Raffles Institution
Year 6 H2 Chemistry 2023
Lecture Notes 15 – Halogen Derivatives

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Content

- Halogenoalkanes
  (i) nucleophilic substitution
  (ii) elimination
- Relative strength of the C–Hal bond
- Unreactivity of halogenoarenes

Learning Outcomes

Candidates should be able to:

(a) recall the chemistry of halogenoalkanes as exemplified by

- **(i)** the following nucleophilic substitution reactions of bromoethane: hydrolysis; formation of nitriles; formation of primary amines by reaction with ammonia
- **(ii)** the elimination of hydrogen bromide from 2-bromopropane

(b) describe and explain the mechanisms of nucleophilic substitutions in halogenoalkanes:

- **(i)** S_N1, in terms of stability of the carbocation intermediates
- **(ii)** S_N2, in terms of steric hindrance of the halogenoalkanes

(c) explain the stereochemical outcome in nucleophilic substitution involving optically active substrates:

- **(i)** inversion of configuration in S_N2 mechanism
- **(ii)** racemisation in S_N1 mechanism

(d) interpret the different reactivities of halogenoalkanes, with particular reference to hydrolysis, and to the relative strengths of the C-Hal bonds

(e) explain the unreactivity of chlorobenzene compared to halogenoalkanes towards nucleophilic substitution, in terms of the delocalisation of the lone pair of electrons on the halogen and steric hindrance

(f) suggest characteristic reactions to differentiate between:

- **(i)** different halogenoalkanes
- **(ii)** halogenoalkanes and halogenoarenes

e.g. hydrolysis, followed by testing of the halide ions

(g) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness

(h) recognise the concern about the effect of chlorofluoroalkanes (CFCs) on the ozone layer
[the mechanistic details of how CFCs deplete the ozone layer are not required]

Lecture Outline

1. Introduction
2. Physical Properties
3. Preparation
4. Characteristic Reactions
5. The S_N2 Mechanism
6. The S_N1 Mechanism
7. Comparison between S_N2 & S_N1
8. Substitution Reactions
9. Elimination Reactions
10. Halogenoarenes
11. Reactions of Halogenoarenes
12. Distinguishing Tests
13. Uses of Halogen Derivatives
14. CFCs and the Ozone Layer
15. Summary

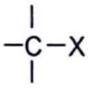
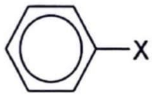
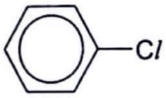
References

1. Cambridge International AS and A Level Chemistry Course Book *by Lawrie Ryan and Roger Norris*
2. Organic Chemistry *by Leroy G. Wade*
3. Organic Chemistry *by Janice Gorzynski Smith*
4. www.chemguide.co.uk

1 Introduction

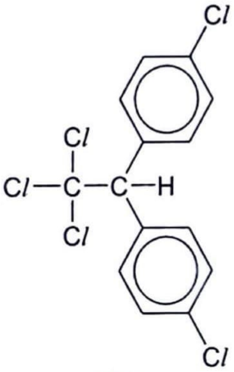
- **Halogen derivatives** are halogen-containing organic compounds. Their molecules contain the **C–X** bond where X = F, Cl, Br or I.

- In H2, the focus will be mainly on halogenoalkanes and halogenoarenes.
  - **Halogenoalkanes** (or **alkyl halides**) are **halogen derivatives of alkanes** in which one or more H atoms of the alkane molecule are replaced by a halogen atom.
  - **Halogenoarenes** (or **aryl halides**) are **halogen derivatives of arenes** in which one or more H atoms of the benzene ring in an arene molecule are replaced by a halogen atom. The **halogen atom is bonded directly to the benzene ring.**

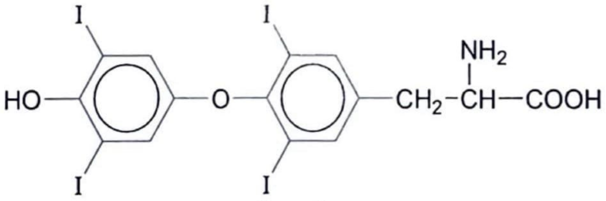
Class of compounds	**Homologous series**	**Structure**	**General formula**	**Example**
Halogen derivatives –X	halogenoalkane (or alkyl halide)	 $-\overset{|}{\underset{|}{C}}-X$	RX	$CH_3CH_2–Cl$ chloroethane
	halogenoarene (or aryl halide)		ArX	 chlorobenzene
Note:		X = F, Cl, Br, I	R = alkyl group or substituted alkyl group Ar = aryl group	

- Examples of halogen derivatives and their usefulness:

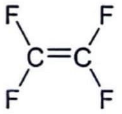
$CHCl_3$	$CHClF_2$	CH_3CCl_3	$CF_3CHClBr$
trichloromethane (chloroform) solvent	chlorodifluoromethane (Freon-22®) refrigerant	1,1,1-trichloroethane cleaning fluid	halothane anaesthetic



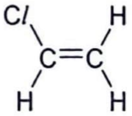
DDT
insecticide



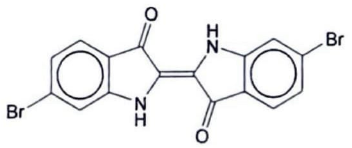
thyroxine
thyroid hormone



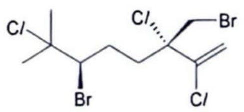
tetrafluoroethene
monomer for Teflon®



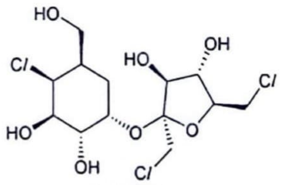
chloroethene
monomer for PVC



Tyrian purple
Isolated from the sea snail *Hexaplex trunculus*, this compound is one of the oldest known dyes and was used to make royal clothing thousands of years ago



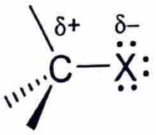
Halomon
Isolated from the red algae *Portieria hornermann*, this compound is currently in clinical trials for use as an antitumour agent



Sucralose
An artificial sweetener, sold under the trade name Splenda®

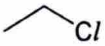
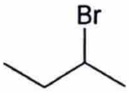
1.1 Halogenoalkanes

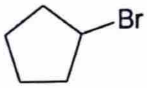
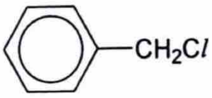
- Halogenoalkanes are commonly denoted by **RX**, where R is an **alkyl** group or a **substituted alkyl** group and X is F, C*l*, Br or I.
- The **general formula** for mono-substituted saturated halogenoalkanes is $C_nH_{2n+1}X$
- Each halogenoalkane has at least one halogen atom bonded to a **sp³ hybridised carbon atom** of an alkyl group.
- The carbon–halogen bond (i.e. C–X bond) in a halogenoalkane (R–X) is **polar** because the halogen atom is **more electronegative** than the carbon atom.



1.2 Nomenclature of halogenoalkanes

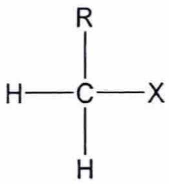
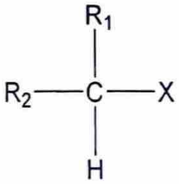
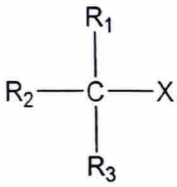
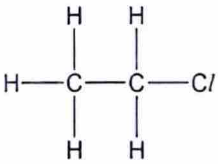
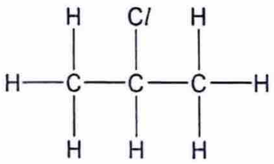
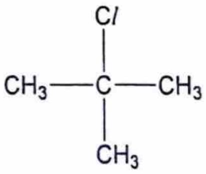
- Halogenoalkanes are named as **derivatives** of the corresponding **alkanes**. The **position** of the halogen atom is indicated (if necessary) by the numbering of the carbon atom to the chain to which it is attached.

Structure	IUPAC Name
CH_3CH_2Cl or 	chloroethane
$Br{-}CH_2CH_2CH_2{-}Br$	1,3-dibromopropane
$CH_3CH_2{-}CHBr{-}CH_3$ or 	2-bromobutane
$CH_3{-}CH{=}CH{-}CHI{-}CH_3$	4-iodopent-2-ene

Structure	IUPAC Name
	bromocyclopentane
	(chloromethyl)benzene **Note!** • an aromatic compound (because a benzene ring is present) • a chloroalkane • **not** a chloroarene (because C*l* is **not** directly bonded to the benzene ring)

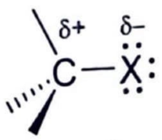
1.3 Classification of halogenoalkanes

- Halogenoalkanes can be classified as **primary** (1°), **secondary** (2°) or **tertiary** (3°) depending on the **number** of **alkyl or aryl** groups that are **attached** to the **carbon** atom that is bonded to the halogen.

Classification of RX	**Primary (1°)**	**Secondary (2°)**	**Tertiary (3°)**
Description	**One** alkyl group is attached to the carbon atom bearing the halogen.	**Two** alkyl groups are attached to the carbon atom bearing the halogen.	**Three** alkyl groups are attached to the carbon atom bearing the halogen.
General Structure	 $\mathrm{H{-}\overset{\displaystyle R}{\underset{\displaystyle H}{C}}{-}X}$	 $\mathrm{R_2{-}\overset{\displaystyle R_1}{\underset{\displaystyle H}{C}}{-}X}$	 $\mathrm{R_2{-}\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{C}}{-}X}$
Example	 $\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}Cl}$ chloroethane	 $\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H}$ 2-chloropropane	 $\mathrm{CH_3{-}\overset{\displaystyle Cl}{\underset{\displaystyle CH_3}{C}}{-}CH_3}$ 2-chloro-2-methylpropane

2 Physical Properties of Halogenoalkanes

- Halogenoalkanes are **polar** compounds. Their molecules contain the **polar C–X** bond.
- The types of intermolecular forces that exist between halogenoalkane molecules are
  - **permanent dipole-permanent dipole** forces, and
  - **instantaneous dipole-induced dipole** forces.



2.1 Boiling point

(a) The boiling point of a halogenoalkane RX is higher than that of the corresponding alkane.

	Boiling point / °C
CH_3CH_2Cl	12
CH_3CH_3	–89

chloroethane (polar)
- permanent dipole-permanent dipole forces and
- instantaneous dipole-induced dipole forces
ethane (non-polar)
- instantaneous dipole-induced dipole forces

(b) For halogenoalkanes RX with the same X, the boiling point increases as the size of R increases.

RX	Boiling point / °C
CH_3Cl	–24
CH_3CH_2Cl	12
$CH_3CH_2CH_2Cl$	47

As the size of R increases, there is a **larger** and **more polarisable** electron cloud as the **number of electrons per molecule** increases.

Hence, the strength of instantaneous dipole-induced dipole increases.

(c) For halogenoalkanes RX with the same R, the boiling point increases as the size of X increases.

RX	Boiling point / °C
CH_3CH_2F	–37
CH_3CH_2Cl	12
CH_3CH_2Br	38
CH_3CH_2I	72

As the size of X increases, there is a **larger** and **more polarisable** electron cloud as the **number of electrons per molecule** increases.

Hence, the strength of instantaneous dipole-induced dipole increases.

2.2 Solubility

- Although halogenoalkanes are polar, they have **poor solubility in water**. This is mainly because they are **not** able to interact with water molecules via hydrogen bonding.
- Halogenoalkanes are **soluble in organic solvents** such as hexane and tetrachloromethane. This is because they are able to interact with these solvent molecules via instantaneous dipole-induced dipole forces.

2.3 Density

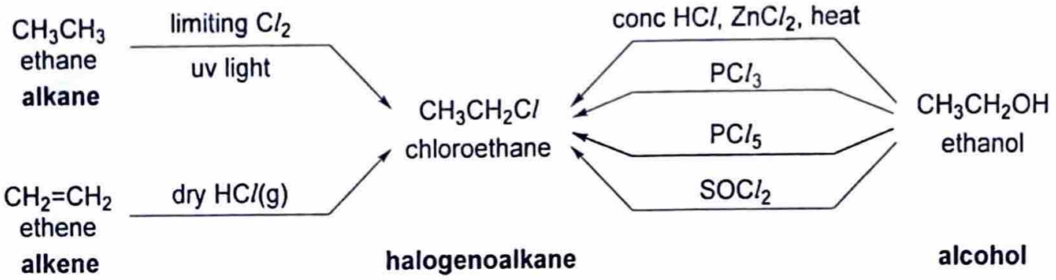
RX	Density at 20 °C/g cm^{-3}
$CH_3CH_2CH_2Cl$	0.890
CH_2Cl_2	1.33
CH_3CH_2Br	1.44

(no need to memorise)

- Fluoroalkanes and monochloroalkanes are less dense than water.
- In general, chloroalkanes with two or more chlorine atoms, bromoalkanes and iodoalkanes are denser than water.

3 Preparation of Halogenoalkanes

- Halogenoalkanes may be prepared in the laboratory from alkanes, alkenes and alcohols.



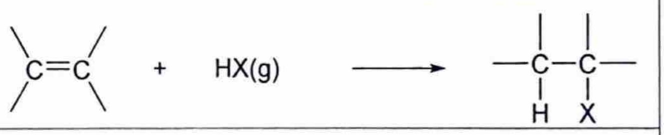
3.1 From alkanes

Reaction	$R{-}H + X_2 \xrightarrow[\text{uv light}]{\text{limiting } X_2} R{-}X + HX$
Reagents and conditions	X_2 (X = Cl or Br), uv light (or sunlight or heat)
Mechanism	free-radical substitution

- **Note:** This is not a good method to prepare a halogenoalkane because poly-substitution can occur, leading to a mixture of products. The use of a limiting amount of X_2 helps to minimise poly-substitution.

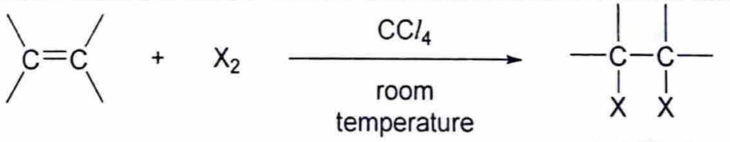
3.2 From alkenes

(a) Preparation of halogenoalkanes with **only one halogen atom per molecule**

Reaction	
Reagents and conditions	dry gaseous HX (X = Cl, Br or I), room temperature
Mechanism	electrophilic addition

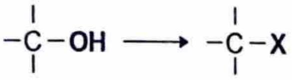
- **Note:** If the alkene is "unsymmetrical", the major product is formed from the more stable carbocation intermediate (refer to lecture notes on Alkenes). For example, when $CH_2{=}CHCH_3$ is reacted with HBr, the major product is $CH_3CHBrCH_3$.

(b) Preparation of halogenoalkanes with **two adjacent halogen atoms per molecule**

Reaction	 vicinal dihalide
Reagents and conditions	X_2 (X = Cl or Br) in CCl_4, room temperature
Mechanism	electrophilic addition

3.3 From alcohols

- Alcohols can undergo **nucleophilic substitution** reactions in which the –OH group is replaced by a halogen atom X. The reaction involves the cleavage of the C–O bond and the formation of the C–X bond.

