2023 JC2 H2 CHEMISTRY (9729)
EXTENSION TOPIC – ORGANIC CHEMISTRY
HALOGEN DERIVATIVES

Name: ____ Civics Group: 22 – ____

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 CONTENT

REFERENCES:

1. **Chemistry (for CIE AS & A Level)** by Peter Cann & Peter Hughes
2. **Cambridge International AS and A Level Chemistry Revision Guide** by Judith Potter and Peter Cann
3. **Understanding Advanced Organic and Analytical Chemistry: The Learner's Approach** by Chan Kim Seng and Jeanne Tan

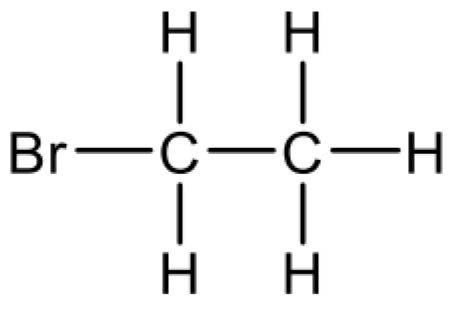
1 Introduction to Halogen Derivatives

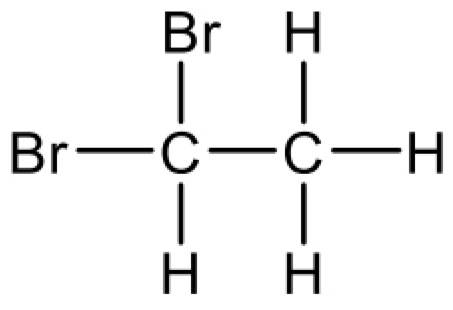
Halogen Derivatives are organic compounds that contain the **C–X functional group (X = F, C*l*, Br or I)**. In this topic, two main types of halogen derivatives will be discussed: **halogenoalkanes** and **halogenoarenes**.

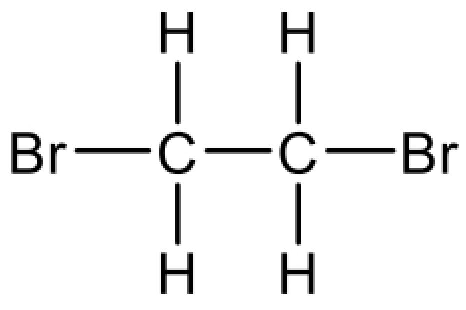
2 Nomenclature and Classification

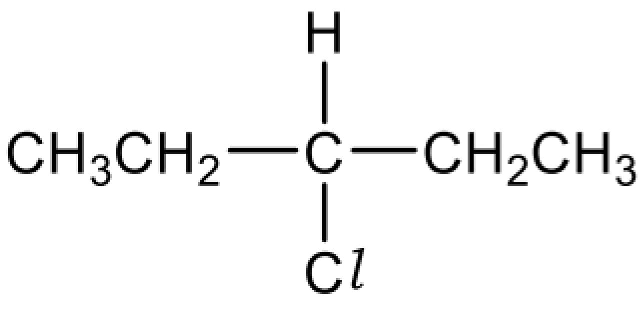
2.1 Halogenoalkanes (Alkyl Halides)

Halogenoalkanes are **alkane molecules which have one or more hydrogen atoms replaced by halogen atoms**. These compounds are named similarly to alkanes, with the suffix ending with *–ane* and the halogens as prefixes (recall the hierarchy of functional groups covered in IOC). Below are some examples:

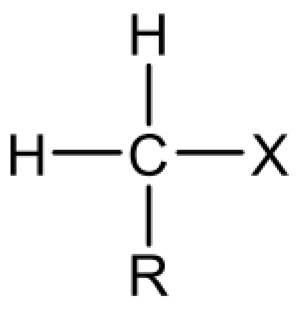

bromoethane


1,1-dibromoethane


1,2-dibromoethane

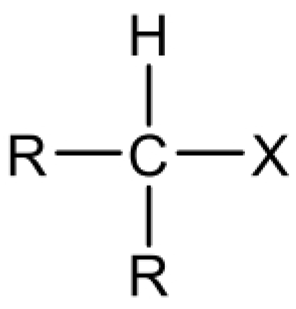

3-chloropentane

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



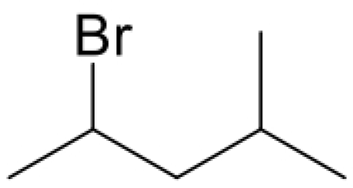
Primary (1°) halogenoalkanes – each alkane molecule contains only **<u>one</u>** alkyl or other carbon-containing group attached to the α-carbon bonded to the halogen atom.

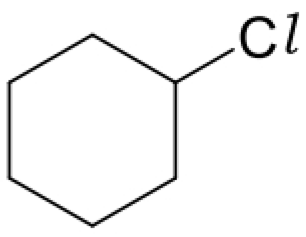
e.g. CH_3CH_2Br

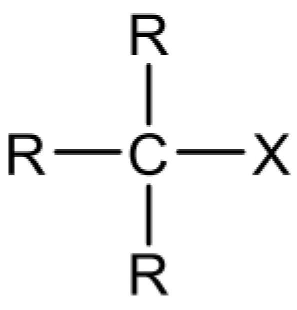


Secondary (2°) halogenoalkanes – each alkane molecule contains **two** alkyl or other carbon-containing group attached to the α-carbon bonded to the halogen atom.

e.g.

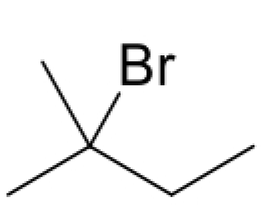


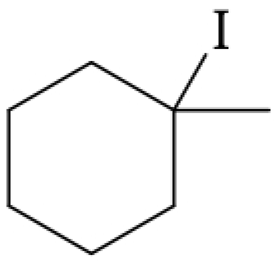




Tertiary (3°) halogenoalkanes – each alkane molecule contains **three** alkyl or other carbon-containing group attached to the α-carbon bonded to the halogen atom.

e.g.

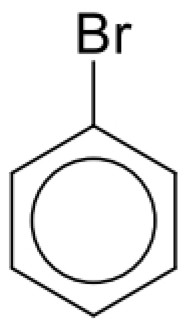




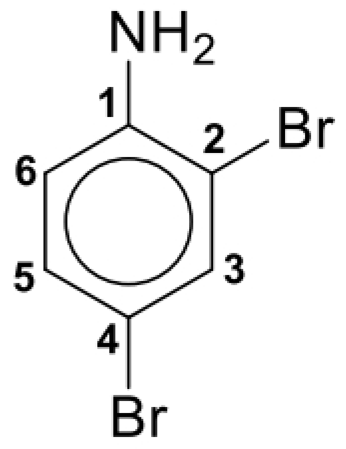
(X = halogen atom, R = alkyl group)

2.2 Halogenoarenes (Aryl halides) (not in H1 syllabus)

Halogenoarenes are **derivatives of benzene** which have **one or more hydrogen atoms present in the aromatic ring replaced by halogen atoms**. Unlike halogenoalkanes, there is no classification of halogenoarenes. These compounds are named similarly to arenes with the halogens as prefixes. Numbering of the position starts from the carbon atom with the principal functional group and in the direction that utilises the lowest possible numbers for the substituents. Below are some examples:



bromobenzene



2,4-dibromophenylamine

Self Check 2A

(a) Draw five isomers (both structural and stereoisomers) with the molecular formula, C_4H_9Br. Annotate chiral carbons with an *, if any.

(b) Classify these isomers as primary, secondary or tertiary halogenoalkanes.

(c) Give the IUPAC names of the five isomers.

At the end of this section, you should know that:

1. Halogenoalkanes and halogenoarenes are alkanes and arenes that have at least one hydrogen atom substituted by a halogen atom.
2. Halogenoalkanes are classified into primary, secondary, and tertiary, depending on the number of alkyl groups directly bonded to the α-carbon bonded to the halogen atom.
3. There is no classification applicable to halogenoarenes.

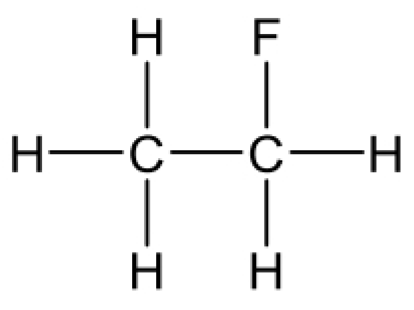
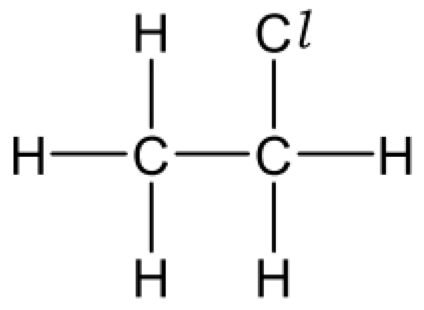
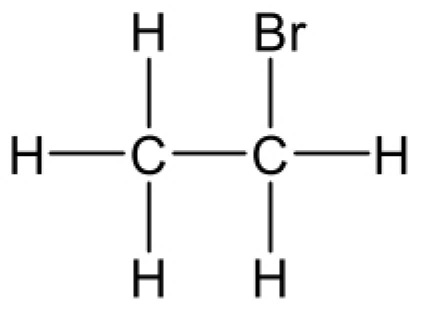
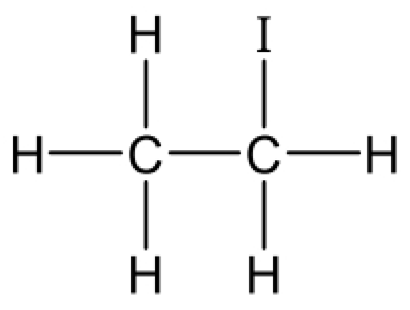
3 Physical Properties

3.1 Melting and Boiling points

- **Most halogenoalkanes are polar** and thus have intermolecular **permanent dipole–permanent dipole attractions**, which are stronger than the intermolecular instantaneous dipole–induced dipole attractions for alkanes. Hence, we expect the melting/boiling point of halogenoalkanes to be higher than that of alkanes with similar number of electrons.

- For halogenoalkanes with the same halogen atom, both the melting point and boiling point:
  - increase with increasing chain length due to the **increasing number of electrons, which makes the electron cloud is more polarisable** and hence **stronger instantaneous dipole-induced dipole attractions between molecules.**
  - decrease with increasing degree of branching due to the **decreasing surface area of contact between the molecule** and hence **weaker instantaneous dipole-induced dipole attractions between molecules.**

- For **halogenoalkanes of the same chain length but with different halogen atoms**, the **melting and boiling point was found to increase with increasing number of electrons, which makes the electron cloud is more polarisable** (see table below), thus leading to **stronger instantaneous dipole-induced dipole attractions between molecules**. This implies that the different strength of the intermolecular instantaneous dipole-induced dipole attractions is the more significant factor than differences in polarity of the molecule, if any.

compound	fluoroethane	chloroethane	bromoethane	iodoethane
structural formula				
boiling point (ºC)	–37.1	12.3	38.3	71.0

3.2 Solubility

Halogenoalkanes/halogenoarenes although polar, have **poor solubility in water**, especially for molecules with higher molecular weight. This is due to **energetic considerations**.

The halogenoalkane forms permanent dipole-permanent dipole interactions with water molecules. The energy that is released from this interaction is insufficient to overcome the strong hydrogen bonding between water molecules.

However, halogenoalkanes/halogenoarenes are **soluble in non-polar solvents**. This is due to the presence of **non-polar alkyl groups or benzene rings** of the respective compounds and thus can form **instantaneous dipole-induced dipole attractions of similar strength with the non-polar solvent molecules.**

3.3 Density

Halogenoalkanes/halogenoarenes are generally denser than both water and the alkane/arene which they are derived from. This is due to the presence of the halogen atom, which increases the molecular mass.

Self Check 3A

The boiling points of some organic compounds are as shown.

compound	structural formula	name	boiling point / ºC
A	$CH_3CH_2CH_2CH_3$	butane	–1
B	$CH_3CH_2CH_2CH_2Cl$	1-chlorobutane	78
C	$CH_3CH_2CH_2CH_2Br$	1-bromobutane	101
D	$CH_3CH_2CH_2CH_2I$	1-iodobutane	130

Explain each of the following.

(a) The boiling point of compound **B** is higher than that of **A**.

