

# ALKYL and ARYL HALIDES

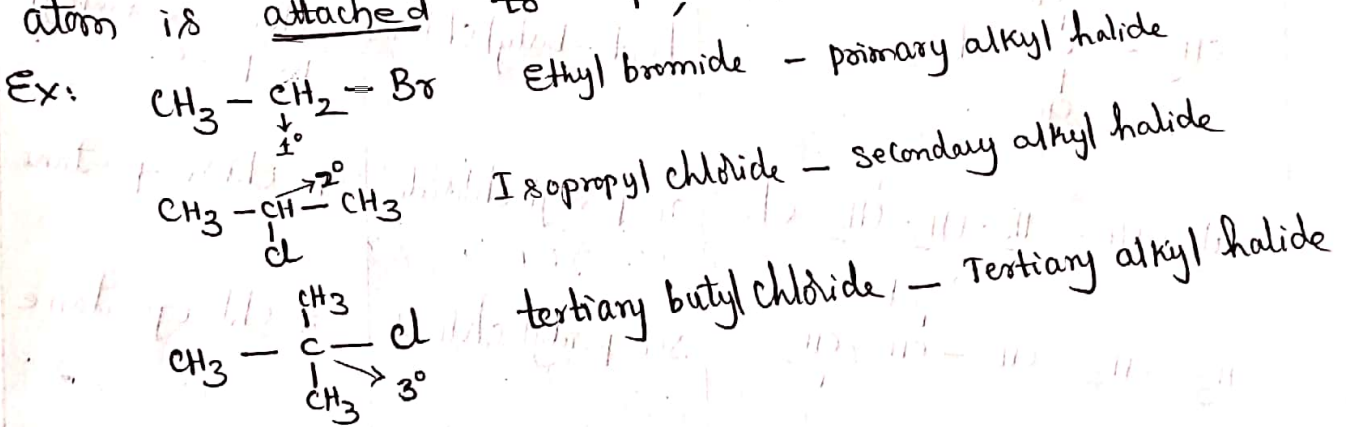
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## ALKYL HALIDES

Mono halogen derivatives of alkanes are called alkyl halides. They are having G.F.  $C_nH_{2n+1}-X$  (or  $R-X$ ). Where  $C_nH_{2n+1}$  is an alkyl group and  $X$  is a halogen atom (Cl, Br or I). In all haloalkanes, halogen atom is bonded to  $sp^3$  hybridised carbon atom.

### Classification of alkyl halides:

Alkyl halides are classified into three types primary ( $1^\circ$ ), Secondary ( $2^\circ$ ) and Tertiary ( $3^\circ$ ) alkyl halides, depending on whether the halogen atom is attached to  $1^\circ$ ,  $2^\circ$ ,  $3^\circ$  carbon atom respectively.



### Nomenclature

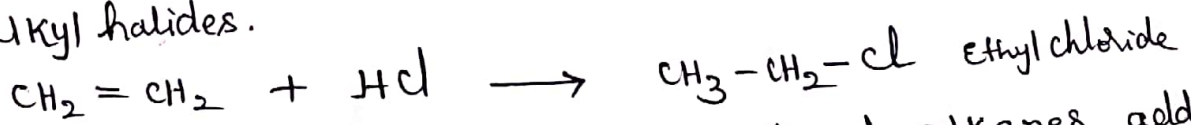
- (a) Common names: - "alkyl halide". Suitable prefixes such as 'n', 'iso', 'sec', 'ter' and 'neo' are used to differentiate the isomers.
- (b) IUPAC names: - In IUPAC system alkyl halides are named as "haloalkane".

formula	Common name	IUPAC name	Type
$\text{CH}_3 - \text{I}$	methyl iodide	iodomethane	1°
$\text{CH}_3 - \text{CH}_2 - \text{Br}$	Ethyl bromide	1-bromo ethane	1°
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$	n-propyl chloride	1-chloropropane	1°
$\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{Cl}}{\text{CH}}} - \text{CH}_3$	iso-propyl chloride	2-chloropropane	2°
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$	n-butyl chloride	1-chlorobutane	1°
$\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{Cl}}{\text{CH}}} - \text{CH}_2 - \text{Cl}$	iso-butyl chloride	1-chloro-2-methyl propane	1°
$\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{Cl}}{\text{CH}}} - \text{CH}_2 - \text{CH}_3$	sec-butyl chloride	2-chlorobutane	2°
$\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{Cl}$	tert-butyl chloride	2-chloro-2-methyl propane.	3°
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$	n-pentyl chloride	1-chloro-pentane	1°
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{Cl}}{\text{CH}}} - \text{CH}_3$	sec-pentyl chloride	2-chloropentane	2°
$\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{CH}_2 - \text{Cl}$	neo-pentyl chloride	1-chloro-2,2-dimethyl propane.	1°

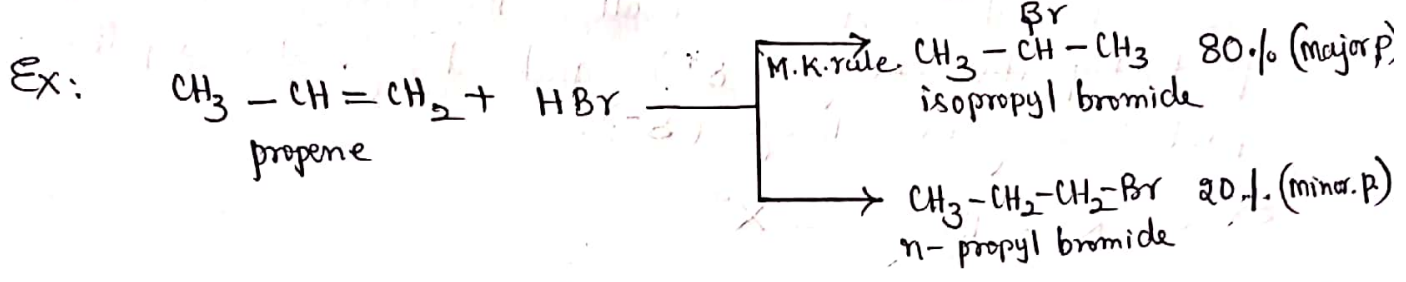
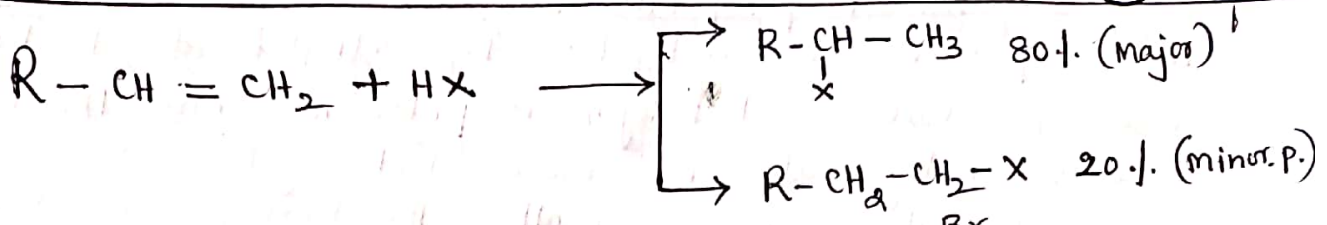
### Methods of preparation

(1) From alkenes:

Alkenes reacts with halogen acids (HCl, HBr, HI) forming alkyl halides.

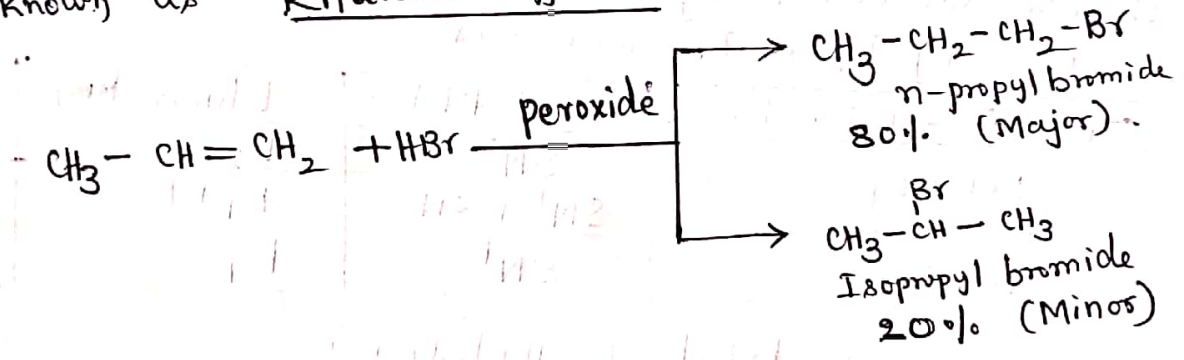


Addition of hydrogen halide to symmetrical alkenes, addition takes place according to Markownikoff's rule.