$R\text{–}OH \longrightarrow R\text{–}X$	 $-\overset{\vert}{\underset{\vert}{C}}-OH \longrightarrow -\overset{\vert}{\underset{\vert}{C}}-X$	**Reagents and conditions:** (a) dry HX, heat (X = Cl, Br or I) (b) PX_3 (X = Cl, Br or I) (c) PCl_5 (d) $SOCl_2$

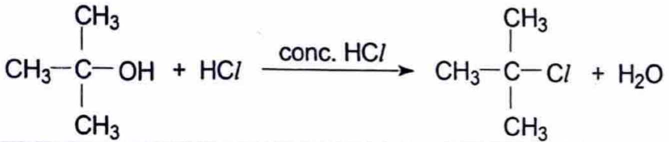
(a) Using dry hydrogen halides and heat

- With hydrogen chloride and heat (or concentrated HCl and heat)

$$R\text{–}OH + HCl \xrightarrow[\text{heat}]{} R\text{–}Cl + H_2O$$

Examples:

$$CH_3CH_2OH + HCl \xrightarrow[\text{heat}]{\text{conc. HCl, ZnCl}_2} CH_3CH_2\text{–}Cl + H_2O$$



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + HCl \xrightarrow{\text{conc. HCl}} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl + H_2O$$

Note:
- **$ZnCl_2$** (a Lewis acid) is sometimes added to promote this reaction.

- With hydrogen bromide and heat

$$R\text{–}OH + HBr \xrightarrow[\text{heat}]{} R\text{–}Br + H_2O$$

$$R\text{–}OH + HBr \xrightarrow[\text{heat}]{\text{KBr(s), conc. H}_2\text{SO}_4} R\text{–}Br + H_2O$$

Note:
- HBr is generated *in situ* from the reaction between conc. H_2SO_4 and KBr.

  $KBr(s) + H_2SO_4(l) \longrightarrow KHSO_4(s) + HBr(g)$
  (not in syllabus)

- With hydrogen iodide and heat

$$R\text{–}OH + HI \xrightarrow[\text{heat}]{} R\text{–}I + H_2O$$

$$R\text{–}OH + HI \xrightarrow[\text{heat}]{\text{KI(s), conc. H}_3\text{PO}_4} R\text{–}I + H_2O$$

Note:
- HI is generated *in situ* from the reaction between conc. H_3PO_4 and KI.

  $KI(s) + H_3PO_4(l) \longrightarrow KH_2PO_4(s) + HI(g)$

(not in syllabus: HI(g) ***cannot*** *be prepared with conc. H_2SO_4 + KI because conc. H_2SO_4 would oxidise I^- to I_2 instead of producing HI. Hence conc. H_3PO_4,* ***a non-oxidising agent****, is used in place of conc. H_2SO_4.)*

(b) Using phosphorus trihalides, PX_3 (where X = Cl, Br or I)

$3R{-}OH + PX_3 \longrightarrow 3R{-}X + H_3PO_3$

Examples:

$3CH_3CH_2{-}OH + PCl_3 \longrightarrow 3CH_3CH_2{-}Cl + H_3PO_3$

$3CH_3CH_2{-}OH + PBr_3 \longrightarrow 3CH_3CH_2{-}Br + H_3PO_3$

$3CH_3CH_2{-}OH + PI_3 \xrightarrow{\text{red P, } I_2} 3CH_3CH_2{-}I + H_3PO_3$

Note:
PI_3 is not sufficiently stable to be stored, but it can be generated *in situ* (in the reaction mixture) by the reaction of red phosphorus with iodine.

$$2P + 3I_2 \longrightarrow 2PI_3$$

Note:
Anhydrous condition must be used because PX_3 reacts with water.
(refer to Periodic Table I notes)

(c) Using phosphorus pentachloride at room temperature

- Solid phosphorus pentachloride reacts with alcohols at room temperature, producing steamy, acidic hydrogen chloride fumes.

$R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$

Example:

$CH_3CH_2{-}OH + PCl_5 \longrightarrow CH_3CH_2{-}Cl + POCl_3 + HCl$

Note:
Anhydrous condition must be used because $PCl_5(s)$ reacts with water.

Note:
- This reaction is one of the tests for the alcohol –OH group.

  Observation: white fumes of hydrogen chloride, which turns damp blue litmus paper red.

(d) Using thionyl chloride at room temperature

- $SOCl_2$ reacts with alcohols at room temperature to produce a chloroalkane. SO_2 and HCl are also produced. Care would have to be taken because both of these gases are toxic.

$R{-}OH + SOCl_2 \longrightarrow R{-}Cl + SO_2 + HCl$

Example:

$CH_3CH_2{-}OH + SOCl_2 \longrightarrow CH_3CH_2{-}Cl + SO_2 + HCl$

Note:
Anhydrous condition must be used because $SOCl_2$ reacts with water.

Note:
- This reaction is sometimes preferred than those using PCl_3 or PCl_5 because the other two products of the reaction (i.e. SO_2 and HCl) are gases and can be separated from the reaction mixture relatively easily.
- $SOBr_2$ is available but it is less stable and less widely used than $SOCl_2$.

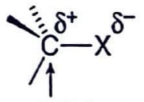
(e) Summary of nucleophilic substitutions of alcohol to obtain halogenoalkane

Reaction	Reagents and condition	Others
$R{-}OH \longrightarrow R{-}Cl$	**PCl_5 or $SOCl_2$, room temperature**	PCl_3 or dry HCl with heating
$R{-}OH \longrightarrow R{-}Br$	**PBr_3 or dry HBr, heat**	red P, Br_2 or $SOBr_2$
$R{-}OH \longrightarrow R{-}I$	**red P, I_2**	dry HI with heating

4 Characteristic Reactions of Halogenoalkanes

4.1 The polar carbon-halogen bond

- The carbon–halogen bond (i.e. C–X bond) in a halogenoalkane (R–X) is **polar** because the halogen atom is **more** electronegative than the carbon atom.
- In this case, the carbon atom bearing the halogen atom acquires a **partial positive charge** and is said to be **electron deficient**.
- This electron-deficient carbon atom is susceptible to attack by **nucleophiles.**

 electron-deficient site - is electrophilic - attracts nucleophiles such as OH^-, CN^- and NH_3	**What is a nucleophile?** A nucleophile is a species that is able to donate an electron pair to an electron-deficient atom **to form a covalent bond.**

- Hence one characteristic reaction of halogenoalkanes is **nucleophilic substitution**. Another characteristic reaction is **elimination.**

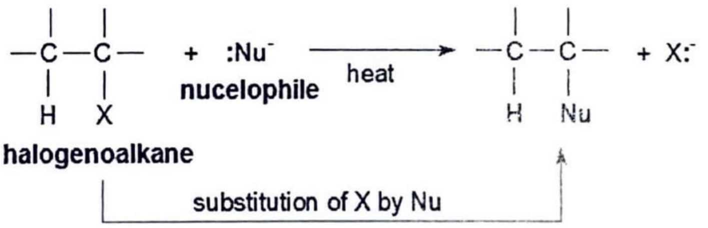
Characteristic reactions of halogenoalkanes

with **nucleophile**

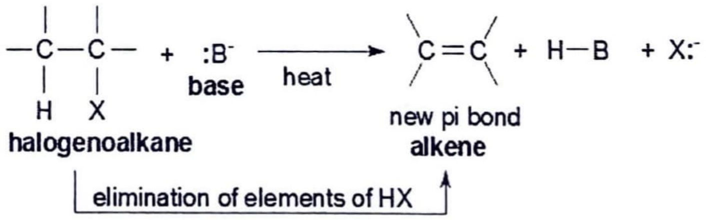
nucleophilic substitution

with **Brønsted-Lowry base**

elimination



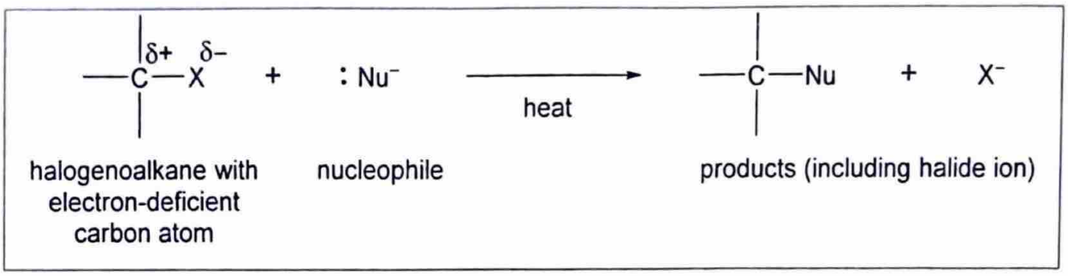
In this nucleophilic substitution reaction, the nucleophile attacks the electron-deficient C atom that is bonded to the halogen atom X. The C–X bond undergoes heterolytic fission and the C–Nu bond is formed. The overall reaction involves the replacement of the halogen atom X by an electron-rich nucleophile.



In this elimination reaction, the base abstracts a proton from the halogenoalkane. The C–X bond and a C–H bond are broken while a π bond is formed. The overall reaction involves the removal of the elements of HX leading to the formation of an alkene.

4.2 Nucleophilic substitution

- The general form of **nucleophilic substitution** involving halogenoalkane is shown below.



- **Nucleophiles are electron-pair donors** which are attracted to **electron-deficient sites**. They contain either at least a lone pair of electrons or a π bond but are not necessarily charged.
  - Examples of **neutral** nucleophiles: H_2O, ROH, NH_3 and RNH_2
  - Examples of **anionic** nucleophiles: OH^-, RO^-, CN^-, and X^-

- Nucleophilic substitution may occur via

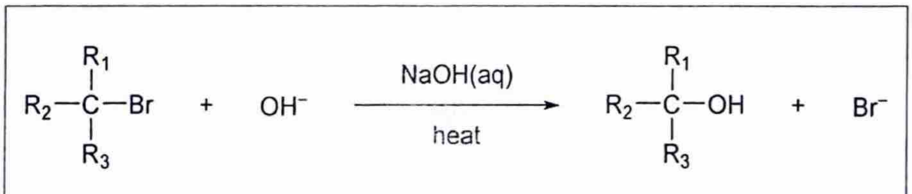
the S_N2 mechanism or the S_N1 mechanism

4.3 Proposing a mechanism

- In Chemistry, mechanisms are proposed based on data obtained from experiments that Chemists perform.

- A mechanism must:
  - match the kinetics of the reaction (e.g. number of species in the slow step); and
  - account for all observations (e.g. stereochemical outcomes) of the reaction.

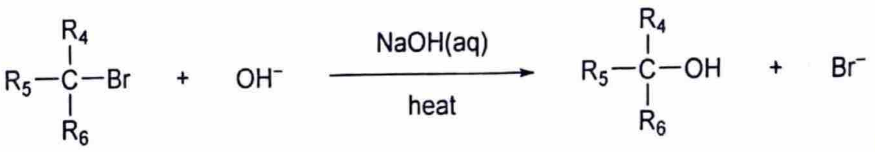
- Consider the reaction between a bromoalkane and hot aqueous sodium hydroxide.



R_1, R_2, R_3: alkyl or H

Observation	**Deduction**
An pale cream precipitate was observed when the resultant mixture was acidified with HNO_3(aq) and $AgNO_3$(aq) was added.	Br^- is present in the resultant mixture. C–Br bond is broken.
When the concentration of OH^- was doubled, the rate of reaction was doubled.	Order of reaction with respect to OH^- is 1.
When the concentration of the bromoalkane was doubled, the rate of reaction was doubled.	Order of reaction with respect to bromoalkane is 1.
	Since the overall order of reaction is 2, it involves both halogenoalkane and nucleophile in the slow single step. Hence, we can conclude that the reaction is Single - step and bimolecular. This is known as **S_N2 mechanism**.

- Consider another reaction between a different bromoalkane and hot aqueous sodium hydroxide.



$R_5C(R_4)(R_6)Br + OH^- \xrightarrow[\text{heat}]{NaOH(aq)} R_5C(R_4)(R_6)OH + Br^-$

R_4, R_5, R_6: large alkyl

Observation	Deduction
A pale cream precipitate was observed when the resultant mixture was acidified with HNO_3(aq) and $AgNO_3$(aq) was added.	Br^- is present in the resultant mixture. C–Br bond is broken.
When the concentration of OH^- was doubled, the rate of reaction was the same.	Order of reaction with respect to OH^- is 0.
When the concentration of the bromoalkane was doubled, the rate of reaction was doubled.	Order of reaction with respect to bromoalkane is 1.
	Since the overall order of reaction is 1, it involves only halogenoalkane in the slow step. Hence, we can conclude that the reaction is more than one step and unimolecular. This is known as **S_N1 mechanism**.

- The stereochemical outcomes for the above reactions were also found to be different (see **Section 5.2** and **Section 6.2**). Key differences in observations between the two reactions are summarised below:

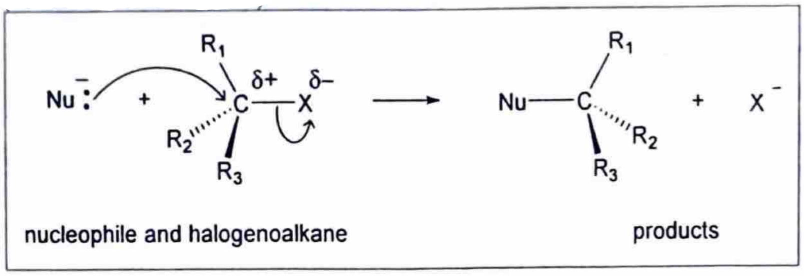
	First Reaction - S_N2 mechanism (R_1, R_2, R_3: alkyl or H)	**Second Reaction - S_N1 mechanism** (R_4, R_5, R_6: large alkyl)
Kinetics	Rate is directly proportional to $[OH^-]$.	Rate is independent of $[OH^-]$.
Stereochemistry	Enantiomerically pure reactant gives enantiomerically pure product.	Enantiomerically pure reactant gives racemic mixture of product.

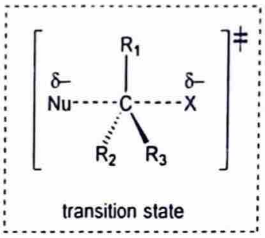
- Whether a reaction proceeds by the S_N2 or the S_N1 mechanism is generally dependent on whether the reactant is a 1°, 2° or 3° halogenoalkane (see **Section 7.2**).

5 Nucleophilic Substitution – S$_N$2 Mechanism

5.1 The S$_N$2 mechanism

- In H2, the **S$_N$2** mechanism is described as:





- ○ **S** stands for Substitution,
- ○ **N**(subscript) stands for Nucleophilic, and
- ○ **2** stands for Two reactant particles involved in the rate-determining step (i.e. this is a **bimolecular** reaction).

Nucleophilic attack

- In the halogenoalkane molecule, the **C–X bond is polar** with the C atom acquiring a partial positive charge since it is less electronegative than the halogen atom.
- During the reaction, the **nucleophile** attacks the partially positively charged C atom from the side directly opposite the halogen atom (i.e. a Backside **attack** occurs).
- **Why must the nucleophile attack from the backside?**

  The X$^{\delta-}$ blocks the approach of the nucleophile from the front side. It also repels the nucleophile since both are electron rich.
- The reaction is a **concerted reaction**, taking place in a **single step** with bond breaking and bond making occurring **at the same time**.

