpendicular to the direction of propagation of light

Monochromatic light → It consists of rays of light of single wavelength vibrating in different plane perpendicular to the direction of propagation of light.

Plane Polarised light (PPL) → It consists of rays of light of single wavelength vibrating in single plane perpendicular to the direction of propagation of light.

Optical Activity → The property of organic substances to rotate the plane of plane polarized light towards right (clockwise) or left (anticlockwise) is called optical activity.

Optically active substance → The substance which can rotate the plane of plane polarized light towards the right (clockwise) or left (anticlockwise) is called optically active substance.
eg glucose, lactic acid

Dextro rotatory ^{substance} molecules → Molecules which rotate the plane An optically active substance which can rotate the plane of plane polarized light to the right hand side (clockwise) is called dextro rotatory substance. It is denoted by 'd' or '+'
eg d-glucose or (+) glucose

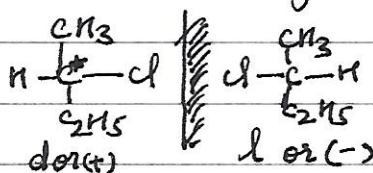
Laevorotatory substance → An optically active substance which rotates the plane of plane polarized light to the left hand side (anti-clockwise) is called laevorotatory substance.

It is denoted by l or $(-)$
eg l -glucose or $(-)$ glucose

Asymmetric Carbon atom → A tetrahedral carbon atom which is bonded to four different atoms or groups is called an ~~ass~~ asymmetric or chiral carbon atom. It is denoted by asterisk (*)

[Any molecule which contains an asymmetric carbon atom will exist as a pair of isomers, which are non superimposable mirror images of each other.

eg 2-Chlorobutane.



Chirality → Any object which is non superimposable with its mirror image is said to be chiral and this property is known as chirality.

Enantiomers → optical/stereo isomers which are non superimposable mirror images of each other and rotate the plane of plane polarized light through the same angle but in opposite direction are known as enantiomers or enantiomorphs.

Racemic mixture or racemates → when equimolar quantities of dextro and laevo isomers are mixed, the resulting mixture is found to be optically inactive due to external compensation. It is

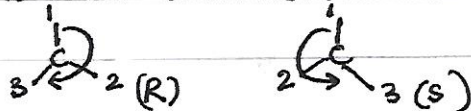
represented as (+) or dl eg (+) lactic acid.

R and S configuration

R \rightarrow latin Rectus (right)

S \rightarrow latin sinister (left)

[Atom with lowest atomic number given lowest priority]



Reaction Mechanism (SN' & SN²)

Mechanism \rightarrow It is a step by step description of exactly how reactants are transformed into products

SN' Mechanism (Alkaline hydrolysis of tertiary butyl bromide)

When tertiary butyl bromide is heated with an aqueous solution of a base NaOH or KOH, it undergoes hydrolysis

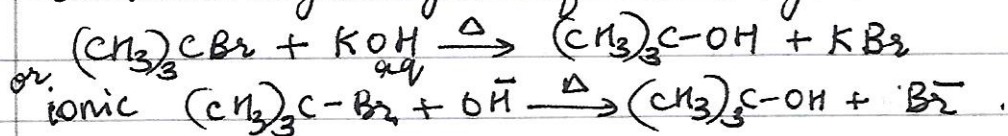
The reaction follows SN' mechanism, where

S \rightarrow Substitution

N \rightarrow Nucleophilic

1 \rightarrow unimolecular (1st order)

consider hydrolysis of tert: butyl bromide



In this reaction the stronger nucleophile OH^- displaces the weaker one Br^- , hence it is a nucleophilic substitution reaction

Kinetics

$$\text{Rate} \propto [(\text{CH}_3)_3\text{C-Br}]$$

\therefore 1st order

2 steps.

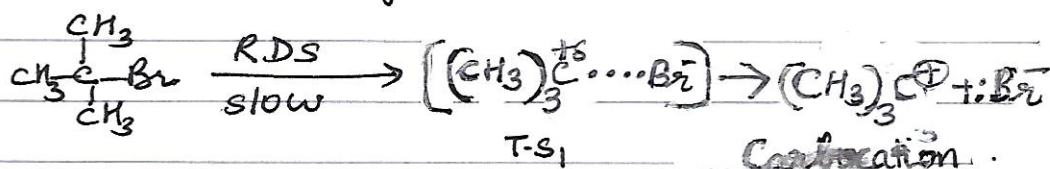
Mechanism

i) Formation of Carbonium ion

Nucleophile OH^- cannot attack from the same side of leaving group Br^- , since Br^- also strong nucleophile. OH^- cannot attack from backside of leaving group due to presence of bulky alkyl group.

