MIND MAP

Haloalkanes and Haloarenes

Electrophile (Electron Loving)

An electrophile is a positively charged species or neutral molecule with electron deficient centre.

Types of Electrophiles

(1) Positively charged electrophiles

$H^+, Br^+, Cl^+, I^+, \overset{+}{N}O_2, R_3C^+, \overset{+}{N}O$ etc.

(2) Neutral Electrophiles

In these electrophiles central atom has an incomplete octet or at least one vacant orbital SO3, BF3, AlCl3, ZnCl2, FeCl3, RCOCl, (RCO)2O etc.

Nucleophiles (Nucleus Loving)

It is an electron rich.

$\overline{C}N, OH^-, Br^-, I^-, \ddot{N}H_3, H_2\ddot{O}$ etc.

Types of Nucleophiles

(1) Negatively charged nucleophiles

$\overline{H}$, $\overline{O}H$, $\overline{O}-R$, $\overline{C}H_3$, $\overline{X}$, $\overline{S}H$, $\overline{R}-\overline{S}$, $N\overline{O}_2$,

(2) Neutral nucleophiles

In these nucleophiles central atom has complete octet and atleast one lone pair of electron

$R-\ddot{O}-H$, $R-\ddot{O}-R$,

$H-\ddot{S}-H$, $R-\ddot{S}-H$, $R-\ddot{S}-R$, $\ddot{P}H_3$,

(3) Pi bonded organic compounds

Organic compounds containing carbon-carbon multiple bonds can also behave as nucleophile, because of pi electron cloud or density.

$CH_2=CH_2$,  , $CH_2=CH-CH=CH_2$, etc.

(4) Ambident Nucleophile

Species having two nucleophilic sides, but only one can donate lone pair of electron at a time, known as Ambident nucleophile.

$\overline{C}\equiv\ddot{N}$, $\overline{O}-\ddot{N}=O$, etc.

1. Non Polar Solvents

These solvents have overall zero dipole moment. It does not solvate both cation and anion

(2) Polar protic solvent

Solvents in which H atom is directly attached with highly electronegative atom (acidic or active hydrogen).

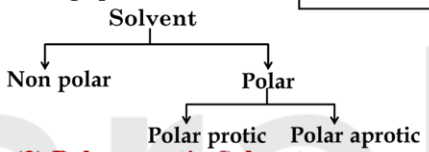
In polar protic solvents cation are solvated by ion dipole interaction while an anion is solvated by hydrogen bonding.

Polar protic solvent can give H+

H_2O, C_2H_5OH, CH_3COOH etc.,

Solvent & it's Role

A Solvent provides a medium, a place, for the substrate and attacking specie to react.



(3) Polar aprotic Solvents

These are the solvents in which H is not attached with highly electronegative atom. These solvents can not give H bonding.

In polar aprotic solvents cation are solvated by ion dipole interaction while an anion is not solvated by solvent

Steric Effects on Nucleophilicity

$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O^-$ t - butoxide (Stronger base, yet weaker nucleophile. Cannot approach the carbon atom so easily.)

$CH_3-CH_2-O^-$ ethoxide (Weaker base, yet stronger nucleophile)

Order Of Leaving Ability Of Some Groups

(1) -I > -Br > -Cl > -F

(2) $CH_3^- < NH_2^- < OH^- < F^-$

(3) $\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\|}{\underset{\|}{O^-S}}}}-CH_3 > R-COO^- > PhO^- > HO^- > RO^-$

Nucleophilicity Vs Basic strength

Nucleophilicity	Base Strength	Remarks
1. $CH_3^- > NH_2^- > OH^- > F^-$	$CH_3^- > NH_2^- > OH^- > F^-$	If donor atoms belong to same period, Nucleophilicity and basic strength order is same
2. $F^- < Cl^- < Br^- < I^-$	$F^- > Cl^- > Br^- > I^-$	In a group Nucleophilicity increases while basic strength decreases in a polar protic solvent. On moving top to bottom.

