St Andrew's Junior College

H2 Chemistry 2026

Lecture Notes 13

Halogen Derivatives

Assessment Objectives:
Candidates should be able to:

(a) recall the chemistry of halogenoalkanes as exemplified by
- **(i)** the following nucleophilic substitution reactions of bromoethane:
  - hydrolysis using NaOH(aq) and heat
  - formation of nitriles using KCN in ethanol and heat
  - formation of primary amines by reaction with ammonia in ethanol heated under pressure
- **(ii)** the elimination of hydrogen bromide from 2-bromopropane using NaOH in ethanol and heat

(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 in the halogenoalkanes

(c) explain the stereochemical outcome in nucleophilic substitution involving optically active substrates (see also (b)):
- **(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 carbon-halogen 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 halogenalkanes (see also (d))
- **(ii)** halogenalkanes and halogenoarenes (see also (e))
  e.g. hydrolysis, followed by testing the halide ions

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

(h) recognise the effect of chlorofluoroalkanes (CFCs) on the ozone layer, and that their proposed replacements, hydrofluoroalkanes (HFCs) and hydrochlorofluoroalkanes (HCFCs), have significant environmental impact too
[the mechanistic details of how CFCs and HCFCs deplete the ozone layer are **not** required]

Lecture Outline:

1. Introduction
2. Physical properties
3. Preparation
4. Reactions of halogenoalkanes
    - Nucleophilic substitution
    - Elimination
5. Halogenoarenes
6. Distinguishing tests
7. Applications (self read)
8. Appendix

References:

1. Chemistry for advanced level by Peter Cann & Peter Hughes
2. 'A' Level Chemistry by E N Ramsden
3. Chemistry in Context by G C Hill & J S Holman

Useful websites:

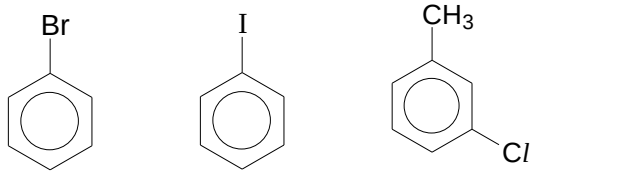
1. http://www.chemguide.co.uk/mechanisms/nucsubmenu.html
2. MOE SLS (requires SLS login)

Lesson 1: Introduction to Common Reactions of Halogenoalkanes
Lesson 2: Nucleophilic Substitution of Halogenoalkanes
Lesson 3: Stereochemical Outcomes of Nucleophilic Substitution Reaction of Halogenoalkanes
Lesson 4: Reactivity of Halogenoalkanes, Halogenoarenes and Acyl Chlorides
Lesson 5: Applications of Halogenoalkanes

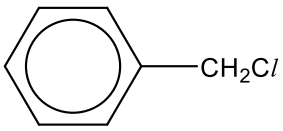
Lesson 1	Lesson 2	Lesson 3	Lesson 4	Lesson 5
	S_N1 and S_N2	Animations of the stereochemical outcomes of S_N1 and S_N2		

1. INTRODUCTION

Halogen derivatives contain a **polar C−X bond**, where **X is a halogen atom** (Group 17 – F, C*l*, Br or I).

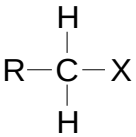
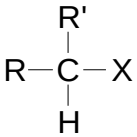
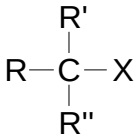
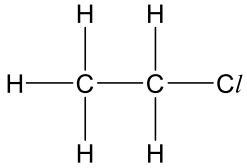
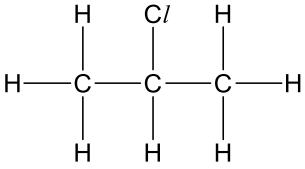
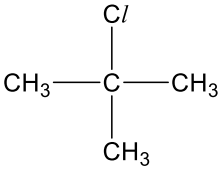
Halogenoalkanes (alkyl halides)	**Halogenoarenes (aryl halides)**
• Halogen derivative of an alkane • R – X, where R is an alkyl group • General formula: **$C_nH_{2n+1}X$**	• Halogen derivative of an arene • Ar – X, where Ar is an aryl group • Halogen atom is attached directly to the aromatic ring
Examples CH_3Cl chloromethane CH_3CH_2Br bromoethane $CH_3CH_2CH_2I$ 1-iodopropane	**Examples**  bromobenzene iodobenzene 3-chloromethylbenzene

Is chloromethylbenzene (benzyl chloride) a halogenoalkane or halogenoarene?



It is a halogenoalkane. It is not a halogenoarene as the halogen is not directly attached to the aromatic ring.

Halogenoalkanes can be classified as **primary**, **secondary** or **tertiary** depending on the number of R groups attached to the C atom bonded to the halogen.

Primary (1°) RX 1 R group	**Secondary (2°) RX** 2 R groups	**Tertiary (3°) RX** 3 R groups
		
 chloroethane	 2-chloropropane	 2-chloro-2-methylpropane

2. PHYSICAL PROPERTIES

2.1 Boiling Points

Comparison between halogenoalkanes and alkanes

Halogenoalkanes have **higher** boiling points than the corresponding alkanes of the **same carbon chain length**. E.g.

Compound	Boiling Point / °C
CH_3Cl	−24
CH_4	−162

- CH_4 has **simple molecular structure** with **instantaneous dipole-induced dipole (id–id)** interactions between **molecules.**
- CH_3Cl has **simple molecular structure** with **permanent dipole-permanent dipole (pd–pd)** interactions between **molecules.**
- **More energy** is required to overcome the **stronger** pd-pd interactions, CH_3Cl has higher boiling point than CH_4.

  Furthermore, the **id–id** between CH_3Cl molecules are stronger than that of CH_4 due to the **greater number of electrons** / **larger electron cloud size**.

Comparison between halogen derivatives with similar number of C atoms

For halogenoalkanes with the same alkyl group but different halogen atoms, the boiling points generally **increase down Group 17**. E.g.

Compound	Boiling Point / °C
CH_3CH_2F	−37.1
CH_3CH_2Cl	12.5
CH_3CH_2Br	38
CH_3CH_2I	72

- **Number of electrons increases** from $CH_3CH_2F < CH_3CH_2Cl < CH_3CH_2Br < CH_3CH_2I$
- Strength of **instantaneous dipole-induced dipole (id–id)** interactions **between molecules increases** from $CH_3CH_2F < CH_3CH_2Cl < CH_3CH_2Br < CH_3CH_2I$ (due to more polarizable electron cloud)
- **More energy** required to overcome the stronger id-id interactions, boiling point increases from $CH_3CH_2F < CH_3CH_2Cl < CH_3CH_2Br < CH_3CH_2I$

2.2 Solubility

Since halogenoalkanes and halogenoarenes are **polar** molecules, they usually dissolve in **polar** organic solvents, such as ethanol and propanone, as the **energy released** on formation of **permanent dipole – permanent dipole (pd-pd) interactions** between the solute and solvent is **sufficient** to overcome the **pd-pd interactions between the solute molecules** and **pd-pd interactions between the solvent molecules**.

However, halogenoalkanes and halogenoarenes are largely **insoluble in water** as the **energy released on formation of pd-pd interactions** between the halogen derivatives and water molecules is **insufficient** to overcome the (stronger) **hydrogen bonding between water molecules** and **pd-pd interactions between halogenoalkane molecules**.

3. PREPARATION OF HALOGENOALKANES AND HALOGENOARENES

3.1 Nucleophilic **substitution** of alcohols
(Refer to hydroxy compound notes)

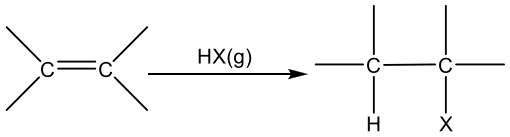
Halogenoalkanes are mainly prepared from alcohols. The hydroxyl (–OH) group is **substituted** by the halogen atom.