Products

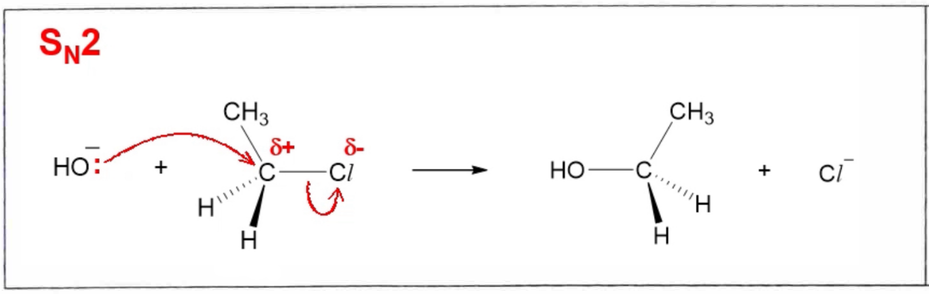
- Eventually the C–X bond breaks and the C–Nu bond forms yielding X$^-$ and the product.
- If Nu ≠ R_1, R_2 or R_3, the chiral carbon is still chiral.
- During the reaction, the three C–R bonds associated with the δ+ C atom turn inside out.
- This results in a stereochemical inversion of the tetrahedral arrangement of bonds to the C atom at which substitution occurs.
- The reaction is said to have occurred with **inversion of configuration** with respect to the C atom at which substitution occurs (i.e. the chiral C atom).

Transition State

- In the transition state, there is Simultaneous partial formation of the C–Nu bond and partial cleavage of the C–X bond.
- The transition state (or activated complex) cannot be isolated.

Try it yourself!

Complete the S$_N$2 mechanism for the reaction between OH$^-$ and chloroethane.



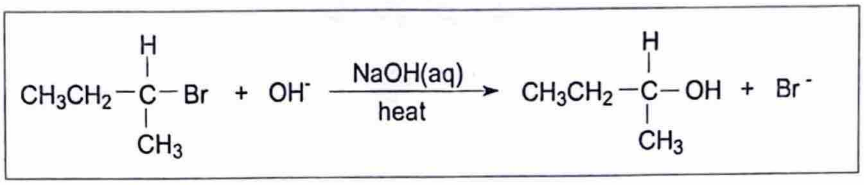
Checklist for S$_N$2 mechanism:

- ☐ name of mechanism
- ☐ δ+ on C, δ– on X
- ☐ lone pair of electrons on Nu$^-$
- ☐ curly arrows to show flow of electrons
- ☐ inverted product

Halogenoalkanes Supplementary Notes – Transition State in S_N2 mechanism

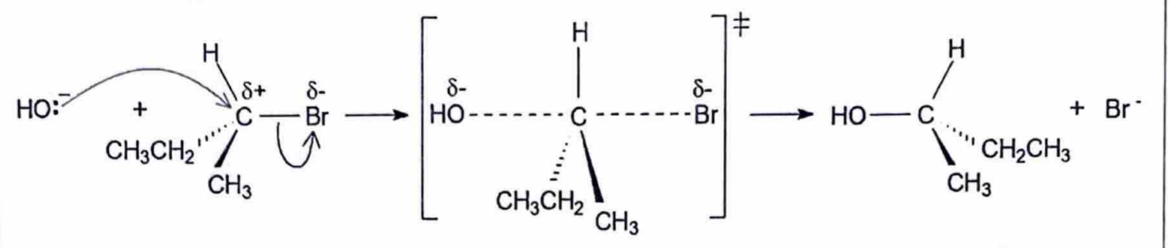
1.1 The S_N2 mechanism

- The reaction between **2-bromobutane and hot, aqueous sodium hydroxide** can proceed via the **S_N2** mechanism – a one-step mechanism where the rate-determining step involves 2 reactant species.



$$CH_3CH_2-\overset{H}{\underset{CH_3}{C}}-Br + OH^- \xrightarrow[heat]{NaOH(aq)} CH_3CH_2-\overset{H}{\underset{CH_3}{C}}-OH + Br^-$$

- Description of the **S_N2** mechanism



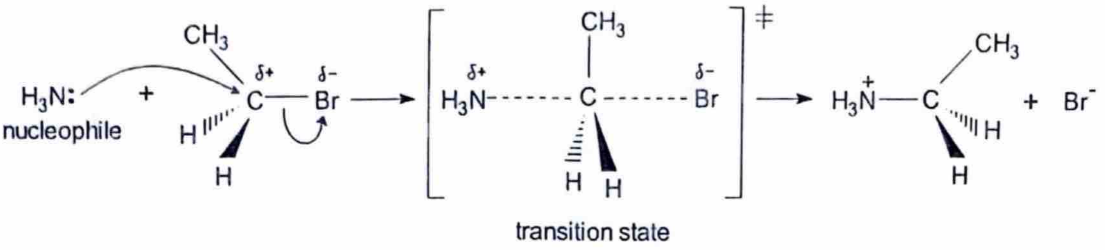
nucleophile and halogenoalkane | transition state | alcohol and bromide ion

- The transition state needs to be included for the S_N2 mechanism.
- The reaction takes place in a single step with bond breaking and bond forming at the same time.
- The ----- lines show the forming of the C–O bond and breaking of the C–Br bond, which take place simultaneously.
- As the C–O bond forms, O gradually loses its negative charge and this is reflected by a δ– charge in the transition state.
- As the C–Br bond breaks, Br gradually gains a full negative charge and this is reflected as a δ – charge in the transition state.
- Due to the presence of five groups around the central carbon, it is said to be a pentavalent transition state.

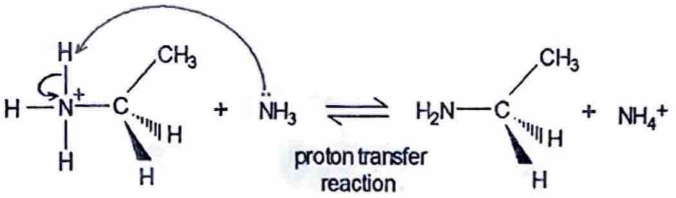
To draw the transition state, take note of the following.

1. Central carbon with 5 groups.
2. Depict bond forming and bond breaking with ----.
3. Partial charges on the attacking nucleophile and leaving halide.
4. Square brackets and ‡ symbol for transition state.

- The reaction between **bromoethane and hot excess concentrated NH_3** proceeds via a S_N2 mechanism.



This is followed by a proton transfer reaction.

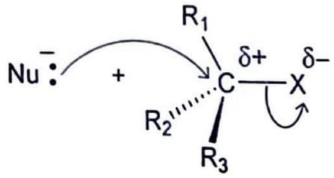
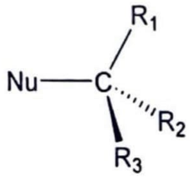
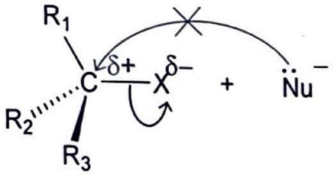
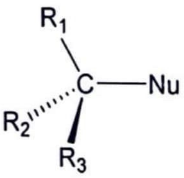


For the transition state here, take note of the following.

- The ----- lines show the forming of the C–N bond and breaking of the C–Br bond, which take place simultaneously.
- As the C–N bond forms, N gradually gains a positive charge until it becomes $-NH_3^+$ in the product. Take note that a N atom with 4 covalent bonds has a positive charge. Therefore, the N atom in the transition state has a δ+ charge.
- As the C–Br bond breaks, Br gradually gains a full negative charge and this is still reflected as a δ– charge in the transition state.

5.2 Stereochemistry and kinetics of the S_N2 mechanism

- Inversion of configuration

	Nucleophilic attack	Product	Remarks
backside attack ✓		 **inversion of configuration (observed)**	• Experimentally, the S_N2 reaction has been found to occur with complete inversion **of configuration** with respect to the chiral C atom at which substitution occurs. • This is only possible if backside attack occurs during the reaction.
front-side attack X		 **retention of configuration (not observed)**	• The S_N2 reaction does **not** occur with **retention of configuration** with respect to the chiral C atom at which substitution occurs. • This indicates that a front-side attack by the nucleophile does **not** occur.

Therefore, the **S_N2 mechanism accounts for the stereochemical outcome** of the reaction.

- Rate of reaction and its relation to the mechanism

The mechanism shows only one step, which must be the rate-determining step.
One molecule of the halogenoalkane and one Nu^- are involved in the slow step.
In other words, the order of reaction is 1 with respect to halogenoalkane, and is also 1 with respect to Nu^-.

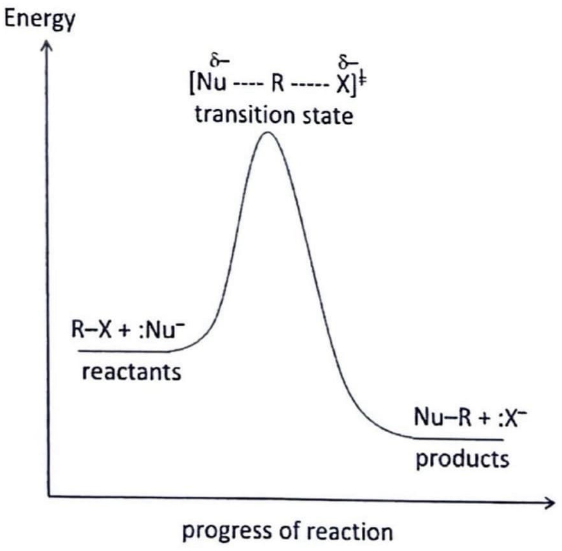
Therefore, the **S_N2 mechanism matches the observed kinetics** obtained from experimental data.

For a S_N2 reaction involving a halogenoalkane, the rate equation and overall order of reaction are:

rate = k[halogenoalkane][nucleophile]	Overall order of reaction = 2

5.3 Energy profile of the S_N2 reaction

Reaction:
$R{-}X + :Nu^- \longrightarrow R{-}Nu + :X^-$



5.4 Factors affecting the reactivity of halogenoalkanes in S$_N$2 reactions

(a) Strength of the carbon-halogen (i.e. C–X) bond

- The S$_N$2 (i.e. bimolecular nucleophilic substitution) reaction for halogenoalkanes involves the **heterolytic fission of the C–X bond** (where X = F, C*l* Br or I).
- Experiments have shown that the **weaker** the C–X bond is, the Faster is the rate of the reaction.
- Hence, the **order of reactivity of halogenoalkanes RX towards S$_N$2 reactions** depends on **the strength of the C–X bond** and **increases** in the following order:

R-F R-Cl < R-Br < R-I

no reaction slowest ⟶ fastest

increasing rate of S$_N$2 reaction

Note:
- The **C–F bond is too strong** to be broken under normal laboratory conditions.
- CH_3CH_2F does **not** undergo hydrolysis even with prolonged heating under reflux with NaOH(aq).

The above **order of reactivity of RX towards S$_N$2 reactions** arises because the strength of the C–X bond decreases in the following order:

C–F > C–Cl > C–Br > C–I

strongest ⟶ weakest

decreasing
C–X bond strength

Note: Relevant data from *Data Booklet*

Bond	**Bond Energy / kJ mol^{-1}**
C–F	485
C–C*l*	340
C–Br	280
C–I	240

Why does the C–X bond strength decreases down Group 17?

- Down Group 17, the size of the halogen atom X increases and the valence atomic orbitals of the halogen atom X become **bigger and more diffuse**. As such, the **overlap of orbitals** which forms the C–X bond becomes **less effective** down the group. Hence the **strength of the C–X bond decreases** down the group.
- In addition, the **electronegativity value** of the halogen atom X decreases down the group. This causes the **polarity** of the C–X bond and hence the **ionic character** of the C–X bond to decrease down the group. Consequently, the strength of the C–X bond decreases down the group.

- Electronegativity data

Bond	**Electronegativity of X**
C–F	4.0
C–C*l*	3.0
C–Br	2.8
C–I	2.5

- **Note:**

The C–C*l* bond is more polar than the C–Br bond, since the C*l* atom is more electronegative than the Br atom. This implies that the C atom in the C–C*l* bond has a **larger** Partial positive **charge** and **should attract nucleophiles more** Strongly than the C atom in the C–Br bond.

However, **despite having a more electron-deficient carbon** to attract nucleophiles, R–C*l* is found to undergo S$_N$2 reactions at a **slower** rate than R–Br.

Hence the order of reactivity of halogenoalkanes RX towards S$_N$2 reactions **does not depend** on the magnitude of the partial positive charge on the carbon in the C–X bond.

(b) Steric effect of R groups in S_N2 reactions

- Studies carried out indicate that there are large differences in the rates at which the various classes of halogenoalkanes – methyl, primary, secondary or tertiary – undergo nucleophilic substitution by the S_N2 mechanism.

- These differences in the rates reflect the **steric hindrance** of each class of halogenoalkane during nucleophilic attack.

- During the S_N2 reaction, the nucleophile must approach the halogenoalkane molecule and attack the electron-deficient carbon atom **from the side directly opposite the halogen atom** (i.e. a backside attack) and **this approach and attack is hindered by alkyl substituents** bonded to the carbon atom that is being attacked.

- In general, the S_N2 mechanism is **favoured by** Less **steric hindrance** around the carbon atom bonded to the halogen atom.

- Hence the **order of reactivity of halogenoalkanes (with the same halogen atom X) towards S_N2 reactions** decreases in the following order:

CH_3X > 1° halogenoalkane > 2° halogenoalkane > 3° halogenoalkane

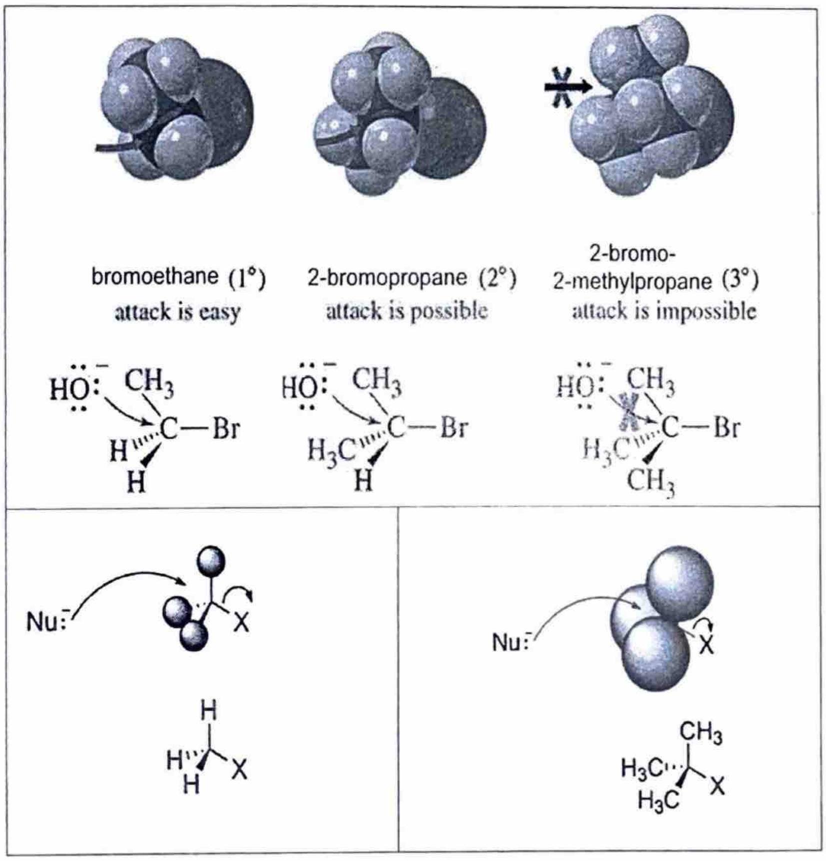
least crowded ⟶ most crowded

increasing steric hindrance around the carbon bonded to the X atom

most reactive ⟶ least reactive

decreasing rate of substitution by the S_N2 mechanism

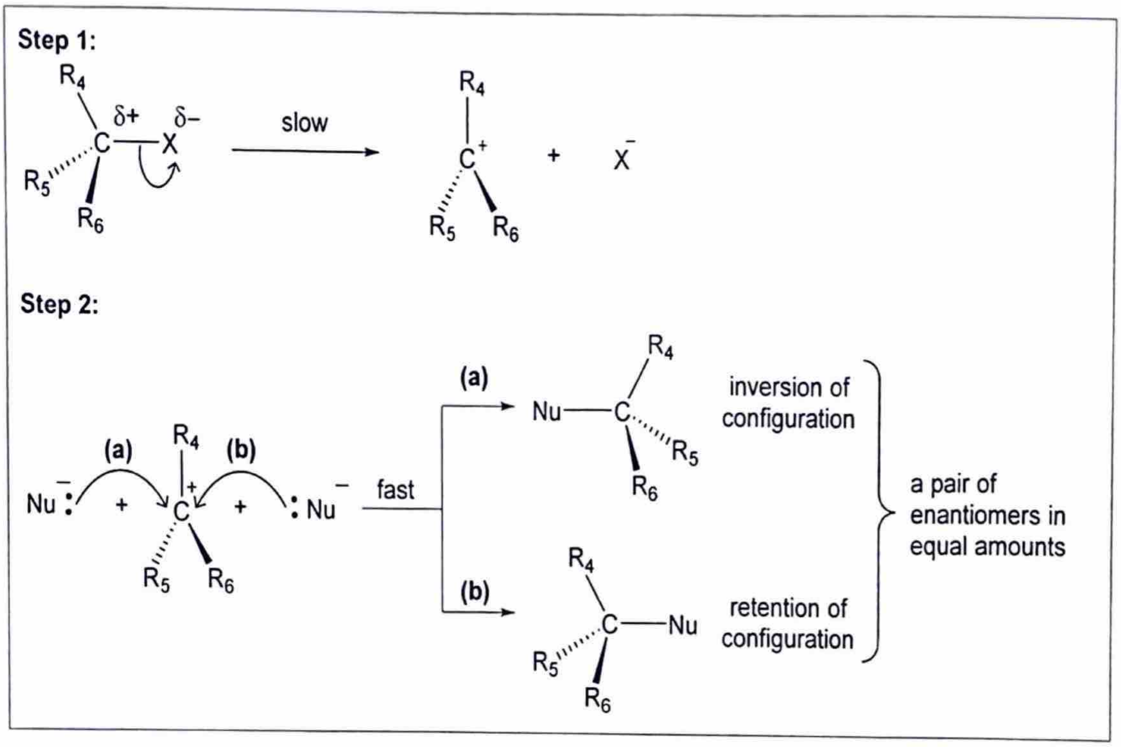
- Diagrammatic representation of **steric hindrance** offered by different bromoalkanes:



6 Nucleophilic Substitution: S_N1 Mechanism

6.1 The S_N1 mechanism

- In H2, the **S_N1** mechanism is described as:



- **S** stands for Substitution,
- **N**(subscript) stands for Nucleophilic, and
- **1** stands for One reactant particle involved in the rate-determining step (i.e. this is a **unimolecular** reaction).

Step 1: Formation of carbocation

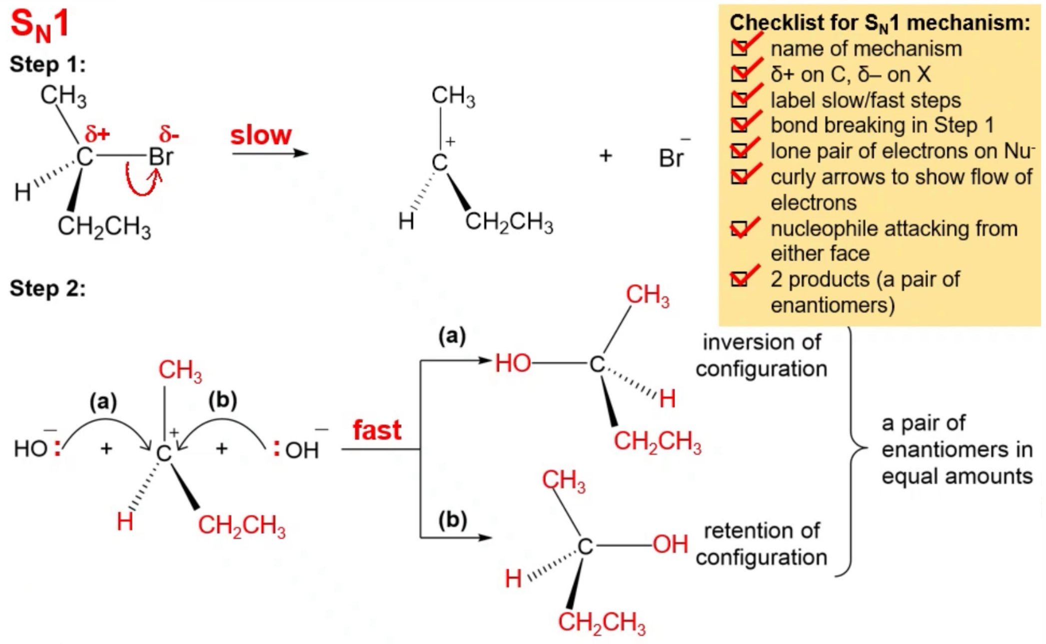
- In step 1, the **C–X bond** undergoes **heterolytic fission** to give a **carbocation** intermediate.
- This is the **rate-determining step** since it involves bond breaking which is endothermic.
- The carbocation formed is **trigonal planar** in shape with respect to the positively charged C.
- Note that the δ+ C is **sp^3 hybridised** while the positively charged C is **sp^2 hybridised**.

Step 2: Nucleophilic attack on the carbocation

- In step 2, the nucleophile attacks the positively charged C of the carbocation from **either side** (i.e. pathways **(a)** and **(b)**) of the trigonal planar structure with **equal likelihood**.
- This yields equal amounts of a **pair of enantiomers** as products, i.e., a **racemic mixture** is produced.
- In this case, the S_N1 reaction proceeds with **racemisation** at a single chiral carbon centre.
- **Racemisation** involves the formation of equal amounts of two enantiomeric products from a single starting material.

Try it yourself!

Complete the S$_N$1 mechanism for the reaction between OH$^-$ and 2-bromobutane.



Checklist for S$_N$1 mechanism:

☑ name of mechanism
☑ δ+ on C, δ– on X
☑ label slow/fast steps
☑ bond breaking in Step 1
☑ lone pair of electrons on Nu$^-$
☑ curly arrows to show flow of electrons
☑ nucleophile attacking from either face
☑ 2 products (a pair of enantiomers)

Checklist for S$_N$1 mechanism:

☐ name of mechanism
☐ δ+ on C, δ– on X
☐ label slow/fast steps
☐ bond breaking in Step 1
☐ lone pair of electrons on Nu$^-$
☐ curly arrows to show flow of electrons
☐ nucleophile attacking from either face
☐ 2 products (a pair of enantiomers)

6.2 Stereochemistry and kinetics of S$_N$1 mechanism

- Racemisation

From the mixture of products obtained, an **S$_N$1 reaction** is said to occur with **racemisation**. The substitution reaction takes place with 50% of the product molecules showing **retention of configuration** about the chiral carbon atom and the other 50% showing **inversion of configuration** about the chiral carbon atom.

Note: A reaction that transforms an optically active compound into a racemic form is said to proceed with **racemisation**.

Therefore, the **S$_N$1 mechanism accounts for racemisation**.

- Rate of reaction and its relation to the mechanism

The mechanism's slow step (rate-determining step) involves only the halogenoalkane. The nucleophile does not appear in the slow step.
In other words, the order of reaction is 1 with respect to halogenoalkane but 0 with respect to Nu$^-$.

Therefore, the **S$_N$1 mechanism matches the observed kinetics** obtained from experimental data.

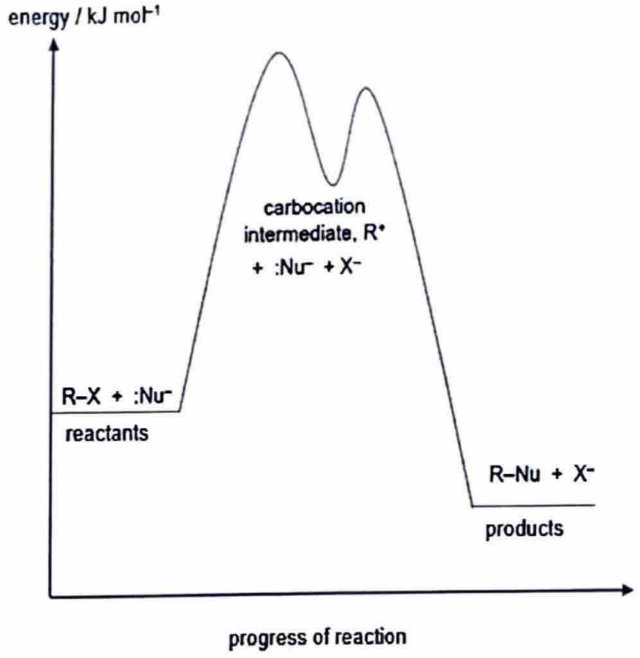
For a S$_N$1 reaction involving a halogenoalkane, the rate equation and overall order of reaction are:

rate = k[halogenoalkane]	Overall order of reaction = 1

6.3 Energy profile of the S_N1 reaction

Reaction:

R–X + :Nu⁻ $\longrightarrow$ R–Nu + :X⁻



6.4 Factors affecting the reactivity of halogenoalkanes in S_N1 reactions

(a) Strength of the carbon-halogen (i.e. C–X) bond

- The rate-determining step of an S_N1 reaction involves the **cleavage of the C–X bond** (X = F, C*l*, Br or I) in the halogenoalkane molecule. Studies have shown that the **weaker** the C–X bond is, the **faster** is the rate of the reaction.
- Hence the **order of reactivity of halogenoalkanes RX towards S_N1 reactions** depends on **the strength of the C–X bond** and **increases** in the following order:

<table>
<tr><td>R–F R–C<i>l</i> < R–Br < R–I
no reaction slowest ⟶ fastest
increasing rate of S_N1 reaction</td><td>Note:
• The C–F bond is too strong to be broken under normal laboratory conditions.
• CH₃CH₂F does not undergo hydrolysis even with prolonged heating under reflux.</td></tr>
<tr><td colspan="2">Note: The above order of reactivity of halogenoalkanes is the same as that towards S_N2 reactions and arises because the C–X bond strength decreases in the following order:
C–F > C–C<i>l</i> > C–Br > C–I</td></tr>
</table>

(b) Stability of carbocation in $\mathrm{S_N1}$ reactions

- The **rate of a $\mathrm{S_N1}$ reaction** depends on the **rate of formation of the carbocation** (the product of the rate-determining step) via the heterolytic fission of the C–X bond.

- Thus, the rate of a $\mathrm{S_N1}$ reaction **increases** as the **stability of the carbocation increases.** This is because a **more stable carbocation is formed faster** due to a **lower activation energy** needed for its formation.

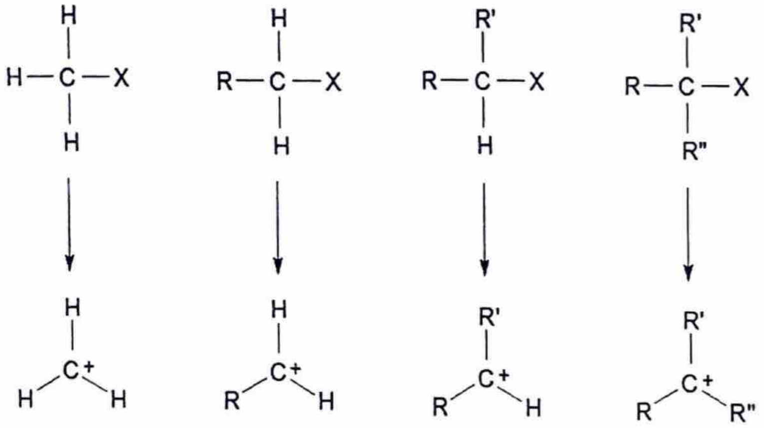
- In general, the $\mathrm{S_N1}$ mechanism is **favoured by factors that stabilise the carbocation.**
  - **Electron-donating groups** such as **alkyl groups** stabilise the carbocation by **dispersing the positive charge** at the carbon atom.
  - As such, the stability of the carbocation increases as the **number of alkyl groups** attached to the positively charged carbon atom of the carbocation increases.

- Hence the **order of reactivity of halogenoalkanes** (with the same halogen atom X) towards $\mathrm{S_N1}$ reactions increases in the following order:

least reactive ⟶ most reactive

increasing rate of substitution
by the $\mathrm{S_N1}$ mechanism

CH_3X < 1° halogenoalkane < 2° halogenoalkane < 3° halogenoalkane

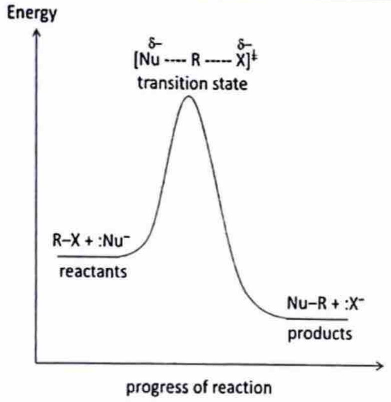
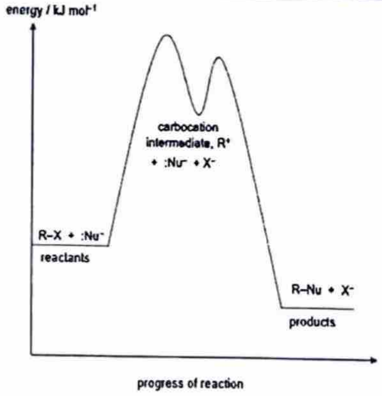


least stable ⟶ most stable

increasing stability of carbocation
due to increasing number of electron-donating alkyl groups

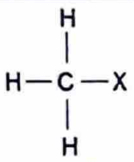
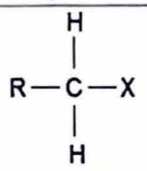
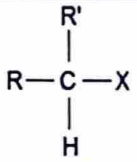
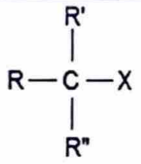
7 Comparison between S_N2 and S_N1 Mechanisms

7.1 Summary table

	S_N2 mechanism	**S_N1 mechanism**
Kinetics	• a second-order reaction	• a first-order reaction
Molecularity	• bimolecular reaction	• unimolecular reaction
Rate equation	• rate = k [RX] [:Nu^-]	• rate = k [RX]
Stereochemistry	• nucleophile attacks the electron-deficient carbon atom from the side directly opposite the halogen atom (i.e. a **backside attack**) • **inversion of configuration** at the chiral carbon atom occurs (if the carbon atom at which substitution occurs is chiral)	• formation of **carbocation** intermediate which is **trigonal planar** with respect to the positively charged carbon atom • attack of nucleophile from both sides of the trigonal plane with equal probability. • **racemisation** occurs (if the carbon atom at which substitution occurs is chiral)
Product formed if the starting material is one enantiomeric form of RX	• one enantiomeric form of product • optically active product	• racemic mixture • optically inactive product mixture
Number of steps	• one step	• two steps
Energy profile diagram		
Order of reactivity (with the same X)	• CH_3X > 1° RX > 2° RX > 3° RX fastest slowest	• CH_3X < 1° RX < 2° RX < 3° RX slowest fastest
Contributing factor (with the same X)	• **steric hindrance** due to the alkyl groups around the carbon atom bonded to the X atom	• **carbocation stability** based on the number of electron-donating alkyl groups bonded to the positively charged carbon
Order of reactivity (with the same R)	• R–C*l* < R–Br < R–I slowest fastest	• R–C*l* < R–Br < R–I slowest fastest
Contributing factor (with the same R)	• decreasing strength of the C–X bond C–C*l* > C–Br > C–I	• decreasing strength of the C–X bond • C–C*l* > C–Br > C–I

7.2 When is the mechanism S_N2 or S_N1?

- Given a particular starting halogenoalkane and nucleophile, how do we know whether a reaction occurs by the S_N2 or S_N1 mechanism?
- For **simplicity at A-level**, the factor to consider is the **structure of the halogenoalkane**.