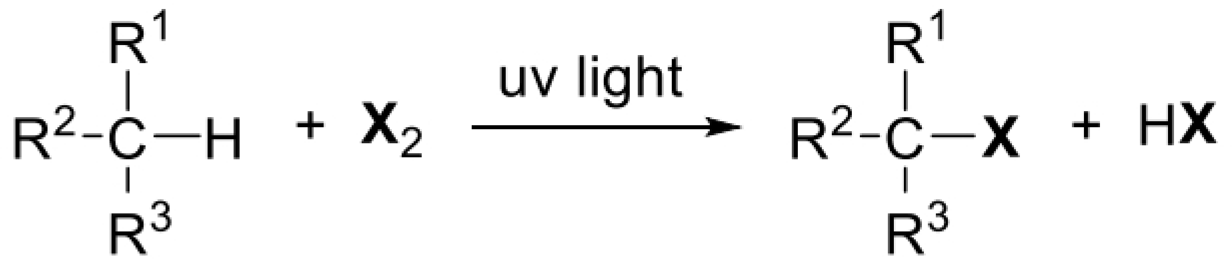
(b) The boiling point increases in the order of **B < C < D**.

At the end of this section, you should know that:

1. Halogenoalkanes and halogenoarenes are polar compounds, with intermolecular permanent dipole-permanent dipole interactions between molecules.
2. Halogenoalkanes and halogenoarenes are insoluble in water but are soluble in organic solvents.
3. Halogenoalkanes and halogenoarenes are generally denser than water and the hydrocarbon that they were derived from.

4 Preparation of Halogenoalkanes and Halogenoarenes

4.1 Free Radical Substitution of Alkanes



(**X** = Cl, Br)

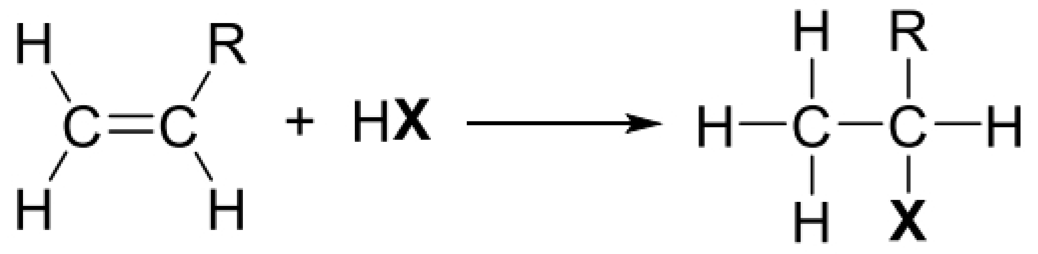
where R^1, R^2 and R^3 are either H atoms or alkyl group

Reagents and conditions: Cl_2(g) or Br$_2$(l); uv light
Observations: *Greenish yellow Cl_2(g) or reddish-brown Br$_2$(l) decolourises

Free radical substitution of alkanes is **seldom used** due to the formation of a **mixture of products** (*e.g.* if we use propane and Br$_2$(l), we may get 1-bromopropane, 2-bromopropane, 1,1-dibromopropane, *etc*. due to **random and/or multiple substitution of H atoms**)

4.2 Electrophilic Addition of Alkenes

4.2.1 Electrophilic Addition of hydrogen halides

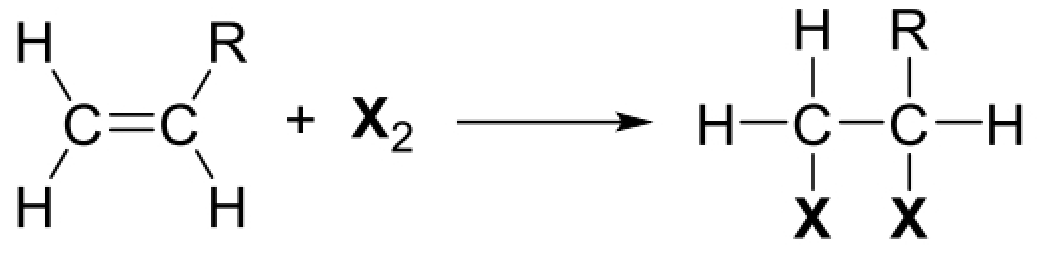


(**X** = Cl, Br, I)

Reagents and conditions: HCl(g), HBr(g) or HI(g); room temperature

Recall from ‘Alkenes’ topic that **Markovnikov’s rule** can be used to predict the major product in the addition of HX to an asymmetrical alkene.

4.2.2 Electrophilic Addition of halogen



(**X** = Cl, Br)

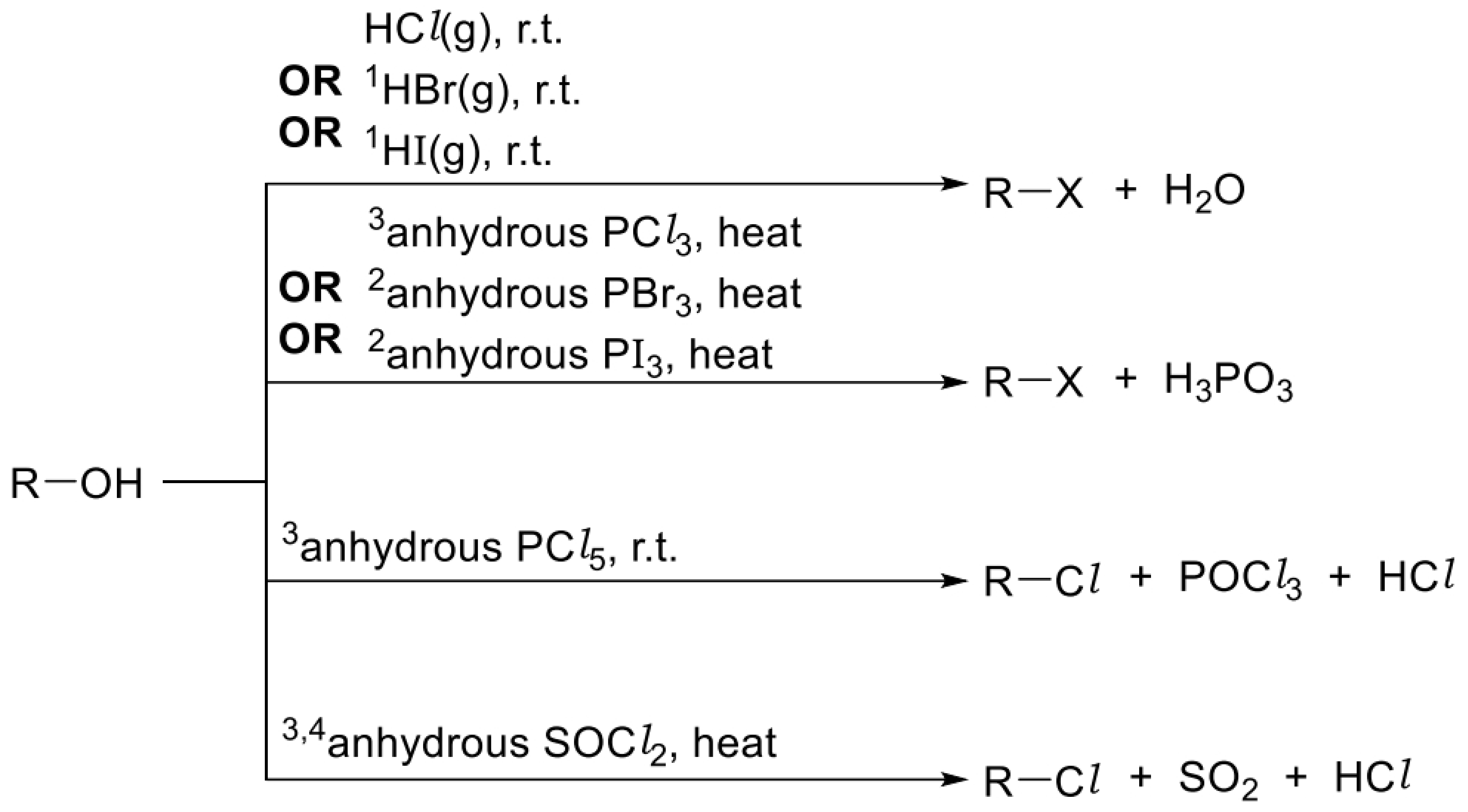
Reagents and conditions: Cl_2 in CCl_4 or Br$_2$ in CCl_4; room temperature, in the dark
Observation: *Pale yellow Cl_2 or orange-red Br$_2$ decolourises

* The decolourisation of greenish yellow Cl_2 gas or pale yellow Cl_2 in CCl_4 may be difficult to observe depending on the intensity of the colour. The use of Cl_2 for distinguishing tests is thus not advisable.

4.3 Nucleophilic Substitution of Alcohols (not in H1 syllabus)

(will revisit in Hydroxy Compounds)

Reagents and Conditions:



Observations: For reaction with PCl_5 and $SOCl_2$, **white fumes of HCl** are produced, which **turn damp blue litmus paper red**.

This is useful as a **chemical test for alcohols**.
However, **carboxylic acids give the same observations**.

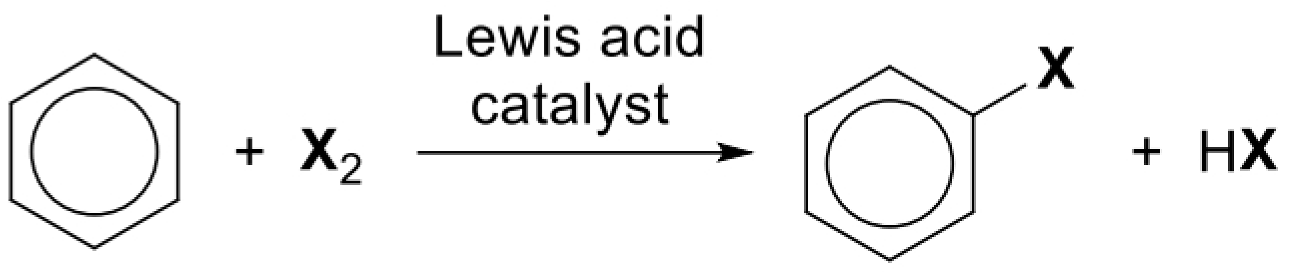
1. $HBr(g)$ may be prepared by reacting solid NaBr with concentrated H_2SO_4 and heat, while $HI(g)$ may be prepared by reacting solid NaI with concentrated H_3PO_4 and heat.

2. PBr_3 or PI_3, is prepared *in situ* by heating red phosphorus with liquid bromine or solid iodine respectively.
   $2P + 3X_2 \rightarrow 2PX_3$ X = Br, I

3. **When using PCl_3, PCl_5 and $SOCl_2$, ensure that there is absence of water.**
   These compounds hydrolyse in water.
   $PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$
   $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$
   $SOCl(l) + H_2O(l) \rightarrow SO_2(g) + 2HCl(g)$

4. The **advantage of using $SOCl_2$** is that the two **by-products are both gases (SO_2 and HCl), so they separate themselves from the RCl product easily**.