- Using phosphorus chloride, PCl_5
  General equation: $R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$ (white fumes)

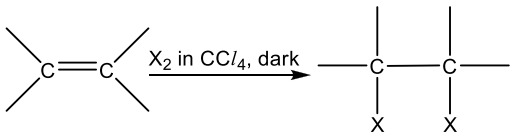
- Using HX(g) (where X = Cl, Br or I)
  General equation: $R{-}OH + HX \longrightarrow R{-}Cl + H_2O$
  Refer to Appendix 1 for more details on the generation of HX.

3.2 Electrophilic **addition** of alkenes
(Refer to alkene notes)

- Using HX (g)



- Using X_2 in CCl_4



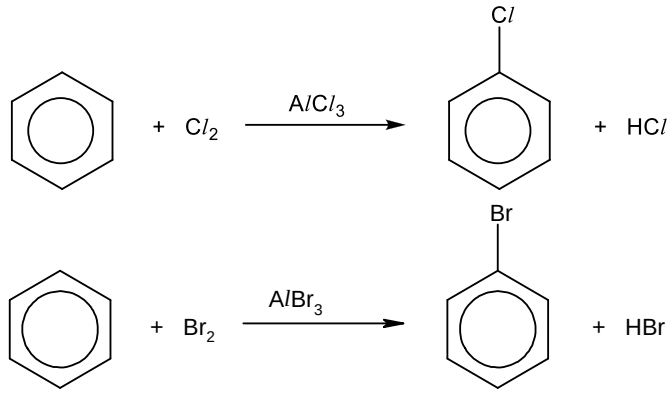
3.3 Free radical **substitution** of alkanes
(Refer to alkanes notes)

- Using limited $X_2(g)$ in UV light
  General equation: $R{-}H + X_2 \longrightarrow R{-}X + HX$

  FRS is not a recommended method to obtain a specific halogenoalkane as a mixture of monosubstituted and polysubstituted halogeneoalkanes will be obtained.

3.4 Electrophilic substitution of benzene
(Refer to arenes notes)

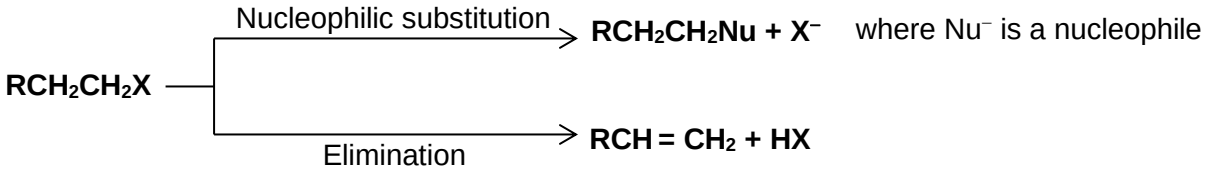
- Using Cl_2 with $AlCl_3$ catalyst or Br_2 with $AlBr_3$ catalyst



4. REACTIONS OF HALOGENOALKANES

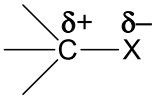
(b)	describe and explain the mechanisms of nucleophilic substitutions in halogenoalkanes:
	(i) S_N1, in terms of stability of the carbocation intermediates
	(ii) S_N2, in terms of steric hindrance in the halogenoalkanes
(c)	explain the stereochemical outcome in nucleophilic substitution involving optically active substrates (see also (b)):
	(i) inversion of configuration in S_N2 mechanism
	(ii) racemisation in S_N1 mechanism

Halogenoalkanes undergo mainly **<u>nucleophilic substitution</u>** and **<u>elimination</u>** reactions.



4.1 <u>Nucleophilic substitution</u>

Halogenoalkanes have a **polar C–X bond**. As X is more electronegative than C, the C bonded to X is electron deficient and is susceptible to attack by nucleophiles.



Recall (introduction to organic chemistry):
A nucleophile is an **electron-pair donor**. Nucleophiles are **electron-rich** species.

- Examples of neutral nucleophiles: H_2O, ROH, NH_3, RNH_2
- Examples of anionic nucleophiles: OH^-, RO^-, CN^-, NH_2^-, $RCOO^-$, X^-

A reaction where a halogen atom in a halogenoalkane is substituted by a nucleophile (Nu^-) is known as **<u>nucleophilic substitution (S_N)</u>**.

$$R–X + Nu^- \longrightarrow R–Nu + X^-$$

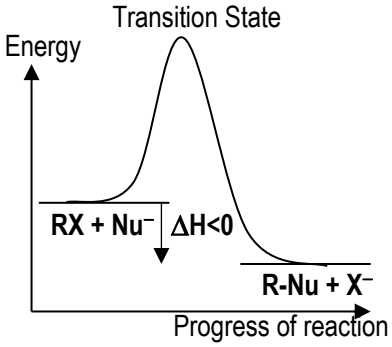
Nucleophilic substitution may occur via an
<u>S_N2</u> (**s**ubstitution, **n**ucleophilic, **bi**molecular) or an
<u>S_N1</u> (**s**ubstitution, **n**ucleophilic, **uni**molecular) mechanism.

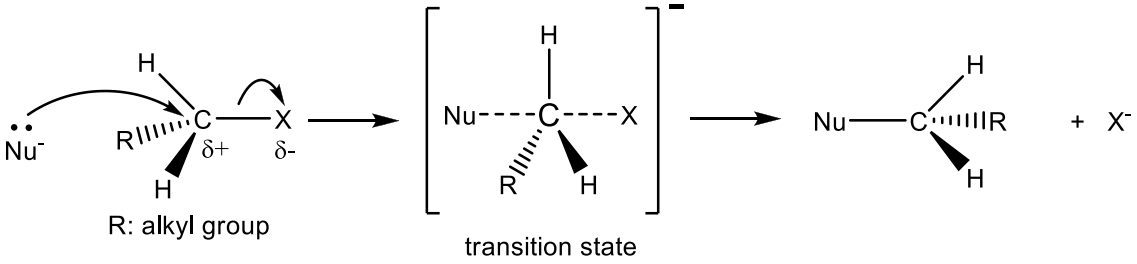
4.1.1 S_N2 mechanism

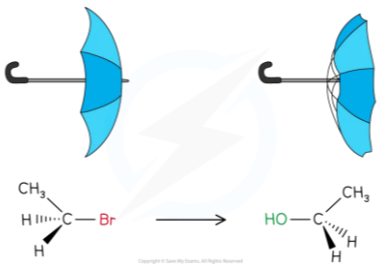
S_N2 (**s**ubstitution, **n**ucleophilic, **bi**molecular) involves the collision of **2** species (Nu^- and RX) in the rate determining (slow) step. The reaction rate is dependent on the concentrations of the nucleophile and RX.

$$\textbf{Rate} = k[Nu^-][RX]$$

Energy Profile of S_N2 reaction





Nucleophilic Attack	**Transition State**	**Product Formation**
• The C–X bond is polar. • Nu^- attacks the δ+ carbon from the **opposite** side of the halogen atom (backside attack). Reasons for backside attack: 1) large X blocks the approach of incoming Nu–. 2) $X^{\delta-}$ and Nu^- will repel each other	• Bond forming and bond breaking occur in a **concerted** manner (i.e. the new C–Nu bond is forming at the same time as the old C–X bond is breaking) • In the transition state, the C–X bond is partially broken and the C–Nu bond is partially formed. • The transition state is an energy maximum and cannot be isolated. • Note conservation of charge when forming the transition state.	• X^- is formed. • There is **inversion of configuration** at the carbon centre (i.e. the 3 bonds that are attached to the carbon centre are turned inside out) 

In general, **primary** halogenoalkanes undergo S_N2.

Exercise 1

Describe the mechanism for the reaction of 1-bromopropane with aqueous KOH in the presence of heat.