CH_3X	1° halogenoalkane	2° halogenoalkane	3° halogenoalkane
			
mechanism	mechanism	and/or mechanisms	mechanism

- **less steric hindrance** for backside attack by the nucleophile
  ⇒ **favours** S_N2 mechanism
- formation of unstable / less stable carbocation
  ⇒ **unlikely to be** S_N1 mechanism

- could be S_N2 **and/or** S_N1
- obtain experimental data to determine mechanism (see "**Note**")

- formation of **more stable carbocation**
  ⇒ **favours** S_N1 mechanism
- more steric hindrance for backside attack by the nucleophile
  ⇒ **unlikely to be** S_N2 mechanism

Note:
Other information (e.g. kinetics data, optical activity data, etc.) **should also be used** to determine whether the reaction proceeds by the S_N2 or the S_N1 mechanism.

Even a primary halogenoalkane can sometimes proceed via S_N1 mechanism! (see Section 7.3)

7.3 Some special cases to take note

- There are some primary halogenoalkanes that undergo nucleophilic substitution reactions via the **S_N1** mechanism (and **not** the **S_N2** mechanism).
- **Example 1:** Hydrolysis of 3-bromopropene (an allylic halide)

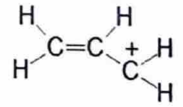
$$CH_2{=}CH{-}CH_2{-}Br + OH^- \xrightarrow[\text{heat}]{NaOH(aq)} CH_2{=}CH{-}CH_2{-}OH + Br^-$$

3-bromopropene

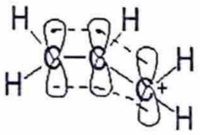
Mechanism: S_N1

Note:
- An allylic halide has the X atom bonded to the carbon atom adjacent to a C=C bond.

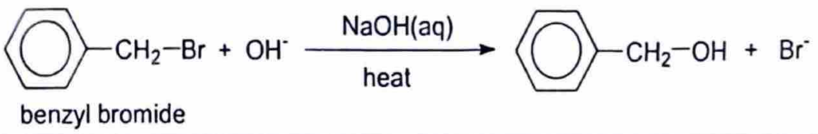
- **Explanation:**
  - 3-Bromopropene undergoes nucleophilic substitution reactions via the S_N1 mechanism because it is able to form a stable carbocation.
  - In this case, it forms a carbocation in which the **positively charged carbon is adjacent to a C=C bond** (i.e. an allylic carbocation).
  - In the carbocation formed, the empty p orbital of the positively charged carbon overlaps with the π-electron cloud of the adjacent C=C bond.
  - This allows the π electrons of the C=C bond to delocalise over the positively charged carbon and disperse the positive charge, thus stabilising the carbocation (i.e., **the carbocation is resonance-stabilised**).



allyl carbocation
(an allylic carbocation)



- **Example 2:** Hydrolysis of (bromomethyl)benzene or benzyl bromide (a benzylic halide)



$$C_6H_5CH_2{-}Br + OH^- \xrightarrow[\text{heat}]{NaOH(aq)} C_6H_5CH_2{-}OH + Br^-$$

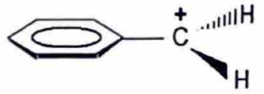
benzyl bromide

Mechanism: S_N1

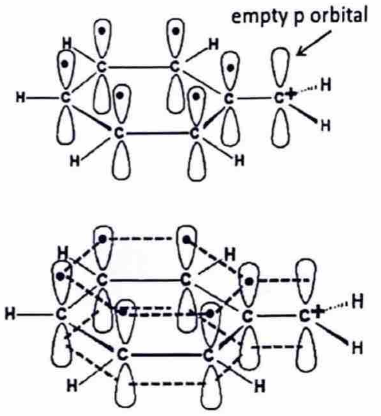
Note:

- A benzylic halide has the X atom bonded to the carbon atom adjacent to a benzene ring.

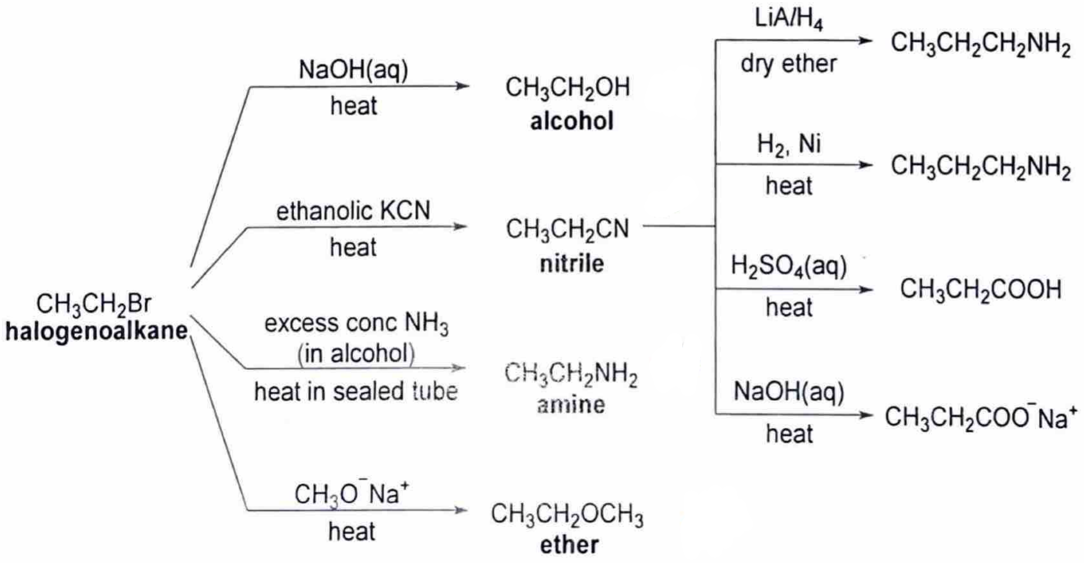
- **Explanation (similar to Example 1):**
  - Benzyl bromide can undergo nucleophilic substitution reactions via the S_N1 mechanism because it is able to form a stable carbocation.
  - In this case, it forms the benzyl carbocation in which the **positively charged carbon is adjacent to the benzene ring** (i.e. a benzylic carbocation).
  - In this carbocation, the empty p orbital of the positively charged carbon overlaps with the π electron cloud of the benzene ring.
  - This allows the π electrons of the benzene ring to delocalise over the positively charged carbon and disperse the positive charge, thus stabilising the carbocation(i.e., **the carbocation is resonance-stabilised**).



benzyl carbocation
(a benzylic carbocation)



8 Examples of Nucleophilic Substitution Reactions of Halogenoalkanes



$$CH_3CH_2Br \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CH_2OH$$

CH$_3$CH$_2$Br **halogenoalkane** → CH$_3$CH$_2$OH **alcohol**

$$CH_3CH_2Br \xrightarrow[\text{heat}]{\text{ethanolic KCN}} CH_3CH_2CN$$

nitrile

$$CH_3CH_2Br \xrightarrow[\text{heat in sealed tube}]{\text{excess conc } NH_3 \text{ (in alcohol)}} CH_3CH_2NH_2$$

amine

$$CH_3CH_2Br \xrightarrow[\text{heat}]{CH_3O^-Na^+} CH_3CH_2OCH_3$$

ether

$$CH_3CH_2CN \xrightarrow[\text{dry ether}]{LiA/H_4} CH_3CH_2CH_2NH_2$$

$$CH_3CH_2CN \xrightarrow[\text{heat}]{H_2,\ Ni} CH_3CH_2CH_2NH_2$$

$$CH_3CH_2CN \xrightarrow[\text{heat}]{H_2SO_4(aq)} CH_3CH_2COOH$$

$$CH_3CH_2CN \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CH_2COO^-Na^+$$

8.1 Formation of alcohols (R–OH)

- This nucleophilic substitution reaction of halogenoalkanes with aqueous sodium hydroxide is commonly termed **hydrolysis** (or more correctly, **alkaline hydrolysis**).

Reaction X = Cl, Br or I	$\textbf{R–X + NaOH(aq)} \xrightarrow[\textbf{heat}]{} \textbf{R–OH + NaX(aq)}$
Reagents and conditions	NaOH(aq) or KOH(aq) heat (or heat under reflux)

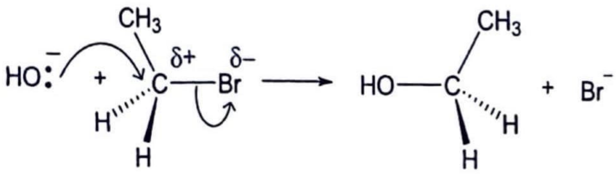
- **Aqueous medium** must be used to help ensure that nucleophilic substitution reaction occurs. Hence the **state symbol "(aq)" for NaOH** must be stated explicitly. Should **alcoholic (or ethanolic) medium** be used, elimination reaction will take preferentially.

- **Example 1:** Hydrolysis of bromoethane

CH_3CH_2Br + NaOH(**aq**) $\xrightarrow[\text{heat}]{}$ CH_3CH_2OH + NaBr(aq)

bromoethane ethanol

The mechanism is **S$_N$2**, since it is a primary halogenoalkane.



Note: Though the bromoethane molecule does not contain a chiral carbon, **3-D diagrams must be drawn to show the backside attack clearly.**

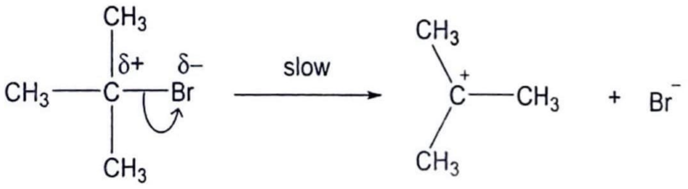
In this case, some chemists still speak of bromoethane as undergoing nucleophilic substitution with inversion of configuration. By this they meant that tetrahedral inversion of the bonds to carbon occurs as the reactant proceeds to the product.

- **Example 2:** Hydrolysis of 2-bromo-2-methylpropane

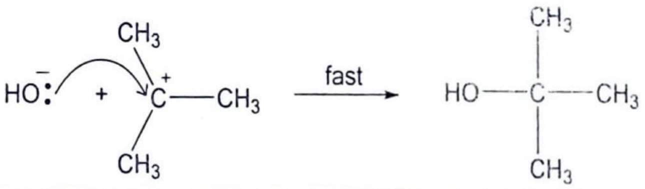
$(CH_3)_3CBr$ + NaOH(**aq**) $\xrightarrow[\text{heat}]{}$ $(CH_3)_3COH$ + NaBr(aq)

The mechanism involved is **S$_N$1**.

Step 1: Formation of carbocation



Step 2: Nucleophilic attack by OH⁻



Note:
In this case, the 3° halogenoalkane does not contain a chiral carbon atom.

Hence the equations used to describe the S$_N$1 mechanism can **be simplified without having to draw 3-D structures**.
(compare with mechanism shown on page 16)

8.2 Formation of nitriles (R–C≡N)

- This nucleophilic substitution reaction of halogenoalkanes with potassium cyanide in ethanol is useful in the synthesis of organic compounds because it is a method of **increasing the length of a carbon chain by one carbon atom**.

Reaction X = Cl, Br or I	$\mathrm{R{-}X + KCN \xrightarrow[heat]{ethanolic\ KCN} R{-}CN + KX}$ a nitrile
Reagents and conditions	alcoholic KCN or ethanolic KCN heat (or heat under reflux)

- *(FYI: In practice, a mixed solvent (water-ethanol) is used for the reaction to improve the miscibility of the reactants. In this case, KCN dissolves in water whereas RX dissolves in ethanol.)*

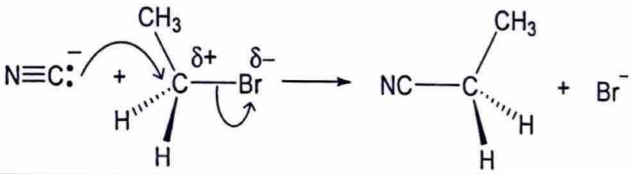
- **Example:** Reaction of bromoethane with ethanolic KCN

$$\mathrm{CH_3CH_2Br + KCN \xrightarrow[heat]{ethanolic\ KCN} CH_3CH_2CN + KBr}$$

bromoethane — propanenitrile

2-carbon chain — 3-carbon chain

The mechanism is S_N2.



- Nitriles are useful intermediate compounds in synthesis. They can be reduced to a primary amine or be hydrolysed to a carboxylic acid or a carboxylate salt.

(a) Reduction of nitriles to primary amines

$\mathrm{R{-}C{\equiv}N + 2H_2 \xrightarrow[heat]{H_2,\ Ni\ (catalyst)} R{-}CH_2{-}NH_2}$ a primary amine	**Note:** $\mathrm{LiAlH_4}$ is "lithium aluminium hydride".
$\mathrm{R{-}C{\equiv}N + 4[H] \xrightarrow[in\ dry\ ether]{LiAlH_4} R{-}CH_2{-}NH_2}$ a primary amine	

(b) Hydrolysis of nitriles to carboxylic acids

$\mathrm{R{-}CN + H^+ + 2H_2O \xrightarrow[heat]{H_2SO_4(aq)} RCOOH + NH_4^+}$ carboxylic acid	Type of reaction: **acidic hydrolysis**
$\mathrm{R{-}CN + OH^- + H_2O \xrightarrow[heat]{NaOH(aq)} RCOO^- + NH_3}$ carboxylate ion	Type of reaction: **basic hydrolysis**

8.3 Formation of primary amines

- The nucleophilic substitution reaction of halogenoalkanes with excess concentrated ammonia in ethanol can produce primary amines.