Nucleophilicity is defined as the tendency of any species to give electron pair to an electron deficient centre, while basic strength is the ability of the species to remove H+ ion from an acid.

Effect of The Solvent

In polar protic solvent large nucleophiles are good, and the Nucleophilicity of halide ions follows the order as $F- < Cl- < Br- < I-$

In polar aprotic solvent, the relative order of Nucleophilicity of halide ions is given as

$F- > Cl- > Br- > I-$

Basic strength of halides follows the same order as nucleophilicity in polar aprotic solvent but in polar protic solvent like H2O they follow the reverse order of Nucleophilicity.

Relative Nucleophilicity in polar protic solvent

$HO^- > H_2O$

$NH_2^- > NH_3$

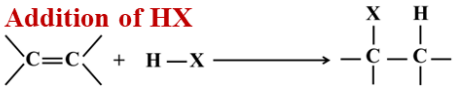
$CF_3SO_3^- < PhCOO^- < PhO^- < RO^-$

MIND MAP

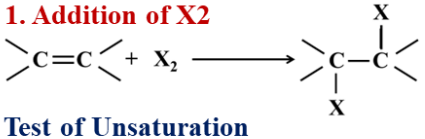
Haloalkanes and Haloarenes

Preparation of Alkyl Halide

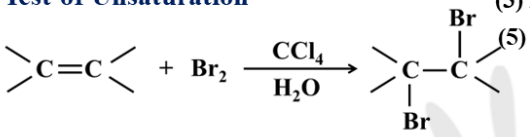
Addition of HX



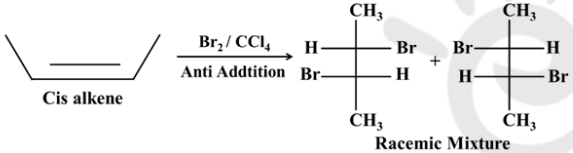
1. Addition of X2



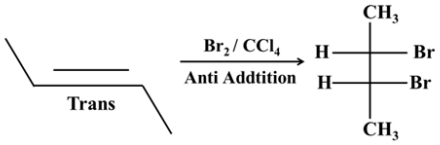
Test of Unsaturation



(Reddish brown) (Colourless)



Cis alkene — Racemic Mixture



Trans — (Meso/POS)

For Symmetric Alkene

Alkene Type	Type of Addition	Product Type
Cis	Syn	Meso
Cis	Anti	Racemic Mixture
Trans	Anti	Meso
Trans	Syn	Racemic Mixture

Favourable conditions

(1) Smaller least sterically hindered substrate. (2) Strong nucleophile.
(3) High concentration of nucleophile. (4) In alkaline medium.
(5) In presence of polar aprotic solvent.

Reactivity Order Towards S_N2 Reaction

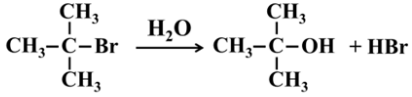
CH3 – X > 1° alkyl halide > 2° alkyl halide >> 3° alkyl halide

(B) Presence of Unsaturation on β-Carbons :-

Presence of unsaturation on β carbon in primary alkyl halide increases rate of SN2 , that's why allyl halide and benzyl halides are good substrate for SN2
As transition state is negatively charged so presence of electron withdrawing group or negative charge stabilising factors increases the rate of SN2 reaction.

Unimolecular Nucleophilic Substitution Reaction (SN1)

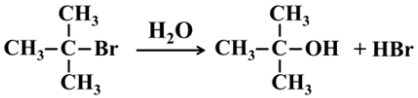
S_N1 in Haloalkanes



(3° alkyl halide)

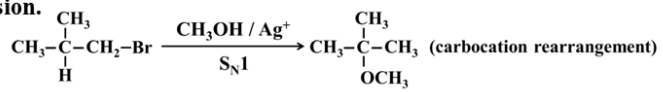
(1) Substrate must be bulky.
(2) Weak or neutral nucleophile with low concentration
(3) In presence of polar protic solvent.
(4) In presence of Lewis acid .