4.4 Electrophilic Substitution of Arenes (not in H1 syllabus)

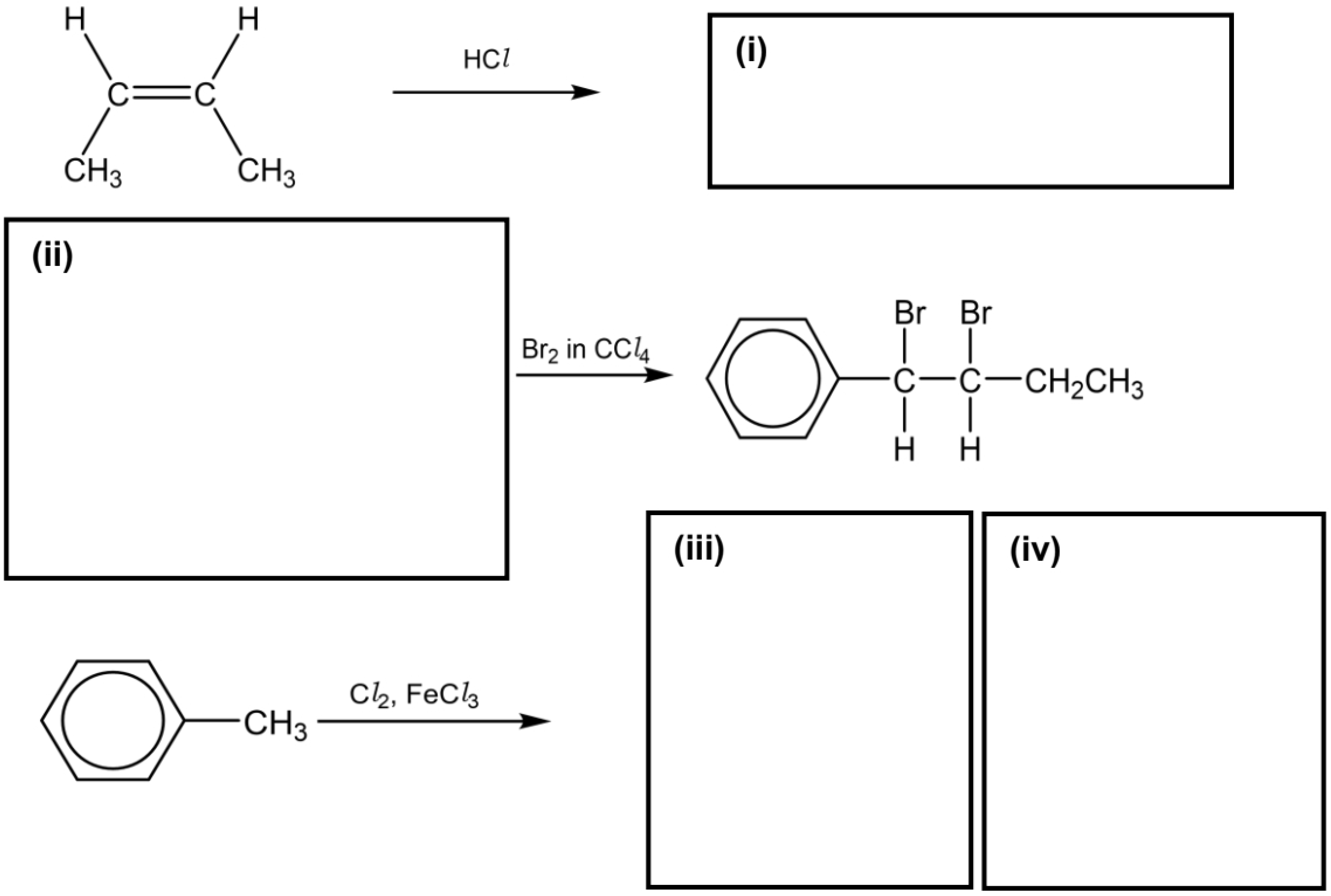


Reagents and conditions: X_2 with anhydrous FeX_3 or anhydrous AlX_3 or Fe as catalyst; room temperature [X = C*l* or Br]

Self Check 4A

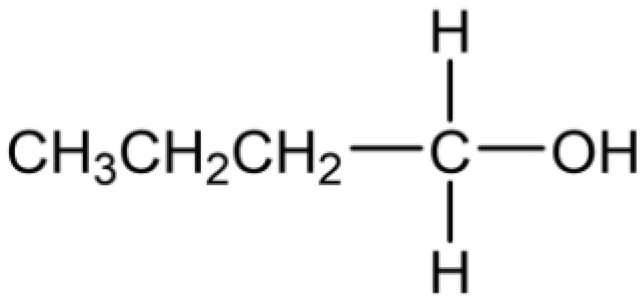
(a) Draw the structures of four possible organic products that may be obtained when propane, $CH_3CH_2CH_3$, is reacted with chlorine in UV light.

(b) Draw the structure of the organic compound in each box below.



Self Check 4A

(c) Draw the structure of the organic product obtained when the alcohol is heated with the following reagents.



$$CH_3CH_2CH_2-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH$$

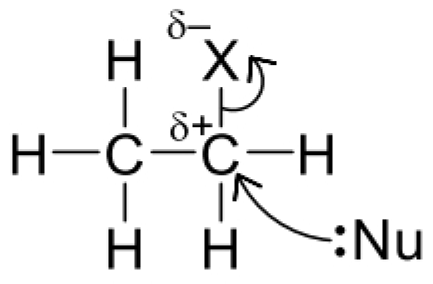
(i) anhydrous thionyl chloride

(ii) phosphorus triiodide

At the end of this section, you should know that:

1. Alkanes undergo free radical substitution with X_2 (where X = Cl, Br) in UV light to give a halogenoalkane and HX gas (appear as white fumes).
2. Alkenes undergo electrophilic addition with X_2(g) or X_2 dissolved in CCl_4 in the dark to give halogenoalkanes as the only product.
3. Halogenoalkanes can be prepared by reacting alcohols with either HX, PX_3, PCl_5, or $SOCl_2$ (X = Cl, Br, I).
4. Halogenoarenes can be prepared by reacting the benzene with X_2 in the presence of Fe, anhydrous FeX_3, or anhydrous AlX_3.

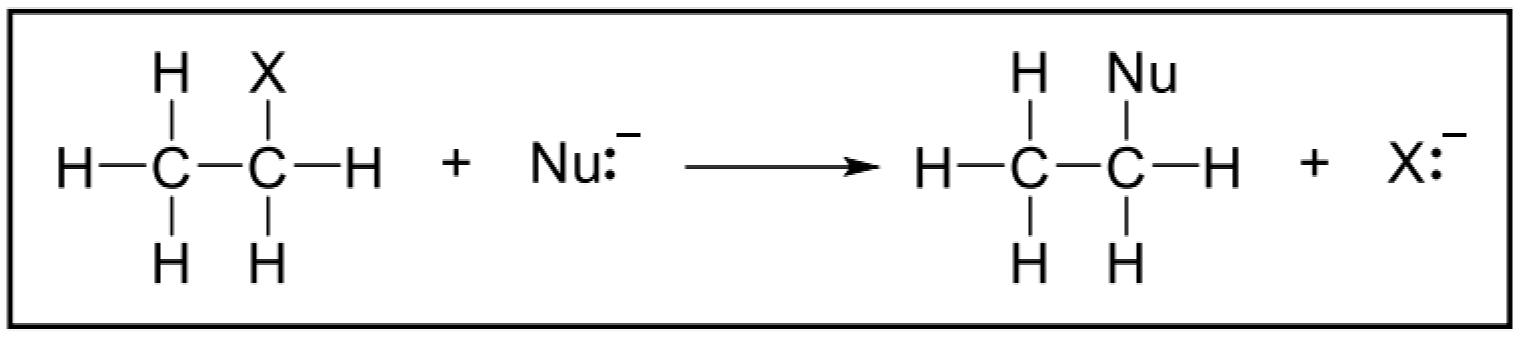
5 Nucleophilic Substitution Reactions of Halogenoalkanes



- Halogenoalkanes are often polar molecules with the C atom of the C–X bond having a partial positive charge. This imparts **electrophilic** character to this C atom.

- **Nucleophilic substitution reactions** occur when a **nucleophile (electron pair donor, Lewis Base)** is attracted to the **electron-deficient C atom (Lewis Acid)**, which is **susceptible to attack** by these nucleophiles, where **the nucleophile substitutes the halogen atom**.

- The overall reaction for nucleophilic substitution can be represented as:

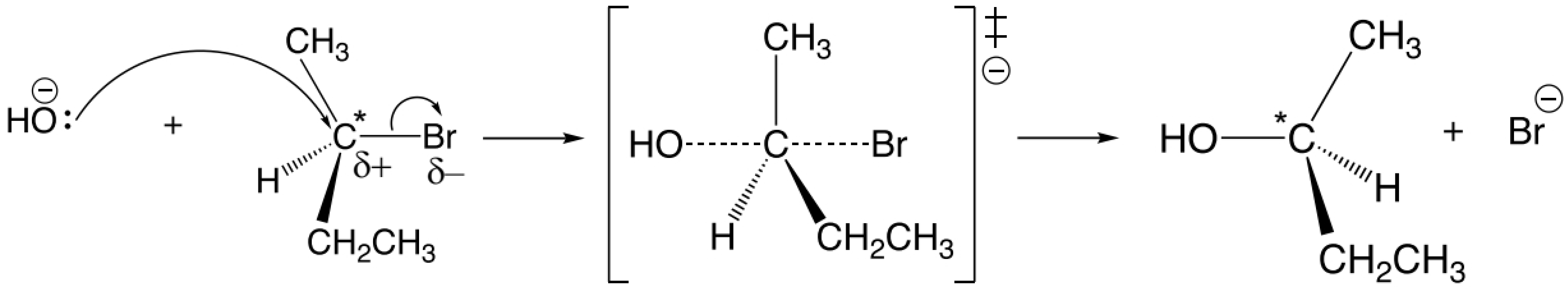


$$\mathrm{CH_3CH_2X} + \mathrm{Nu}{:}^{-} \longrightarrow \mathrm{CH_3CH_2Nu} + \mathrm{X}{:}^{-}$$

- Nucleophilic substitution reactions can proceed by either a **one-step mechanism (S_N2)** or a **two-step mechanism (S_N1)**.
  - **Primary** halogenoalkanes **generally** undergo the **S_N2 mechanism**.
  - **Tertiary** halogenoalkanes **generally** undergo the **S_N1 mechanism**.
  - **Secondary** halogenoalkanes may proceed via **both mechanisms**.

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

5.1 Mechanism of S_N2 reactions (not in H1 syllabus)



pentavalent
transition state

- The **OH⁻ nucleophile**, attacks the $^{\delta+}$C atom (α-carbon) from the side **opposite** to that of the C–Br bond in what is known as the **rear-side attack**.

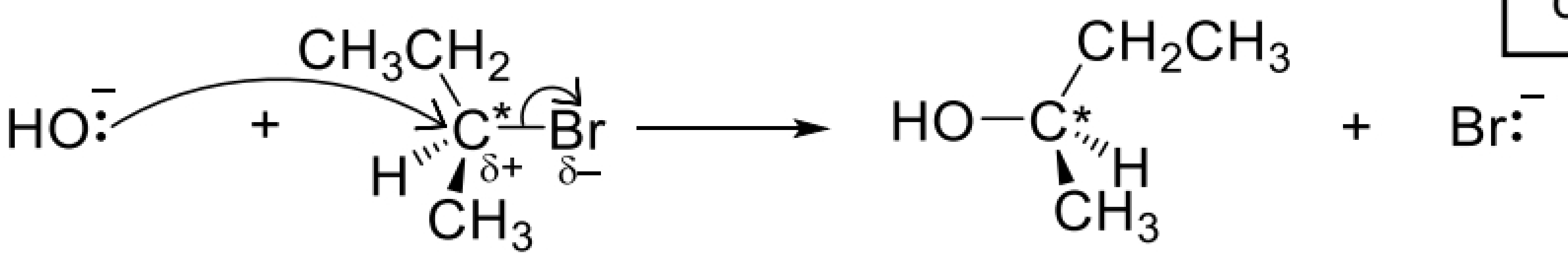
- The OH⁻ donates one of its lone pair to the carbon atom, a **bond begins to form between O of OH⁻ and the C of the halogenoalkane**.

- Simultaneously, the **C–Br bond is weakened and begins to break (heterolytic cleavage)**. Both the bonding electrons in the C–Br bond are gradually transferred to the Br atom to form Br⁻, the leaving group.

- The reaction takes place in a single step *via* a transition state.

- If **other anionic nucleophiles** are used **(*e.g.* CN⁻, X⁻, *etc.*)**, the **mechanism will be similar to what is shown above**.

