VICTORIA JUNIOR COLLEGE

CHEMISTRY DEPARTMENT

Halogen Derivatives

(Halogenoalkanes and Halogenoarenes)

Lesson outline

Lesson	1	2
Pages	1 – 8	9 – 18
Complete by	09/02/25	09/02/25
Tutorial Qns	1 – 4	5 – 10

(I) Halogenoalkanes

1 Introduction

2 Physical Properties
- 2.1 Boiling point
- 2.2 Solubility

3 Laboratory Preparation
- 3.1 From alcohols
- 3.2 From alkenes

4 Reactions
- 4.1 Nucleophilic substitution
- 4.2 Elimination

5 Effect of halogen atoms
- 5.1 Distinguishing tests for RX
- 5.2 Effect of different halogen atoms on reactivity of halogenoalkanes

6 Nucleophilic Substitution Mechanism

7 Fluoroalkanes and Fluorohalogenoalkanes
- 7.1 Uses
- 7.2 Effect of CFCs on the Ozone Layer

(II) Halogenoarenes

1 Introduction

2 Preparation

3 Chemical Properties
- 3.1 Reactions involving halogen atom
- 3.2 Reactions involving benzene ring

Learning Objectives

Students 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

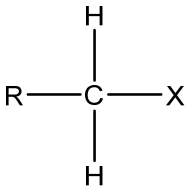
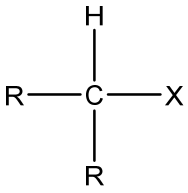
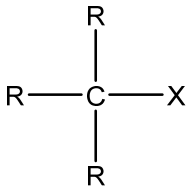
(g) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness

(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]

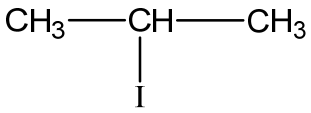
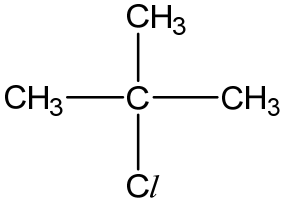
I HALOGENOALKANES

1 Introduction

- General formula: $\mathbf{C_nH_{2n+1}X}$
- Halogenoalkanes are also known as alkyl halides.
- They can be classified as **primary, secondary or tertiary** halogenoalkanes depending on the number of alkyl or aryl groups attached to the C atom of the C–*X* bond.

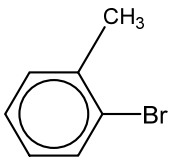
Type of halogenoalkane	**Primary**	**Secondary**	**Tertiary**
Structure			
Carbon bonded to halogen X is bonded to	1 alkyl or aryl group	2 alkyl or aryl groups	3 alkyl or aryl groups

Note: R groups **may or may not** be the same.

- <u>Nomenclature</u>
  Halogenoalkanes are named in a similar manner to alkanes where the suffix ends in –ane and the halogens are treated as substituents and named as prefixes such as chloro–, bromo–, iodo–.
  Examples:
  (i) CH_3CH_2Br (ii)  (iii) 

  bromoethane 2–iodopropane 2–chloro–2–methylpropane

Quick Check 1:
Give the IUPAC name of the following compounds.

(a) $CH_3CH_2CH(CH_3)CH_2C\mathit{l}$ **(b)** $CH_3CH{=}CHCH_2Br$ **(c)** 

2 Physical Properties

2.1 Boiling Point

- Halogenoalkanes have a **higher boiling point** than alkanes with the same number of carbon atoms as there are **permanent dipole–permanent dipole** attractions between polar R*X* molecules and also **stronger instantaneous dipole–induced dipole interactions** due to the **greater number of electrons** present.

- For a given alkyl group, boiling point increases with increasing A_r of the halogen.
  i.e. boiling point of RC*l* < RBr < RI

2.2 Solubility

- In spite of the C–*X* bond being polar, halogenoalkanes are **insoluble in water** due to their **inability to form hydrogen bonds with water**.

- They are **soluble** in **organic solvents** whereby the energy released from solute–solvent interactions is sufficient to overcome the solute–solute and the solvent–solvent interactions.

3 Preparation of halogenoalkanes

3.1 Nucleophilic substitution of alcohols (using ethanol as an example)

- $CH_3CH_2\mathbf{OH} + PCl_5 \rightarrow CH_3CH_2\mathbf{Cl} + HCl + POCl_3$ ***Remember the by-products HCl (steamy white fumes) and $POCl_3$***

  Reagents and conditions: PCl_5

  Note: PCl_5 provides the nucleophile, Cl^-

- $3CH_3CH_2\mathbf{OH} + PX_3 \rightarrow 3CH_3CH_2\mathbf{X} + H_3PO_3$ (*X*= C*l*, Br) ***Remember the by-product H_3PO_3***

  Reagents and conditions: PCl_3 or PBr_3, heat

  PX_3 provides the nucleophile, X^-

  Note:
  - Phosphorus triiodide, PI_3 is very **unstable** and so it is prepared ***in situ*** (at site of reaction). The alcohol is heated with red P and I_2 to produce PI_3 in situ which then reacts with the alcohol to form the iodoalkane.
    $2P + 3I_2 \rightarrow 2PI_3$

- $CH_3CH_2\mathbf{OH} + SOCl_2 \rightarrow CH_3CH_2\mathbf{Cl} + HCl + SO_2$ ***Remember the by-products HCl (steamy white fumes) and SO_2***

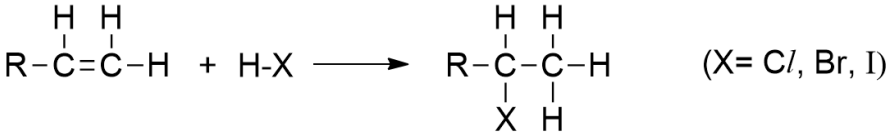
Reagents and conditions: $SOCl_2$, heat

Note: $SOCl_2$ provides the nucleophile, Cl^-

- $CH_3CH_2\mathbf{OH} + HX \rightarrow CH_3CH_2\mathbf{X} + H_2O$ (where X=Cl, Br, I) *Remember the by-product H_2O*

Reagents and conditions: HX(g), heat
Note: For HCl(g), $ZnCl_2$ catalyst is needed.

3.2 Electrophilic addition of hydrogen halides (HX) to alkenes



Reagents and conditions: HX(g)

Note: Markovnikov's rule is followed.

You are ready to attempt Qn 1 of tutorial.

4 Reactions of halogenoalkanes

- C–X bond is **polar** due to the presence of the **electronegative** halogen atom. Hence, halogenoalkanes are chemically very reactive.
- Halogenoalkanes undergo **nucleophilic substitution** as the electron–deficient C atom in the C–X bond carries a partial positive charge which enabled it to attract a nucleophile, leading to substitution of the halogen.
- Halogenoalkanes also undergo **elimination** (using alcoholic OH^-).