S_N1 in Haloalkanes



(3° alkyl halide)

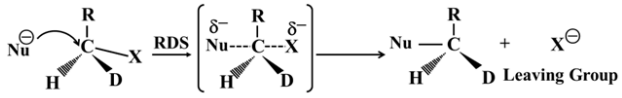
In most of the case the product has usually of 5-20% inverted product and 80-95% racemised species. Thus reaction proceeds with partial racemisation and some inversion.



(carbocation rearrangement)

Bimolecular Nucleophilic Substitution Reaction (SN2)

Mechanism

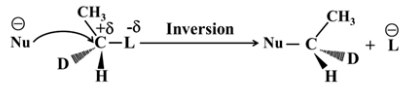


Transition state — Leaving Group

(1) Characteristics of SN2 Reactions

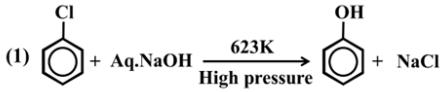
(A) Nucleophile attacks on the substrate from just opposite side to the leaving group.
(B) Hybridisation of the carbon at which substitution occurs changes from sp3 to sp2 in the transition state
(C) It is bimolecular, one step concerted process
rate ∝ [alkyl halide] [nucleophile]
rate = k[alkyl halide] [nucleophile]
This mode of attack causes an inversion of configuration at the carbon atom that is the target of nucleophilic attack.
This inversion is also known as Walden inversion.

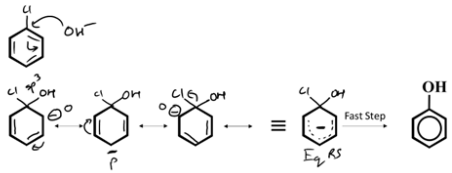
Important Point



It is always not necessary that absolute configuration will change.

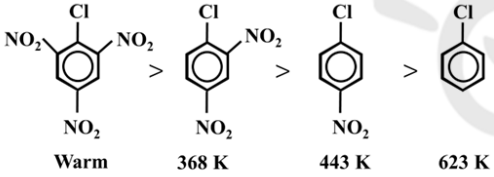
Chemical Properties of Aryl Halides

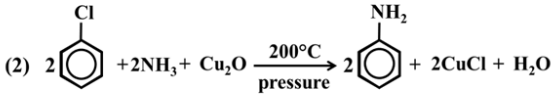


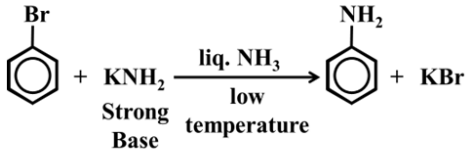


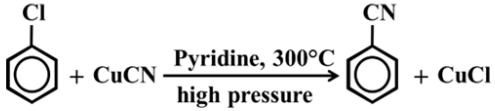
Presence of deactivating group in ortho and para position makes the nucleophilic substitution easier.

Reactivity Order (Towards Nucleophilic Substitution)





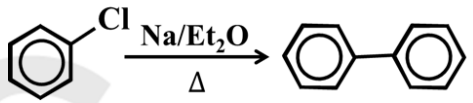


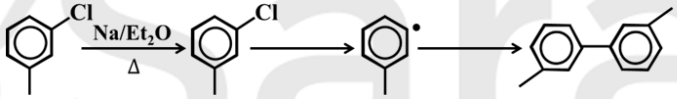


MIND MAP

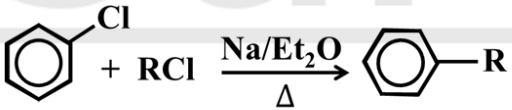
Haloalkanes and Haloarenes

Fitting Reaction (Aryl Halide)