Name of mechanism:

☞ **Self- Check: Q1**

Criteria of Success for S_N2 mechanism:

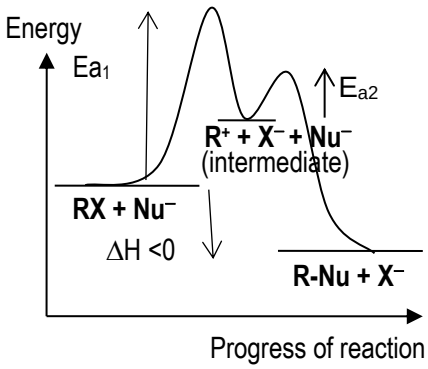
- ☐ Name of mechanism: **Nucleophilic substitution, S_N2**
- ☐ 3D representation of reactant and product
- ☐ δ+ on C, δ– on X
- ☐ Lone pair of electrons on Nu
- ☐ Nu attack from the side opposite to X
- ☐ Curly arrows to show flow of a pair of electrons
- ☐ Bond breaking and bond forming in transition state
- ☐ Overall charge on transition state if Nu^- was used
- ☐ Inverted product

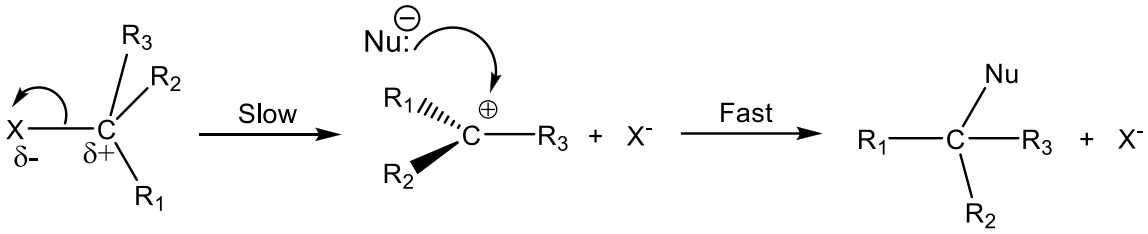
4.1.2 S_N1 mechanism

S_N1 (**s**ubstitution, **n**ucleophilic, **uni**molecular) involves only 1 species (RX) in the rate determining (slow) step. The reaction rate is dependent only on the concentration of RX as the nucleophile is not involved in the rate determining step.

Rate = k[RX]

Energy Profile of S_N1 reaction

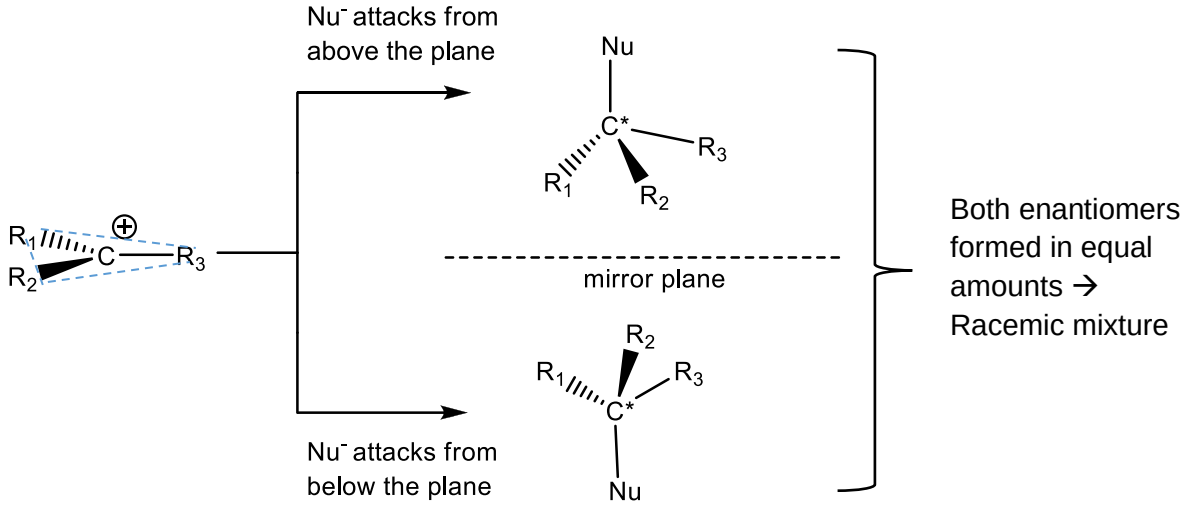




Step 1 **Formation of carbocation (slow):**	**Step 2** **Attack by Nu^- (fast):**
• The C–X bond breaks heterolytically to form a **trigonal planar carbocation intermediate** • The positively charged C atom in the carbocation intermediate is sp^2 hybridised. • The intermediate is at an energy minimum.	• Since the carbocation intermediate is trigonal planar, the nucleophile may attack the positively charged C atom from **above or below the plane with equal probability**. • If the resulting sp^3 carbon is chiral (i.e. R_1, R_2 and R_3 are different groups), a racemic mixture (a mixture with both enantiomers present in equal amounts) will be obtained. • A racemic mixture does not rotate plane polarised light.

Criteria of Success for S_N1 mechanism:

- ☐ Name of mechanism: **Nucleophile Substitution, S_N1**
- ☐ δ+ on C, δ– on X
- ☐ Curly arrows to show flow of a pair of electrons
- ☐ Lone pair of electrons on Nu
- ☐ Trigonal planar carbocation intermediate
- ☐ Nu attack from either side of the trigonal plane
- ☐ Label slow and fast steps
- ☐ If chiral C exists, a pair of optical isomers as products



In general, **tertiary** halogenoalkanes undergo S_N1.

4.2 Factors affecting nucleophilic substitution

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

4.2.1 C–X Bond Strength

During nucleophilic substitution (both S_N1 and S_N2), the C–X bond is broken in the slow step.

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

Based on C–X bond energies, expected ease of bond breaking is:

C – F < C – C*l* < C – Br < C – I

Down the group, **size of the halogen atom increases** and the valence orbitals of the halogen atom become bigger and more diffuse. **Orbital overlap is less effective** and **C – X bond strength decreases**. Less energy is required to break the C – X bond.

Hence, the order of reactivity of halogenoalkanes towards nucleophiles is:

R – I > R – Br > R – C*l* > R – F

Most reactive Least reactive

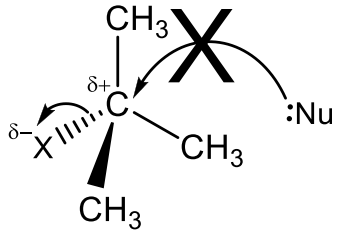
The C–F bond is so strong that fluoroalkanes are **chemically inert / unreactive** and seldom undergo nucleophilic substitution or elimination.

4.2.2 S_N1 vs S_N2

Generally (there are exceptions), primary halogenoalkanes prefer to undergo S_N2 while tertiary halogenoalkanes prefer to undergo S_N1.

Steric factors

S_N2 is favoured for primary halogenoalkanes as there is minimal **steric hindrance**. As S_N2 involves backside attack of the nucleophile, bulky alkyl groups bonded to the reactive C centre will block the approach of the nucleophile from the back. This is why it is unfavorable for tertiary halogenoalkanes to undergo S_N2.



Electronic factors

Alkyl groups are electron donating. The **greater the number of alkyl groups** present, the **less electron deficient** the C centre is, making it **less susceptible** to nucleophilic attack.

Therefore the order of reactivity of RX to S_N2:

(slowest) 3° RX < 2° RX < 1° RX < CH_3X (fastest)

Stability of carbocation

S_N1 involves the formation of a carbocation intermediate and is therefore favoured by factors that stabilise the carbocation.

The greater the number of electron donating alkyl groups, the more dispersed the positive charge on the carbocation, the more stable the carbocation.