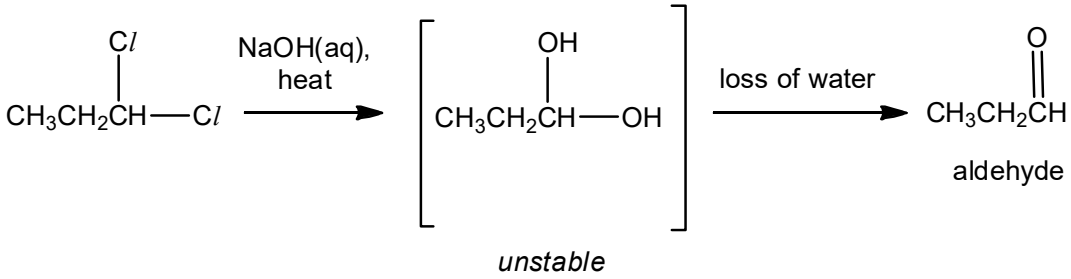
4.1 Nucleophilic substitution *Learning objective: (a)(i)*

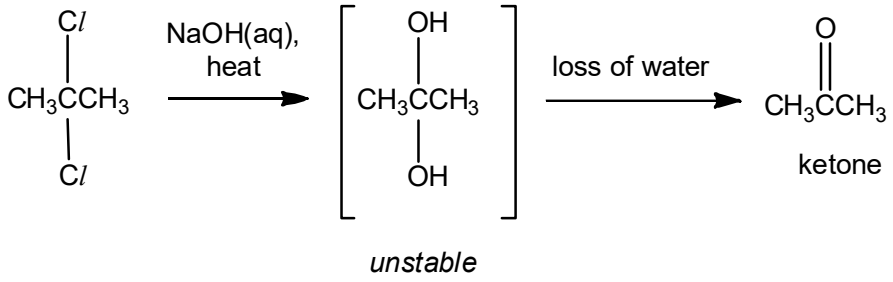
(a) Formation of alcohol

$CH_3CH_2\mathbf{Br} + OH^- \rightarrow CH_3CH_2\mathbf{OH} + Br^-$ *Remember the by-product Br^-*

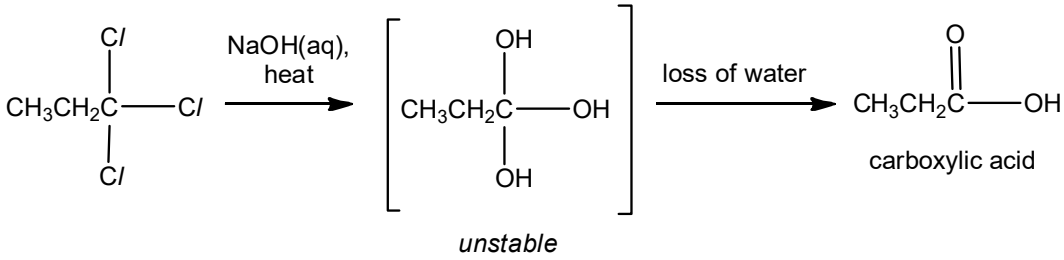
- Nucleophile: OH^-
- Reagents and conditions: NaOH(aq) or KOH(aq), heat *MUST specify the state symbol (aq)*
- This reaction is also known as alkaline hydrolysis.

- For geminal–dihalides (where two halogen atoms are attached to the **same** carbon atom), it would form a germinal diol which would undergo spontaneous dehydration to form a carbonyl compound.





- For geminal–trihalides (where three halogen atoms are attached to the **same** carbon atom), it would form a germinal triol which would undergo spontaneous dehydration to form a carboxylic acid.



(b) Formation of nitrile

$CH_3CH_2\mathbf{Br} + CN^- \rightarrow CH_3CH_2\mathbf{CN} + Br^-$ ***Remember the by-product Br^-***

- Nucleophile: CN^-
- Reagent and condition: KCN in ethanol or ethanolic KCN, heat ***MUST include the solvent eg ethanol***
- This reaction can be applied to **lengthen** the carbon chain known as a **step–up** reaction.
- Nitriles are useful intermediates in synthesis. They can be **hydrolysed to carboxylic acids.**

$RCN + 2H_2O + H^+ \rightarrow RCO_2H + NH_4^+$ *Know how to write the balanced equation*

Reagents and conditions: H_2SO_4(aq), heat *MUST include the state symbol (aq)*

- Nitriles can also be **reduced to primary amines**.

$RCN + 4[H] \rightarrow RCH_2NH_2$ *Know how to write the balanced equation*

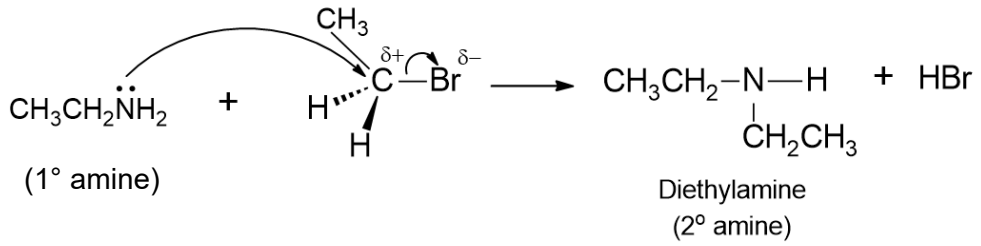
Reagents and conditions: $LiAlH_4$ in dry ether
: H_2, Ni catalyst, heat
: H_2, Pt or Pd catalyst

(c) Formation of amine

$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$ *Remember the by-product HBr*

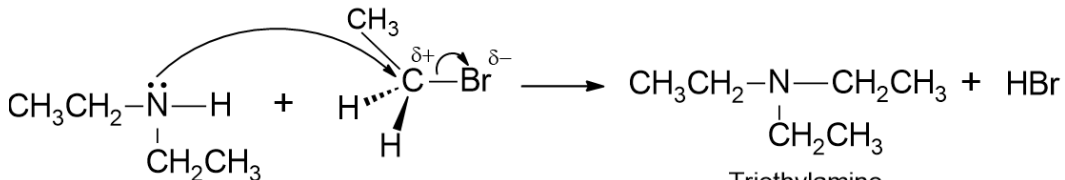
- Nucleophile: NH_3
- Reagents and conditions:
  Excess NH_3 in ethanol or **excess** ethanolic NH_3, heat in sealed tube *MUST specify "excess", the solvent eg ethanol and "heat in sealed tube"*
- If **limited NH_3 in ethanol which means excess CH_3CH_2Br is used**, the primary amine that is formed initially would get a chance to react with another halogenoalkane, resulting in the formation of more highly substituted amines in a series of reactions as shown below.