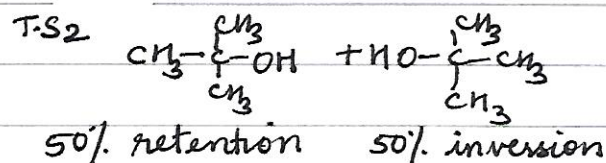
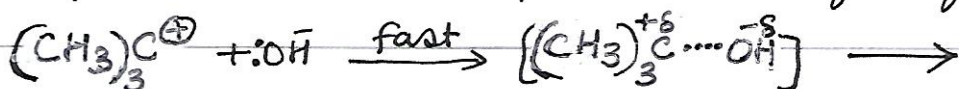
Therefore there is slow heterolytic fission of bond between carbon and bromine, forming tertiary butyl carbonium ion.

It is slow step & called Rate determining step (RDS). It involves only one molecule, it is unimolecular.

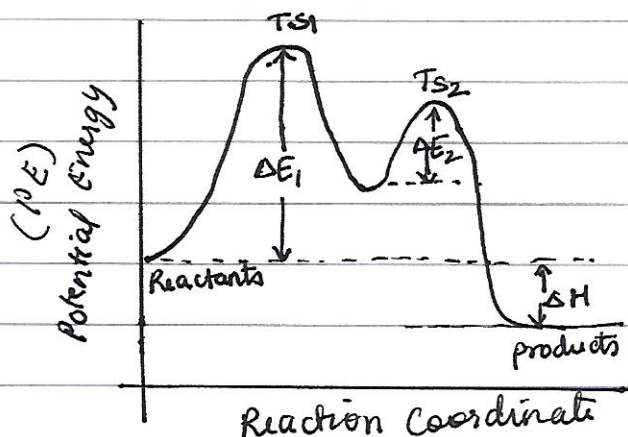


ii) Attack of Nucleophile

The nucleophile OH^- attacks the carbocation from all sides. It is a fast step. It forms products with 50% retention and 50% inversion of configuration.



EPD (S_N' Mechanism)



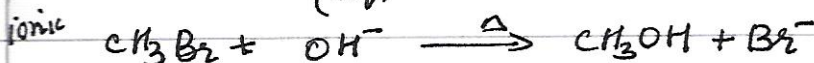
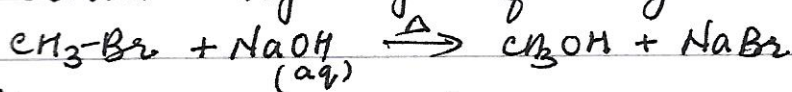
SN² mechanism (Alkaline hydrolysis of Methyl Bromide)
 when Methyl bromide is heated with an aqueous solution of a base NaOH or KOH, it undergoes hydrolysis. The reaction follows SN² mechanism, where

S → Substitution

N → Nucleophilic

2 → bimolecular (2nd order)

Consider hydrolysis of Methyl bromide



Kinetics

$$\text{Rate} \propto [\text{CH}_3\text{Br}] [\text{OH}^-]$$

∴ 2nd order, 1 step.

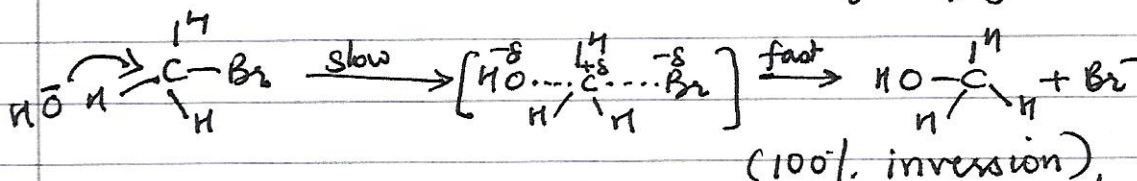
Mechanism

i) Back-side attack of Nucleophile

The Nucleophile OH⁻ attacks Methyl bromide from back side of the leaving group Br⁻. [cannot attack from same side of leaving group Br⁻ as Br⁻ is also strong Nucleophile]

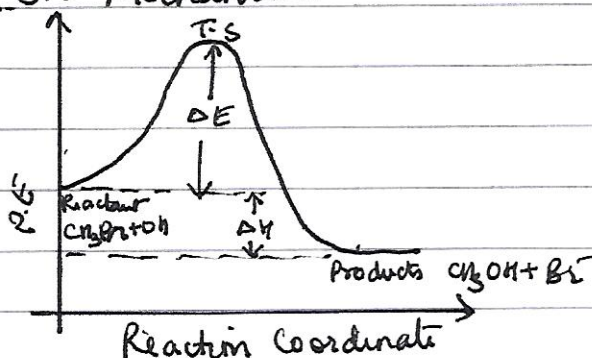
ii) Formation of transition state

It forms a transition state where central carbon atom is bonded to five different atoms or groups. It is highly unstable and breaks to form products Methyl alcohol and bromide with 100% inversion of configuration.



Rate depends on concentration of Methyl bromide & OH⁻ ∴ 2nd order.