M-K rule: Addition of  $HX^-$  to unsymmetrical alkenes, the negative part of the reagent goes to Carbon containing least no. of H-atom across the  $C=C$ .

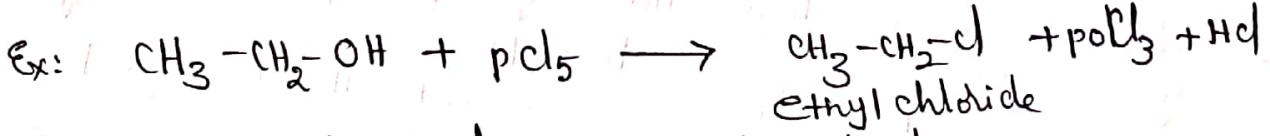
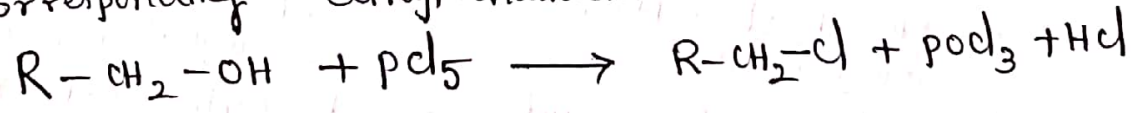
Note: In presence of peroxide as a catalyst, HBr adds to unsymmetrical alkene against to Markownikoff's rule, which is called Anti-Markownikoff's rule. which is also known as "Kharasch effect".



(2) From alcohols:

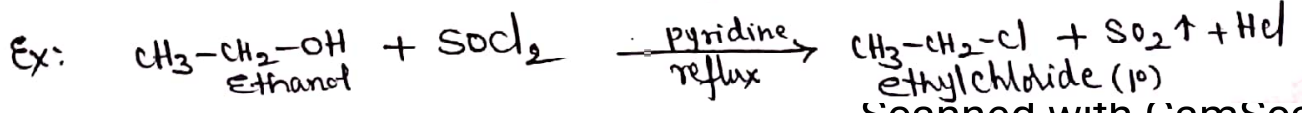
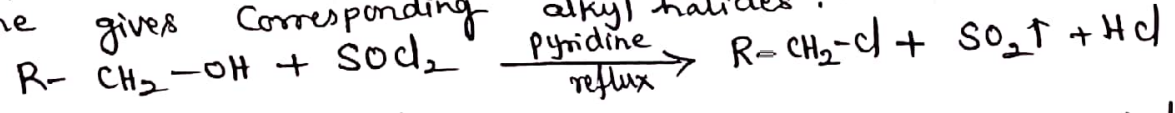
(a) By the action of  $PCl_5$  :-

Alcohols react with phosphorus pentachloride gives corresponding alkyl halides.



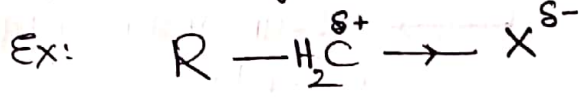
(b) Action with  $SOCl_2$  - Darzen's method

Alcohols when refluxed with thionyl chloride in presence of pyridine gives corresponding alkyl halides.



Chemical properties:

Nature of Carbon-halogen bond: In alkyl halides, the bond between Carbon and halogen is polar in nature. This is because halogen atom is more electronegative when compared to Carbon atom. As a result, the Carbon atom acquires partial positive charge ( $\delta^+$ ) and halogen atom acquires partial negative charge ( $\delta^-$ ).



Nucleophilic Substitution reactions

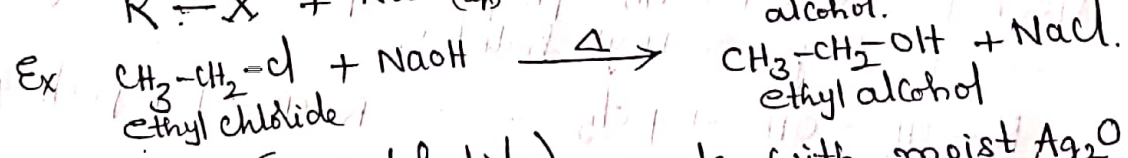
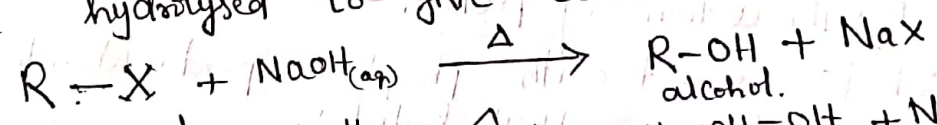
A reaction in which weaker nucleophile is substituted by stronger nucleophile is called nucleophilic substitution reaction ( $S_N$ ). The substitution takes place either by  $S_N^1$  or  $S_N^2$  mechanism or by a combination of both.

Depending on the nature of alkyl halides, they undergo nucleophilic substitution by  $S_N^1$  or  $S_N^2$  mechanism and elimination by  $E_1$  or  $E_2$  mechanism

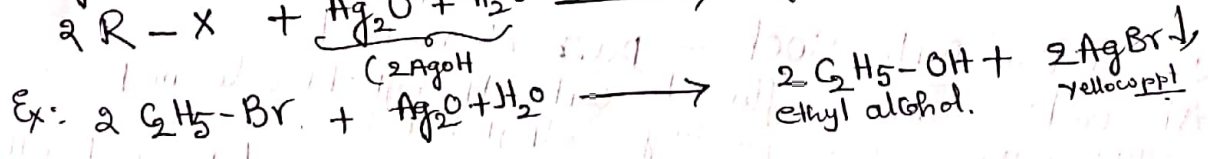
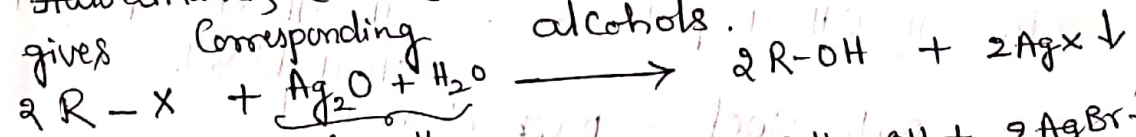
Type of alkyl halide	Substitution	Elimination
primary	$S_N^2$	$E_2$
Secondary	$S_N^1 + S_N^2$	$E_1 + E_2$
Tertiary	$S_N^1$	$E_1$

(1) Formation of alcohols (or Hydrolysis)

(a) When alkyl halides are boiled with aqueous NaOH (or KOH) they are hydrolysed to give alcohols.

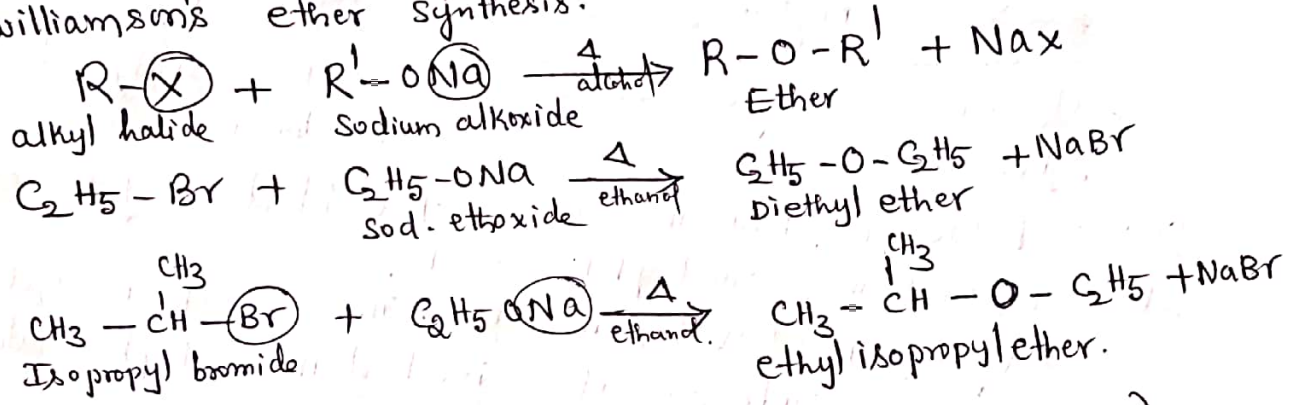


(b) Haloalkanes (or alkyl halide) reacts with moist  $Ag_2O$  gives corresponding alcohols.