(most stable) **3°** carbocation > **2°** carbocation > **1°** carbocation (least stable)

Therefore the order of reactivity of RX to S_N1:

(slowest) CH_3X < 1º RX < 2º RX < 3º RX (fastest)

Secondary halogenoalkanes can undergo both S_N1 and S_N2. To decide on the mechanism, refer to **data provided** in the question (e.g. rate equation). Data provided takes priority over the classification of RX.

Why does 2-bromo-2-methylpropane undergo S_N1 instead of S_N2?

2-bromo-2-methylpropane is a tertiary RX.

S_N2 is not favorable because:

- There is **steric hindrance** by the 3 bulky alkyl groups, preventing backside attack by the nucleophile.
- The reactive C centre is less electron deficient and **less susceptible to nucleophilic attack** due to the presence of 3 electron-donating alkyl groups

S_N1 mechanism is favourable because the 3 electron-donating alkyl groups disperse the positive charge, stabilising the **3° carbocation intermediate** formed.

Exercise 2

The reaction of CH_3CHDBr with hot aqueous sodium hydroxide yields only 1 optically active product. However, the reaction of 2-bromo-2-ethylpentane with hot aqueous sodium hydroxide yields an optically inactive (racemic) mixture. Explain why.

Thinking process:

- What are the structures of CH_3CHDBr and 2-bromo-2-ethylpentane?
- What type of RX are they?
- What is the mechanism for their reactions with NaOH?
- Under what circumstances would a compound be optically active?
- What is a racemic mixture and under what circumstances would it be formed?

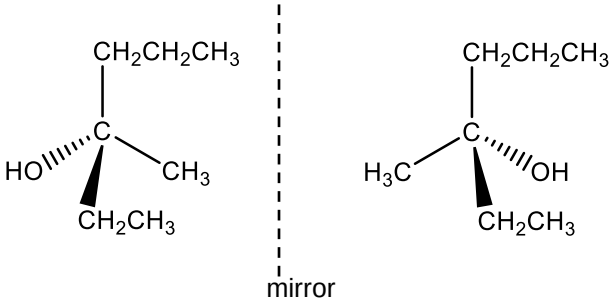
CH_3CHDBr is a RX.

It undergoes to give only 1 enantiomer which is optically active.

2-bromo-2-ethylpentane is a RX.

It undergoes .

As the carbocation intermediate is trigonal planar, OH^- can attack from above or below the plane with equal probability to give a racemic mixture of 2 enantiomers in equal proportion.



4.3 Examples of nucleophilic substitution reactions

(a) recall the chemistry of halogenoalkanes as exemplified by

(i) the following nucleophilic substitution reactions of bromoethane:

- hydrolysis using NaOH(aq) and heat
- formation of nitriles using KCN in ethanol and heat
- formation of primary amines by reaction with ammonia in ethanol heated under pressure

(ii) the elimination of hydrogen bromide from 2-bromopropane using NaOH in ethanol and heat

4.3.1 Formation of alcohols

➢ **Reagents and Conditions**

NaOH(aq), heat (OH^- is the nucleophile, Na^+ is just a spectator ion, water is the solvent)

General Equation: $R–\mathbf{X} + \mathbf{OH^-}(aq) \xrightarrow{\text{heat}} R–\mathbf{OH} + \mathbf{X^-}$

E.g.: $CH_3CH_2Cl + OH^-(aq) \xrightarrow{\text{heat}} CH_3CH_2OH + Cl^-$

- **Type of reaction**: nucleophilic substitution (hydrolysis)
- It is not possible to perform hydrolysis using water alone as water is a weaker nucleophile as compared to OH^- and rate of hydrolysis will be too slow.
- Water must be the solvent instead of alcohol to prevent elimination (See Section 4.4)

4.3.2 Formation of nitriles

➢ **Reagents and Conditions**

KCN in ethanol, heat (CN^- is the nucleophile, K^+ is just a spectator ion, ethanol is the solvent)

General Equation: $R–\mathbf{X} + \mathbf{CN^-} \xrightarrow{\text{heat}} R–\mathbf{CN} + \mathbf{X^-}$

E.g.: $CH_3CH_2Cl + CN^- \xrightarrow{\text{heat}} CH_3CH_2CN + Cl^-$

- This is a **step-up** reaction as the carbon chain is lengthened by 1. The nitrile can then be converted to other useful functional groups.

- **Acid hydrolysis** of nitriles to form carboxylic acids

  ➢ **Reagents and Conditions**

  $H_2SO_4(aq)$, heat

  General Equation: $R–\mathbf{CN} + H^+ + 2H_2O \longrightarrow R\mathbf{COOH} + NH_4^+$

  E.g.: $CH_3CH_2CN + H^+ + 2H_2O \longrightarrow CH_3CH_2COOH + NH_4^+$

- **Basic hydrolysis** of nitriles to form carboxylate salts

  ➢ **Reagents and Conditions**

  NaOH(aq), heat

  General Equation: $R–\mathbf{CN} + OH^- + H_2O \longrightarrow R\mathbf{COO^-} + NH_3$

  E.g.: $CH_3CH_2CN + NaOH + H_2O \longrightarrow CH_3CH_2COO^- Na^+ + NH_3$

- **Reduction** of nitriles to form primary amines

  ➢ **Reagents and Conditions**
  $LiAlH_4$ in dry ether OR
  $H_2(g)$, Ni catalyst, heat

	$LiAlH_4$ in dry ether (use [H] to balance)	**H_2, Ni, heat (use H_2 to balance)**
Equation	$R–CN + 4[H] \rightarrow R–CH_2NH_2$	$R–CN + 2H_2 \rightarrow R–CH_2NH_2$
E.g.	$CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$	$CH_3CH_2CN + 2H_2 \rightarrow CH_3CH_2CH_2NH_2$

Exercise 3

Propose a reaction scheme to synthesise propanoic acid from ethanol in 3 steps. Suggest structures for all intermediates and suggest the reagents and conditions for each step.

Thinking process:
- What is the number of C in ethanol and propanoic acid?
- How can we increase the C chain by 1 C?

4.3.3 Formation of amines

➢ **Reagents and Conditions**
NH_3 in ethanol, heat under pressure (NH_3 is the nucleophile, ethanol is the solvent)
Refer to Appendix 2 for detailed mechanism

General Equation: $R–X + NH_3 \longrightarrow R–NH_2 + HX$

E.g.: $CH_3CH_2Br + NH_3 \longrightarrow CH_3CH_2NH_2 + HBr$

FYI: The reaction is carried out in a sealed tube to prevent the gaseous NH_3 from escaping. The sealed tube creates high pressure, so reaction can take place at a faster rate.

Exercise 4

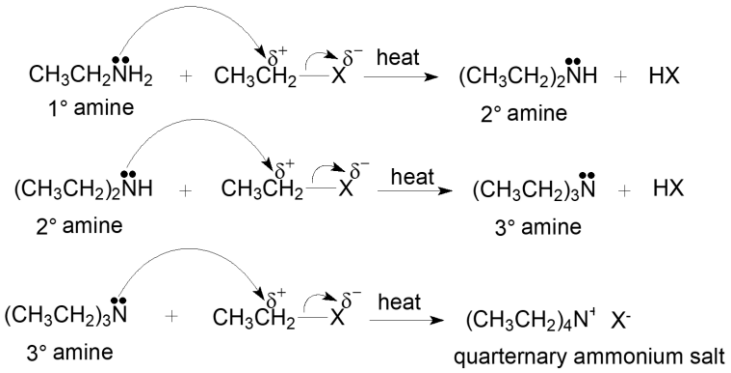
Draw the mechanism for the reaction of CH_3CH_2CI with NH_3.

By conservation of charge, the transition state must be neutral (no overall charge) as the nucleophile used is neutral.

FYI: Polyalkylation

For nucleophilic substitution with NH_3, NH_3 must be in excess to prevent polyalkylation.