Reaction X = C*l*, Br or I	$R{-}X + NH_3 \xrightarrow[\text{sealed tube, heat}]{\text{excess conc. } NH_3 \text{ (in alcohol)}} \underset{\text{primary amine}}{R{-}NH_2} + HX$	• For simplicity, this equation is commonly used to represent the nucleophilic substitution reaction.
Reagents and conditions	excess conc. NH_3 (in alcohol or ethanol), sealed tube, heat	

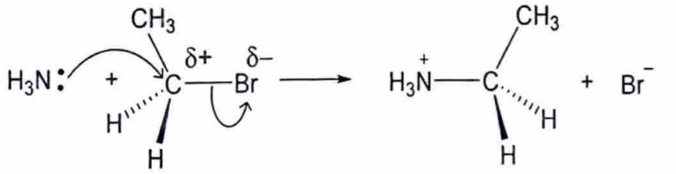
- Other possible equations

$R{-}X + NH_3 \xrightarrow[\text{sealed tube, heat}]{\text{excess conc. } NH_3 \text{ (in alcohol)}} \underset{\text{1° amine salt (alkylammonium salt)}}{R{-}NH_3^+ X^-}$ $R{-}NH_3^+ + NH_3 \longrightarrow \underset{\text{1° amine}}{R{-}NH_2} + NH_4^+$	• In the presence of **excess NH_3**, the reaction mixture contains – the 1° amine – the 1° amine salt – the ammonium salt
$R{-}X + 2NH_3 \xrightarrow[\text{sealed tube, heat}]{\text{excess conc. } NH_3 \text{ (in alcohol)}} \underset{\text{1° amine}}{R{-}NH_2} + NH_4X$	• This equation is sometimes used to represent the reaction between ammonia and R–X to produce a 1° amine.
$R{-}X + NH_3 \xrightarrow[\text{sealed tube, heat}]{\text{excess conc. } NH_3 \text{ (in alcohol)}} \underset{\text{1° amine salt (alkylammonium salt)}}{R{-}NH_3^+ X^-}$	• In practice, an amine salt (or an alkylammonium salt) is formed in the reaction mixture.
$R{-}NH_3^+ X^- + NaOH(aq) \longrightarrow \underset{\text{1° amine}}{R{-}NH_2} + NaX + H_2O$	• An alkali can be added to the mixture to liberate the free amine.

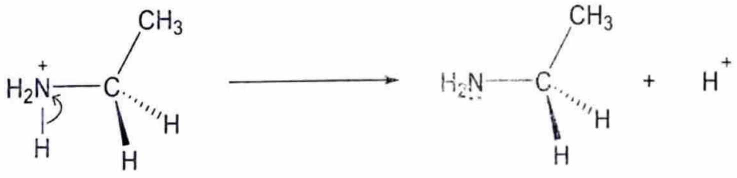
- Example: Reaction of bromoethane with ammonia

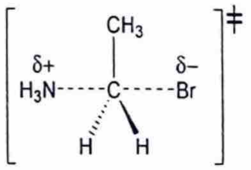
$$\underset{\text{bromoethane}}{CH_3CH_2Br} + NH_3 \xrightarrow[\text{sealed tube, heat}]{\text{excess conc. } NH_3 \text{ (in alcohol)}} \underset{\text{ethylamine}}{CH_3CH_2NH_2} + HBr$$

The mechanism is S_N2.



Then,





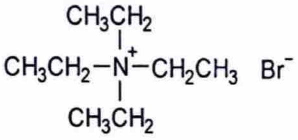
Note:
- Conservation of charge applies.
- This transition state has a net charge of zero because both reactants are uncharged.

- A problem encountered with this method of preparation of amines: a mixture of products is obtained due to **polyalkylation**. The simplified nucleophilic substitution reactions for polyalkylation are shown below.

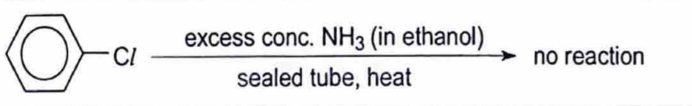
$NH_3 + CH_3CH_2Br \longrightarrow CH_3CH_2NH_2 + HBr$	• Since the 1° amine formed is also nucleophilic, it may undergo further reaction giving a 2° amine.
$CH_3CH_2NH_2 + CH_3CH_2Br \longrightarrow (CH_3CH_2)_2NH + HBr$	• By similar equilibria and further alkylation, the 3° amine and even the quaternary ammonium compound may be formed.
$(CH_3CH_2)_2NH + CH_3CH_2Br \longrightarrow (CH_3CH_2)_3N + HBr$	• The actual result is a complex mixture of products.
$(CH_3CH_2)_3N + CH_3CH_2Br \longrightarrow \mathbf{(CH_3CH_2)_4N^+\,Br^-}$	• On an industrial scale, the products are separated by the addition of alkali to liberate the free amines, followed by fractional distillation.

- The use of **an excess of NH_3** minimises polyalkylation.

With an excess of NH_3, the probability of polyalkylation is reduced because there are so many more molecules of NH_3 surrounding the halogenoalkane. Before the halogenoalkane can meet and react with the desired product (primary amine), it would have reacted with an NH_3 molecule.

$CH_3CH_2Br \xrightarrow[\text{sealed tube, heat}]{\textbf{excess}\ \text{conc. } NH_3 \text{ in alcohol}} CH_3CH_2NH_2 + NH_4Br$	• Intended product is $CH_3CH_2NH_2$.
 $\mathbf{CH_3CH_2Br\ (excess)} \xrightarrow[\text{sealed tube, heat}]{\text{conc. } NH_3 \text{ in alcohol}} (CH_3CH_2)_4N^+\ Br^-$ quaternary ammonium salt	• Intended product is $(CH_3CH_2)_4N^+Br^-$.

- This method is limited to the formation of **aliphatic amines** because aryl halides will **not** undergo nucleophilic substitution reactions with ammonia under such conditions (see **Section 11**).

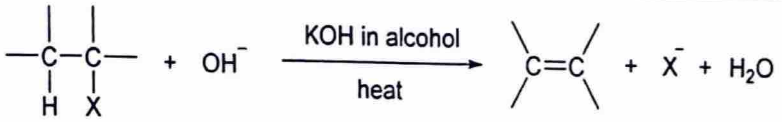


9 Elimination Reactions of Halogenoalkanes

9.1 Elimination reaction

- An **elimination reaction** involves loss of atoms from the starting material to form a new π bond in the product.

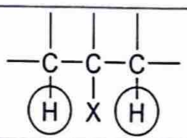
- Halogenoalkanes can undergo elimination reactions when heated with alkali (e.g. KOH) **in the presence of alcohol as solvent**.

Reaction X = C*l*, Br or I	
Reagents and conditions	**alcoholic** KOH (or NaOH) or **ethanolic** KOH (or NaOH) heat

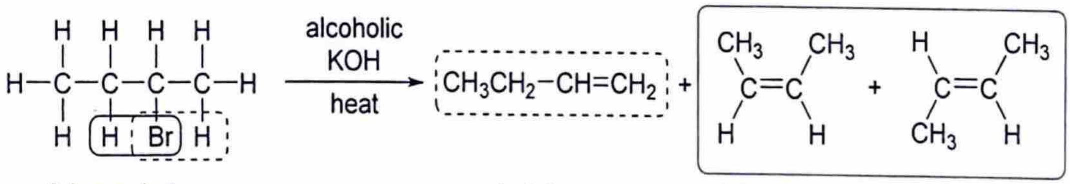
- **Alcoholic KOH** is used instead of aqueous KOH because OH^- in **alcoholic medium** behaves better as a **base** than as a nucleophile.

- During the reaction, HX is lost and an alkene is formed. The type of reaction is **elimination**. The reaction is sometimes called dehydrohalogenation since the elements of HX are eliminated from the halogenoalkane molecule.

- Elimination of HX is possible for a halogenoalkane only if the halogenoalkane molecule **contains an H atom that is bonded to an C atom that is adjacent to the C atom bonded to the halogen**.

• **Either of the H that is circled** must be present for elimination of HX take place.	

- **Example**: Reaction of 2-bromobutane with hot alcoholic KOH



2-bromobutane

but-1-ene

cis-but-2-ene

trans-but-2-ene (major product)

Note:
The ***trans***-product is favoured due to steric factor. There is less repulsion of the methyl groups in ***trans***-but-2-ene. Hence, it is more stable and is the major product.

- **Saytzeff's (or Zaitsev's) rule:**

For elimination reactions of alcohols or halogenoalkanes to alkenes, the preferred alkene is the alkene with the **most alkyl groups attached to the doubly bonded carbon atoms**, i.e. the **most highly substituted** alkene.

In the above example, but-2-ene is preferentially formed over but-1-ene.

Note: Do refer to the **lecture notes on Alkenes** for more worked examples.

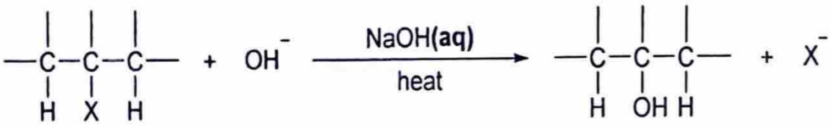
9.2 Competition between nucleophilic substitution and elimination reactions

- Many nucleophiles can also act as bases. Hence, nucleophilic substitution reactions involving halogenoalkanes are usually accompanied by elimination reactions. A mixture of products is usually obtained.

- However, by choosing the suitable conditions such as the appropriate nucleophile, temperature and solvent, we can optimise the production of the desired product.

- For **simplicity at A-level,**

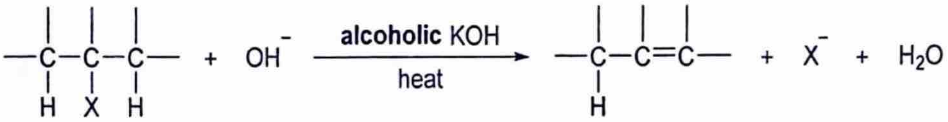
Nucleophilic substitution (S_N2 or S_N1)



$$-\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}- + OH^- \xrightarrow[\text{heat}]{\text{NaOH(aq)}} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}- + X^-$$

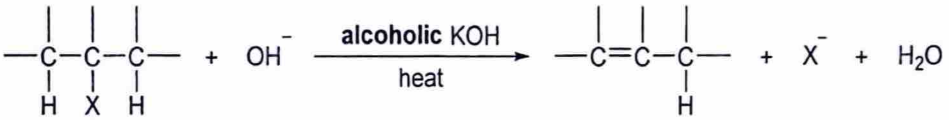
Note: OH^- acts as a **nucleophile** in **aqueous** medium.

Elimination



$$-\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}- + OH^- \xrightarrow[\text{heat}]{\text{alcoholic KOH}} -\underset{H}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}- + X^- + H_2O$$

OR



$$-\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}- + OH^- \xrightarrow[\text{heat}]{\text{alcoholic KOH}} -\overset{|}{C}=\overset{|}{C}-\underset{H}{\overset{|}{C}}- + X^- + H_2O$$

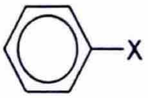
Note: OH^- acts as a **base** in **alcoholic** medium.

10 Halogenoarenes

- **Halogenoarenes** (or **aryl halides**) are **halogen derivatives of arenes** in which one or more hydrogen atoms of the benzene ring in the arene molecule is replaced by a halogen atom.

- Hence, the molecules of halogenoarenes contain one or more halogen atoms **directly attached to a benzene ring**. Each halogen atom is bonded to a sp^2 hybridised carbon of a benzene ring.

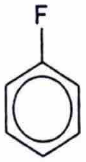
- The simplest halogenoarene is commonly written as

C_6H_5X or 

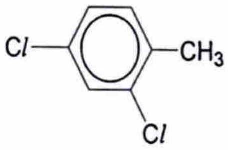
where X = F, Cl, Br or I

- Halogenoarenes are also known as **aryl halides** and are generally represented as **ArX** where **Ar** denotes an aryl group.

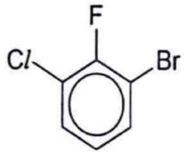
(a) Nomenclature



fluorobenzene



2,4-dichloro-1-methylbenzene



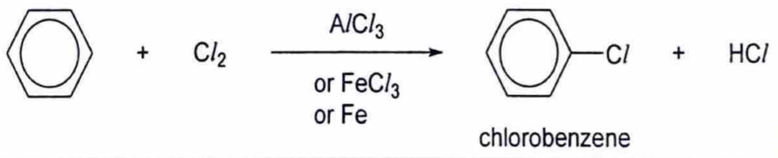
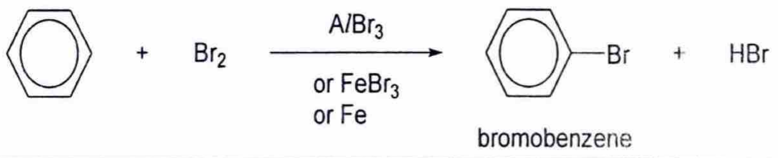
1-bromo-3-chloro-2-fluorobenzene

(b) Physical properties

- Halogenoarenes burn with a sooty, luminous flame, which is characteristic of unsaturated compounds containing a benzene ring.
- C_6H_5Cl, C_6H_5Br and C_6H_5I are colourless liquids which are **<u>insoluble</u> in water** and **denser than water**.

(c) Preparation of halogenoarenes

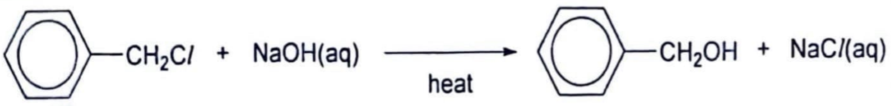
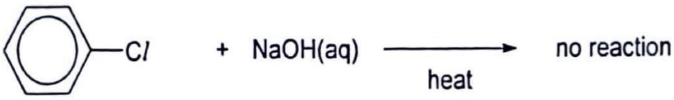
- Chlorobenzene and bromobenzene can be prepared from the electrophilic substitution reactions of benzene with halogens in the presence of a suitable catalyst.

	Mechanism: electrophilic substitution
	Mechanism: electrophilic substitution

- Refer to the **lecture notes on Arenes** for details.

11 Reactions of Halogenoarenes

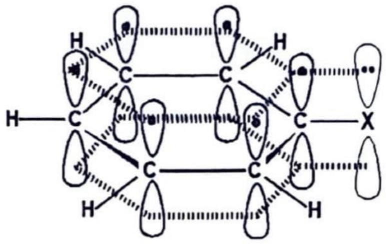
- Unlike halogenoalkanes, halogenarenes generally **do not undergo nucleophilic substitution**.

	Nucleophilic substitution occurs.
	**No nucleophilic substitution.**

- Reasons:

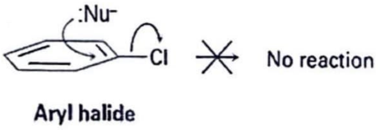
1. **Partial double bond character in the carbon-halogen bond**

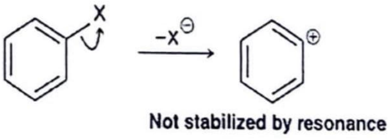
   - In the halogenoarene molecule, a p orbital of the halogen atom overlaps with the π electron cloud of the benzene ring.
   - This allows The lone pair of electrons in the p orbital of the halogen atom **to delocalise into the benzene ring.**
   - This results in Partial double bond character in the carbon–halogen (C–X) bond. More energy is required to break this stronger carbon-halogen bond.
   - This bond is **strengthened** and hence not easily broken.