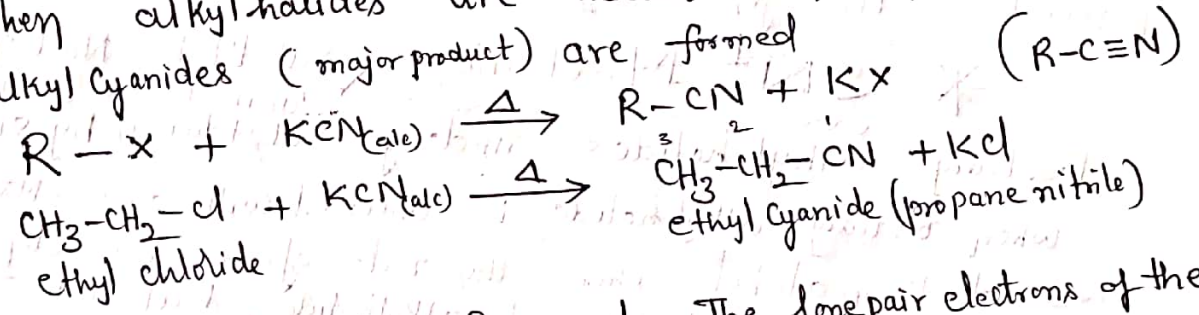
(2) Formation of Ethers (or Williamson's ether synthesis)

When alkyl halides are heated with sodium alkoxides gives corresponding ethers. This reaction is known as Williamson's ether synthesis.



(3) Formation of alkyl cyanides (or alkane nitrile)

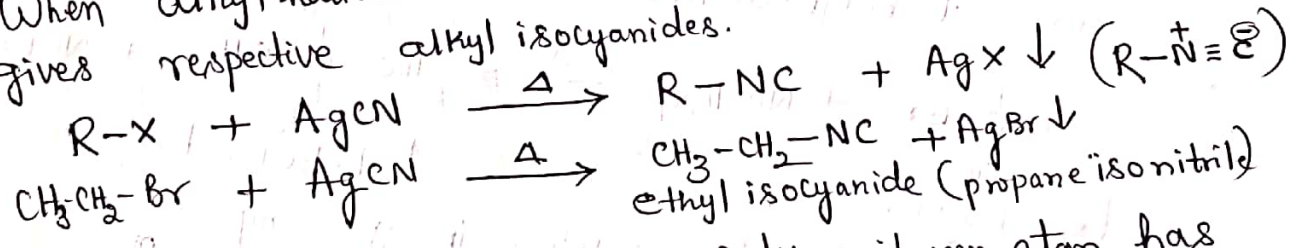
When alkyl halides are heated with aq. alcoholic KCN, alkyl cyanides (major product) are formed



Note: KCN is an ionic compound. The lone pair electrons of the carbon atom involved in the nucleophilic attack.

(4) Formation of alkyl isocyanide (or alkane isonitrile)

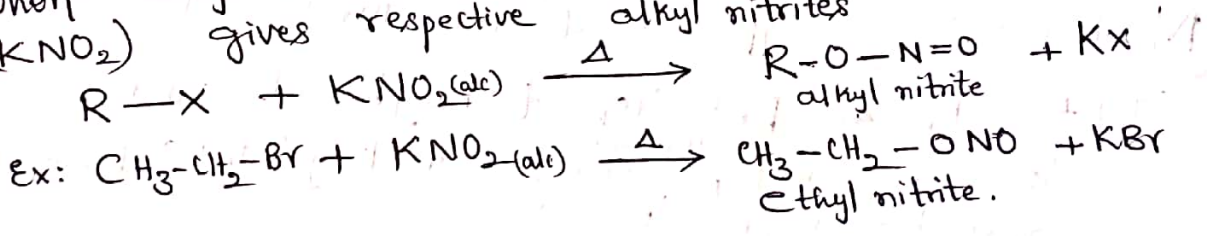
When alkyl halide are warmed with alcoholic silver cyanide gives respective alkyl isocyanides.



Note: AgCN is covalent in nature. Only nitrogen atom has lone pair electrons involved in nucleophilic attack.

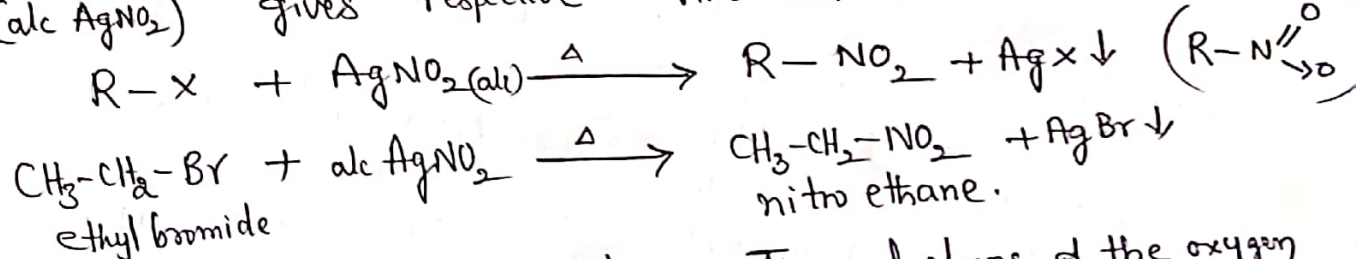
(5) Formation of alkyl nitrites :-

When alkyl halides are warmed with alcoholic potassium nitrite (KNO<sub>2</sub>) gives respective alkyl nitrites



(6) Formation of nitroalkane :

When alkyl halides are warmed with alcoholic silver nitrite (alc AgNO<sub>2</sub>) gives respective nitroalkane.



Note : KNO<sub>2</sub> is ionic in nature, The electrons of the oxygen atom involved in nucleophilic attack. AgNO<sub>2</sub> is Covalent in nature. The lone pair electrons of less electronegative nitrogen atom involved in nucleophilic attack.

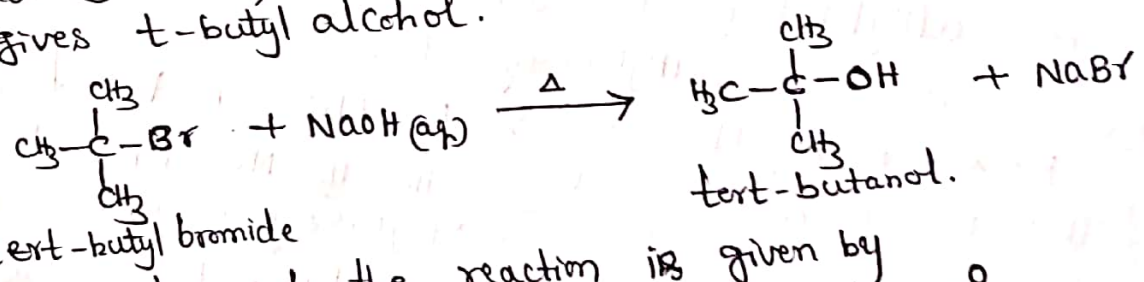
Halalkanes undergo nucleophilic substitution reaction proceeds through different mechanism namely SN<sup>1</sup> & SN<sup>2</sup>.

\* SN<sup>1</sup> Mechanism (Substitution Nucleophilic unimolecular @ 1<sup>st</sup> order reaction)

Tertiary alkyl halides undergo substitution by SN<sup>1</sup> mechanism.

When tertiary alkyl halide is warmed with aqueous NaOH @ KOH gives tertiary alcohol, where the rate of the reaction depends only on the concentration of alkyl halide, but not on the conc<sup>n</sup> of nucleophile (NaOH).

Ex:- When a tertiary butyl bromide is warmed with aqueous NaOH @ KOH, it undergoes nucleophilic substitution reaction gives t-butyl alcohol.