As the amines formed are also nucleophiles (nitrogen has a lone pair of electrons), the amines can react with more RX to yield 2° and 3° amines and quaternary ammonium salts.



A **mixture of products is obtained**, which is difficult to separate and causes poor yield. **To avoid further substitution causing the mixture of products, excess ammonia** is used to consume most of the RX at the first step so that there is little RX left for further substitution.

If the halogenoalkane was in excess, the major product formed would be the quaternary ammonium salt, as each substituted amine would react with more R-X at an even greater speed. This is because alkyl groups are electron-donating, enhancing the availability of lone pair of electrons on nitrogen.

Strength of nucleophile: NH_3 < 1° amine < 2° amine < 3° amine

Summary of nucleophilic substitution reactions of RX:

Nucleophile	Reagents and Conditions	Product	Remarks
OH^-	NaOH(aq), heat You might see KOH used in questions	alcohol	Solvent must be aqueous to prevent elimination
CN^-	KCN in ethanol, heat You might see NaCN used in questions	nitrile	Step up reaction, extend carbon chain by 1 C
NH_3	NH_3 in ethanol, heat under pressure	amine	Polyalkylation occurs when RX is in excess

☞ **Self- Check: Q2(a) – (b), 3 – 5**

4.4 Elimination

(a)	recall the chemistry of halogenoalkanes as exemplified by
(ii)	the elimination of hydrogen bromide from 2-bromopropane using NaOH in ethanol and heat

Elimination of H and X atoms from **adjacent** carbon atoms of halogenoalkanes results in the formation of a C=C double bond i.e. alkenes. Elimination can take place only if there is a H atom on the adjacent C such that HX can be eliminated.

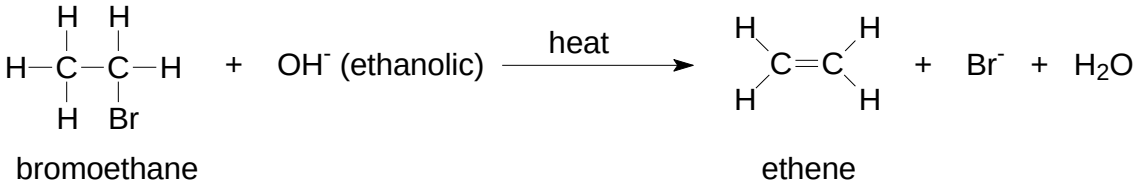
Under ethanolic conditions, OH^- acts as a strong **base** (proton acceptor) rather than a nucleophile and abstracts a proton (H^+) readily.

➢ **Reagents and Conditions**

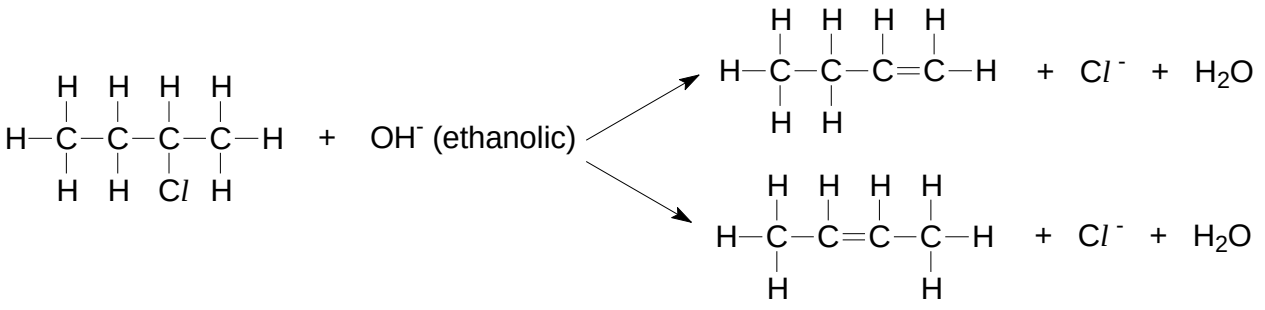
NaOH in ethanol, heat

Recall: NaOH(aq), heat results in nucleophilic substitution instead of elimination.

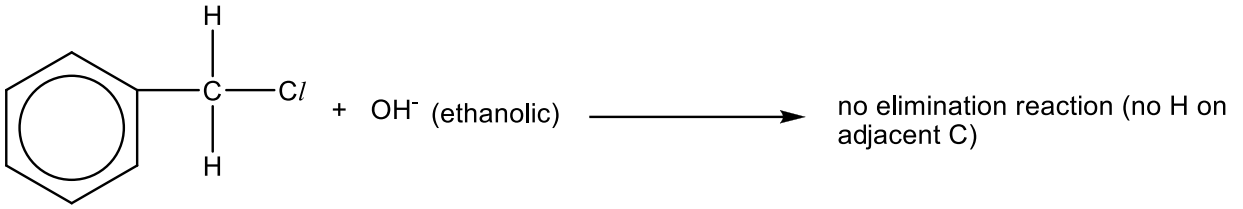
E.g.



bromoethane ethene



a mixture of products are obtained, the major product is the more substituted alkene



☞ **Self- Check: Q2(c), Q6 - 7**

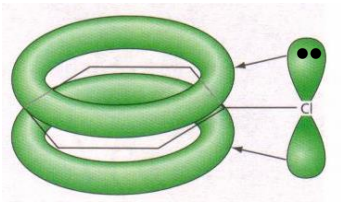
5. HALOGENOARENES

5.1 Unreactivity of halogenoarenes to nucleophilic substitution

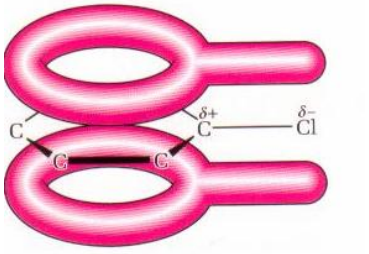
(e)	explain the unreactivity of chlorobenzene compared to halogenoalkanes towards nucleophilic substitution, in terms of the delocalisation of the lone pair of electrons on the halogen and steric hindrance

Halogenoarenes, e.g. chlorobenzene, are unreactive towards nucleophilic substitution compared to halogenoalkanes.

Reason 1: Partial double bond character of C–X bond in halogenoarenes



- The p orbital of the halogen atom overlaps with the π electron cloud of benzene
- **Lone pair of electrons of the halogen atom delocalise into the benzene ring**.
- The C–X bond has **partial double bond** character (shortened and strengthened bond)
- **More energy** is required to break the **stronger C–X** bond



Reason 2: Steric factors

- The benzene ring is bulky and will block the approach of the incoming nucleophile (steric hindrance)

Reason 3: Electronic factors

- The benzene ring is electron-rich and will repel the electron-rich nucleophile

For example, unlike typical nucleophilic substitutions of halogenoalkane RX to form alcohol ROH, phenol C_6H_5OH **CANNOT** be formed by heating chlorobenzene with NaOH(aq).

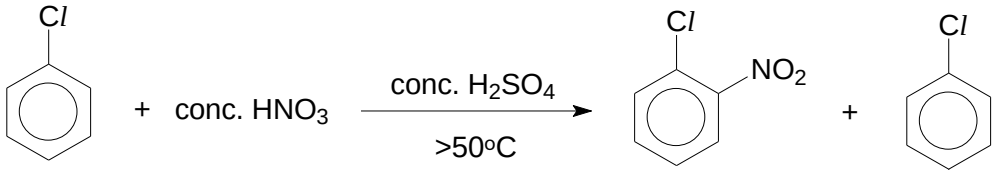
$$C_6H_5Cl + OH^-(aq) \xrightarrow[\text{heat}]{\not\longrightarrow} C_6H_5OH + Cl^-(aq)$$

☞ **Self- Check: Q8**

5.2 Electrophilic substitution of halogenoarenes
(Refer to arenes notes)

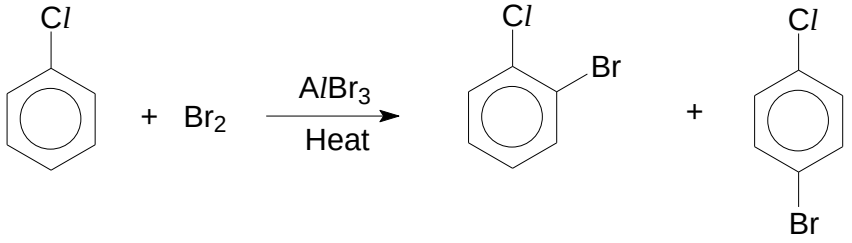
While halogenoarenes are unreactive to nucleophilic substitution, they can undergo **electrophilic substitution** at the ring, similar to benzene and methylbenzene.