$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$
Ethylamine
(1° amine)



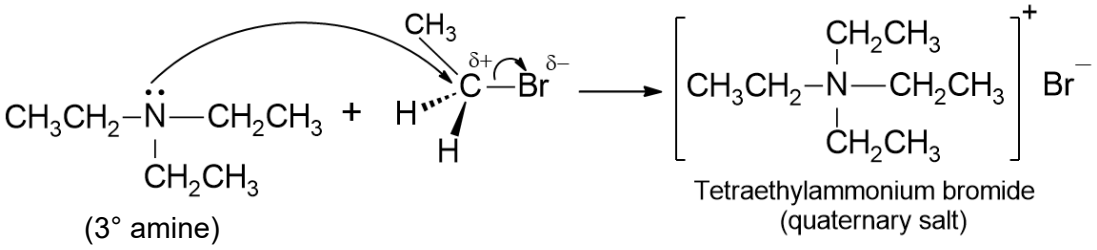
(1° amine)

Diethylamine
(2° amine)



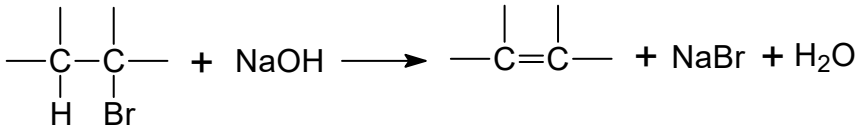
(2° amine)

Triethylamine
(3° amine)



Disadvantage: A **mixture** of different polysubstituted products results and fractional distillation is needed to separate the products.

4.2 Elimination Reaction *Learning objective: (a)(ii)*



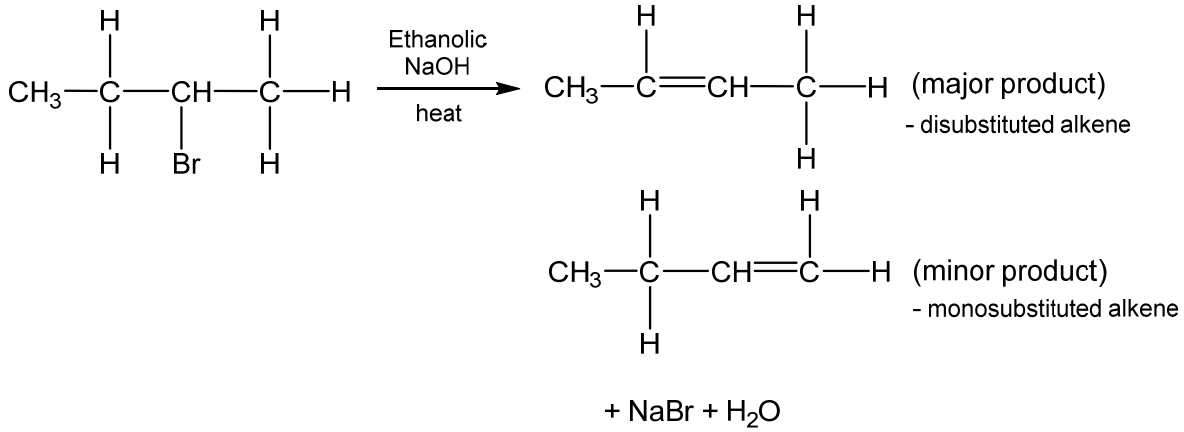
Remember the by-products NaBr and H_2O

MUST specify the solvent eg ethanol
RX → ROH use NaOH(aq)
RX → alkene use NaOH in ethanol

- Reagents and conditions:
  NaOH in ethanol or KOH in ethanol, heat
  (Can also be written as ethanolic NaOH or ethanolic KOH respectively)

- The major product formed is the **<u>more substituted</u>** alkene.

  For e.g.



You are ready to attempt Qn 2 – Qn 4 of tutorial.

5 Effect of halogen atoms

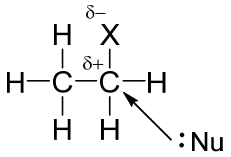
5.1 Distinguishing Tests for R*X* (RC*l*, RBr, RI) *Learning objective: (f)(i)*

- Procedure
  1. **Heat R*X* with NaOH(aq)**.
     $RX + OH^- \rightarrow ROH + X^-$ *This is one of the nucleophilic substitution reactions to free the X^-.*
  2. **Acidify with HNO_3(aq)**. *The <u>only</u> acid that can be used is HNO_3. This step must be done before adding $AgNO_3$(aq).*
     [to prevent brown AgOH ppt. or Ag_2O ppt. formation in step 3].
  3. **Add $AgNO_3$(aq)**.
     $Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$
     ppt.

  Note: Using HNO_3 instead of HC*l* or H_2SO_4 for acidification prevents introducing anions into the system that may be precipitated out by the Ag^+ ion.

- Observations:
  - **White** ppt of AgC*l* if RC*l* is present *The observations excluding the formula can be found in Qualitative Analysis notes of the Data Booklet*
  - **Cream** ppt of AgBr if RBr is present
  - **Yellow** ppt of AgI if RI is present

5.2 Effect of different halogen atoms on reactivity of halogenoalkanes *Learning objective: (d)*



- The **larger** the halogen atom X, the **less effective is the overlap of orbitals** between the carbon atom and halogen atom.
- This results in a **longer** and **weaker** C–X bond.

Bond	C-C*l*	C-Br	C-I
Bond energy / kJ mol^{-1}	340	280	240

- Since bond energy of C-C*l* > C-Br > C-I, ease of bond breaking of C-C*l* < C-Br < C-I.

- Hence, the least energy is needed to break the C-I bond, and reactivity of halogenoalkanes increases in the order: **RC*l* < RBr < RI**.

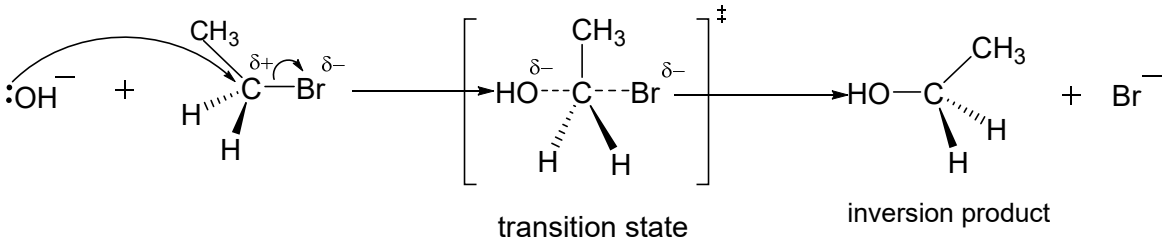
6 Nucleophilic Substitution Mechanism

- Halogenoalkanes undergo **nucleophilic substitution** as the electron–deficient C atom in the C–X bond carries a partial positive charge and hence it is susceptible to attack by a nucleophile (e.g. OH^-, $:CN^-$, NH_3, RO^-, RCO_2^-) leading to substitution of the halogen.

(a) Mechanism for primary halogenoalkanes

<u>Bimolecular Nucleophilic Substitution (S_N2)</u>

e.g. CH_3CH_2**Br** + NaOH → CH_3CH_2**OH** + NaBr *Learning objective: (b)(ii) and (c)(i)*



transition state inversion product

- Nucleophile OH^- approaches the **electron deficient** carbon atom from the side **opposite** to the bromine atom, leading to the spatial configuration of the product being **inverted** from that of the starting organic molecule.
- The OH^- supplies the lone pair of electrons, which forms the new bond and the pair of electrons in the C–Br bond is gradually acquired completely by the bromine atom.
- The transition state cannot be isolated (i.e. it does not exist as a stable intermediate).
- The mechanism consists of only **one step** in which two reactant particles, i.e. the single step is the rate determining step, which consists of one CH_3CH_2Br molecule and one OH^- ion. Hence it is described as *bimolecular.*
- What is the rate equation of an S_N2 reaction?