The rate of the reaction is given by

$$Rate \propto [tert\text{-butyl bromide}]^1 \times [NaOH]^0$$

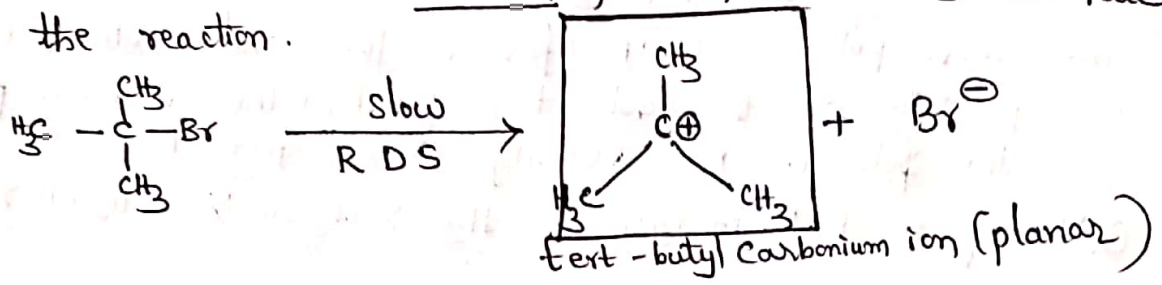
$$Rate = k [tert\text{ butyl bromide}]^1 [NaOH]^0$$

$$Order = 1 + 0 = 1$$

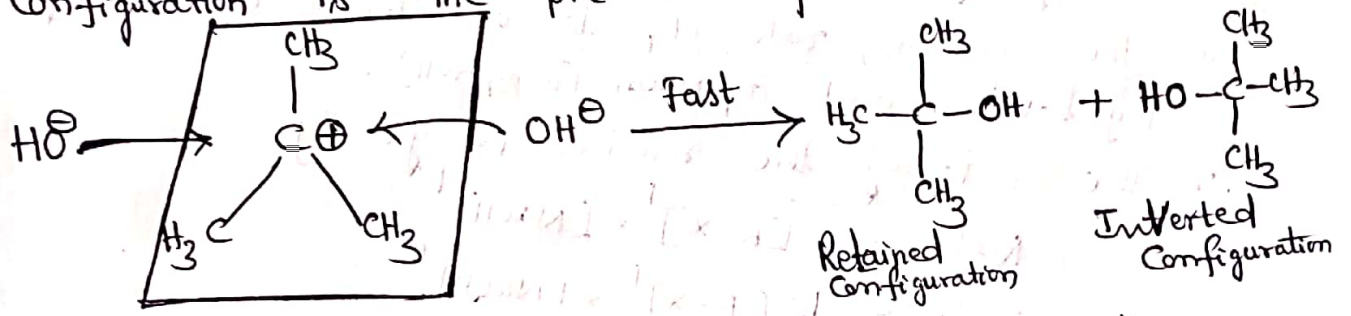
Mechanism : The mechanism involves two steps.

Step 1 : In the first step t-butyl bromide undergoes slow ionisation (or dissociation) + forming tertiary butyl Carbonium ion and bromide (Br<sup>-</sup>) ion.

First step is the slow step, which determines the rate of the reaction.



Step (2): The nucleophile  $\text{OH}^{\ominus}$  can attack the planar Carbonium ion from either side (direction) forming two enantiomers with inversion and retention of configuration (t-butyl alcohol). Enantiomer with Inverted configuration is the predominant product.



The rate of the reaction depends only on the concentration of tertiary butyl bromide and not on the concentration of aq. NaOH (or KOH). Hence, it is a unimolecular reaction or 1<sup>st</sup> order reaction.

\* Factors affecting the SN1 reaction:

① Structure of alkyl halide: → The rate of SN1 reaction depends on the stability of the carbocation formed. Higher the stability of carbocation, higher is the rate of SN1 reaction. The stability of the carbocations are in the order: Benzyl > Allyl > 3° > 2° > 1° >  $\text{CH}_3^{\oplus}$ .

② Nature of the leaving group: - Better the leaving group, easier is the formation of carbocation, higher the rate of reaction.  $\text{R-I} > \text{R-Br} > \text{R-Cl}$ .

③ Nature of the Nucleophile: Weaker nucleophile can favour the SN1 reaction.

④ Concentration of the nucleophile: Lower concentration of the nucleophile favour the SN1 reaction. (Since nucleophile not take part in the slow step reaction)

### (5) Nature of the Solvent :

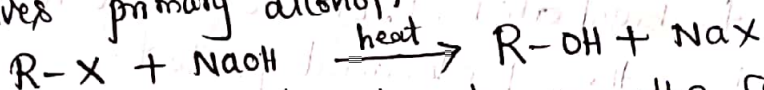
The more polar solvent favour the  $S_N1$  reaction. Greater (more) the polarity of the solvent, greater is the ionising power of the solvent. more easily cation formed.

Order of reactivity in case of  $H_2O > CH_3OH > C_2H_5OH > CH_3COOH$ .

### \* $S_N2$ Reaction Mechanism

(Substitution nucleophilic Bimolecular)  $\textcircled{2}$  2<sup>nd</sup> order reaction

When a primary alkyl halide is warmed with aq. NaOH  $\textcircled{2}$  KOH gives primary alcohol.



In this reaction, rate depends on the concentration of both alkyl halide and aq. NaOH (or aq. KOH).

$\therefore$  The rate of the reaction is given by

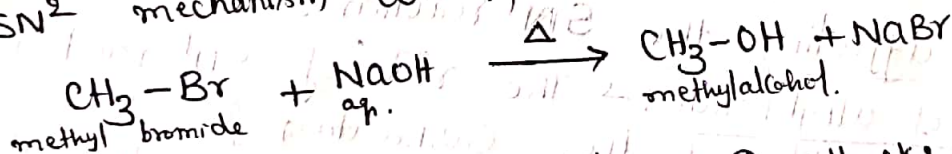
$$\text{Rate} \propto [R-X]^1 \times [NaOH]^1$$

$$\text{Rate} = k [R-X]^1 \times [NaOH]^1$$

$$\text{Order} = 1+1 = 2$$

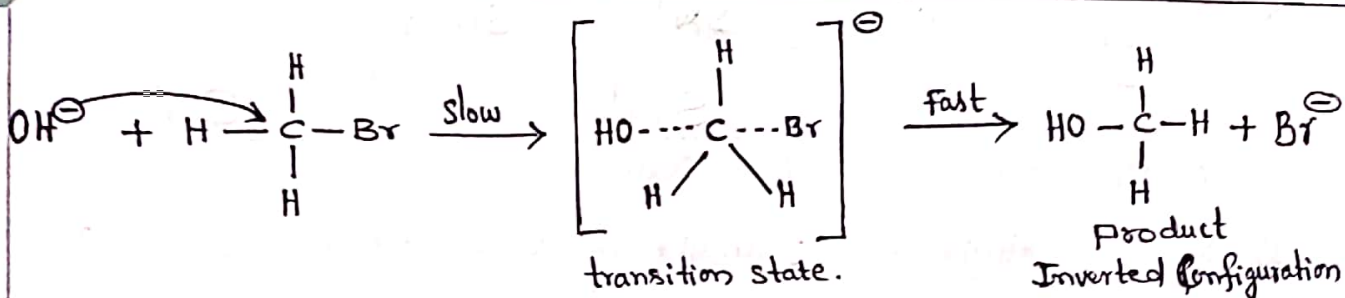
Hence it is Bimolecular reaction or 2<sup>nd</sup> order reaction.

Ex when methyl bromide (primary alkyl halide) is warmed with aq. NaOH (or KOH) gives methyl alcohol. The reaction follows  $S_N2$  mechanism which occurs in a single step.



Mechanism: The nucleophile  $OH^-$  attacks the primary-carbon atom from the opposite side of the outgoing nucleophile ( $Br^-$ ) forming a transition state. i.e. The new bond between the carbon and nucleophile is slowly formed, simultaneously the  $C-Br$  bond becomes gradually weakened. The half bonded state is known as "transition state". As the transition state is unstable it decomposes giving an inverted product.





The halide ion ( $\text{Br}^-$ ) leaves the transition state rapidly and the product has inverted configuration (Walden inversion).

The reaction occurs in single step in which the slow step involves both alkyl halide and  $\text{NaOH}$ . Hence, the rate of the reaction depends on the concentration of both primary alkyl halide and  $\text{NaOH}$ .  
 $\therefore$  It is a bimolecular reaction or 2<sup>nd</sup> Order reaction.