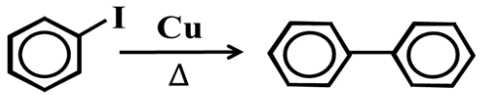


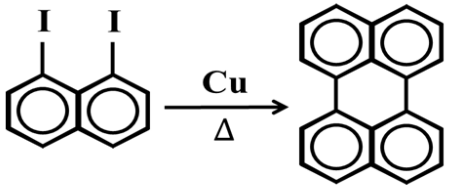


Wurtz-Fitting Reaction(Alkyl-Aryl)



Ullmann Reaction





Physical Properties

(a) The lower member CH3F, CH3Cl, CH3Br, C2H5Cl and C2H5F are gases at room temp.
CH3I and members upto C18 are colourless sweet smelling liquids.

(b) Higher B.P. than parent alkanes

Decreasing order of B.P. is

R – I > R – Br > R – Cl > R – F

Among isomeric R – X decreasing order of B.P. is

Primary > Secondary > tertiary

(c) R – F and R – Cl ⟶ Lighter than water

R – Br and R – I ⟶ Heavier than water

Decreasing order of density is

R – I > R – Br > R – Cl > R –F

(d) R–X are polar covalent compounds but insoluble in water because they can not form H–bonds. They dissolve in organic solvents.

(e) R – X burns with a green flame with Cu wire.(Beilstein test)

(f) The stability order is

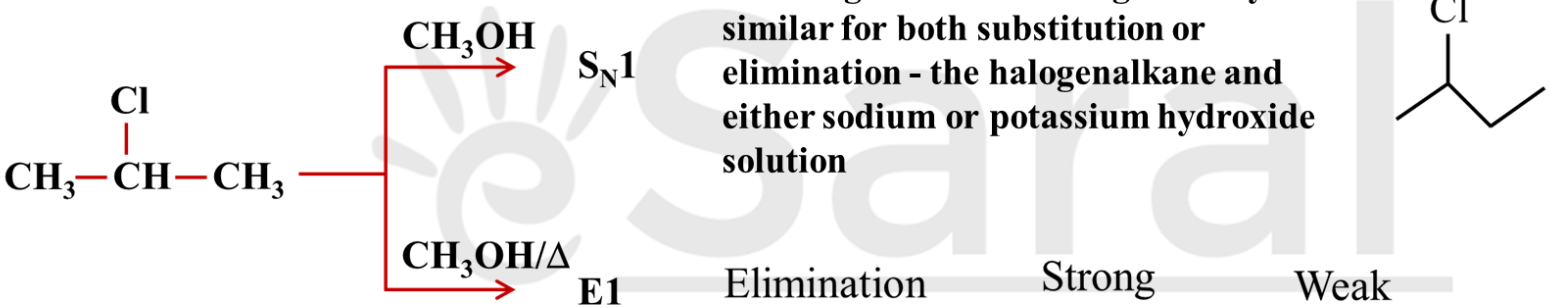
R – F > R – Cl > R – Br > R – I

R – I is least stable and darken in light due to photodecomposition.

$2R - I \xrightarrow{hv} R - R + I_2$

MIND MAP

Substitution vs Elimination reaction



The reagents we are using are very similar for both substitution or elimination - the halogenalkane and either sodium or potassium hydroxide solution

Alc KOH, Δ → E_2

NaCN, ΔMSO → S_N2

H_2O → S_N1

EtO4, Δ → E_1

Elimination Strong Base

Strong Nu/Base

Weak Nucleophile

Substrate	Alc. KOH	Aq. KOH	H_2O
1° halide	$S_N < E$	$S_N2 > E$	X
2° halide	$S_N < E$	$S_N2 \geq E_2$	$S_N1 > E$
3° halide	$S_N < E$	$S_N1 < E_1$	$S_N1 > E$

MIND MAP

Alkyl Halide

1. By alcohols

S_N1 Path

$$R-CH_2-OH \xrightarrow[\text{Lewis Acid}]{H-Cl,\ ZnCl_2} RCH_2-Cl$$

Reactivity order for alcohol

Reactivity ∝ stability of intermediate carbocation

Reactivity order is

Tertiary alc. > Secondary alcohol > Pri. alc.