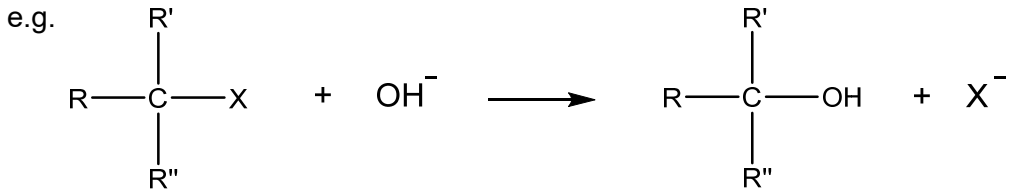
_____

Checklist for drawing S_N2 mechanism
√ mechanism name (S_N2)
√ lone pair on nucleophile
√ two FULL arrows occurring in ONE step: from lone pair to electron deficient carbon AND showing C-X bond breaks
√ dipole on C-X bond (partial charges)
√ structure of transition state (dotted bonds means about to break and about to form)
√ show the spatial configuration of product inverted from starting organic molecule
√ must remember to include by-product the X^- ion

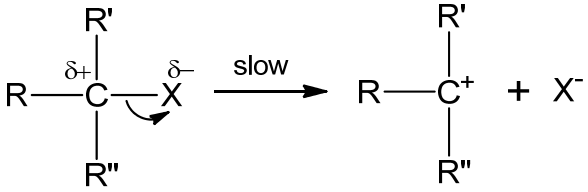
(b) Mechanism for tertiary halogenoalkanes

Unimolecular Nucleophilic Substitution (S_N1) *Learning objective: (b)(i) and (c)(ii)*

e.g.

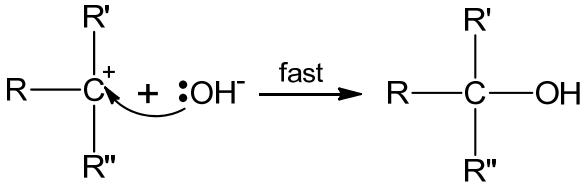


Step 1: Tertiary halogenoalkane undergoes heterolytic fission to form a halide ion and a carbocation.



Carbocation (intermediate)

Step 2: Carbocation is readily attacked by nucleophiles such as OH^- to form the final alcohol product.



- The carbocation formed in step 1 is **trigonal planar** with respect to the positively charged carbon. As a result, the OH^- nucleophile can attack this positively charged carbon in step 2 from **either side of the trigonal plane with equal chance**. The product will thus be a **racemic mixture** which contains a 50:50 mixture of enantiomers if the starting halogenoalkane is chiral and optically pure.

- The mechanism consists of **two steps**. Since only one reactant particle (i.e. CR_3X) participates in the slow step (rate determining step), it is described as *unimolecular.*

- What is the rate equation of an S_N1 reaction?

_____

Checklist for drawing S_N1 mechanism
√ mechanism name (S_N1)
√ lone pair on nucleophile
√ TWO steps: first step showing C-X bond breaks draw FULL arrow, second step showing from lone pair to carbon with positive charge in carbocation
√ dipole on C-X bond (partial charges)
√ write "slow" and "fast" step
√ must remember to include by-product the X^- ion

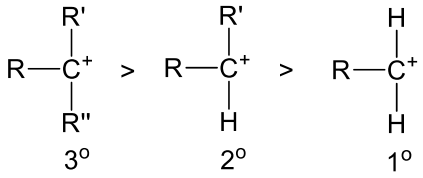
(c) *Factors that favour S_N1 and S_N2 mechanisms*

Learning objective: (b)(i) and (b)(ii)

Differences in the mechanism undergone by the various classes of halogenoalkanes are due to the following factors:

(1) Stability of the carbocation intermediate

The more stable the carbocation intermediate, the more favoured the S_N1 mechanism. Stability of carbocations decreases in the order:



Recall: why does the stability of carbocations decrease in this manner?

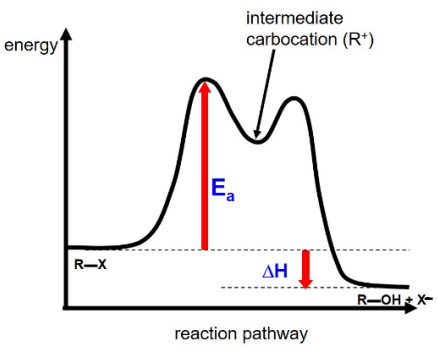
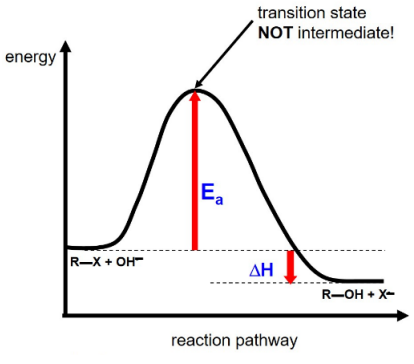
Hence, tertiary halogenoalkanes, which will form a highly stable tertiary carbocation intermediate, undergo the S_N1 mechanism more readily than primary and secondary halogenoalkanes.

Summary of why tertiary RX favours S_N1 mechanism:
Tertiary carbocation most stable as 3 alkyl groups exert electron donating inductive effect, disperse the positive charge on carbocation

(2) Steric factors

As alkyl groups are **bulkier** than H atoms, their presence will hinder the approach of the nucleophile to the halogenoalkane in an S_N2 mechanism (steric hindrance).

A primary halogenoalkane has the least number of alkyl groups attached to the reactive carbon, hence posing the least amount of steric hindrance to an approaching nucleophile. As a result, primary halogenoalkanes undergo the S_N2 mechanism most readily.

	S_N1	**S_N2**
Class of RX	Tertiary	Primary
No. of steps in mechanism	2	1
Energy profile diagram		

Summary of why primary RX favours S_N2 mechanism:
Least amount of steric hindrance to an approaching of the nucleophile as there is only one bulky alkyl group bonded to electron deficient carbon

	S_N1	S_N2
No of reactant particles in rate equation	1	2
Stereochemistry	Product is a racemic mixture consisting of 2 enantiomers	Product consists of 1 enantiomer with spatial arrangement inverted from that of starting reactant.
Factors that favour the mechanism	High stability of carbocation	Low steric hindrance

- In the substitution reactions of secondary halogenoalkanes, both mechanisms occur.

Quick Check:

Describe the mechanisms for the following reactions.

i) $CH_3CH_2\mathbf{C}\boldsymbol{l} + KCN \rightarrow CH_3CH_2\mathbf{CN} + KC\boldsymbol{l}$

ii) $(CH_3)_3C\mathbf{Br} + NH_3 \rightarrow (CH_3)_3C\mathbf{NH_2} + HBr$

You are ready to attempt Qn 5 – Qn 6 of tutorial.