### \* Factors affecting $\text{SN}^2$ reaction:

(1) Structure of alkyl halide (steric effect): Less bulkier (smaller) the group, more is the reactivity of the alkyl halide towards  $\text{SN}^2$  reaction  
 $\text{CH}_3\text{-X} > 1^\circ > 2^\circ > 3^\circ$

(2) Strength (Nature) of nucleophile:  
 Higher the electron donating tendency, higher the reactivity of  $\text{SN}^2$  reaction, i.e. the stronger nucleophile favour the  $\text{SN}^2$  reaction.  
 $\text{CN}^- > \text{I}^- > \text{C}_2\text{H}_5\text{O}^- > \text{OH}^- > \text{C}_6\text{H}_5\text{O}^- > \text{Cl}^- > \text{CH}_3\text{COO}^-$

(3) Nature of the leaving group:  
 Rate of  $\text{SN}^2$  reaction depends on the basicity of the leaving group, weaker the base best is the leaving group.  
 $\text{I}^- > \text{Br}^- > \text{OH}^- > \text{CH}_3\text{COO}^- > \text{C}_2\text{H}_5\text{O}^-$

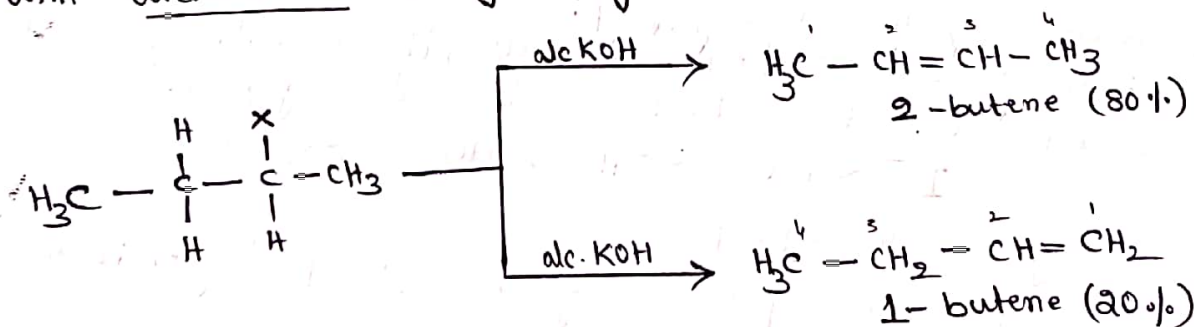
(4) Polarity of the solvent:  
 Lesser the polarity of the solvent higher is the reactivity.

\* Difference between SN<sup>1</sup> and SN<sup>2</sup> mechanism:

Factors	SN <sup>1</sup>	SN <sup>2</sup>
1) Reaction Kinetics	First Order reaction	Second order reaction
2) Nature of alkyl halides	3° alkyl halides more reactive	1° alkyl halides more reactive.
3) Nature of nucleophile	weaker and stronger nucleophiles favours SN <sup>1</sup> .	Stronger nucleophiles favours SN <sup>2</sup> .
4) Concentration of nucleophile	Lower Concentration of nucleophile favours SN <sup>1</sup> .	Higher Concentration of nucleophile favours SN <sup>2</sup> .
5) Reactive intermediate	Carbocation	Transition state
6) Nature of solvent	polar solvent favour SN <sup>1</sup>	non-polar solvent favours SN <sup>2</sup>
7) Stereochemistry	Inversion and Retention of Configuration of product.	Inversion of Configuration of product (Walden Inversion)

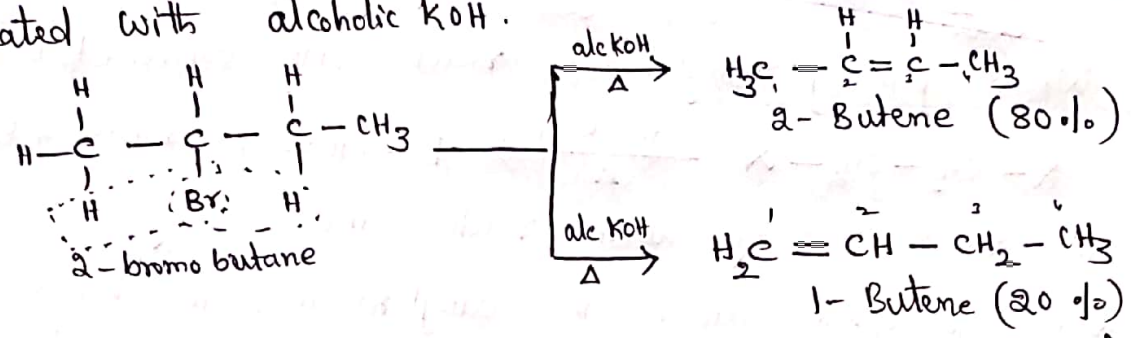
Elimination Reactions

\* "The reaction in which the atoms (groups) are lost from the adjacent Carbon atoms results in the formation of C=C (or) C≡C are called 1,2-elimination reaction or β-elimination reaction. When alkyl halides containing β-hydrogen atom, when treated with alcoholic KOH dehydrohalogenation takes place to give alkene."



\* Saytzeff's Rule: State Saytzeff's rule with an Example.  
 "In the dehydrohalogenation reactions, the preferred product is the more substituted alkene. Alkene formed has greater number of alkyl groups attached to the doubly bonded Carbon atom."

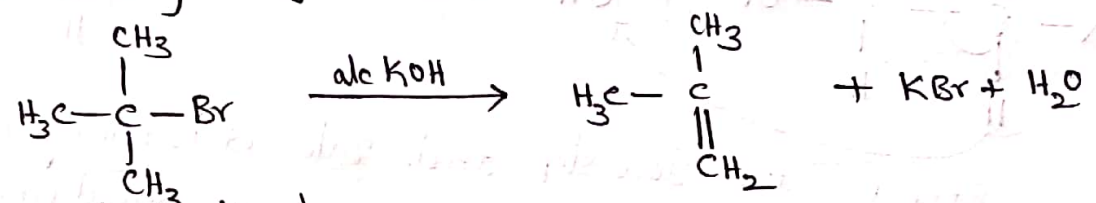
Ex: Two alkenes are possible when 2-bromo butane is heated with alcoholic KOH.



2-Butene is more substituted alkene than 1-Butene, hence 2-Butene is the major product.

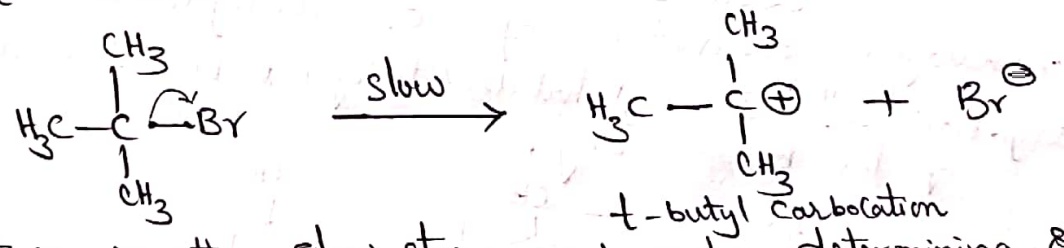
E<sub>1</sub> or E<sub>N</sub><sup>1</sup> mechanism

When tertiary alkyl halide react with alcoholic KOH gives alkene.



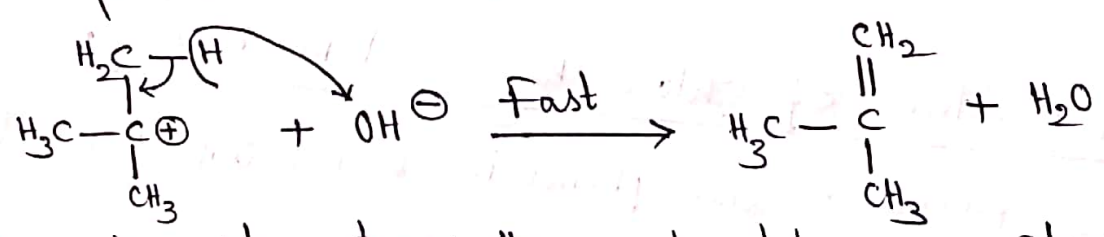
The mechanism of above reaction involves two steps.

Step(i) The Carbon-halogen bond breaks heterolytically forming the intermediate Carbocation.



This is the slow step and rate determining step.

Step(ii) The nucleophile (OH<sup>-</sup>) abstracts proton from the β-Carbon to form alkene.