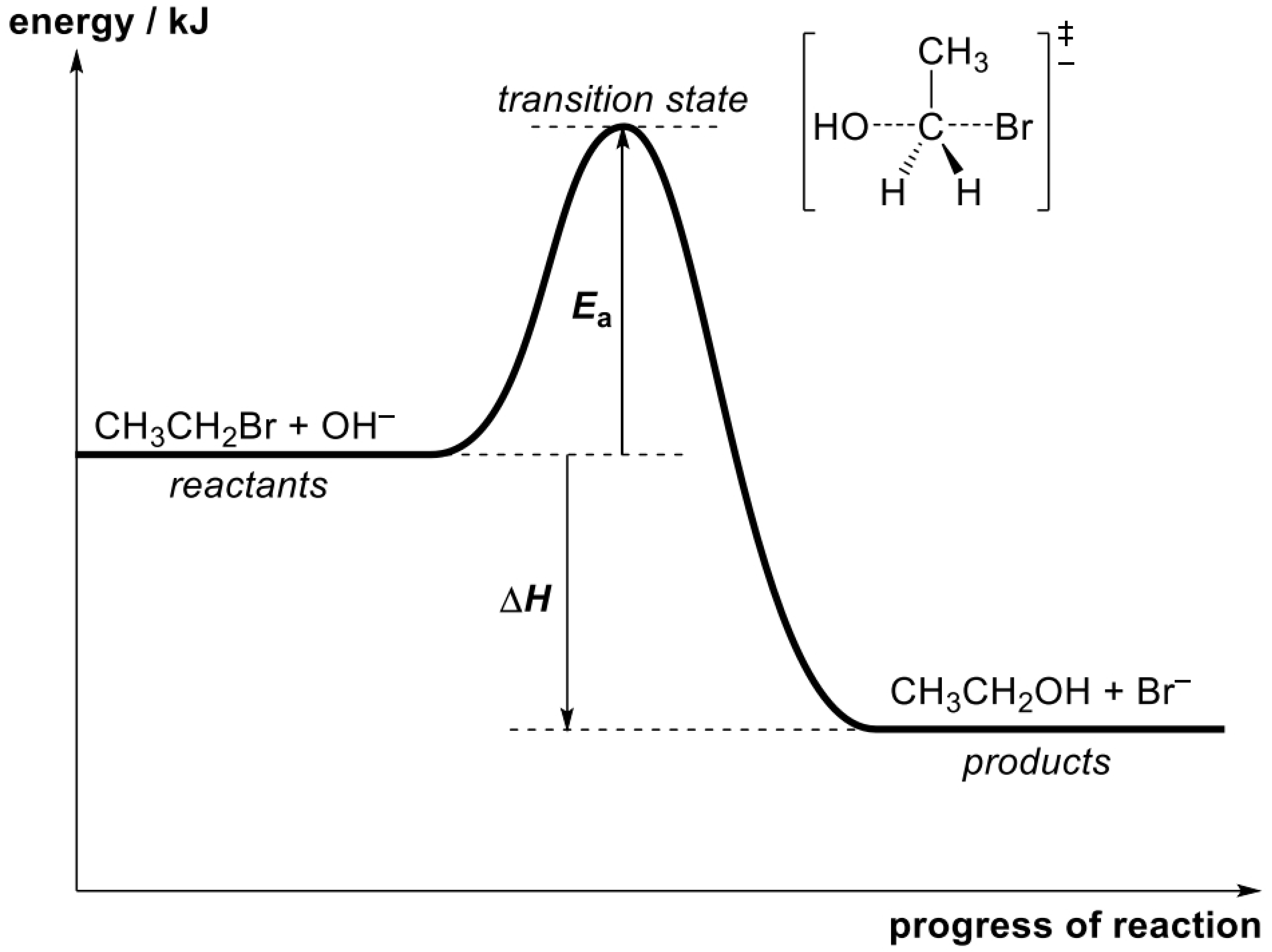
- If the halogenoalkane has a **chiral α-carbon**, due to the **rear-side attack**, there will be an **inversion of configuration** at the α-carbon.



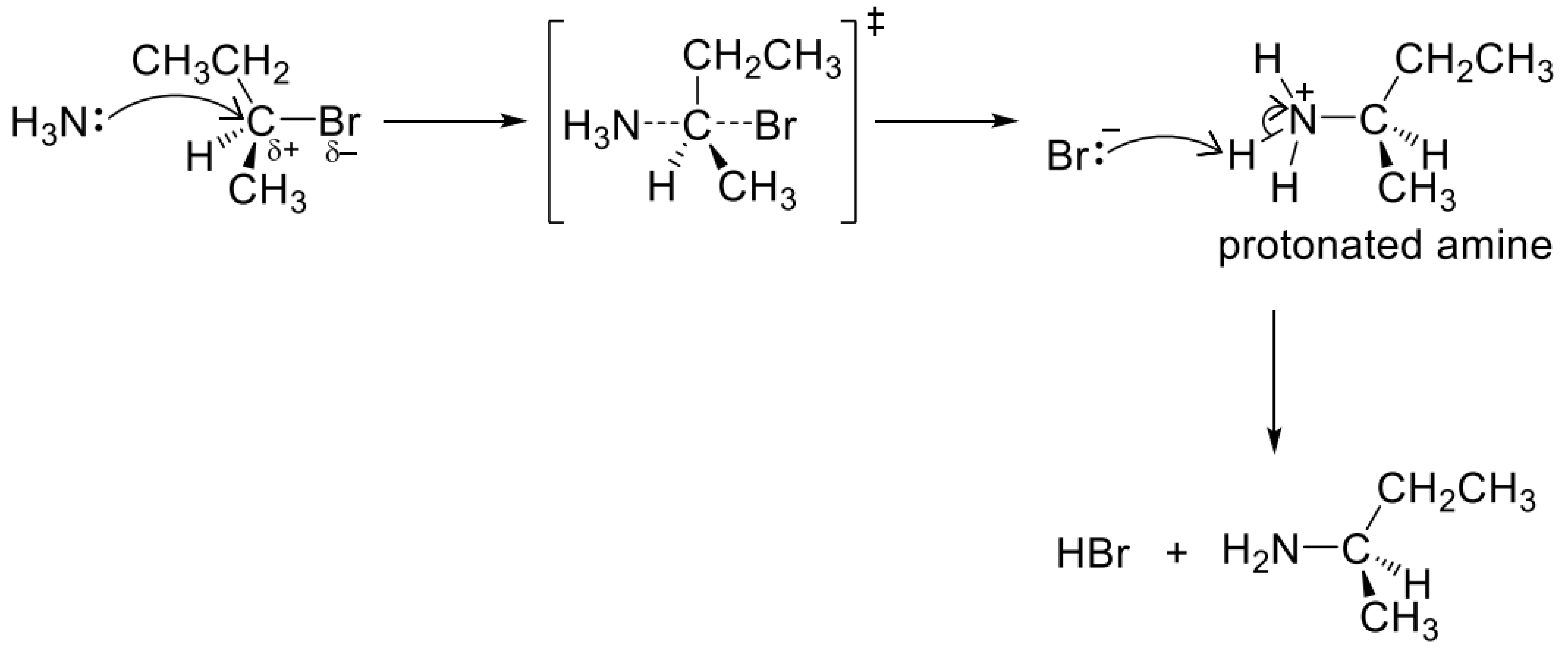
* chiral carbon

- The rate equation for this mechanism is **rate = *k*[RX][nucleophile]**, where the rate is dependent on the concentration of both RX and the nucleophile.
  - The mechanism is known as **S_N2** (substitution, nucleophilic, bimolecular), because **<u>two species are involved in the rate-determining step</u>**.

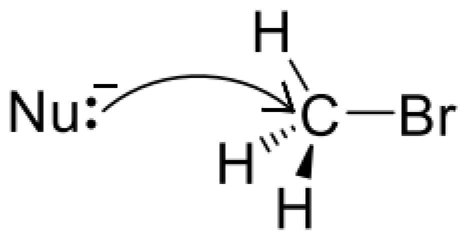
- The energy profile diagram for the S_N2 mechanism is as shown.



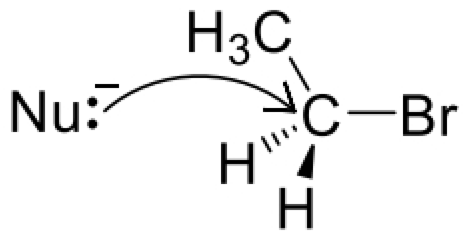
- If **neutral nucleophiles** such as NH_3 and amines (*e.g.* RNH_2, R_2NH, R_3N) are used, the mechanism will be as shown (For NH_3. Amines behave similarly). The protonated amine product formed undergoes deprotonation by a base such as X^-.



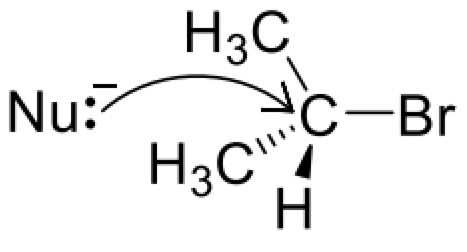
- **<u>Steric hindrance increases as additional alkyl groups are bonded to the α–carbon</u>**. Hence, generally **<u>primary halogenoalkanes undergo S_N2 reactions more readily</u>** and tertiary halogenoalkanes do not and the **<u>rate of the nucleophilic substitution reaction decreases from methyl > 1° > 2° > 3° halogenoalkane</u>**.



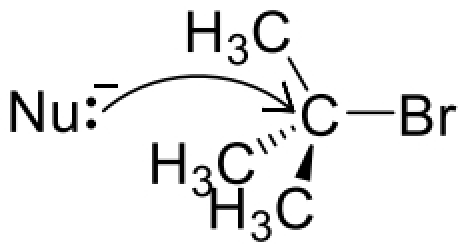
methyl



1°



2°



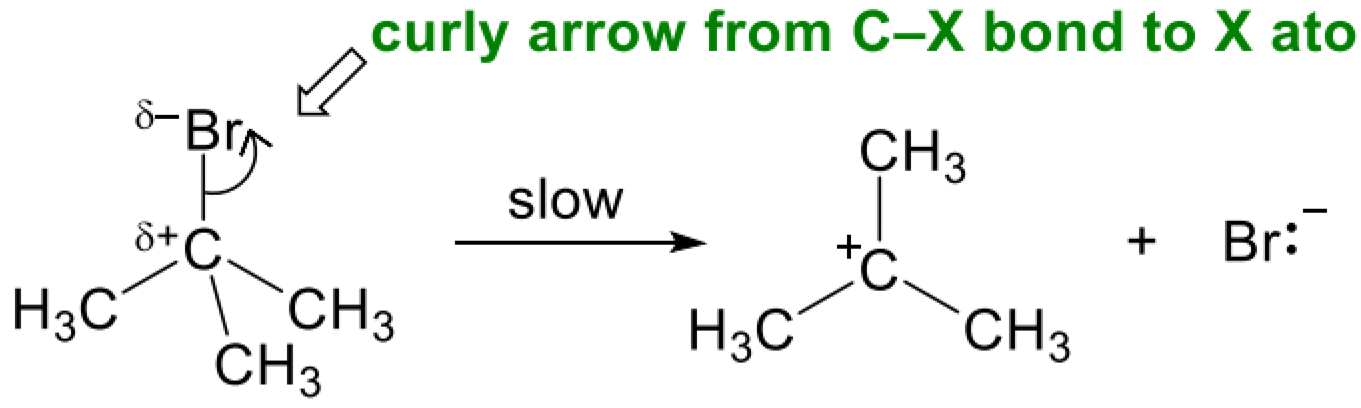
3°

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

5.2 Mechanism of S_N1 reactions (not in H1 syllabus)

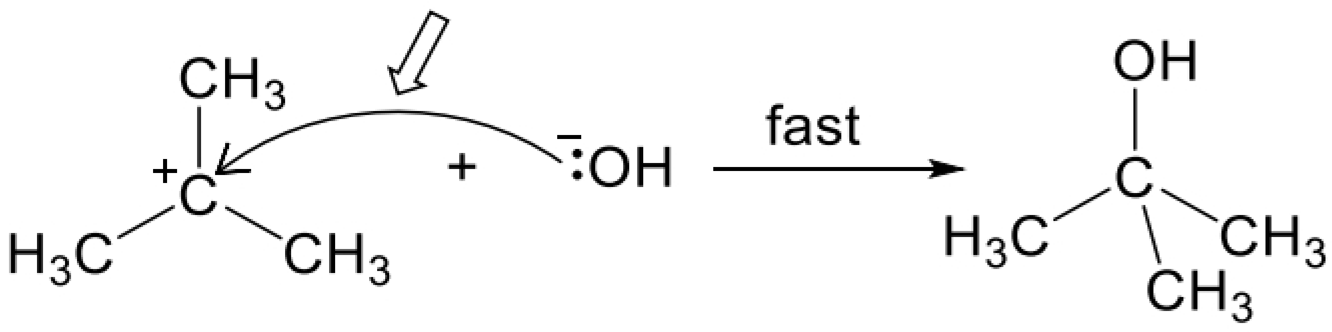
Step 1: C–X bond breaks to form the carbocation and halide ion

curly arrow from C–X bond to X atom



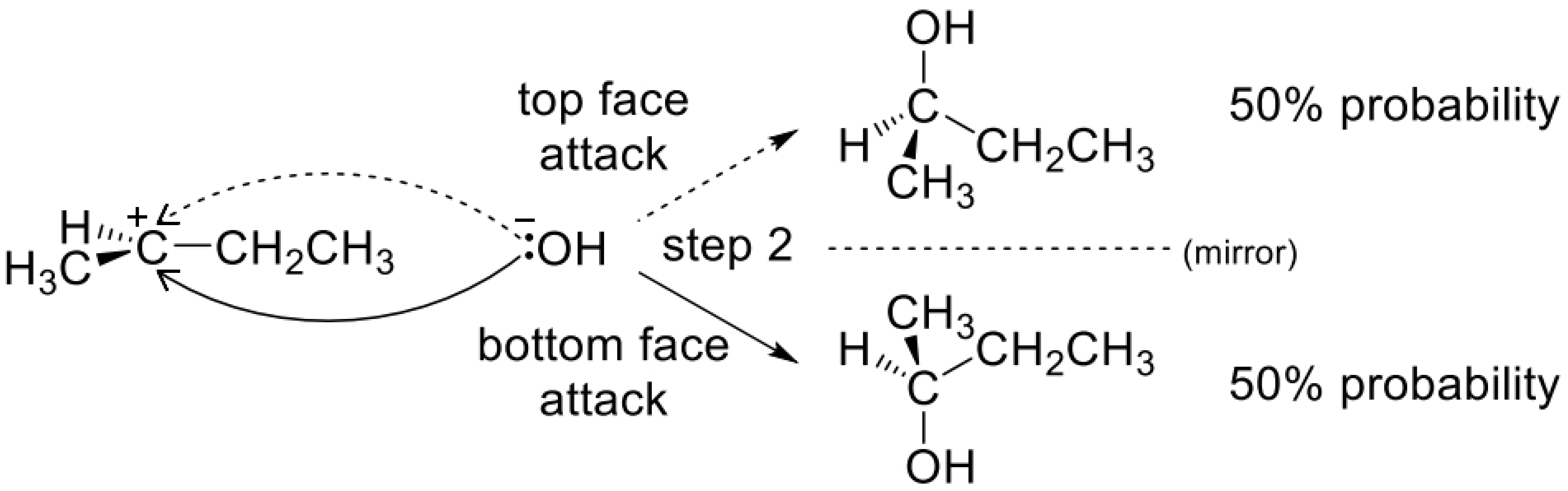
Step 2: Nucleophile attacks the carbocation to form the product