Reactivity order of H—X is

HI > HBr > HCl

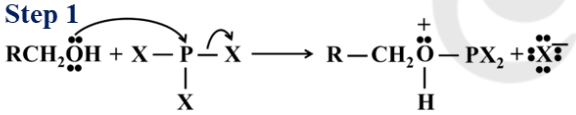
Note

HCl + ZnCl2 is called as Lucas reagent, alcohol gives turbidity with Lucas reagent.

2. By the action of Phosphorus Halides (SN2 Path)

$$R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$$

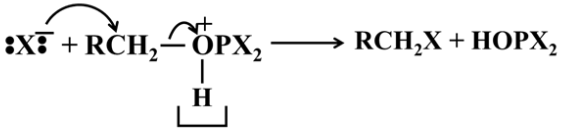
Step 1



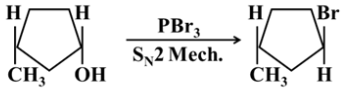
Protonated alkyl dihalophosphite

Step 2

Attack from back side



A good leaving group



Inverted Product

3. By reaction with Thionyl Chloride - (Darzens Reaction)

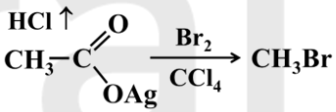
$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2\uparrow + HCl\uparrow$$

The usefulness of this method is that there is no side product, which has to be separated.

Also the side products are gaseous, which escape from the reaction mixture and hence giving very good yield.

4. By reaction with Thionyl Chloride - (Darzens Reaction)

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



5. By halide exchange

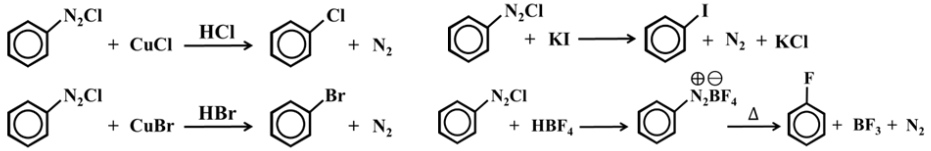
Finkelstein reaction

$$R-Cl \text{ or } R-Br + KI \xrightarrow[S_N2\ Path]{\text{Dry Acetone}} R-I + KCl \text{ or } KBr$$

Swarts Reaction

$$2CH_3Cl + HgF_2 \xrightarrow[S_N2\ Path]{} 2CH_3-F + HgCl_2$$

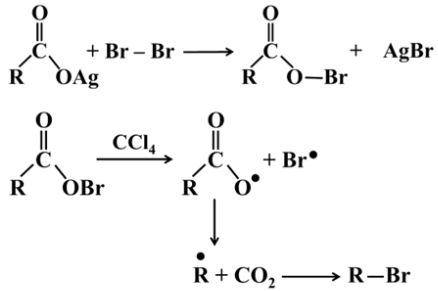
Sandmeyer's Reaction



Borodine Hunsdiecker Reaction

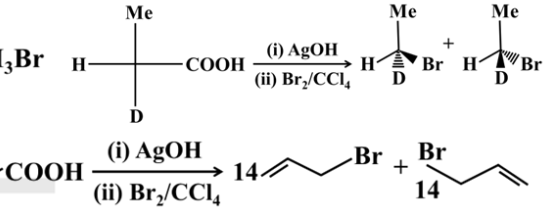
$$R-C-OOAg + Br_2 \xrightarrow{CCl_4} R-Br + CO_2 + AgBr$$

Mechanism



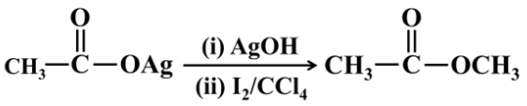
(i) Radical intermediate is involved.