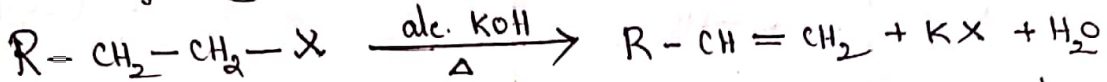


Since the slow step is the rate determining step and it involves only one reactant, hence it is a first order reaction.

The order of reactivity of an alkyl halide having different alkyl groups towards E<sub>1</sub> reaction is 3° > 2° > 1°.

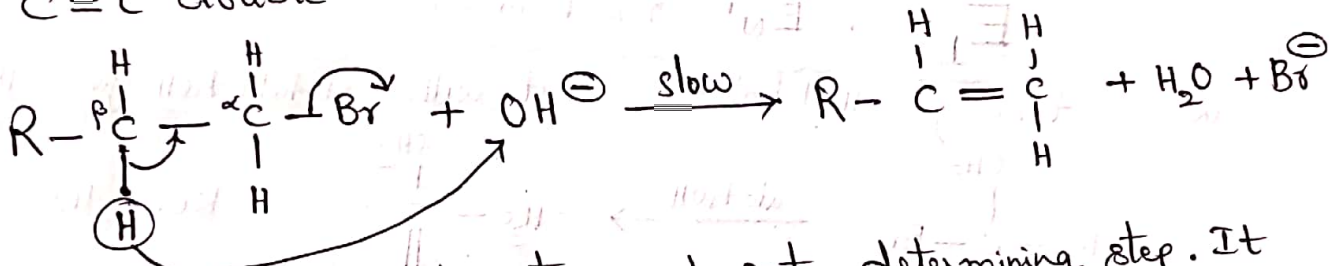
E<sub>2</sub> or E<sub>N2</sub> Mechanism

When primary alkyl halide react with alcoholic KOH gives alkenes.



The mechanism of above reaction involves only one step.

When nucleophile attack the alkyl halide, the removal of hydrogen atom from  $\beta$ -Carbon atom, and removal of halide ion from  $\alpha$ -Carbon atom are occur simultaneously to form C=C double bond.

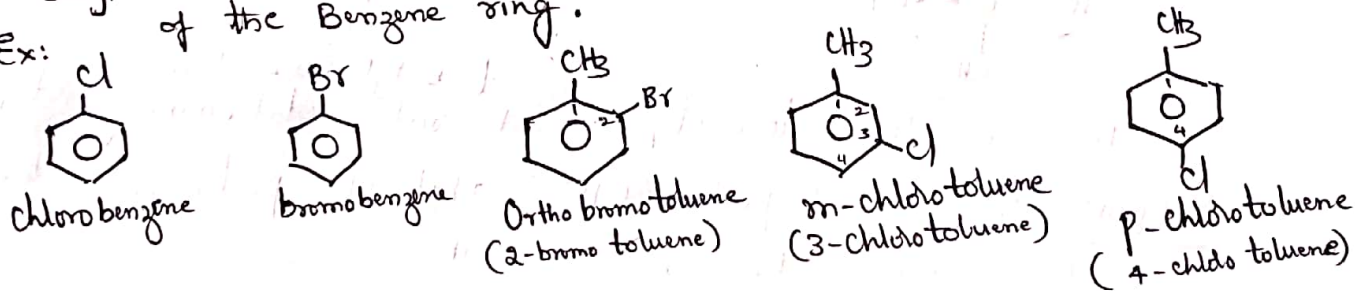


This step is the slow step and rate determining step. It involves two reactant molecules, hence it is second order reaction.

ARYL HALIDES

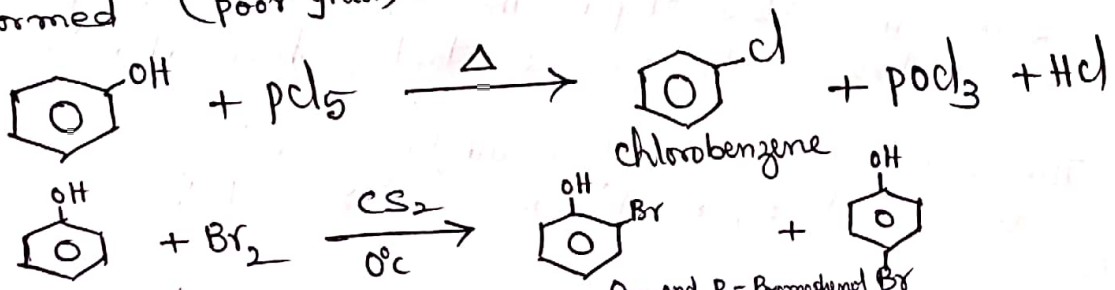
"Monohalogen derivatives of aromatic hydrocarbons are called aryl halides". In aryl halides, halogen is bonded directly to a Carbon of the Benzene ring.

Ex:



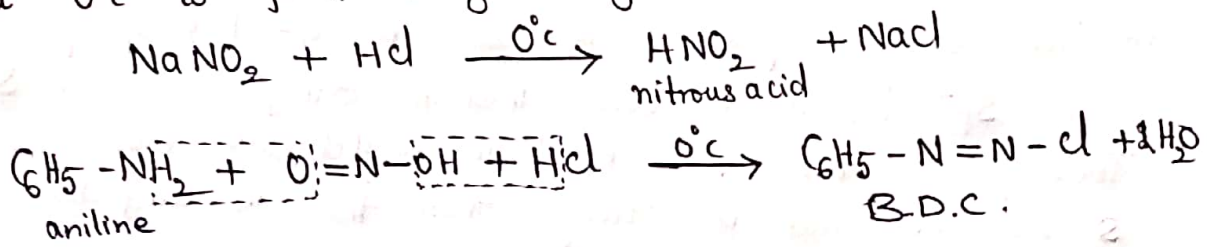
Preparation of chloro, bromo and iodobenzenes:

① From Phenol: When phenol is heated with PCl<sub>5</sub>, chlorobenzene is formed (poor yield).



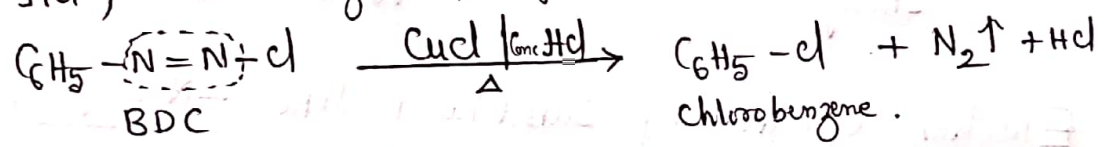
\* (2) From Aniline (By diazotisation followed by Sandmeyer's reaction)

step (i) Diazotisation: Aniline is treated with sodium nitrite and dil HCl at 0°C to form benzene diazonium chloride. (BDC).

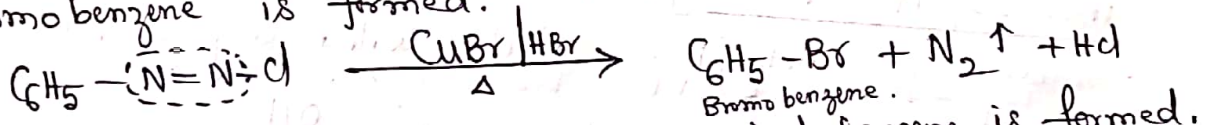


step (ii) Sandmeyer's reaction:

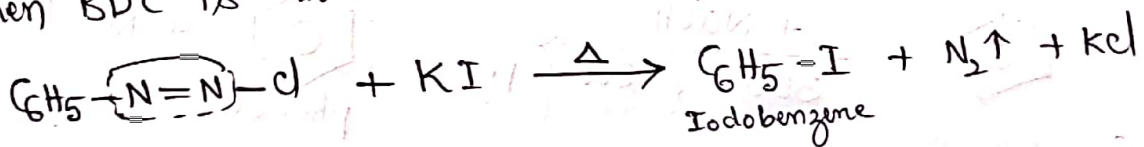
When Benzene diazonium chloride is heated with cuprous chloride (CuCl) in HCl, chlorobenzene is formed. This type reaction is called Sandmeyer's reaction.



When BDC is heated with cuprous bromide (CuBr) in HBr, bromobenzene is formed.



When BDC is heated with KI, iodo benzene is formed.