7 Fluoroalkanes (RF) & Fluorohalogenoalkanes (RFX) *Learning objective: (g)*

7.1 Uses

Fluoroalkanes (RF) and fluorohalogenoalkanes (RFX) are useful because of the following properties:

- Chemically **inert** due to **strong** C–F bond.
- RF and RFX with small alkyl groups have **low** boiling points and so are easily vapourised. (they can be kept as liquid at high pressure and released as gas at atmospheric pressure).
- **Non–toxic** and odourless.
- Those without H atoms such as CF_2Cl_2, $CClBrF_2$ are non–flammable and can be used in **fire extinguishers** as they will not undergo combustion.

Compounds	Uses
$CF_2=CF_2$	making **Teflon** used in non–stick pans or water–proof cloth
CF_2Cl_2 (*Freon 12*)	propellant gases in **aerosols**
$CFCl_3$ (*Freon 11*)	**refrigerant** in air–conditioner
$C_2F_3Cl_3$ (*Freon 113*)	**solvents** for cleaning electronic circuit boards
$CClBrF_2$	In **fire extinguishers**

7.2 Effect of chloro–fluoro compounds (CFC) on Ozone Layer *Learning objective: (h)*

Natural equilibrium in the ozone layer

- O_3 is formed at the upper atmosphere (stratosphere) via the following reactions:

$$O_2 \rightarrow 2O$$
$$O + O_2 \rightarrow O_3$$

- O_3 also absorbs ***ultra–violet (UV)* radiation** which is harmful to living organisms. *UV* radiation can cause skin cancer in people and damage vegetation, including food crops.
- By absorbing *UV* radiation, O_3 is split into O atoms and O_2 molecules which readily recombine to give back O_3. This naturally maintains the level of ozone in the stratosphere.

O_3 cycle:

$$O_3 \xrightarrow{uv} O + O_2$$
$$O + O_2 \rightarrow O_3$$

Effect of CFCs

- CFC molecules are chemically **inert**. They do not react with air or water and are not biodegradable. As they rise into atmosphere, the C–C*l* bond is broken in the presence of *UV* light, forming highly reactive C*l* radicals.

  Example:

  $$CF_2Cl_2 \rightarrow CF_2Cl + Cl\bullet$$

- C*l* radicals react with O_3 thus, destroying ozone layer. C*l* radicals act as **catalysts** as they are *not consumed* in the reaction mechanism.

  Mechanism:

  $$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$$
  $$ClO\bullet + O \rightarrow Cl\bullet + O_2$$

  Overall reaction: $O_3 + O \rightarrow 2O_2$

  Note: There is no need to memorise the mechanism.

  Hence C*l* radicals *catalyse* the destruction of ozone.

- Note that C–F bond is **not broken** in the stratosphere as it is much stronger than C–C*l*.

- Measures to protect O_3 layer include reducing the use of CFCs and finding substitutes for CFCs such as HFC (hydrofluorocarbons) and HCFC (hydrochlorofluorocarbons).

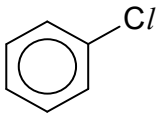
You are ready to attempt Qn 7 – Qn 8 of tutorial.

(II) HALOGENOARENES

1 Introduction *Learning objective: (e) and (f)(ii)*

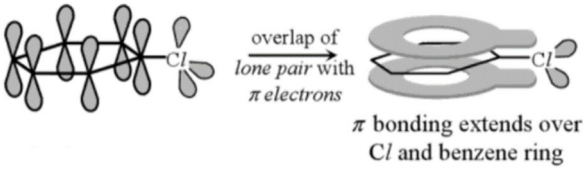
- Halogenoarenes are also known as aryl halides.

  e.g. chlorobenzene



- Colourless liquid; pleasant smell
- Insoluble in water but soluble in non–polar solvents such as benzene.
- C*l* atom here is very much **less** reactive than that in halogenoalkanes. This is due to two reasons:

  ➢ The **p–orbital** of the **halogen atom overlaps** with the **p–orbitals** of carbon atom in **benzene** ring, leading to delocalisation of the lone pair of electrons on halogen atom into the ring.



  This confers **partial double bond** character on the C–C*l* bond, thus **strengthening** the bond and making the halogen atom difficult to be replaced.

  C–C*l* bond length in chlorobenzene = 0.169 nm
  C–C*l* bond length in CH_3CH_2Cl = 0.179 nm

  NB: S_N1 involving the breaking of C–X bond to form the carbocation would be difficult.

  ➢ The **benzene ring** poses **steric hindrance**, making it difficult for the nucleophile to approach the electron–deficient carbon. It also hindered the **rear attack** of the nucleophile.

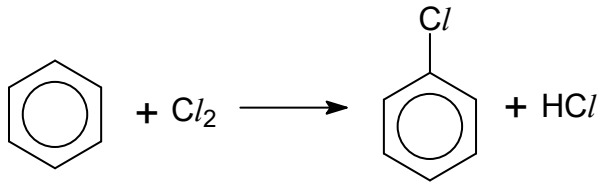
  NB: S_N2 involving rear attack of nucleophile on the electron–deficient C would be difficult.

You are ready to attempt Qn 9 of tutorial.

Summary of unreactivity of chlorobenzene compared to halogenoalkanes:

1. *p orbital of Cl overlap with p orbitals of benzene => C-Cl has partial double bond character => C-Cl bond is strengthened*
2. *benzene ring poses steric hindrance, hindering rear attack of the nucleophile*