(ii) Degradation (Carbon length reduces) reaction.



(iii) If I2 is taken instead of Br2 ester is formed.

It is called Birnbaum Simonini reaction.



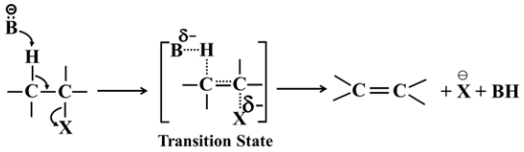
MIND MAP

Elimination Reaction

Bimolecular Elimination Reaction (E2)

Dehydrohalogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene.

Mechanism

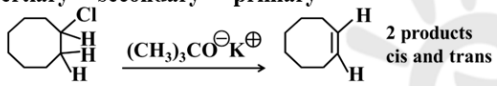


(i) This is a single step, bimolecular reaction

Rate = k [R – X] [B⁻]

Reactivity order for alkyl group towards E2 reaction is given as

Tertiary > secondary > primary



Chlorocyclooctane

Step 2

Formation of the Hoffmann Product

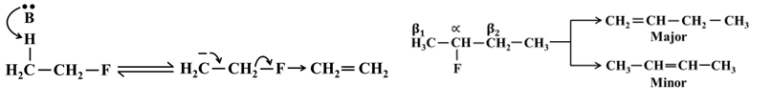
Bulky bases can also accomplish dehydrohalogenations that do not follow the Saytzeff rule.

First step consists of the removal of a proton, , by a base generating a carbanion

In second step carbanion looses a leaving group to form alkene

Stereo Chemistry of E2 reactions

E2 reaction is an example of anti-elimination in which both H and leaving group are anti to each other.



4. Unimolecular Conjugate Base Reaction (E1cB Reaction)

In the E1cB H leaves first and then the X(when X is a poor leaving group). This is a two step process, the intermediate is a carbanion.

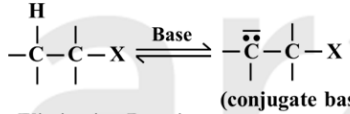
For E1cB

(i) Substrate must be containing acidic hydrogens

(ii) Poor leaving groups(For example F and NR3.)

Mechanism

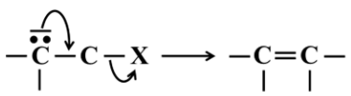
Step 1



Elimination Reaction

E2	E1	E1cB	E_i
Elimination Reaction With molecularity = 2	Unimolecular Elimination Reaction	Elimination Conjugate Base Reaction	Elimination Internal Reaction

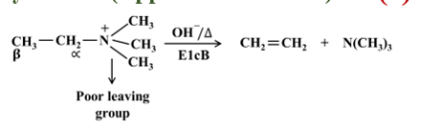
Step 2



First step consists of the removal of a proton, , by a base generating a carbanion

In second step carbanion looses a leaving group to form alkene

Pyrolysis of Tetra Alkyl Ammonium Hydroxide (Application of E1cB)

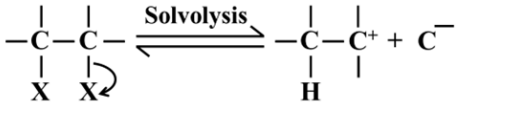


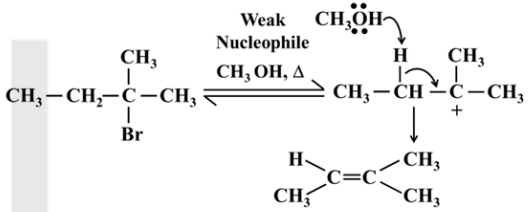
Unimolecular Elimination Reaction (E1)

First step - Slow step involves ionisation to form carbocation

Second step - Abstraction of proton

Mechanism





3. Elimination Internal (Ei) Or Pyrolytic Syn-elimination

These elimination reaction occur through formation of cyclic transition state involving only one molecule of substrate.

(1) Pyrolysis of Esters (Ei)