curly arrow from lone pair of nucleophile to C atom of carbocation



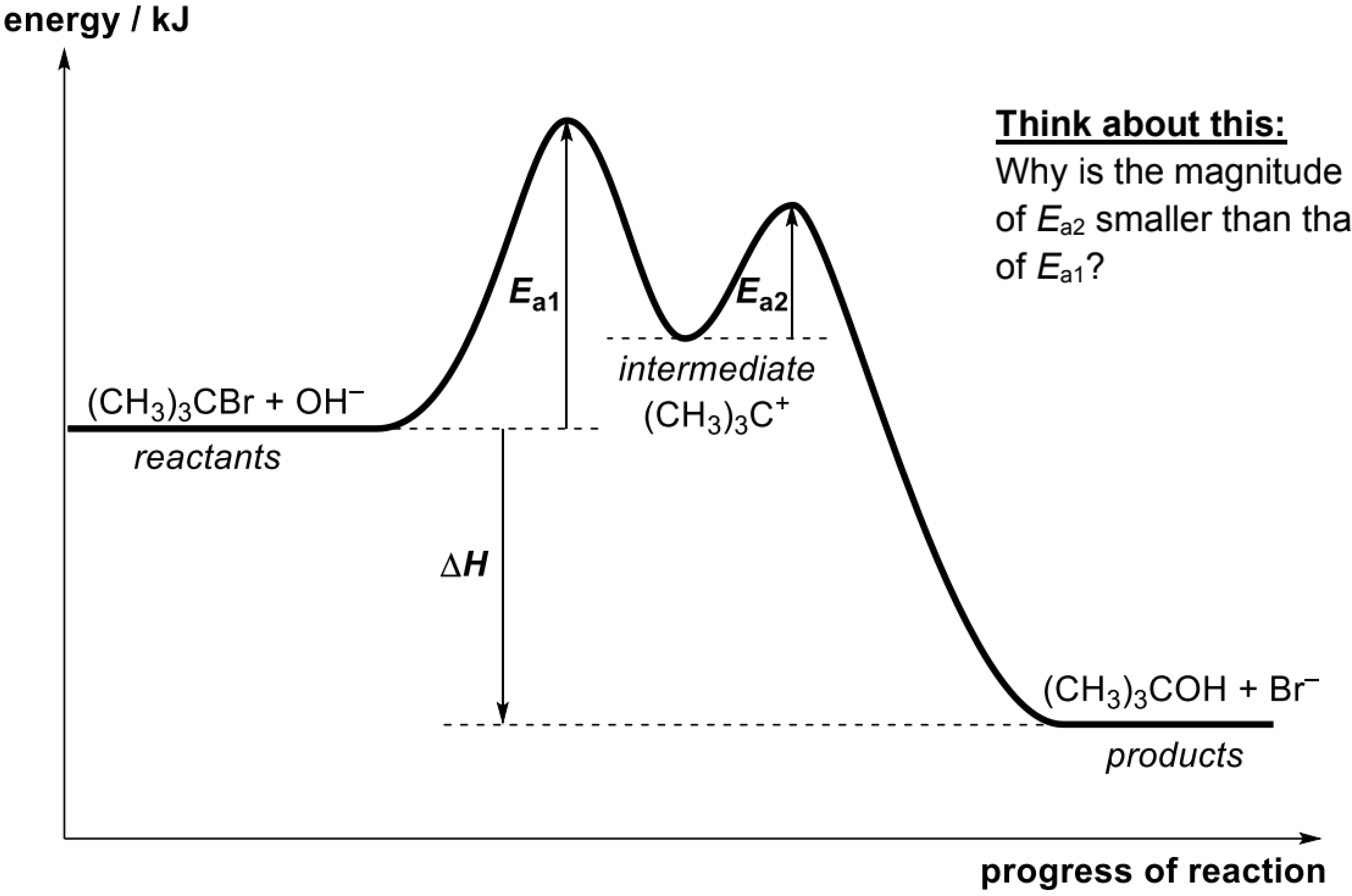
- The **first step**, which is the **slow step**, involves the **heterolytic cleavage** of the **C–Br bond** in the halogenoalkane to form a **carbocation intermediate** and Br^- ion.
- The **<u>electron-donating alkyl groups</u>** help to **<u>stabilise the carbocation</u>**.
- The **second step**, which is the **fast step**, involves **bond formation between nucleophile (OH^-) and cationic carbon of the highly reactive carbocation** to form the product.

- As the **<u>carbocation intermediate is trigonal planar with respect to the cationic carbon</u>**, the **<u>nucleophile can attack from either face (top and bottom) with equal probability</u>**.
- If nucleophilic attack of the electron-deficient carbon gives rise to a **chiral carbon**, a **racemic mixture** is formed as both enantiomers would be formed in equimolar amounts**.**



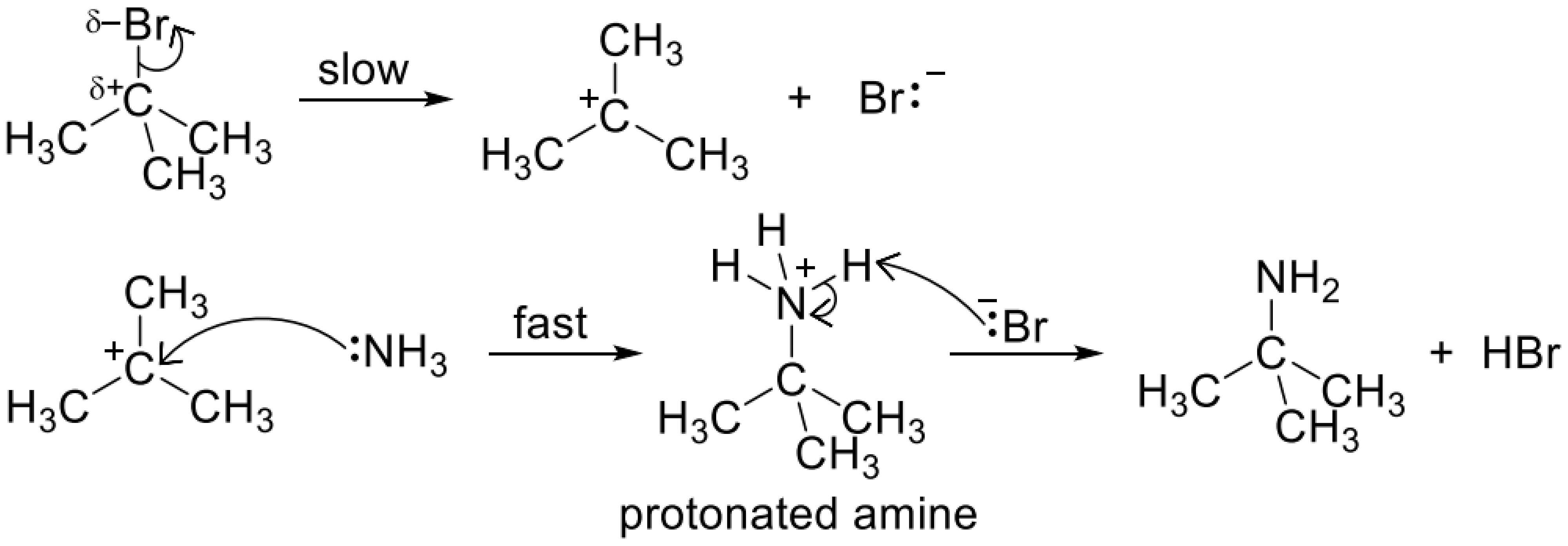
- The derived rate equation for this mechanism is **rate = *k*[RX],** where the rate is dependent on the concentration of RX only.
  - The mechanism is known as **S_N1** (Substitution, Nucleophilic, unimolecular), because **<u>only one species is involved in the rate-determining step</u>**.

- The energy profile diagram for the S_N1 mechanism is as shown.

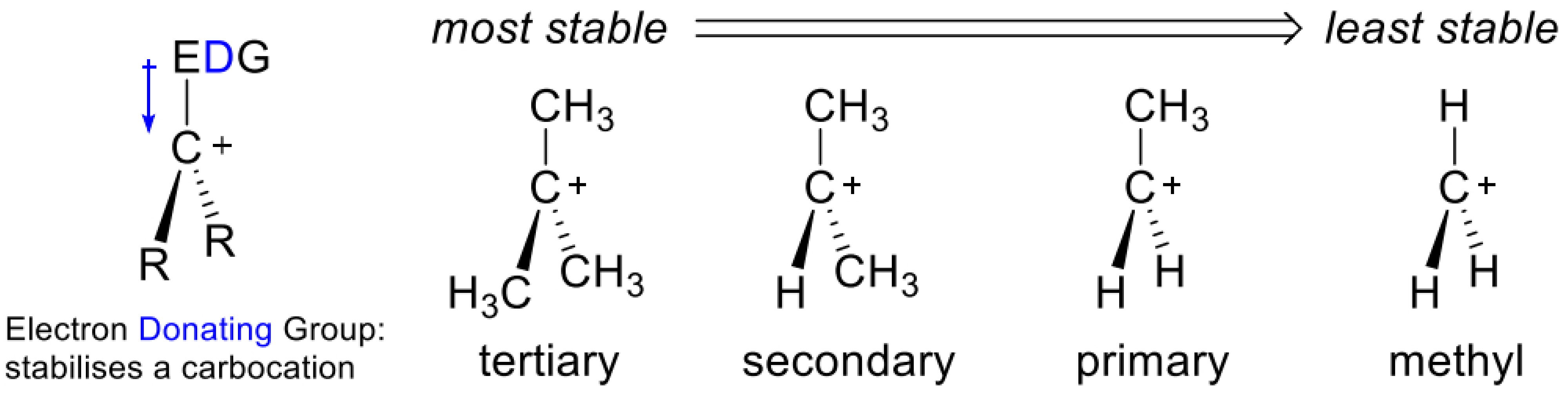


Think about this:
Why is the magnitude of E_{a2} smaller than that of E_{a1}?

- If **neutral nucleophiles** such as NH_3 and amines (*e.g.* RNH_2, R_2NH, R_3N) are used, the mechanism (for NH_3) will be as shown (amines behave similarly). The protonated amine product formed undergoes deprotonation by a base such as X^-.



- **<u>Stability of carbocation increases as additional electron-donating alkyl groups are bonded to the positively charged carbon</u>**. Hence, generally **<u>tertiary halogenoalkanes undergo S_N1 reactions more readily</u>** and primary halogenoalkanes do not and the **<u>rate of the nucleophilic substitution reaction decreases from 3° > 2° > 1° > methyl halogenoalkane</u>**.



5.3 Comparison of S_N2 and S_N1 mechanisms (not in H1 syllabus)

	S_N2	**S_N1**
mechanism	• Nucleophile approaches the electron-deficient α-carbon from the side **opposite** to the leaving halide. • The other 3 groups attached to the α-carbon would hinder the approach of the nucleophile if they are bulky (**steric hindrance**).	• The C-X bond first breaks heterolytically to form the carbocation intermediate and halide ion. • Electron-donating alkyl groups attached to the α-carbon of a halogenoalkane help to **stabilise the carbocation intermediate** formed.
kinetics	**overall 2nd order** reaction rate = k[RX][Nu]	**overall 1st order** reaction rate = k[RX]
energy profile diagram	single step	two steps
stereochemistry of products (if any)	**inversion of configuration** about the α-carbon of chiral halides	**racemisation** of chiral halides
type of RX	**1° halogenoalkanes** usually undergo nucleophilic substitution via **S_N2** mechanism and 3° halogenoalkanes do not. (CH_3 > 1° > 2° > 3°)	**3° halogenoalkanes** usually undergo nucleophilic substitution via **S_N1** mechanism and 1° halogenoalkanes do not. (CH_3 < 1° < 2° < 3°)

- For 2° halogenoalkanes, nucleophilic substitution can proceed via both **S_N1** and **S_N2** mechanisms.