2 Preparation (from chlorination of benzene)

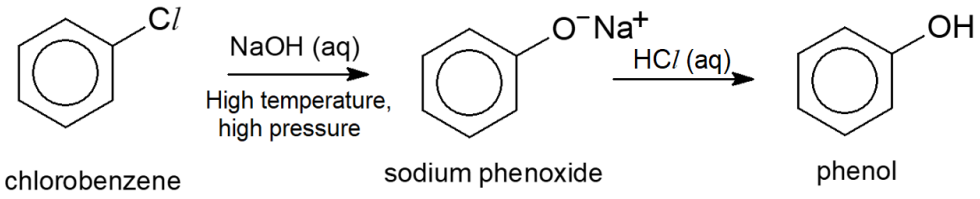


- Reagents and conditions: **Cl_2, anhydrous $FeCl_3$ catalyst**

3 Chemical Properties

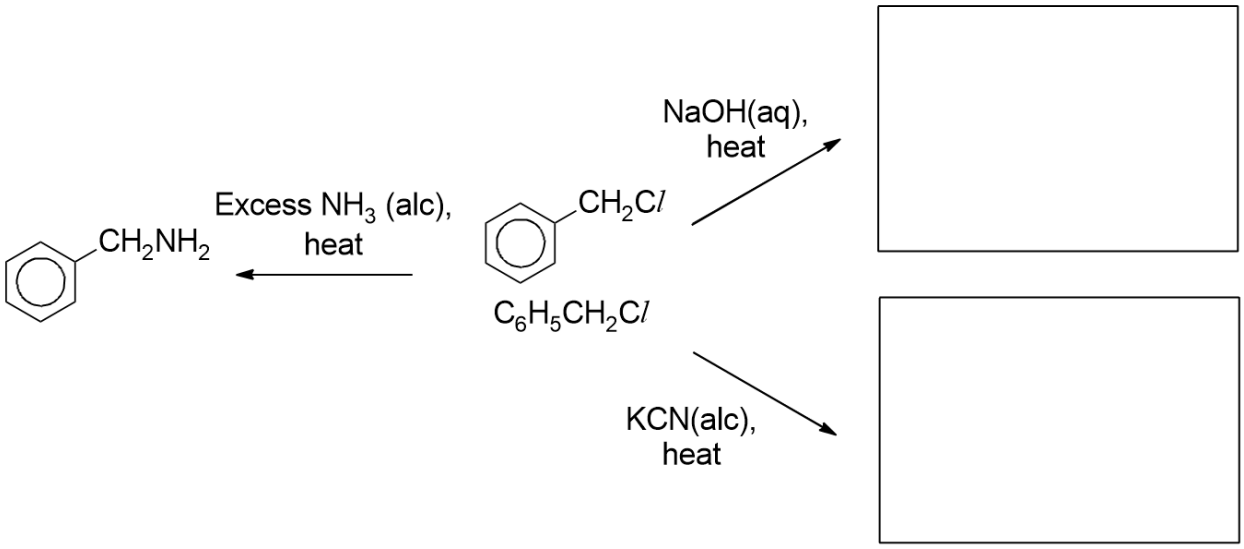
3.1 Reactions involving halogen atom

- No nucleophilic substitution under normal laboratory conditions in contrast to CH_3CH_2Cl, i.e. no reaction with OH^-, CN^-, NH_3.
- Nucleophilic substitution (or hydrolysis) with NaOH will only occur under **drastic** conditions of high temperature and high pressure.



Reagents and conditions:
NaOH(aq) at high temperature and high pressure, followed by HCl(aq)

- The behaviour of Cl atom in $C_6H_5CH_2Cl$ is similar to CH_3CH_2Cl.



- The behaviour of C*l* atom in CH_2=CHC*l* is similar to C_6H_5C*l*.

  CH_2=CHC*l* is an example of a **vinyl halide**. The p–orbital of halogen atom overlaps with p–orbitals of the alkene carbons, resulting in delocalisation of lone pair of electrons on halogen atom over the π electron cloud of C=C bond. This confers **partial double bond character** to the carbon–halogen bond. Thus more energy is needed to break the carbon-halogen bond.

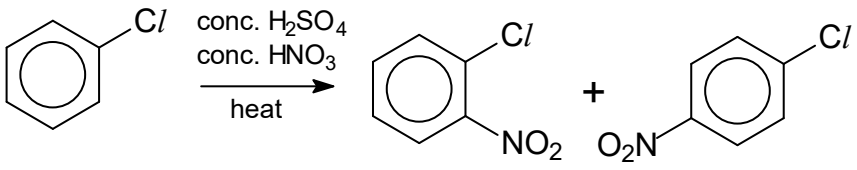
  notice this is similar to unreactivity of chlorobenzene explanation

  Hence, vinyl halides are in general **unreactive** towards nucleophiles.

3.2 Reaction involving benzene ring

- Undergoes the usual **electrophilic substitution** such as halogenation, nitration and alkylation.

  e.g.



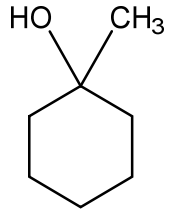
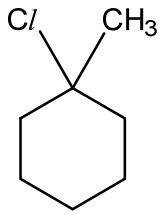
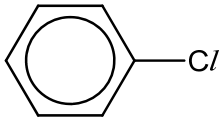
- C*l* substituent:
  - deactivates benzene nucleus towards electrophilic substitution [*see data booklet*]
  - is 2– and 4–directing [*see data booklet*]

You are ready to attempt Qn 10 of tutorial.

VICTORIA JUNIOR COLLEGE
CHEMISTRY DEPARTMENT
Halogen Derivatives (Halogenoalkanes and Halogenoarenes)
Tutorial Questions

Complete the following tables:

(1) Preparation of halogen derivatives

Preparation of halogenoalkanes		
Starting compound	Reagents and conditions	Product
		
	HC*l*(g)	
Preparation of halogenoarenes		
	Cl_2, anhydrous A*l*Cl_3	

(2) Reactions of halogen derivatives

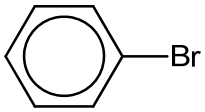
(a) Halogenoalkanes

Starting compound	Reaction type	Reagents and conditions	Product
$CH_3CHClCH_3$		NaOH(aq), heat	
			$CH_3CH(NH_2)CH_3$
		Limited NH_3 in ethanol, heat in sealed tube	

Starting compound	Reaction type	Reagents and conditions	Intermediate	Reaction type, reagents and conditions	Final product
CH_3CHC/CH_3			$CH_3CH(CN)CH_3$	Hydrolysis $H_2SO_4(aq)$, heat	
					CH_3CHCH_3 | CH_2NH_2

Starting compound	Reaction type	Reagents and conditions	Product
$(CH_3)_2CC/CH_2CH_3$		NaOH in ethanol, heat	

(b) Halogenoarenes and vinyl halides

Compound	Reactivity
	No reaction under normal laboratory conditions.
$CH_3CI{=}CH_2$	

Preparation of Halogenoalkanes

1 State the reagents and conditions needed for the conversion of $CH_3CH_2CH_2CH_2OH$ into

(a) 1–bromobutane

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(b) 2–bromobutane (in two steps)

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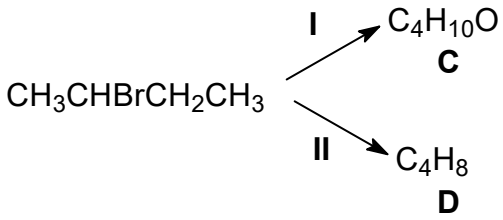
Reactions of halogenoalkanes

2 2–bromobutane can react under two different sets of reaction conditions to give two different product mixtures **C** and **D**.



(a) State the reagents and conditions necessary for each of the reactions **I** and **II**.

……..

……..

……..

(b) Product **D** is a mixture of isomers, all of which decolourise bromine water. Draw displayed formulae of these isomers and explain the reaction with $Br_2(aq)$.

……..

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(c) State the reagents and conditions for the conversion of $CH_3CH(Br)CH_2CH_3$ into $CH_3CH(NH_2)CH_2CH_3$.

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3 A monocarboxylic acid **R** occurs in goat's milk. **R** has the following composition by mass:

C, 62.1%; H, 10.3%; O, 27.6%.

Neutralisation of a sample of 0.10 g of **R** requires 8.6 cm^3 of 0.10 mol dm^{-3} sodium hydroxide.

(a) Determine the molecular formula of **R**.

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(b) **R** can be synthesized in the laboratory from 1–bromo–2,2–dimethylpropane by a 2–stage reaction sequence:

1–bromo–2,2–dimethylpropane → **Q** → **R**

(i) Draw the skeletal formula of 1–bromo–2,2–dimethylpropane.

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(ii) Suggest the reagents and conditions necessary for each step of the synthesis.

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(iii) Predict from this synthesis the structural formulae of **Q** and **R**.