Nitration

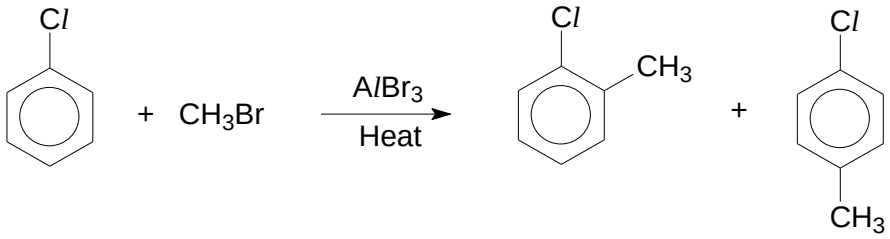


Halogens deactivate the benzene ring and are 2,4-directing. (Refer to Data Booklet)

Halogenation



Friedel-Crafts Alkylation



☞ **Self- Check: Q2(d)**

6. DISTINGUISHING TESTS

(f) suggest characteristic reactions to differentiate between
- **(i)** different halogenalkanes (see also (d))
- **(ii)** halogenalkanes and halogenoarenes (see also (e))
  e.g. hydrolysis, followed by testing the halide ions

6.1 Distinguishing halogenoalkanes and halogenoarenes

Step 1:	Add NaOH(aq) to both compounds and heat.	RX will undergo nucleophilic substitution, no reaction for ArX
Step 2:	Cool and acidify with HNO_3(aq)	HNO_3(aq) removes excess NaOH(aq) present, to prevent formation of insoluble Ag_2O or AgOH (brown ppt) in Step 3. Only HNO_3(aq) can be used for acidification. HC*l*(aq) will introduce the Cl^- ion, leading to a false positive. H_2SO_4(aq) will cause the formation of insoluble Ag_2SO_4 (white ppt) in Step 3.
Step 3:	Add $AgNO_3$(aq)	Ag^+ tests for presence of halide ions AgC*l* – white ppt AgBr – cream ppt AgI – yellow ppt AgX ppt colours can be found in *Data Booklet*.

E.g. Distinguishing chloroethane (RX) and chlorobenzene (ArX)

Reagents and conditions:

1. NaOH(aq), heat. 2. Cool and acidify with HNO_3(aq) 3. $AgNO_3$(aq)

Observations with chloroethane: White ppt formed

Observations with chlorobenzene: No white ppt

Equations:

$CH_3CH_2Cl + OH^-(aq) \longrightarrow CH_3CH_2OH + Cl^-$ nucleophilic substitution

$Cl^-(aq) + Ag^+(aq) \longrightarrow AgCl(s)$ white ppt precipitation

6.2 Distinguishing between different halogenoalkanes

E.g. Distinguishing between RC*l*, RBr and RI

Method 1

Reagents and conditions:

1. NaOH(aq), heat. 2. Cool and acidify with HNO_3(aq) 3. $AgNO_3$(aq)

Observations with RC*l*: White ppt formed

Observations with RBr: Pale cream ppt formed

Observations with RI: Yellow ppt formed

General Equations:

$RX + OH^-(aq) \longrightarrow ROH + X^-$ nucleophilic substitution

$X^-(aq) + Ag^+(aq) \longrightarrow AgX(s)$ precipitation reaction

Method 2

Reagents and conditions: Ethanolic $AgNO_3$, heat

Observations with RC*l*: White ppt formed slowly (last to be formed)

Observations with RBr: Pale cream ppt formed (2nd to be formed)

Observations with RI: Yellow ppt formed quickly (1st to be formed)

In Method 2, ethanol acts as the both the solvent and the nucleophile. The advantage of this one-step method is that we can observe the rate of substitution of RX, based on the rate at which the AgX ppt is formed.

In Method 1, ppt forms immediately regardless of the RX as hydrolysis is already complete when $Ag^+(aq)$ is introduced.

Down the group, **size of the halogen atom increases** and the valence orbitals of the halogen atom become bigger and more diffuse. **Orbital overlap is less effective** and **C – X bond strength decreases**. Less energy is required to break the C – X bond. (Section 4.2.1)

I^- ions are formed first, followed by Br^- ions and C*l*$^-$ ions, so yellow ppt of AgI is observed before cream ppt of AgBr and white ppt of AgC*l*.

- No ppt is observed with CH_3CH_2F as it does not undergo hydrolysis due to the shortest and strongest C–F bond.
- No ppt is observed with C_6H_5Cl as it does not undergo hydrolysis due to partial double bond character and steric hindrance. (Section 5.1)

☞ **Self- Check: Q9**

7. APPLICATIONS

(g)	explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness
(h)	recognise the effect of chlorofluoroalkanes (CFCs) on the ozone layer, and that their proposed replacements, hydrofluoroalkanes (HFCs) and hydrochlorofluoroalkanes (HCFCs), have significant environmental impact too [the mechanistic details of how CFCs and HCFCs deplete the ozone layer are **not** required]

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

Fluoroalkanes and fluorohalogenoalkanes are chemically inert, stable and non-flammable due to their strong C–F bond(s). Refer to Appendix 3 for some uses of fluoroalkanes and fluorohalogenoalkanes based on their chemical properties.

Of all the fluorohalogenoalkanes, **chlorofluorocarbons** are the most widely known. **Chlorofluorocarbons (CFCs)** are halogenoalkanes that contain only **chlorine**, **fluorine** and **carbon**. Their molecules contain only C–F and C–C*l* bonds (and no C–H bond). Examples are $CFCl_3$, CCl_2F_2 and $C_2Cl_2F_4$.

Some properties of CFCs include:

- chemically inert and stable under ambient conditions
- non-flammable
- low toxicity
- volatile i.e. low boiling point
- easily liquefy under pressure

In the 1920s, refrigeration and air conditioning systems used compounds such as ammonia, chloromethane, propane and sulfur dioxide as refrigerants. Though effective, the compounds were **toxic and flammable**, and exposure to them could result in serious injury or death. A team of chemists at Frigidaire led by Thomas Midgely Jr. (1889-1944) worked to develop **nontoxic, nonflammable** alternatives to the refrigerants.

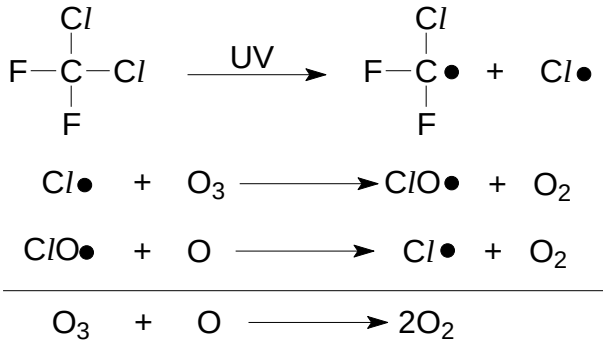
The team focused their effort on compounds containing carbon and halogens such as fluorine and chlorine. Such compounds were known to be **volatile and chemically inert, both important properties for the team studying their use in refrigeration**. The first compound they developed was dichlorodifluoromethane, CCl_2F_2, which they dubbed "Freon."