- The type of mechanism (S_N2 or S_N1) is based on <u>**electronic**</u> and <u>**steric considerations**</u> on the structure of the halogenoalkanes:

structure of halogenoalkane	**stability of carbocation (electronic)**	**steric hindrance (steric)**	**type of mechanism**
methyl	least	least	100% S_N2
1°	↓	↓	↓
2°			
3°	most	most	100% S_N1

Example 5A

The rate equation for the alkaline hydrolysis of the halogenoalkane RBr is

$$\text{rate} = k\,[\text{RBr}]\,[\text{OH}^-]$$

Which of the following statements is inconsistent with this observation?

A The reaction is first order with respect to RBr.
B The reaction is second order overall.
C The final step in the reaction is the attack of OH^- on R^+.
D The rate-determining step is bimolecular.
E OH^- attacks RBr before the R-Br bond is broken.

Self Check 5A

Bromoethane, CH_3CH_2Br, reacts with methanol under suitable conditions to form $CH_3CH_2OCH_3$. Name and describe the mechanism for the reaction, given that the attacking nucleophile is CH_3O^-. [This reaction produces an organic compound containing an ether functional group.]

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

5.4 Reactivity of Halogenoalkanes by Nucleophilic Substitution Reactions

The reactivity of halogenoalkanes by nucleophilic substitution reactions depends on the **ease of cleavage of the C–X bond**. The stronger the bond, the harder it is for the bond to break.

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

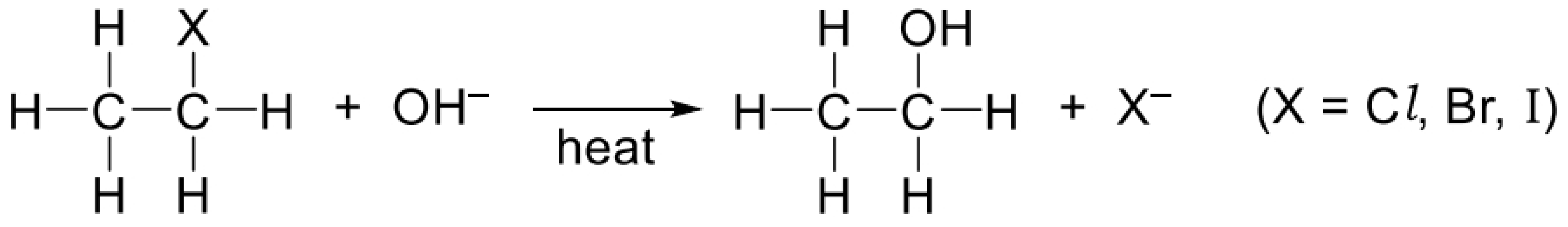
As the **size of the halogens become larger from F to I**, the **valence orbital used for bonding** becomes **larger and more diffuse**. Thus, the **orbital overlap** between the halogen and carbon atoms **becomes less effective**.

<u>**Bond strength: C–I < C–Br < C–C*l* < C–F**</u> and thus, the <u>**reactivity of halogenoalkanes: iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes**</u>.

Due to the <u>**very strong C–F bond**</u>, <u>**fluoroalkanes are generally unreactive**</u> and do not undergo nucleophilic substitution.

LO (a) recall the chemistry of halogenoalkanes as exemplified by:
(iii) the following nucleophilic substitution reactions of bromoethane: hydrolysis; formation of nitriles; formation of primary amines by reaction with ammonia

5.5 Formation of Alcohols



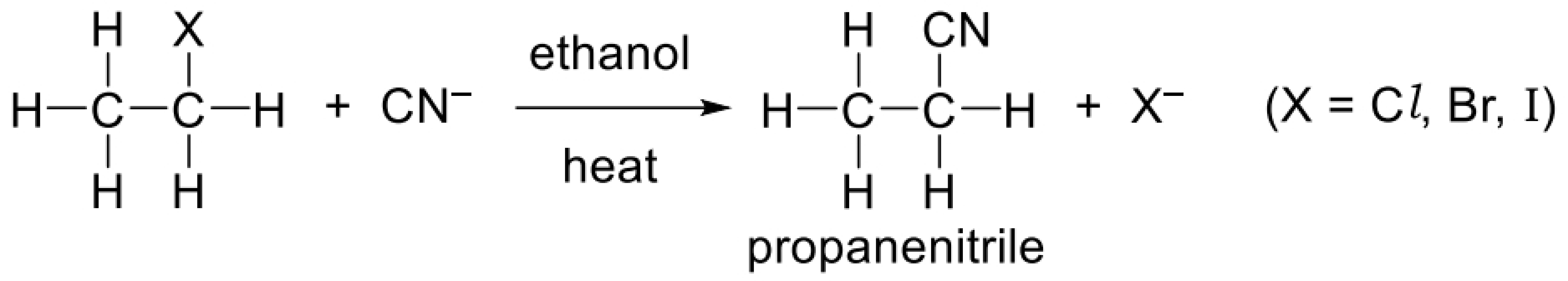
$$\mathrm{CH_3CH_2X + OH^- \xrightarrow[\text{heat}]{} CH_3CH_2OH + X^-}$$

(X = C*l*, Br, I)

Reagents and conditions: NaOH(aq) or KOH(aq); heat

This reaction is also known as **alkaline hydrolysis**, which is carried out in an aqueous medium.

5.6 Formation of Nitriles (not in H1 syllabus)



Reagents and conditions: KCN or NaCN, ethanol; heat

- Nitriles are a class of useful reagents in organic synthesis. Through the formation of a nitrile, the **carbon chain length is extended by one C atom** (step-up reaction). Formation of carbon-carbon bonds is an important part of organic synthesis.

- The nitrile product can be **hydrolysed to form carboxylic acids or carboxylate salts** or be **reduced to form amines**.

5.6.1 Hydrolysis and Reduction of Nitriles (not in H1 syllabus)

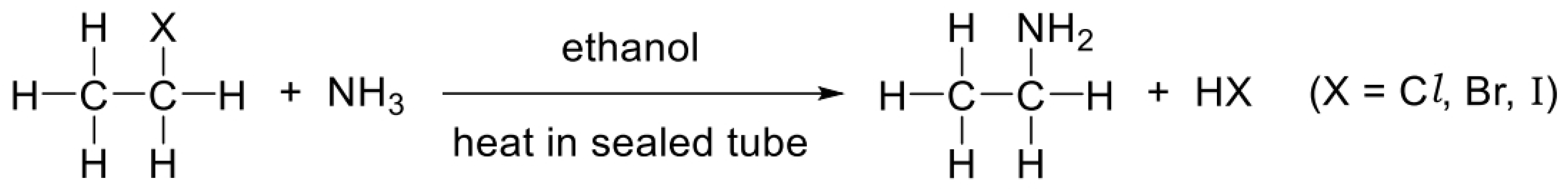
Acidic Hydrolysis: $R\text{–}\mathbf{C{\equiv}N} + 2H_2O + H^+ \rightarrow R\text{–}\mathbf{CO_2H} + NH_4^+$
Reagents and Conditions: $HCl(aq)$ or $H_2SO_4(aq)$, heat

Basic Hydrolysis: $R\text{–}\mathbf{C{\equiv}N} + H_2O + OH^- \rightarrow R\text{–}\mathbf{CO_2^-} + NH_3$
Reagents and Conditions: NaOH(aq) or KOH(aq), heat
(The solution can be acidified to get the carboxylic acid)

Reduction: $R\text{–}\mathbf{C{\equiv}N} + 4[H] \rightarrow R\text{–}\mathbf{CH_2NH_2}$ **(if $LiAlH_4$ is used)**
$R\text{–}\mathbf{C{\equiv}N} + 2H_2 \rightarrow R\text{–}\mathbf{CH_2NH_2}$ **(if H_2 is used)**

Reagents and Conditions:
$LiAlH_4$ in dry ether, r.t. *or* H_2 with Ni or Pd or Pt catalyst, r.t.

5.7 Formation of Amines (not in H1 syllabus)



$$CH_3CH_2X + NH_3 \xrightarrow[\text{heat in sealed tube}]{\text{ethanol}} CH_3CH_2NH_2 + HX \quad (X = Cl, Br, I)$$

Reagents and condition: excess NH_3, ethanol; heat in sealed tube

- A **primary amine** (RNH_2) is formed when a halogenoalkane reacts with ammonia. **Excess ammonia is used to ensure high yield of the primary amine**.

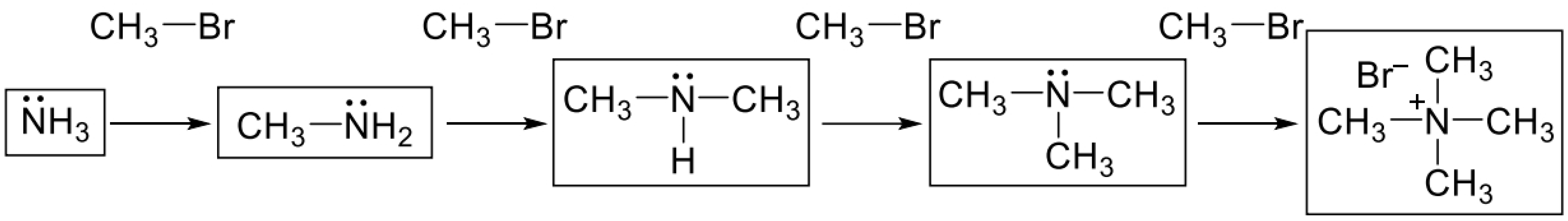
- If equivalent amounts of the halogenoalkane and ammonia are used, the yield of the amine will be lowered. This is because the hydrogen halide formed in this reaction will undergo an acid-base reaction with the ammonia and prevent it from reacting with the halogenoalkane.
  i.e. $HX + NH_3 \rightarrow NH_4X$ (ammonium salt)

- If excess halogenoalkane is used, **secondary and tertiary amines (R_2NH and R_3N respectively), or even quaternary ammonium salts ($R_4N^+X^-$) may be obtained** as the primary amine formed are **stronger nucleophiles** than ammonia and **further nucleophilic substitution reaction may occur**.

- Equations for their formation are as shown.

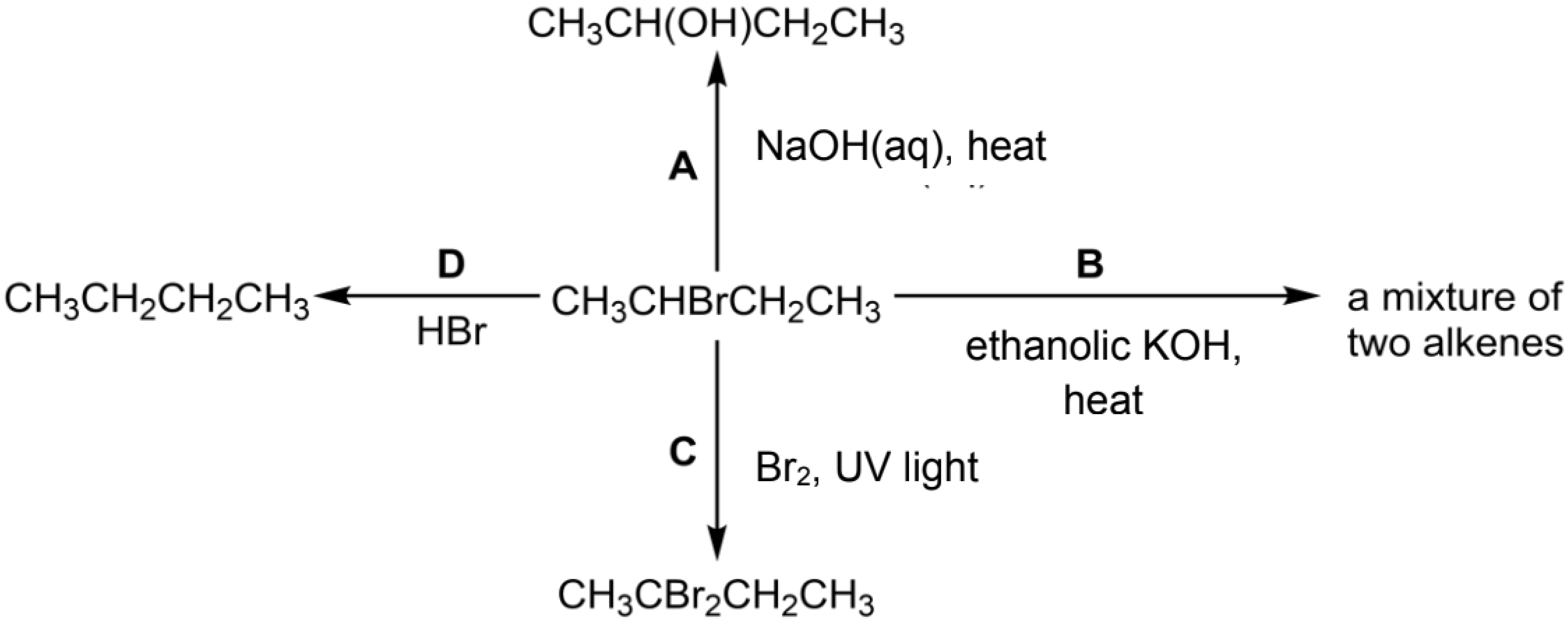
$RX + RNH_2 \rightarrow R_2NH + HX$	(secondary amine formed)
$RX + R_2NH \rightarrow R_3N + HX$	(tertiary amine formed)
$RX + R_3N \rightarrow R_4N^+ X^-$	(quaternary ammonium salt formed)

E.g. Reaction between **excess CH_3Br** and NH_3 (favours further nucleophilic substitution):



Self Check 5B

A reaction scheme using 2-bromobutane is shown. Which of the reactions does **not** take place?