2. **Steric hindrance and electronic repulsion due to the benzene ring**

   - A halogenoarene **cannot react via the S_N2 mechanism**. Sterically, nucleophilic attack at the electron-deficient carbon atom from the side directly opposite the halogen atom is **blocked by the benzene ring**. The **π-electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile**, rendering attack of the nucleophile difficult.
   - A halogenoarene also **cannot react via the S_N1 mechanism**. This is because it is **not able to form a stable carbocation**.





- **Note:**
  Halogenoalkenes (C=C–X) generally **do not undergo nucleophilic substitution** because of similar reasons as given above.

12 Distinguishing Tests

12.1 Using NaOH(aq), dilute HNO_3 and $AgNO_3$(aq) via the 4-step test

(a) Distinguishing between halogenoalkanes, R–C*l*, R–Br and R–I

Step	Procedure	Purpose/Explanation
1	Heat each sample of RX with NaOH(aq) in a test-tube.	- Hydrolysis of RX occurs. - The C–X bond breaks to produce X^-(aq). $RX + NaOH(aq) \xrightarrow[\text{heat}]{} ROH + Na^+(aq) + X^-(aq)$
2	Cool the mixture.	- This is to prevent the thermal decomposition of $AgNO_3$ which will be added in step 4.
3	Acidify the mixture with dilute HNO_3.	- This is to remove any excess NaOH. Otherwise any NaOH present will react with $AgNO_3$(aq) added in step 4 to form a brown precipitate of Ag_2O. $2Ag^+(aq) + 2OH^-(aq) \longrightarrow Ag_2O(s) + H_2O(l)$ - **HC*l*(aq) and H_2SO_4(aq) cannot be used for acidification here** because they will react with $AgNO_3$(aq) added in step 4 to form a white precipitate of AgC*l* and Ag_2SO_4 respectively. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$ $2Ag^+(aq) + SO_4^{2-}(aq) \longrightarrow Ag_2SO_4(s)$
4	Then add $AgNO_3$(aq) to the reaction mixture.	- This is produce a precipitate of AgX. The colour of AgX will help identify which RX is present initially. $Ag^+(aq) + X^-(aq) \longrightarrow AgX(s)$

- If the above 4-step test is carried out, deduction of the halogenoalkane present can be made from the colour of the silver halide precipitate formed.
    - For a chloroalkane, a **white precipitate of AgC*l*** is observed.
    - For a bromoalkane, a **pale cream precipitate of AgBr** is observed.
    - For an iodoalkane, a **yellow precipitate of AgI** is observed.

(b) Distinguishing between halogenoalkanes and halogenoarenes

- **Example:** Chemical test to distinguish between chloroethane and chlorobenzene.

Chemical test	Add NaOH(aq) to each sample in a test-tube and heat each mixture. Cool each mixture and acidify with dilute HNO_3. Then add $AgNO_3$(aq).
Observations	- For chloroethane, a white precipitate of AgC*l* is observed. - For chlorobenzene, no precipitate is observed.
Equations	$CH_3CH_2Cl + OH^-(aq) \longrightarrow CH_3CH_2OH + Cl^-$ $Cl^-(aq) + Ag^+(aq) \longrightarrow \underset{\text{white precipitate}}{AgCl(s)}$

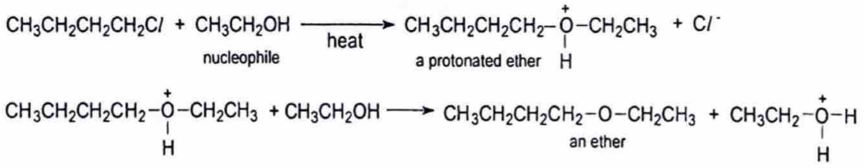
(c) Distinguishing between halogenoalkanes and other functional groups

- The same 4-step test can be carried out to distinguish between a halogenoalkane and other functional groups.
- **Example:** Chemical test to distinguish between 1-chlorobutane and butan-1-ol.

Chemical test	Add NaOH(aq) to each sample in a test-tube and heat each mixture. Cool each mixture and acidify with dilute HNO_3. Then add $AgNO_3$(aq).
Observations	• For 1-chlorobutane, a **white precipitate of AgC*l*** is observed. • For butan-1-ol, **no precipitate** is observed.
Equations	$CH_3CH_2CH_2CH_2Cl + OH^-(aq) \longrightarrow CH_3CH_2CH_2CH_2OH + Cl^-$ $Cl^-(aq) + Ag^+(aq) \longrightarrow \underset{\text{white precipitate}}{AgCl(s)}$

12.2 Using ethanolic $AgNO_3$ (or alcoholic $AgNO_3$)

- Ethanolic $AgNO_3$ is sometimes the preferred reagent to use to test for halogenoalkanes. This is because the ethanol used is able to dissolve both the halogenoalkane and $AgNO_3$.
- Note: In ethanolic $AgNO_3$, the **ethanol molecule** is able to act as a nucleophile.
- **Example:** Chemical test to distinguish between 1-chlorobutane and butan-1-ol

Chemical test	Add ethanolic $AgNO_3$ to each sample in a test-tube and warm each mixture.
Observations	• For 1-chlorobutane, a **white precipitate of AgC*l*** is observed. • For butan-1-ol, **no precipitate** is observed.
Equations	 $CH_3CH_2CH_2CH_2Cl + \underset{\text{nucleophile}}{CH_3CH_2OH} \xrightarrow[\text{heat}]{} \underset{\text{a protonated ether}}{CH_3CH_2CH_2CH_2-\overset{+}{\underset{\underset{H}{\vert}}{O}}-CH_2CH_3} + Cl^-$ $CH_3CH_2CH_2CH_2-\overset{+}{\underset{\underset{H}{\vert}}{O}}-CH_2CH_3 + CH_3CH_2OH \longrightarrow \underset{\text{an ether}}{CH_3CH_2CH_2CH_2-O-CH_2CH_3} + CH_3CH_2-\overset{+}{\underset{\underset{H}{\vert}}{O}}-H$ $Cl^-(alc) + Ag^+(alc) \longrightarrow \underset{\text{white precipitate}}{AgCl(s)}$

(Note : Equation 1 : nucleophilic substitution;
Equation 2 : acid-base reaction;
Equation 3 : precipitation)

13 Uses of Fluoroalkanes and Fluorohalogenoalkanes

- Due to the strength of C–F and C–Cl bonds, **fluoroalkanes** and **fluorochloroalkanes** are stable molecular entities under ambient conditions, exhibiting low toxicity, low reactivity and low flammability.

- Of all the fluorohalogenoalkanes, **chlorofluorocarbons (or CFCs)** manufactured under the trade name Freons are the most widely known.

13.1 Chlorofluorocarbons or CFCs

- **Chlorofluorocarbons or CFCs** are halogenoalkanes that contain only chlorine, fluorine and carbon. Their molecules contain only C–F and C–Cl bonds (and no C–H bond). They are sold under the trade name of Freons®. Examples are $CFCl_3$, CCl_2F_2 and $C_2Cl_2F_4$.

- Since C–F and C–Cl bonds are relatively strong, **CFCs are relatively stable** under normal atmospheric conditions. Of course, in the presence of a nucleophile, CFCs containing C–Cl bonds are reactive.

- CFCs have some desirable properties which make them useful compounds for various applications. Some properties of CFCs and their uses are shown in the table below.

Some properties of CFCs	**Use**	**CFCs or Halons used previously or still in use**	**HCFCs or HFCs or others as replacements**
• stable and chemically unreactive • low toxicity • non-flammable • odourless • volatile i.e. low boiling point • easily liquefy under pressure	refrigerants	CF_2Cl_2	$CHClF_2$, CF_3CH_2F, CF_3CHF_2
	aerosol propellants	CF_2Cl_2, $CClF_2CClF_2$	low-boiling hydrocarbons (flammable) CO_2 (in cooking spray) CF_3CH_2F (in asthma inhalers)
	anaesthetics	$CF_3CHBrCl$ (halothane)	$CF_3CHCl–O–CHF_2$ (isoflurane) $(CF_3)_2CH–O–CH_2F$ (sevoflurane)
	blowing agents for foams	CCl_3F, $Cl_2FCCClF_2$	$CF_3CH_2CHF_2$
	solvents, degreasing agents, cleaning agents	CCl_3F, CCl_2FCClF_2	$CF_3CF_2CHFCHFCH_3$
	fire extinguishers	$CBrClF_2$	CF_3CHCl_2

13.2 Halons

- **Halons** are halogenoalkanes related to CFCs and they contain only carbon, bromine and other halogens (no hydrogen). Examples are $CBrClF_2$ and $CBrF_3$.

- Halons are used in fire extinguisher systems because they are effective fire retardants. Heat-induced cleavage of the weak C–Br bond releases bromine atoms, which suppress combustion by inhibiting the free-radical chain reactions occurring in flames.

13.3 Hydrochlorofluorocarbons (HCFCs) and Hydrofluorocarbons (HFCs)

- Since CFCs and Halons can damage the ozone layer (see **Section 14**), their use has been either discontinued or controlled and chemists have had to find alternatives.

- The interim replacements for CFCs are **hydrochlorofluorocarbons** (HCFCs), which deplete stratospheric ozone, but to a much lesser extent than CFCs. Such compounds with **C–H bonds**, are generally destroyed at lower altitudes before they reach the stratosphere to cause ozone depletion.

- Ultimately, **hydrofluorocarbons** (HFCs) will replace HCFCs. Unlike CFCs and HCFCs, HFCs have an **ozone depletion potential** (ODP) of 0.

- The uses of some HCFCs and HFCs are shown in the table above. Note that HCFCs and HFCs do act as "greenhouse gases" and may contribute to global warming. For this reason, they may be replaced in turn.

14.1 The ozone layer

- The **ozone layer** is present 20–50 km above the Earth's surface in the region of the upper atmosphere known as the **stratosphere**.

- This ozone layer absorbs short wavelength (200 nm to 300 nm) of ultraviolet light very strongly. Such radiation has harmful effects on living organisms as prolonged exposure may cause skin cancer, eye diseases and malfunctioning of the immune system. Thus, the ozone layer protects life at the surface of earth from the harmful ultraviolet radiation.

- The formation and destruction of ozone by natural processes form a dynamic equilibrium that maintains a constant concentration of ozone in the stratosphere.

- Some of the reactions involving O_2 and O_3 are given below.

(a) O_2 molecules absorb ultraviolet radiation and dissociate into oxygen radicals

$$O_2 \xrightarrow{\text{uv light}} 2O\bullet$$

(b) Oxygen radicals react with O_2 molecules to form O_3 molecules

$$O\bullet + O_2 \longrightarrow O_3$$

(c) O_3 molecules absorb ultraviolet radiation and dissociate into O_2 and $O\bullet$

$$O_3 \xrightarrow{\text{uv light}} O_2 + O\bullet$$

(d) O_3 molecules react with oxygen radicals to form O_2 molecules

$$O_3 + O\bullet \longrightarrow 2O_2$$

Overall: No net increase/decrease in both O_2 and O_3.

14.2 Effect of CFCs on the ozone layer

- In the 1930s, CFCs were seen as being the ideal chemicals for refrigerants, aerosol propellants and as blowing agents for 'expanded polystyrene' used for insulation and packaging. They were widely used and people could see no drawbacks to using them, as they were safe and inert.

- However, CFCs were subsequently found to have caused a serious environmental issue – the **depletion of the ozone layer** in the upper atmosphere. The ozone layer protects the Earth by absorbing the harmful ultraviolet radiation arriving from the Sun.

- CFCs are stable and unreactive compounds under normal conditions. When released into the environment, their stability allows them to stay in the atmosphere for a long period of time.

- Eventually the CFCs diffuse to the upper atmosphere. Here they are exposed to the stronger ultraviolet radiation from the Sun. Although the C–F bond is very strong, the C–*Cl* bond is weak enough to be split by the ultraviolet radiation to produce chlorine radicals.

- These chlorine radicals can react with the ozone molecules and upset the delicately balanced equilibrium between ozone formation and ozone breakdown brought about by natural processes.

- The **chlorine radicals** produced from CFCs in the stratosphere act as a **homogeneous catalyst** for the reaction of O_3 with O• to form O_2 as illustrated in the table below.

Step 1: CFC molecules absorb ultraviolet radiation and the C–Cl bond undergoes homolytic fission

$$CCl_2F_2 \xrightarrow{\text{uv light}} \bullet CClF_2 + Cl\bullet$$

Step 2: The chlorine radical then combines with an ozone molecule to form chlorine monoxide and molecular oxygen.

$$Cl\bullet + O_3 \longrightarrow ClO\bullet + O_2$$

Step 3: The ClO• then reacts with an oxygen radical.

$$ClO\bullet + O\bullet \longrightarrow Cl\bullet + O_2$$

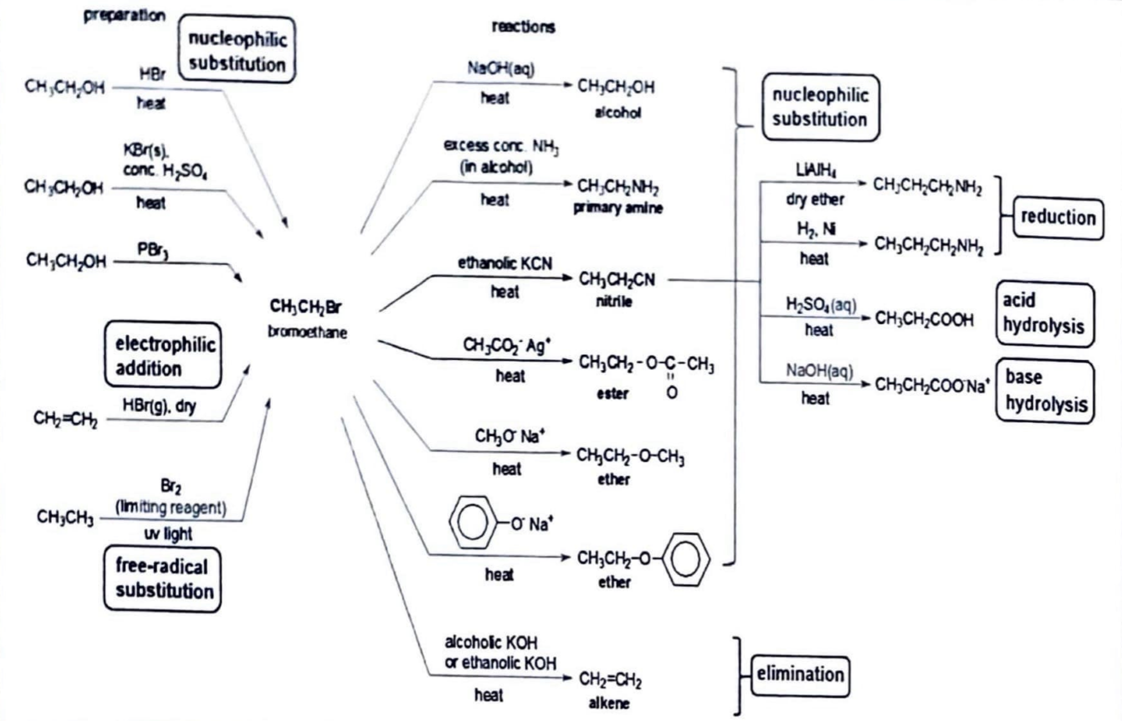
The **chain-propagation steps** can proceed continuously i.e. 2, 3, 2, 3, ...

Note: A single chlorine radical from a CFC molecule can literally lead to the destruction of thousands of ozone molecues.