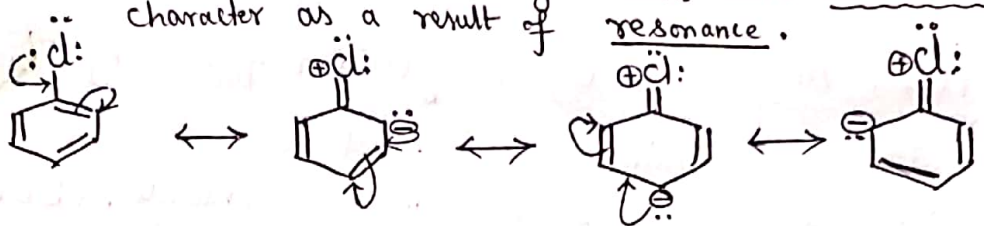
### Reactions of chlorobenzene

#### Aromatic nucleophilic Substitution:

Aryl halides like chlorobenzene, bromobenzene etc are least reactive because Carbon-halogen bond has double bond character as a result of resonance and is very strong. Hence aryl halides (ex chlorobenzene) undergo nucleophilic substitution only under drastic conditions (high temp, high pressure, catalyst etc) with strong bases.

Note: chlorobenzene is less reactive because

(i) The C-Cl bond in chlorobenzene has some double bond character as a result of resonance.

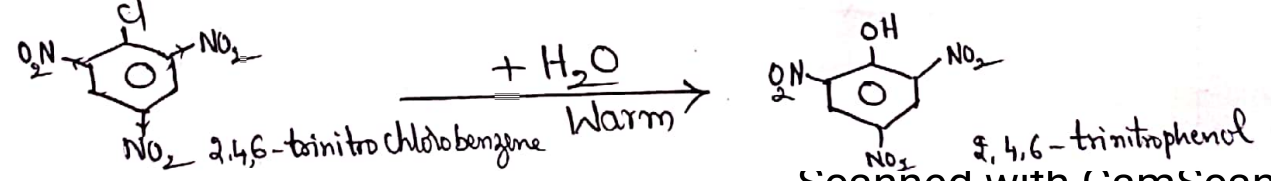
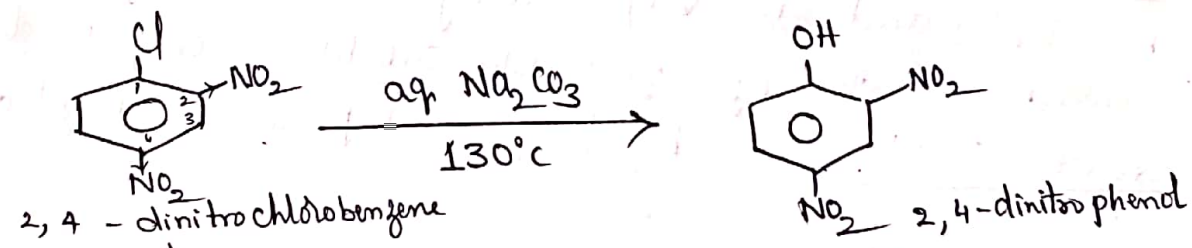
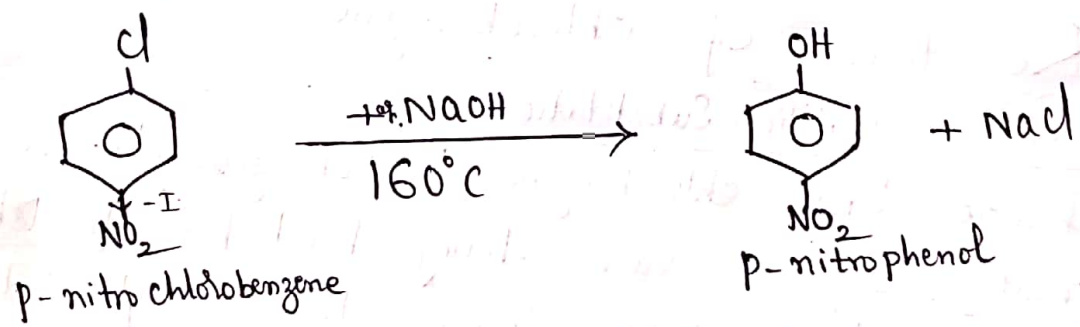
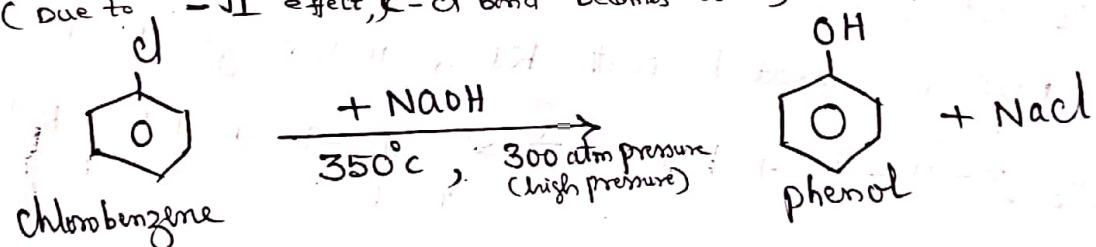


(ii) The orbitals of the Carbon atom in C-Cl bond of aryl halide are  $sp^2$  hybridised while that in alkyl chloride are  $sp^3$  hybridised. Therefore, the C-Cl bond in aryl chloride has more s-character and is stronger than in alkyl chloride.



(3 Marks)  
\*

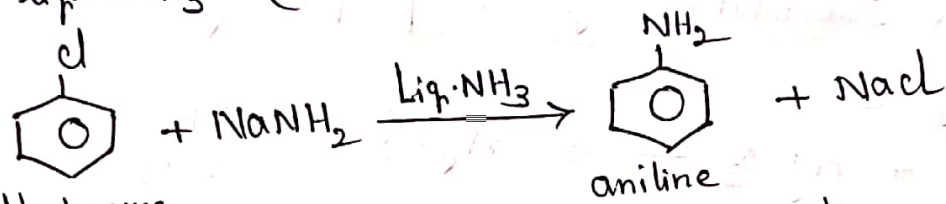
Electron withdrawing substituents like  $-NO_2$  group at Ortho or para positions to chlorine atom (halogen) greatly increases its reactivity. Reactivity increases with increasing number of Ortho/para electron withdrawing substituents ( $NO_2$ ).  
(Due to  $-I$  effect, C-Cl bond becomes weak).



\* Benzene mechanism: (3M)

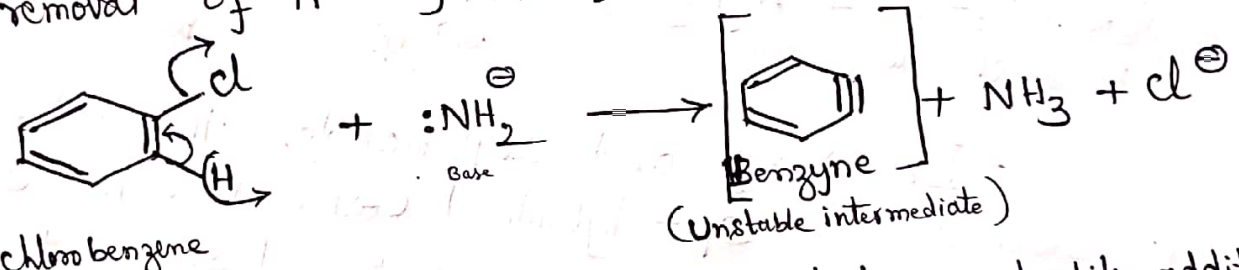
Aryl halides not containing electron withdrawing groups, undergo nucleophilic substitution only with strong bases like Sodamide. An intermediate called 'benzynes' is formed, the mechanism is known as benzyne mechanism or elimination - addition mechanism.

Ex: chlorobenzene (or bromobenzene) reacts with sodamide in  $liq.NH_3$  (or  $KNH_2/liq.NH_3$ ) to form aniline.

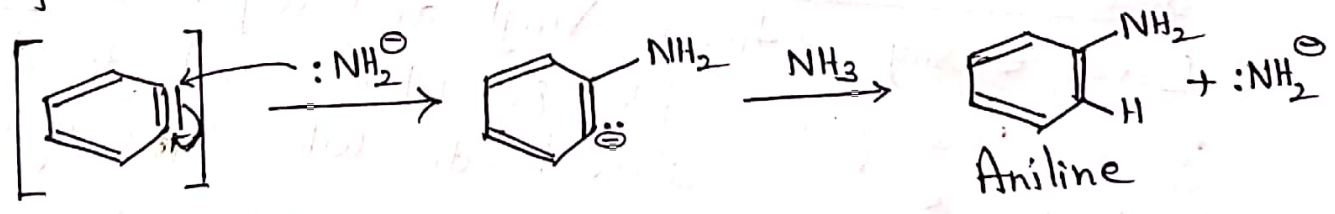


Mechanism involves two steps: elimination and addition.