At the end of this section, you should know that:

1. The C–X bond is polar, with the carbon atom having a partial positive charge and the halogen atom having a partial negative charge, due to the halogen having a higher electronegativity than carbon.

2. The rate equation for an S_N2 nucleophilic substitution is **rate = *k*[RX][Nu]** and usually occurs for primary halogenoalkanes.

3. For an S_N2 nucleophilic substitution, if the α-carbon is a chiral carbon, then it will undergo a chirality inversion when it undergoes an S_N2 nucleophilic substitution.

4. The rate equation for an S_N1 nucleophilic substitution is **rate = *k*[RX]** and usually occurs for tertiary halogenoalkanes.

5. For an S_N1 nucleophilic substitution, if the α-carbon is a chiral carbon, then a racemic mixture will be formed.

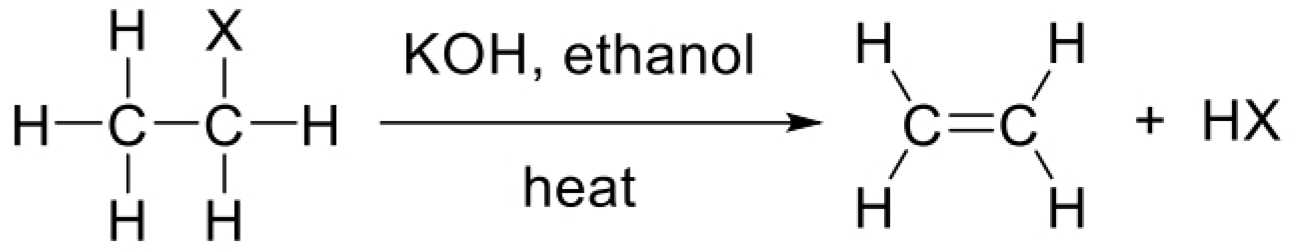
6. Halogenoalkanes react with NaOH(aq) when heated to form alcohols.

7. Halogenoalkanes react with ethanolic KCN when heated to form nitriles.

8. Halogenoalkanes react with excess ethanolic NH_3 when heated in a sealed tube to form primary amines.

6 Elimination Reaction of Halogenoalkanes

Halogenoalkanes take part in elimination reactions, producing alkenes.

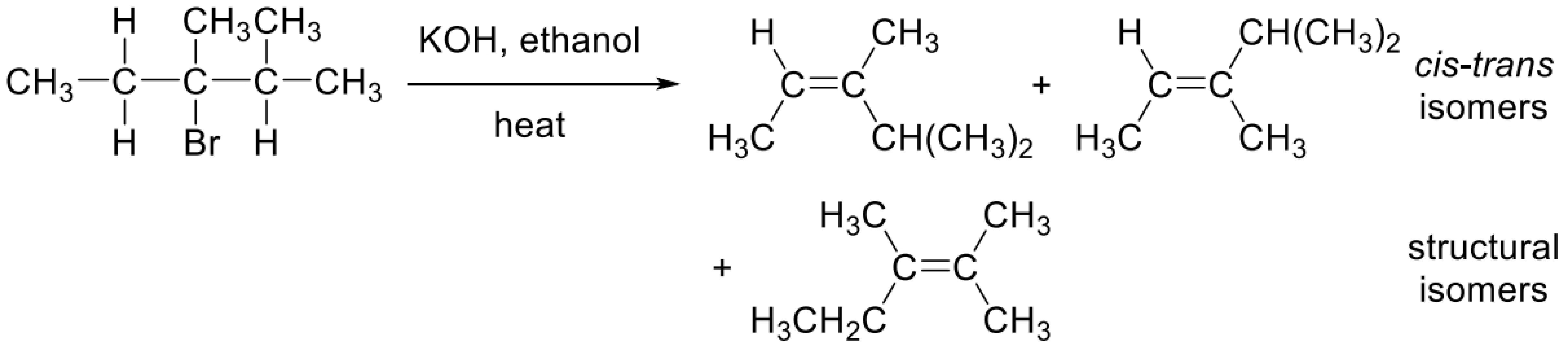


Reagents and conditions: NaOH or KOH, ethanol; heat

- In an ethanolic solution, **OH^- acts as a base and deprotonates the H atom on the C atom adjacent to the C–X bond**. The C–X bond breaks simultaneously, and the alkene is formed.

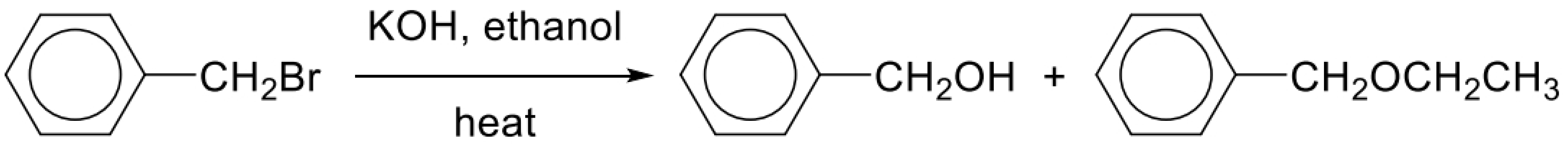
- More than one alkene product can be formed when the carbon bonded to the halogen has **more than one adjacent carbon with hydrogen atom(s) bonded to it**, resulting in **constitutional (structural) and/or *cis-trans* isomers**.

  Example: Elimination of HBr from 3-bromo-2,3-dimethylpentane



- Using **alcoholic solvents favours elimination**, but it is **possible to have nucleophilic substitution occurring as well**. This is because the oxygen atom in alcohols is also nucleophilic in nature. **(WHY?)**

e.g.



- Like the reactivity of halogenoalkanes in nucleophilic substitution reactions, the **ease of elimination reaction is dependent on the strength of the C–X bond**.

Self Check 6A

Draw the structural formulae of the three alkenes formed when 2-bromobutane undergoes elimination with hot ethanolic NaOH.

At the end of this section, you should know that:

1. Halogenoalkanes react with KOH in ethanol, when heated, to produce alkenes.
2. The weaker the C–X bond, the faster the rate of elimination.

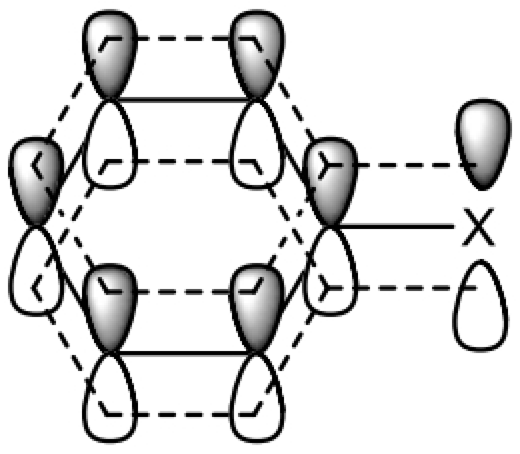
7 Reactions of Halogenoarenes (not in H1 syllabus)

LO (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

In general, **halogenoarenes do not undergo nucleophilic substitution**.

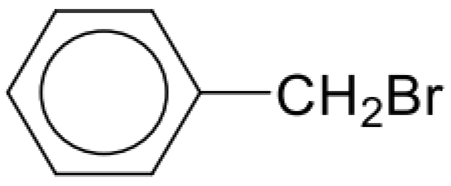
The lack of reactivity towards nucleophilic attack is due to the following reasons.

1) ***The C–X bond is strengthened and not easily cleaved.*** (Main reason)



- The ***p* orbital of the halogen atom can overlap sideway with the π electron cloud of the benzene ring**. As a result, the **lone pair of electrons on the halogen atom can delocalise into the benzene ring**.
- This leads to **partial double bond character in the C–X bond** which makes it **stronger than the C–X bond in halogenoalkanes**.

Note:

(1) For halogenoarenes, **the halogen atom is bonded to the benzene ring**. Hence, compounds such as  are NOT considered as halogenoarenes.

(2) Similarly, **halogenoalkenes (*e.g.* CH_2=CHC*l*)** generally do not undergo nucleophilic substitution as the ***p* orbital of the halogen atom can overlap sideway with the π bond of the alkene**. As a result, the **lone pair of electrons on the halogen atom can delocalise into the C=C bond, thereby imparting partial double bond characteristic to the C–X bond**.

2) ***Steric hindrance*** (*w.r.t.* S_N2 mechanism)

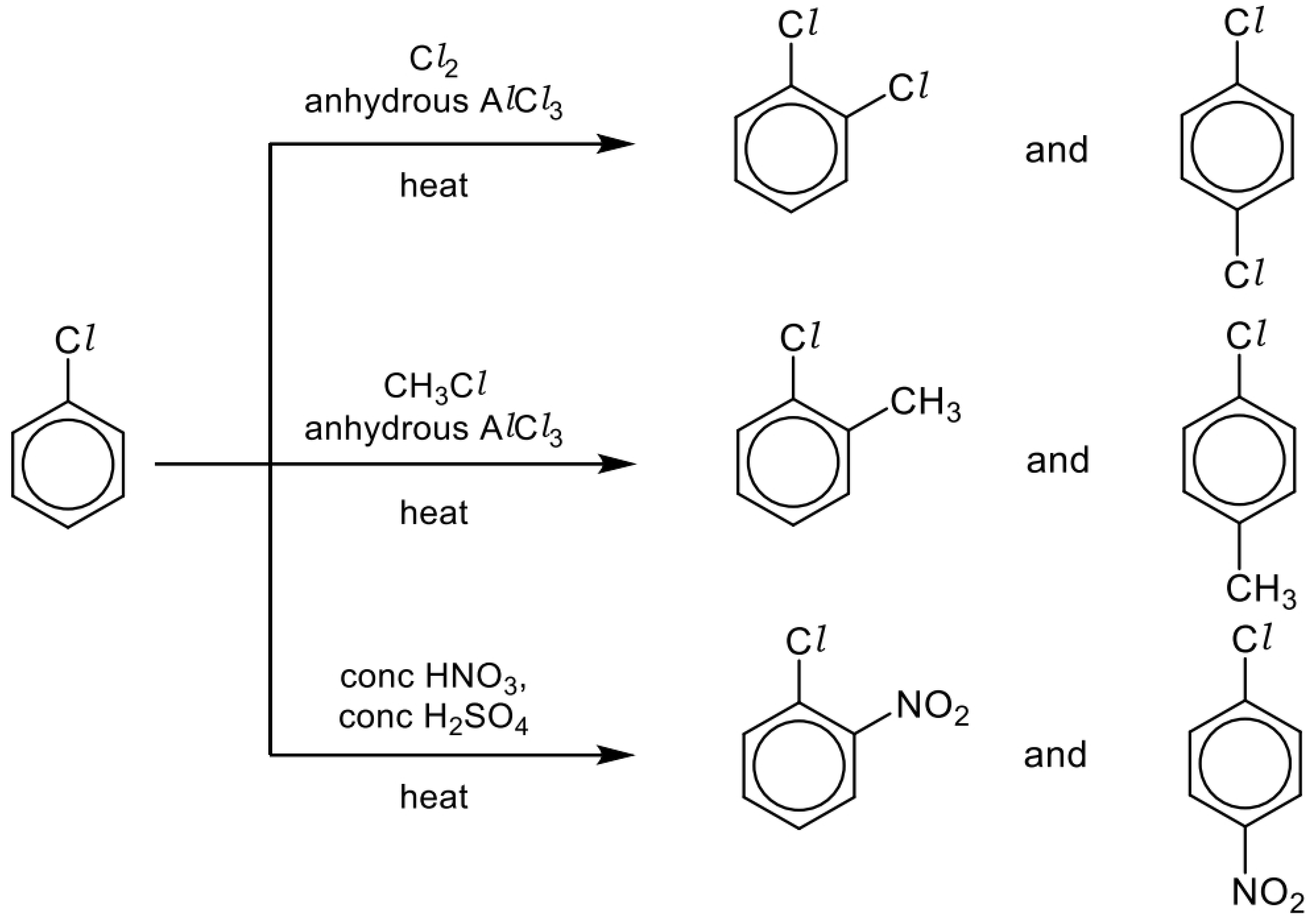
- The **benzene ring sterically hinders S_N2 reactions**. The **C in the C–X bond is not accessible to nucleophilic attack via rear side attack**.