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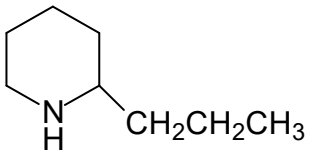
4 The alkaloid *coniine* is the major constituent of oil of hemlock, the poison taken by Socrates when he committed suicide in 399 BCE.



coniine

Coniine can be synthesized by reacting ammonia with a dibromo compound **J**.

$$NH_3 + \underset{\textbf{J}}{C_8H_{16}Br_2} \rightarrow \text{coniine} + 2HBr$$

(a) What *type of reaction* is occurring here?

……..

(b) Suggest the structure and name of compound **J**.

……..

……

Nucleophilic substitution mechanisms

5 **(a)** A sample of (2–chloroethyl)benzene, $C_6H_5CH_2CH_2Cl$, underwent hydrolysis when heated with dilute aqueous NaOH. The kinetics of the study show that the reaction is overall second order. By showing relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs, describe the mechanism for the hydrolysis of (2–chloromethyl)benzene.

(b) (1–chloroethyl)benzene, $C_6H_5CH(Cl)CH_3$, is a positional isomer of (2–chloroethyl)benzene.

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

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

By showing relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs, describe the mechanism for the hydrolysis of (1–chloroethyl)benzene. Explain why the product was optically inactive.

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

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Effect of different halogen atoms on reactivity of halogenoalkanes

6 Why does the reaction $C_2H_5X + OH^- \rightarrow C_2H_5OH + X^-$ take place more rapidly in aqueous solution when *X* is I than when *X* is Br?

A The I^- ion is a stronger nucleophile than the Br^- ion.
B The I^- ion is less hydrated in solution than the Br^- ion.
C The C–Br bond is more polar than the C–I bond.
D The C–Br bond is stronger than the C–I bond. ( )

Additional notes:

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Fluoroalkanes and fluorohalogenoalkanes

7 Which of the following would be suitable for use in a fire extinguisher?

1 $CBrF_3$
2 $CH_3(CH_2)_5CBr_3$
3 HF

A **1**, **2** and **3**
B **1** and **2** only
C **2** and **3** only
D **1** only ( )

Additional notes:

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8 Ozone depletion potential (ODP) is a measure of the effectiveness of chlorofluoroalkanes in destroying stratospheric ozone. In which sequence are compounds listed in increasing order of their ODPs?

A $CHCl F_2 < CH_3CCl_2F < CCl_2FCCl F_2$
B $CHCl F_2 < CCl_2FCCl F_2 < CH_3CCl_2F$
C $CCl_2FCCl F_2 < CHCl F_2 < CH_3CCl_2F$
D $CH_3CCl_2F < CCl_2FCCl F_2 < CHCl F_2$ ( )

Additional notes:

……...

Halogenoarenes

9 A mixture of 1 mol of bromobenzene and 1 mol of 2–bromopropane is heated under reflux for several hours with 2 mol of sodium hydroxide in aqueous solution.

(a) How many moles of bromobenzene and 2–bromopropane are likely to remain?

……..

(b) Give 2 reasons to explain the low reactivity of bromobenzene towards nucleophilic substitution.

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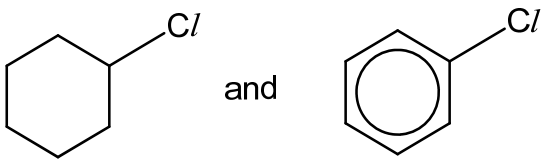
10 Describe how you would distinguish between the following pair of compounds. Indicate clearly in your answer the reagents, conditions and observations for each compound.



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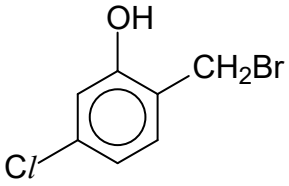
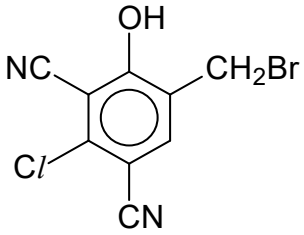
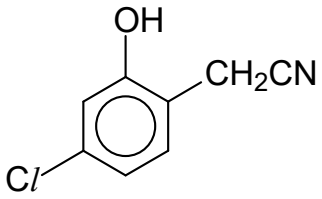
VICTORIA JUNIOR COLLEGE
CHEMISTRY DEPARTMENT
Halogen Derivatives (Halogenoalkanes and Halogenoarenes)
Supplementary Questions

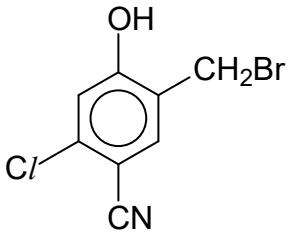
1 A compound has the following structure.

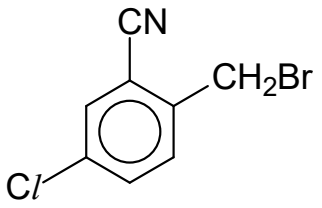


Which compound is obtained by nucleophilic substitution when a cyanide ion reacts with this compound?

A


C


B


D


2 Some chlorobutanes were separately treated with hot ethanolic sodium hydroxide. Two of these gave the same hydrocarbon C_4H_6. From which pair of chlorobutanes was this hydrocarbon obtained?

A $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CH_2CHCl_2$
B $CH_3CHClCHClCH_3$ and $ClCH_2CH_2CH_2CH_2Cl$
C $CH_3CH_2CH_2CH_2Cl$ and $ClCH_2CH_2CH_2CH_2Cl$
D $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CHClCH_3$

3 The reduction of a nitrile produced a compound of formula $C_3H_7NH_2$. Which compound would be produced if the same nitrile was hydrolysed by heating with dilute hydrochloric acid?

A $CH_3CH_2NH_2$
B CH_3CH_2OH
C $CH_3CH_2CO_2H$
D $(CH_3)_2CHCO_2H$

4 **(a)** Suggest reagents, and conditions necessary to convert bromoethane into **(i)** $CH_3CH_2NH_2$ **(ii)** $CH_3CH_2CH_2NH_2$.

(b) A by–product in the formation of $CH_3CH_2NH_2$ in **(a)(i)** above has the formula $C_8H_{20}NBr$ and it gives an immediate precipitate with aqueous silver nitrate. Suggest a structure for this compound.

5 2–iodooctane, $CH_3CHI(CH_2)_5CH_3$, exists as two optical isomers, **A** and **B** which rotate polarized light in opposite direction.

An optically pure sample containing only isomer **A** rotates polarised light by an angle of +33.3°. It reacts with a solution of radioactive iodide, $^{131}I^-$, dissolved in acetone until 1.5% of the original 2–iodooctane is incorporated with radioactive iodide. The product mixture at this point in time is found to rotate polarized light by an angle of +32.3°.

(a) Calculate the percentage composition of **A** and **B** present in the product mixture.

(b) Hence, deduce whether the mechanism proceeds via S_N1 or S_N2.

(c) Describe, with the aid of curly arrows, the stereochemistry of the mechanism stated in **(b)**.