By the **early 1970s, CFCs were in widespread use, and worldwide production of the compounds had reached nearly one million tons per year, representing roughly a $500 million slice of the chemical industry.**

Adapted from ACS educational resources:
https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/cfcs-ozone.html

However, this lack of chemical reactivity also provides CFCs with a **lifespan that can exceed 100 years**, giving them time to **diffuse into the upper stratosphere**, where strong **UV radiation breaks the (weakest) C-C*l* bond** homolytically to **generate C*l*• radicals** that **catalyse the decomposition of ozone into oxygen**.

FYI: Mechanism of ozone decomposition catalysed by CFCs



https://www.youtube.com/watch?v=5BM4wXCP3Vc
How CFCs deplete ozone layer

Hence, CFCs cause thinning of the ozone layer and allow more ultraviolet (UV) radiation from the sun to reach the earth. This is harmful, as excessive exposure to UV radiation would lead to crop damage, skin cancer, cataracts and malfunctioning of the immune system in humans.

The depletion of the ozone layer over Antartica was first discovered in May 1985. This finding led directly to the Montreal Protocol in 1987 where many countries agreed to the following measures to protect the ozone layer*:*

- to reduce CFC production to half of 1986 levels by the year 1999 and a complete phase out of CFC's by the year 2000.
- to find substitutes for CFCs which do not damage the ozone layer e.g. hydrofluoroalkanes (HFCs) as they contain neither chlorine nor bromine and therefore have no detrimental effect on stratospheric ozone.

Today, the use of CFCs is outlawed by 197 countries around the world and scientists concur that the ozone layer is slowly recovering as a result. 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.

Unfortunately, research has shown that replacements for CFCs, hydrofluoroalkanes (HFCs) and hydrochlorofluoroalkanes (HCFCs), have significant environmental impact too. **While HFCs and HCFCs do not contribute to ozone depletion, they are greenhouse gases that trap heat at the magnitude of hundreds to thousands of times higher than carbon dioxide.**

Scientists' search for non-toxic and safe refrigerants that do not harm the ozone layer nor contribute to global warming continues…

☞ **Self- Check: Q10**

8. APPENDIX

Appendix 1 – Details of using HX to prepare RX from ROH

Using **HX(g)**, where X = C*l*, Br or I, **heat**

HC*l* is generated *in situ* from the reaction between conc. H_2SO_4 and NaC*l*.

To prepare	Reagent	Condition	Equation
RC*l*	NaC*l*(s), Conc H_2SO_4	Anhydrous $ZnCl_2$ (catalyst), heat	$NaCl + H_2SO_4 \rightarrow HCl\ (g) + NaHSO_4$ $CH_3CH_2OH + HCl(g) \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$
RBr	NaBr(s), Conc H_2SO_4	Heat	$NaBr + H_2SO_4 \rightarrow HBr\ (g) + NaHSO_4$ $CH_3CH_2OH + HBr(g) \rightarrow CH_3CH_2Br + H_2O$
RI	NaI(s), Conc **H_3PO_4**	Heat	$NaI + H_3PO_4 \rightarrow HI\ (g) + NaH_2PO_4$ $CH_3CH_2OH + HI\ (g) \rightarrow CH_3CH_2I + H_2O$

- HI is generated *in situ* from the reaction between conc. H_3PO_4 and NaI.
- ***To produce HI, conc H_3PO_4 (less oxidising) is used instead of conc H_2SO_4***

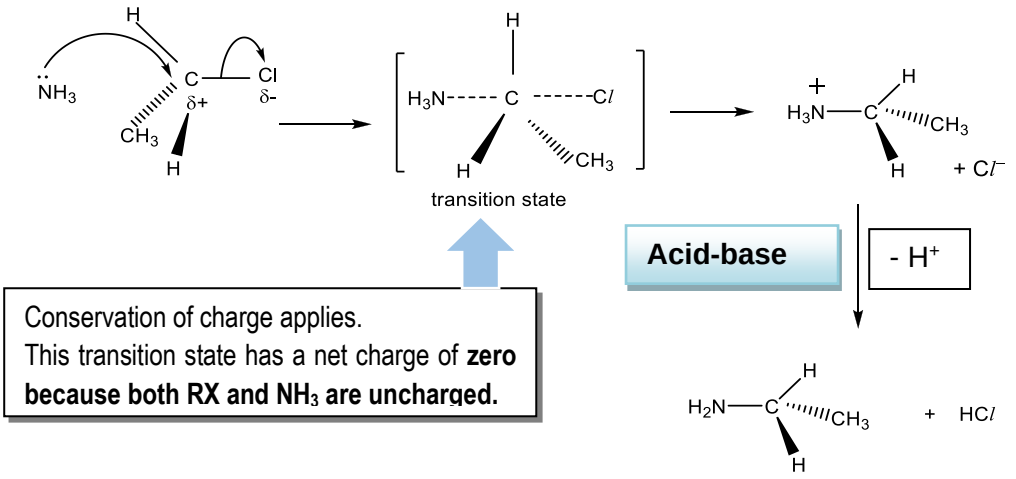
Reason: most of the HI produced would be oxidised by conc H_2SO_4 to give iodine crystals.

$NaI + H_2SO_4 \rightarrow HI + NaHSO_4$

$8HI + H_2SO_4 \rightarrow 4I_2 + 4H_2O + H_2S$

Appendix 2 – Nucleophilic substitution mechanism of RX with NH_3

2 processes: S_N2 followed by acid-base reaction

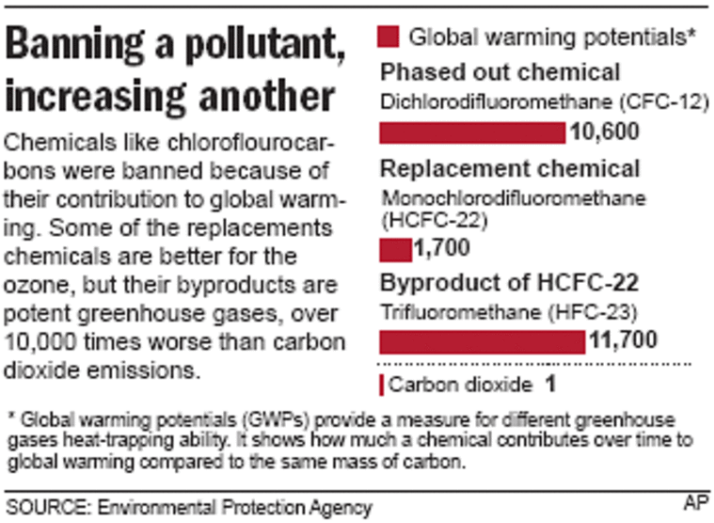


Conservation of charge applies.
This transition state has a net charge of **zero because both RX and NH_3 are uncharged.**