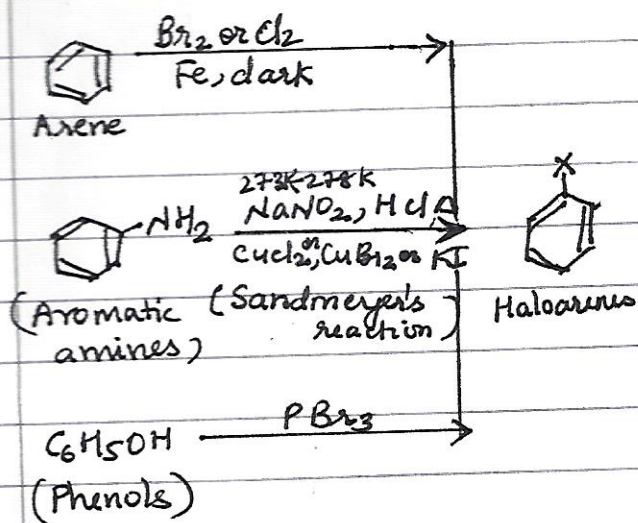
EPD SN² Mechanism



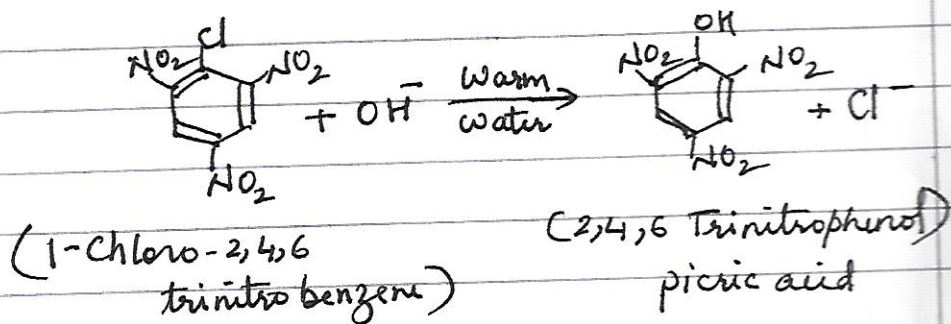
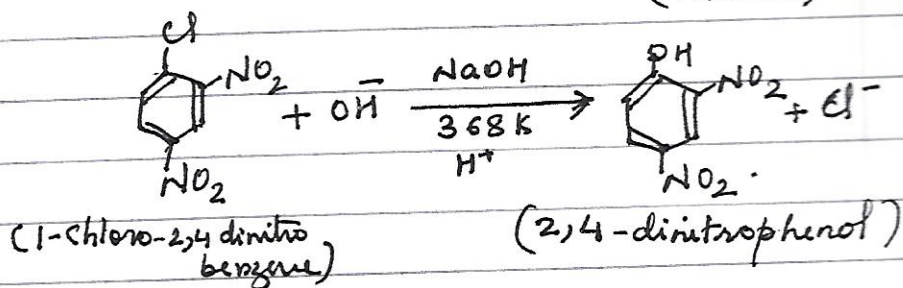
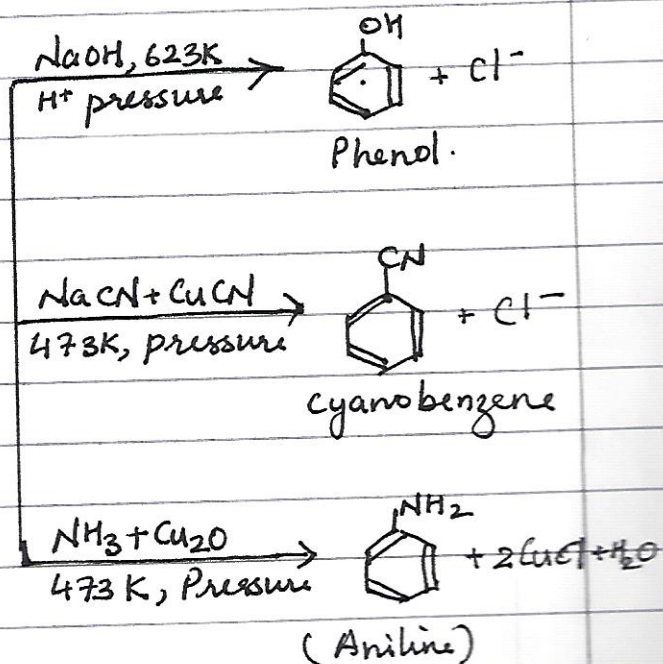
Haloarenes.

Defⁿ: When one or more hydrogen atoms of aromatic hydrocarbon are replaced by corresponding number of halogen atoms, the resulting compound is called haloarenes.

Preparation



Properties (Reactions of Haloarenes)



Reactions of chlorobenzene