In your answer, indicate clearly the presence of any radioactive iodine, ^{131}I, and the relative spatial configuration of the organic reactant and product.

(d) 3–iodo–3–methylhexane exists as a pair of enantiomers. When an enantiomerically pure sample of 3–iodo–3–methylhexane was reacted with excess radioactive iodide, $^{131}I^-$, a racemic mixture was obtained. Describe the mechanism of the reaction, and explain why it results in a racemic mixture.

6 Explain the following observations as fully as you can. (Use of the *Data Booklet* is recommended.)

Compound	*Observations after adding $AgNO_3$ (aq)*
$CH_3CHICH_2CH_3$	Ppt forms almost immediately
$CH_3CHBrCH_2CH_3$	Ppt forms after 2 minutes
$CH_3CHCl CH_2CH_3$	Ppt slowly forms after 10 minutes
$CH_3CHFCH_2CH_3$	No ppt forms
C_6H_5Cl	No ppt forms

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

(a) Suggest and explain how the boiling points of these three compounds differ.

(b) Suggest and explain how the C–*X* bond polarities in these three compounds differ.

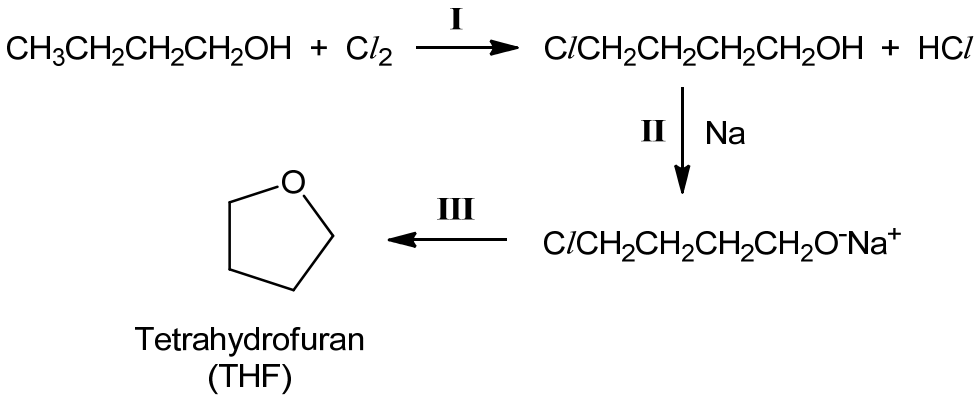
(c) Describe and explain how the reactivities of the three compounds differ towards nucleophilic reagents.

8 When a mixture of beryllium hydroxide pellets and ethanol is added to 2–chlorobutane, **P**, **Q** and **R** are formed. Although **P**, **Q** and **R** do not react with PCl_5, they decolourise potassium manganate (VII), with only **R** giving effervescence.

Suggest the identities of **P**, **Q** and **R**, explaining your reasoning.

9 The common industrial solvent, tetrahydrofuran (THF) is widely used to degrease metal parts.

It can be synthesized from butan–1–ol as shown below.



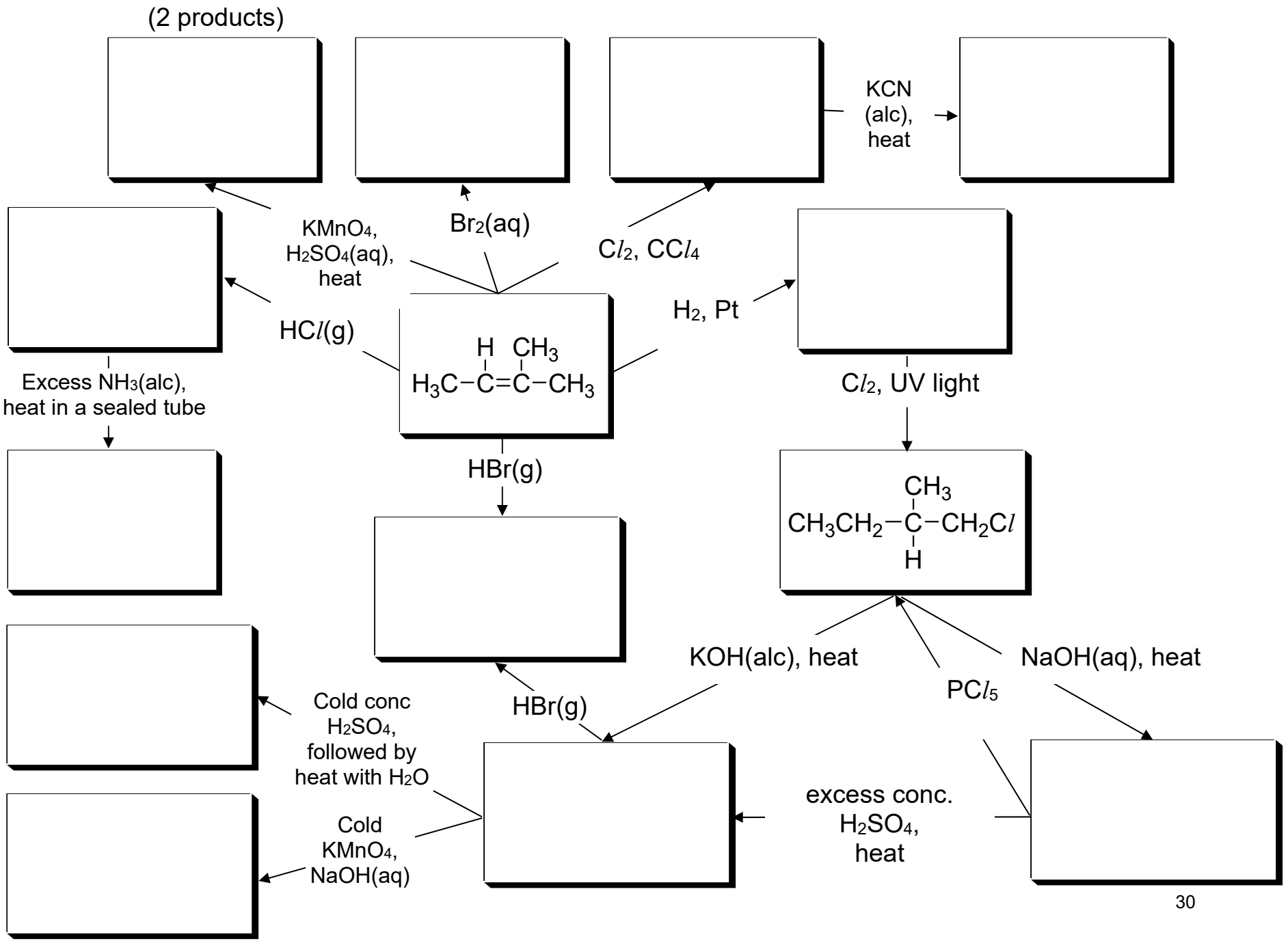
Tetrahydrofuran
(THF)

(a) What types of reaction are steps **I** and **III**?

(b) Draw a mechanism for step **III**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

(c) Comment on the yield of THF in this synthesis. Briefly explain your reasoning.

Alkanes / Alkenes / Halogenoalkanes



Arenes and RX