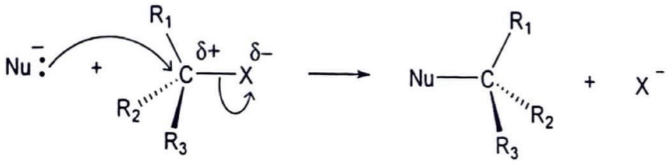
Net reaction is: $O_3 + O\bullet \xrightarrow{Cl\bullet} 2O_2$

- To protect the ozone layer, many countries have agreed to the following measures, under the **Montreal Protocol** (1987) on substances that deplete the ozone layer.
    - to reduce CFC production to half of 1986 levels by the year 1999 and a complete phase out of CFCs by the year 2000.
    - to find substitutes for CFCs which do not damage the ozone layer. For example, HFCs (or HFAs i.e. hydrofluoroalkanes) are the preferred replacements because they contain neither chlorine nor bromine and therefore have no detrimental effect on stratospheric ozone.
- It has been projected that the ozone layer could heal by 2050, but there are some indications that climatic changes, such as global warming due to greenhouse gases would delay the ozone recovery.

15 Summary



The S_N2 mechanism

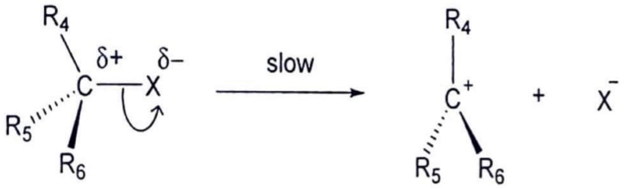


Checklist for S_N2 mechanism:

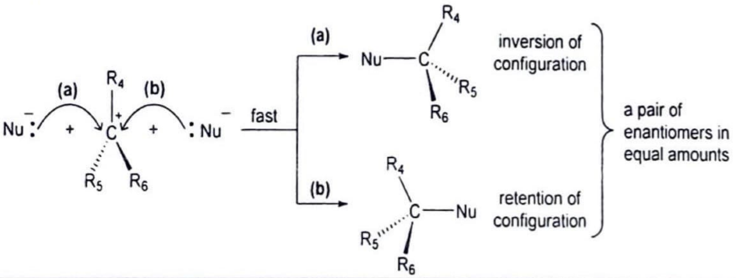
- ☐ name of mechanism
- ☐ $\delta+$ on C, $\delta-$ on X
- ☐ lone pair of electrons on Nu^-
- ☐ curly arrows to show flow of electrons
- ☐ inverted product

The S_N1 mechanism

Step 1:



Step 2:



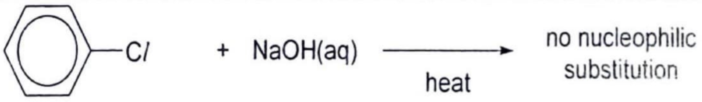
Checklist for S_N1 mechanism:

- ☐ name of mechanism
- ☐ $\delta+$ on C, $\delta-$ on X
- ☐ label slow/fast steps
- ☐ bond breaking in Step 1
- ☐ lone pair of electrons on Nu^-
- ☐ curly arrows to show flow of electrons
- ☐ nucleophile attacking from either face
- ☐ 2 products (a pair of enantiomers)

(can give non 3-D representation if C attached to X is not chiral)

Note:

1° RX	S_N2 mechanism
2° RX	S_N2 mechanism and S_N1 mechanism
3° RX	S_N1 mechanism



- Reasons: (1) C–Cl bond is strengthened due to partial double bond character (why?);
  (2) Steric hindrance and electronic repulsion due to the benzene ring.

Test for RX

1. Add NaOH(aq) to the sample and heat.
2. Cool the mixture.
3. Acidify with dilute nitric acid.
4. Then add $AgNO_3$(aq).

Observation: AgX(s) precipitate

- Create your own summaries and share with your peers!

Raffles Institution
Year 6 H2 Chemistry 2023

Tutorial 15: Halogen Derivatives

Self-Check Questions

1 **A**, **B**, **C** and **D** are four constitutional isomers with molecular formula C_4H_9Br.

- **A** displays stereoisomerism.
- **B** has the highest boiling point among the four isomers.
- **C** reacts with hot aqueous sodium hydroxide via the S_N1 mechanism.
- Both **C** and **D** react with hot ethanolic potassium hydroxide to give the same organic product.

(a) Identity **A**, **B**, **C** and **D** by drawing their skeletal formulae.

(b) Give the systematic names of **A**, **B**, **C** and **D**, and classify each isomer as a primary, secondary or tertiary bromoalkane.

(c) Rank the four isomeric bromoalkanes in order of decreasing reactivity as a substrate in an S_N2 reaction.

2 Deduce if the following halogenoalkanes undergo S_N1 or S_N2 reaction when heated with aqueous NaOH.

Halogenoalkane	**S_N1 or S_N2**	**Explanation**
CH_3CH_2Cl		
$(CH_3)_3CCl$		
(+)–$CH_3CHBrCH_2CH_3$ (Product does **not** rotate plane-polarised light)		
$CH_3CHClCH_2CH_3$ (Reaction is overall 2nd order)		
$C_6H_5CHClCH_3$ (Rate of reaction is independent of [NaOH])		

Discussion Questions

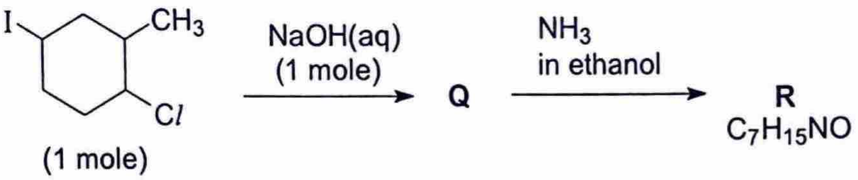
[N2009/P3/Q2 & N2012/P3/Q2(d)(i) modified]

3 The halogenoethanes, C_2H_5Cl, C_2H_5Br and C_2H_5I, differ in their physical properties and reactivities.

(a) Suggest reagents and conditions necessary to synthesise each of the three compounds from ethanol. Write a balanced equation for each reaction.

(b) Using suitable data from the *Data Booklet*, explain how the reactivities of the three compounds differ towards nucleophilic reagents.

(c) The different reactivities of organic halogen compounds can be exploited in successive reactions of dihalogen compounds. Based on your answer to **(b)**, draw the structures of the intermediate product **Q** and the product **R** in the transformation shown below.



4 **(a)** A sample of (2-chloroethyl)benzene underwent hydrolysis when heated with dilute aqueous NaOH. The method of initial rates was used to study the kinetics of the reaction.

By making use of the kinetics data below, deduce the rate equation and hence describe the mechanism for this reaction.

Experiment	Initial [(2-chloroethyl)benzene] /mol dm^{-3}	Initial [NaOH] /mol dm^{-3}	Initial rate /mol dm^{-3} min^{-1}
1	0.010	0.010	0.0025
2	0.010	0.020	0.0050
3	0.020	0.040	0.0200

(b) (1-Chloroethyl)benzene is a positional isomer of (2-chloroethyl)benzene.

(i) State the type of stereoisomerism exhibited by (1-chloroethyl)benzene and draw its stereoisomers.

(ii) When a sample containing purely one of the stereoisomers of (1-chloroethyl)benzene underwent hydrolysis in NaOH(aq), the product solution was found to be optically inactive.

Describe the mechanism for the hydrolysis of (1-chloroethyl)benzene and explain why the product solution was optically inactive. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

(c) Suggest reasons for the difference in mechanisms for **(a)** and **(b)(ii)**.

5 Bromoethane can react with many different nucleophiles to yield different organic products.

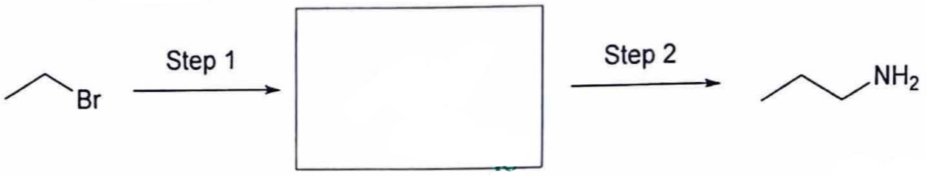
(a) Explain what is a *nucleophile*.

5 **(b)** State the reagents and conditions needed for the following conversions. Draw the structure of the intermediate, if any, in each case.

(i)

Reagents and conditions:

(ii)

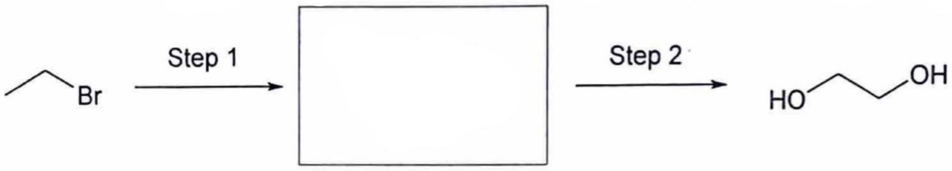


Reagents and conditions

Step 1:

Step 2:

(iii)

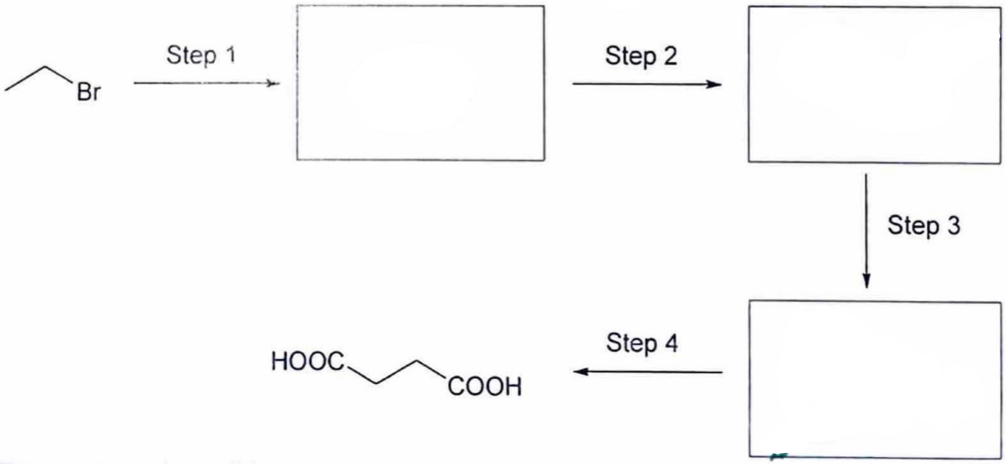


Reagents and conditions

Step 1:

Step 2:

(iv)



Reagents and conditions

Step 1:

Step 2:

Step 3:

Step 4:

(c) Describe the mechanism for the formation of $CH_3CH_2NH_2$ in **(b)(i)**.

(d) A by-product **S** in the formation of $CH_3CH_2NH_2$ in **(b)(i)** above has the formula $C_8H_{20}NBr$ and it gives an **immediate** precipitate with aqueous silver nitrate. Suggest a structure for this by-product **S** and write equations to account for its formation.

6 In an experiment to study the relative rates of nucleophilic substitution of four halogen derivatives, the following procedure was carried out:

- *4 drops of each halogen derivative were added to 4 different test-tubes.*
- *The 4 test-tubes were placed in a water bath maintained at 50 °C.*
- *1 cm^3 of 0.10 mol dm^{-3} $AgNO_3$ solution in ethanol was then added to each test-tube and a stopwatch was started simultaneously for each test-tube.*

The results are tabulated below:

Halogen derivative	**Observation upon adding ethanolic $AgNO_3$**
chlorobenzene	no observable change
2-chlorobutane	slight cloudiness after 3 minutes; still slightly cloudy after 15 min
2-bromobutane	slight cloudiness after 1 minute; pale cream precipitate after 6 min
2-iodobutane	immediately opaque; yellow precipitate within 1 min

The nucleophilic substitution reaction which takes place in some of the test-tubes may be represented by the following equation:

$$R\text{–}X + CH_3CH_2OH + AgNO_3 \longrightarrow R\text{–}OCH_2CH_3 + AgX + H^+ + NO_3^-$$

(a) Explain the varying rate of formation of precipitate in the case of 2-chlorobutane, 2-bromobutane and 2-iodobutane.

(b) Explain why there is no change observed for the test-tube containing chlorobenzene.

(c) Predict and explain what happens when the experiment is repeated with 2-chlorobut-2-ene.

7 Outline a simple chemical test to distinguish between the following pairs of compounds.

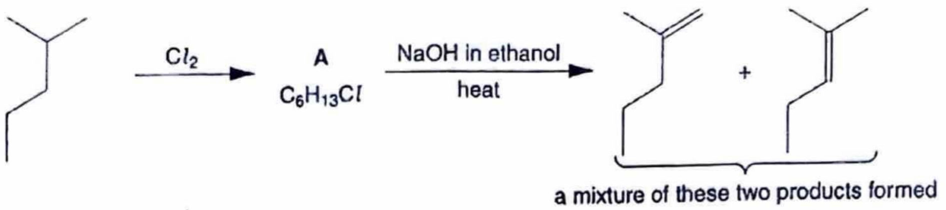
(a) (2-bromoethyl)benzene and 1-bromo-2-ethylbenzene

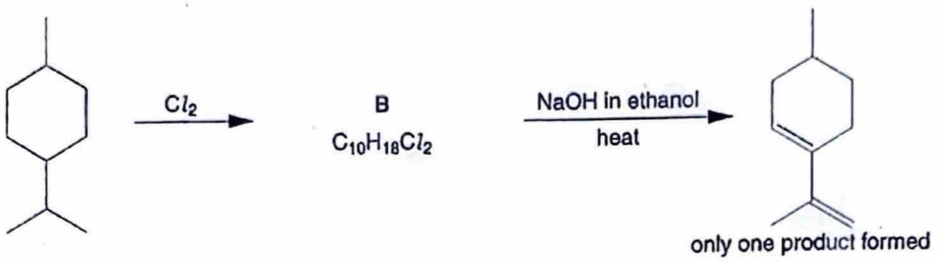
(b) chloroethane and iodoethane

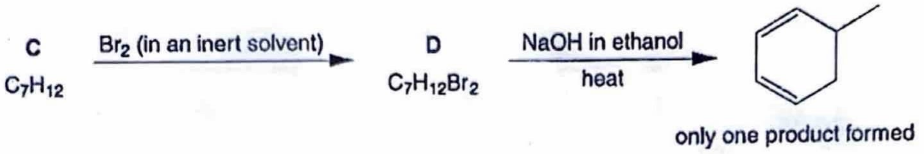
8 When a hydrocarbon **J** (M_r = 92) is treated with chlorine under different conditions, two isomeric chlorides, **K** and **L**, are formed. On heating **K** with aqueous sodium hydroxide, **M**, with molecular formula, C_7H_8O, is formed. On the other hand, **L** is inert towards aqueous sodium hydroxide.

Deduce the identities of compounds **J** to **M** and explain the reactions involved.

9 **(a)** Suggest a structural formula for each of the compounds **A** – **D** in the following schemes.







(b) Chlorofluoroalkanes, CFCs, were once used as refrigerants fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer.

(i) Suggest two reasons why CFCs were originally used for these purposes.

(ii) Explain how CFCs destroy the ozone layer.

(iii) Suggest **one** potential hazard of using alkanes instead of CFCs.