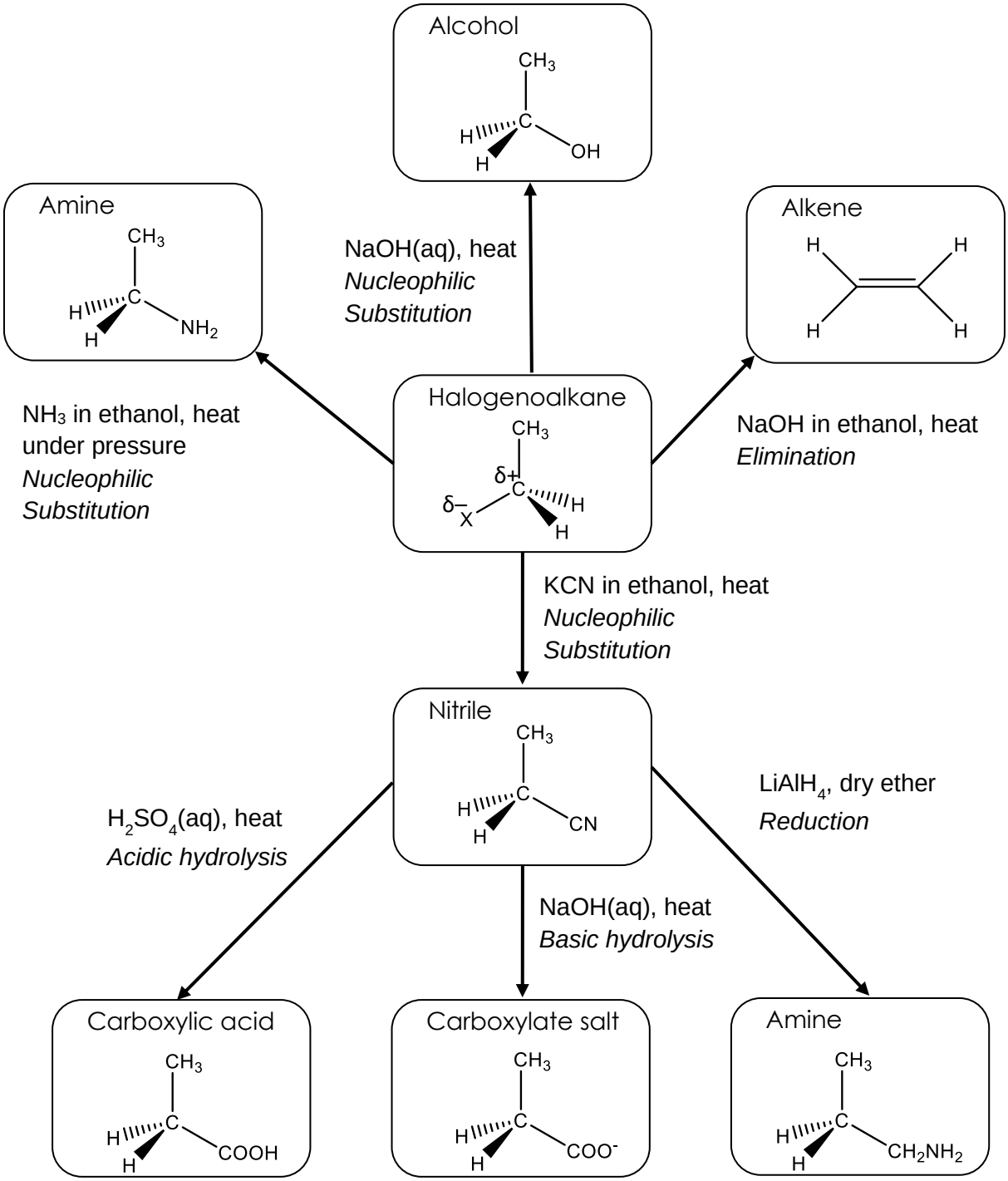
Appendix 3 – Some uses of fluoroalkanes and fluorohalogenoalkanes

refrigerants	Refrigerants readily absorb heat from the environment and can provide refrigeration or air conditioning when compressed and expanded rapidly. Dichlorodifluoromethane, CCl_2F_2 and 1,2-dichloro-1,1,2,2-tetrafluoroethane, $CClF_2$-$CClF_2$ are the most common CFCs used as refrigerants
aerosol propellants	Aerosol cans are a device that uses one highly pressurized liquid (CFCs) to push another fluid (e.g. hairspray, mousse) out of the can. For example, when the hairspray is released from the aerosol can, the liquid propellant becomes a gas and helps break up the hairspray into a fine mist. CFCs were widely used as propellants in the 1970s but today, the most common propellants are naturally occurring hydrocarbons.
fire extinguisher	$CClBrF_2$, bromochlorodifluoromethane, is a common chemical used in fire extinguishers. It does not have hydrogen atoms, so it does not burn. It has high relative molecular mass, and forms a dense gas that settles on fire, cutting off the air supply.
grease solvents	CH_2Cl_2, dichloromethane, and CCl_2=$CHCl$, trichloroethene, are used in dry cleaning and removing oils and greases from metal surfaces.
polymer production	Chloroethene is the monomer for polyvinylchloride, PVC. Poly(tetrafluoroethene), (-CF_2-CF_2-) is used as corrosion proof valves and seals which are resistant to most chemicals. It is also used as non-stick coating (teflon) for cooking pans due to its low coefficient of friction.
pesticides	DDT (dichlorodiphenyltrichloroehane) is used as a pesticide to remove the threat of malaria, stopping the spread of typhus and yellow fever.

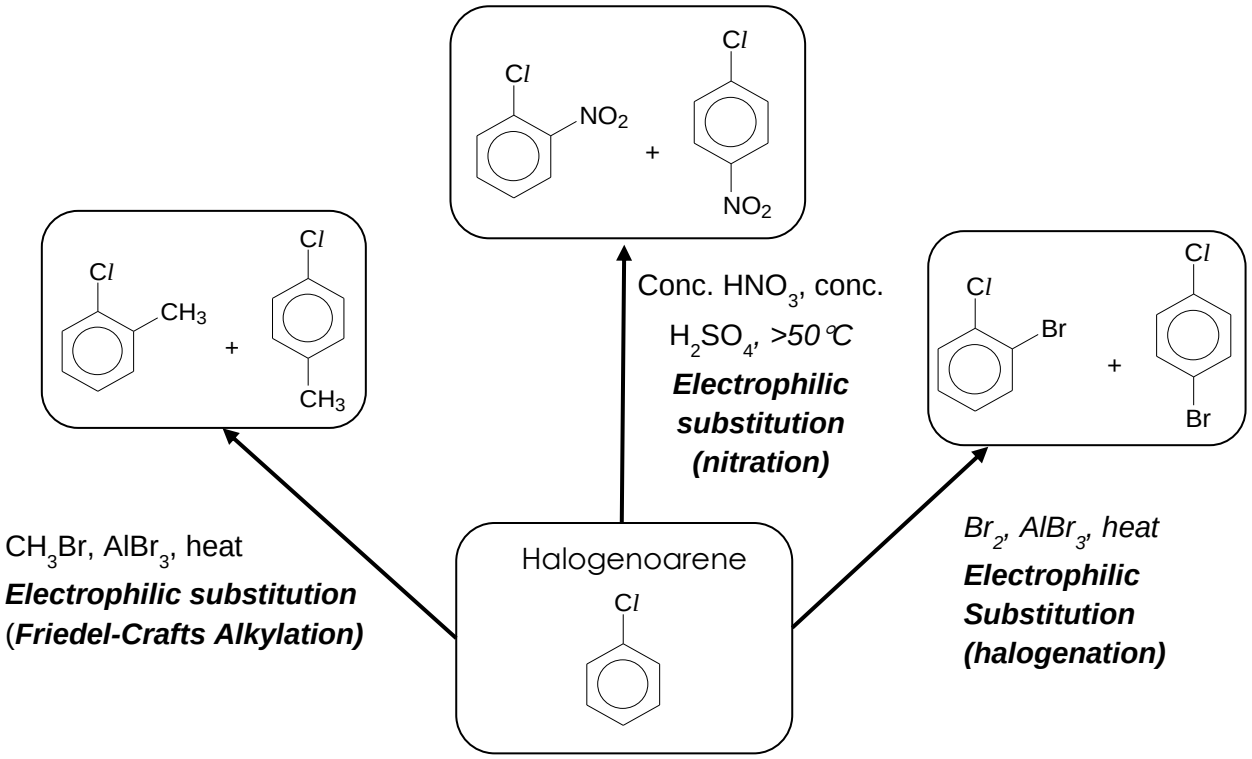
Appendix 4 – HFC and HCFCs contribute to global warming



Summary of RX Reactions



Summary of ArX Reactions



ArX DOES NOT UNDERGO NUCLEOPHILIC SUBSTITUTION WITH NaOH(aq), heat