(i) Elimination Step: Benzynes intermediate is formed through removal of  $H^+$  by  $:NH_2^-$  and loss of  $Cl^-$ .



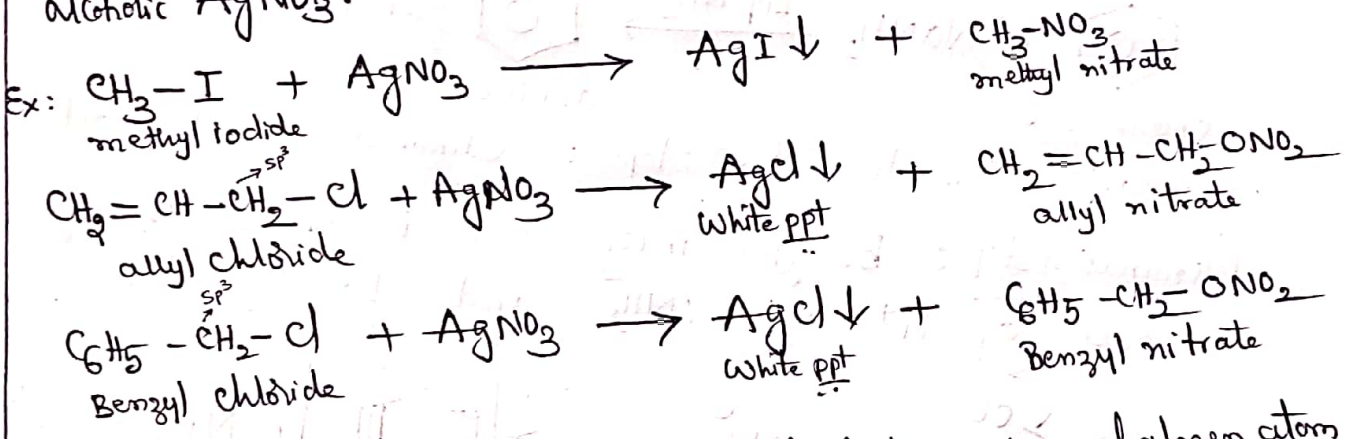
(ii) Addition step: A Carbanion is formed by nucleophilic addition of  $NH_2^-$  to benzyne. The Carbanion abstracts a proton from the solvent ( $NH_3$ ) to give the substitution product.



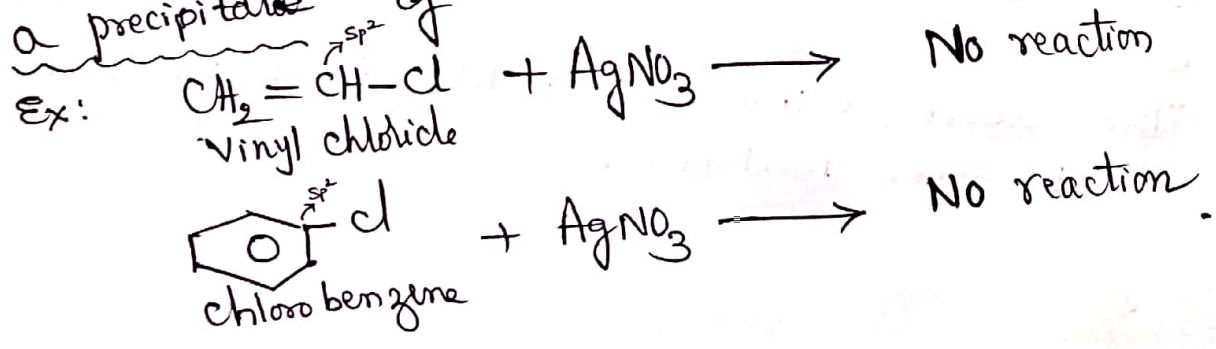
The above elimination - addition mechanism is known as Benzynes mechanism.

\* Reactivity and Relative Strength of C-X bond in alkyl, allyl, benzyl, vinyl and aryl halides.

In alkyl, allyl and benzyl halides the halogen atom is attached to sp<sup>3</sup> hybridised Carbon atom. The C-X bond has less s-character, longer bond length and weaker bond than that in vinyl and aryl halides. The C-X bond can break easily. Hence alkyl, allyl and benzyl halides readily undergo nucleophilic substitution gives a precipitate of silver halide with alcoholic AgNO<sub>3</sub>.



In vinyl and aryl halides, the halogen atom is attached to sp<sup>2</sup> hybridised Carbon atom. The C-X bond has more s-character, shorter bond length and stronger than that in alkyl, allyl and benzyl halides. The C-X bond has double bond character due to resonance, it cannot break easily. Hence vinyl and aryl halides do not readily undergo nucleophilic substitution and do not give a precipitate of silver halide with alcoholic AgNO<sub>3</sub>.





# ALKYL and ARYL HALIDES

17

II SEM BSc.

ASSIGNMENT

HSM

## PART A (2 Marks Questions)

- 1) What are alkyl halides? Give an example.
- 2) What are the types of alkyl halides? Give one example each.
- 3) Give the IUPAC names of the following compounds
  - (i)  $\text{CH}_3 - \overset{\text{FH}_3}{\text{C}} - \text{CH}_2 - \text{Cl}$
  - (ii)  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \overset{\text{Cl}}{\text{C}} = \text{CH}_3$
  - (iii)  $\text{CH}_3 - \overset{\text{H}_2\text{C}}{\text{C}} - \text{CH}_2 - \text{Br}$
  - (iv)  $\text{CH}_3 - \overset{\text{FH}_3}{\underset{\text{CH}_3}{\text{C}}} - \text{Cl}$
- 4) State Markownikoff's rule. with an example.
- 5) What happens when alkyl halides is heated with aq. alk. KCN?
- 6) Explain Williamson's Ether synthesis. with an example.
- 7) How do you prepare alcohols from alkyl halides?
- 8) What are the factors affecting  $\text{SN}^1$  reaction
- 9) What are the factors affecting  $\text{SN}^2$  reaction.
- 10) What are the differences betn  $\text{SN}^1$  and  $\text{SN}^2$  mechanism.
- 11) What are Elimination reactions?
- 12) State Saytzeff rule with an example.
- 13) How can you convert aniline to chlorobenzene
- 14) What is the action of  $\text{PCl}_5$  and  $\text{SOCl}_2$  on alcohols?
- 15) Why chlorobenzene does not give precipitate even on prolonged heating with alc.  $\text{AgNO}_3$ ?
- 16) What are aryl halides? Give two examples.
- 17) How do you convert phenol to chlorobenzene?
- 18) Explain Sandmeyer's reaction with an example.
- 19) Write all the possible isomers of  $\text{C}_4\text{H}_9\text{Cl}$ .
- 20) Write the structural formula of (i) neopentyl chloride  
(ii) Benzynes.

## PART-B (10 Marks. E.)

- (1) (a) Give any two methods of preparation of alkyl halides ?
- (b) Explain Benzyne mechanism with an example.
- (c) Discuss  $S_N^2$  reaction mechanism with an example (4+3+3)
- (2) (a) Discuss  $S_N^1$  reaction mechanism with an example.
- (b) Discuss the effect of  $-NO_2$  group on aromatic nucleophilic substitution of chlorobenzene.
- (c) How are (i) alkyl isonitrite  
(ii) diethyl ether  
(iii) nitro ethane (alkane) is prepared from alkyl halides (4+3+3)
- (3) (a) Compare the reactivity of C-X bond in allyl, vinyl, alkyl and benzyl halides. Justify your answer.
- (b) How is chlorobenzene synthesised from aniline? Name the reaction.
- (c) 2,4,6-trinitrochlorobenzene is easily hydrolysed but chlorobenzene does not explain why? (4+3+3)
- (4) (a) Explain  $E_1$  mechanism with an example
- (b) Allyl chloride gives a white ppt of AgCl with aq.  $AgNO_3$  But vinyl chloride does not. Explain?
- (c) (4+3+3)

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