7.1 Electrophilic Substitution of the Benzene Ring of Halogenoarenes

Halogenoarenes undergo electrophilic substitution of benzene ring just like any other arenes.

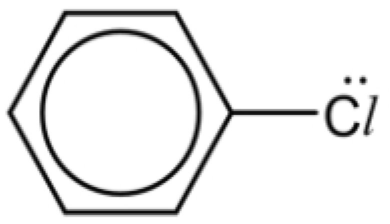
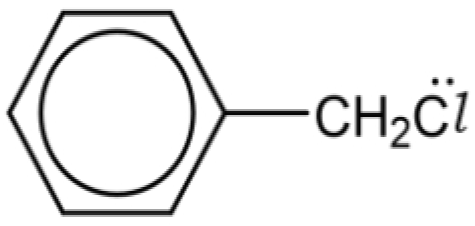
- Electrophilic substitution of halogenoarenes happens at a **lower rate** because the **halogen atoms are very electronegative, thus decreasing electron density of the π electron cloud of the benzene ring (halogen deactivates the benzene ring).**

- Electrophilic attacks are **2-, 4-directed** as this leads to the formation of a more stable arenium intermediate.



Self Check 7A

Complete the table below by writing *Yes* or *No*.

does the following compound exhibit the following properties or undergo the following reactions?	CH_3CH_2Cl		
delocalisation of electrons from chlorine			
nucleophilic substitution			
elimination			
electrophilic substitution			

8 Distinguishing Test for Halogen Derivatives

LO (f) suggest characteristic reactions to differentiate between:
- (i) different halogenoalkanes
- (ii) halogenoalkanes and halogenoarenes

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

To determine if an organic compound is a halogenoalkane (or has a halide functional group), the following chemical tests can be done:

Reagents and conditions:

Step 1: **NaOH(aq) and heat**
[Nucleophilic substitution reaction occurs]
$RX + OH^- \rightarrow ROH + X^-$

Step 2: **Excess dilute HNO_3** after cooling (Cannot use HCl and H_2SO_4) **(WHY?)**
[Removal of excess $OH^-(aq)$ to prevent the formation of Ag_2O]

Step 3: **$AgNO_3(aq)$** and observe for **any precipitation** that may occur
[Detect the presence of X^-]
$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$

OR

Reagents and conditions: $AgNO_3$ in ethanol, heat

The expected observations are given in the table below.

halogenoalkane	R–C*l*	R–Br	R–I
observations	white precipitate AgC*l*(s) formed	cream precipitate AgBr(s) formed	yellow precipitate AgI(s) formed

This chemical test can also be used to **distinguish between halogenoalkanes and halogenoarenes**. Since **halogenoarenes do not undergo nucleophilic substitution in general, there will be no formation of precipitate**.

Note:
- The **rate** at which the silver halide precipitate is formed is determined by the **strength of the C–X bond**.
- Precipitate is **<u>not</u>** formed when **halogenoarenes and fluoroalkanes** undergo the chemical test described above due to the **strong C–X bond**.

9 Uses of Halogenoalkanes and the Impact on the Environment (not in H1 syllabus)

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

Thomas Midgley Jr is widely known as the father of chlorofluorocarbons, a type of halogenoalkanes. First synthesised in 1921, they were touted by Midgley as being ideal compounds that could have multiple applications, such as being used as refrigerants, aerosol propellants and in fire extinguishers in view of their properties: **inert, non-flammable**, odourless and can be liquefied under pressure and vaporise readily when that pressure is released. **CFCs and fluoroalkanes are much less reactive (inert) due to stronger C–F bonds**. After the widespread commercial uses, many halogenoalkanes have also been shown to be serious pollutants and toxins. For example, chlorofluorocarbons been shown to result in ozone depletion.

9.1 Effect of CFCs on the Ozone Layer – Depletion of the Ozone Layer

CFCs in aerosol sprays deplete the ozone (O_3) layer and expose us to ultraviolet (UV) radiation from the sun. The O_3 layer absorbs UV rays and thus screens the earth from excessive UV radiation. Overexposure to UV radiation causes skin cancer in humans and widespread crop failure. Being chemically inert, CFCs can drift upwards to an altitude 20 km above sea level and enter the stratosphere. When exposed to UV radiation (λ = 200–250 nm) at this altitude, photolysis takes place and the C–Cl bond undergoes **homolytic fission**.
(Bond energies: C–Cl = 351 kJ mol^{-1} *vs* C–F = 452 kJ mol^{-1})

$$CF_3Cl \xrightarrow{\text{uv light}} Cl\bullet + \bullet CF_3$$

In the stratosphere, O_2 molecules decompose to oxygen atoms upon absorbing UV light.

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

The oxygen atoms then react readily with O_2 to produce ozone. However, O_3 decomposes to reform oxygen atoms and O_2 molecules by absorbing UV light and equilibrium is set up between the two processes.

formation of ozone : $O + O_2 \rightarrow O_3$
depletion of ozone : $O_3 \rightarrow O + O_2$

Chlorine atom, Cl•, disrupts the equilibrium by acting as a homogeneous catalyst in the destruction of ozone:

$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2 \quad \text{------------------}\ \textbf{(1)}$$
$$ClO\bullet + O \rightarrow Cl\bullet + O_2 \quad \text{------------------}\ \textbf{(2)}$$

As shown by equations **(1)** and **(2)**, the **formation of C*l*• is detrimental as it destroys O_3** as well as removes O, one of the re actants for O_3 formation. Notice that C*l*• is regenerated and thus plays the role of catalyst.

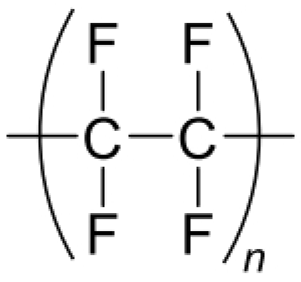
Ozone in the stratosphere is constantly regenerated through natural processes, such as lightning strikes. However, for many decades, the rate of destruction of stratospheric ozone has outpaced the rate at which it is regenerated.

Measures to reduce ozone depletion

- Reduce use of CFCs in industrial and household applications. Since 1987, at the Montreal Protocol, the use of CFCs has been increasingly banned many countries.
- **Substitutes such as hydrocarbons, hydrofluorocarbons or fluorocarbons have been used** in place of CFCs. For example, most aerosols use propane or butane as propellant instead of CFCs. However, **alkanes are highly flammable** and pose a fire hazard.

9.2 Use of Fluoroalkanes in Daily Life and their Associated Problems

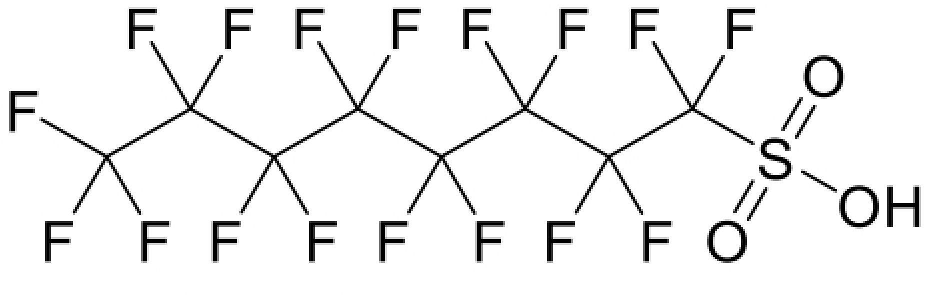
Fluoroalkanes also play significant roles in today's society. One of the most common uses of fluoroalkanes is in the use of the polymer polytetrafluoroethylene (PTFE) in non-stick frying pans.


$-(CF_2-CF_2)_n-$

polytetrafluoroethylene

This polymer is made from tetrafluoroethene and is commonly used in non-stick frying pans because the strength of the C–F bonds prevent reaction with the other substances that are placed on it when cooking. This makes these pans easy to clean after cooking with them.

However, while PTFE is generally considered safe for use in cooking as long as the pan is not overheated, there exists a class of compounds known as polyfluoroalkyl substances (PFAS) that pose severe health hazards to mankind. One such PFAS is perfluorooctanesulfonic acid.

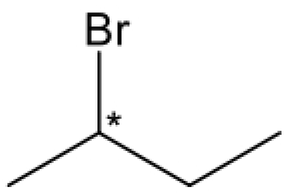
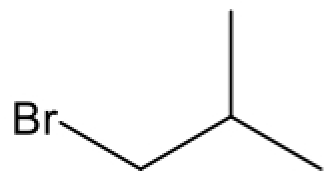
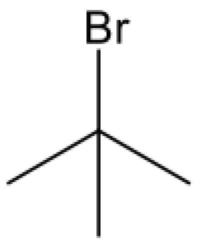


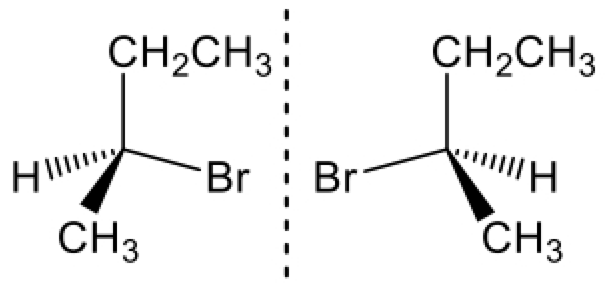
perfluorooctanesulfonic acid

Due to the strength of the C–F bonds, PFAS are extremely difficult to break down. Indeed, PFAS have been dubbed as 'forever chemicals' in certain countries. Due to leaching of these compounds from industries that use them, as well as workers being directly exposed to them, PFAS enter the ecosystem and eventually accumulate in our bodies. High levels of PFAS in the human body have been known to cause thyroid disease and certain types of cancer.

Self-check Answers

2A:

			
1-bromobutane	2-bromobutane	1-bromo-2-methyl-propane	2-bromo-2-methyl-propane
primary	secondary	primary	tertiary



A pair of enantiomers of 2-bromobutane

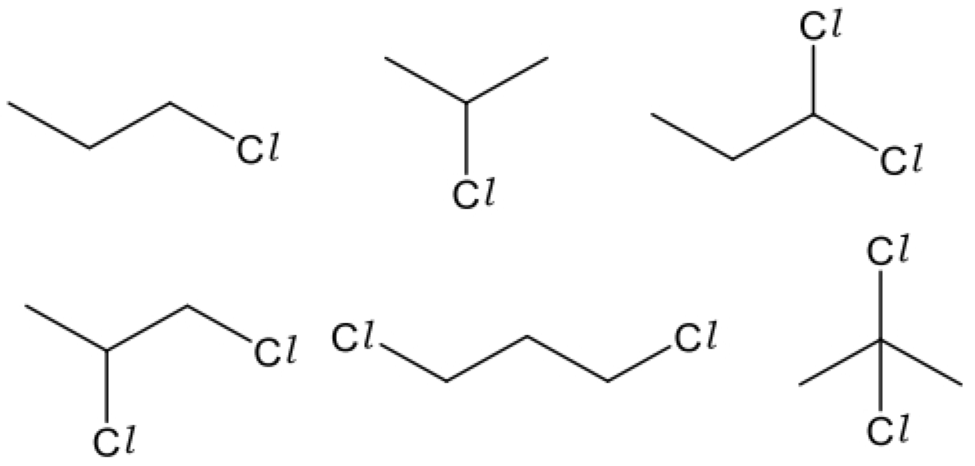
3A:

(a) **More energy** is required to overcome the **stronger permanent dipole-permanent dipole interactions between polar 1-chlorobutane molecules** of **B** as compared to the **weaker instantaneous dipole-induced dipole interactions between the non-polar butane molecules** of **A**.

(b) From **B** to **D**, the **number of electrons increases, electron cloud is more polarisable** and results in the **increasing strength of the instantaneous dipole-induced dipole interactions between molecules**. Thus, there is an increase in energy needed to overcome the increasingly stronger intermolecular forces of attractions. Hence, boiling point increases from **B** to **D**.

4A:

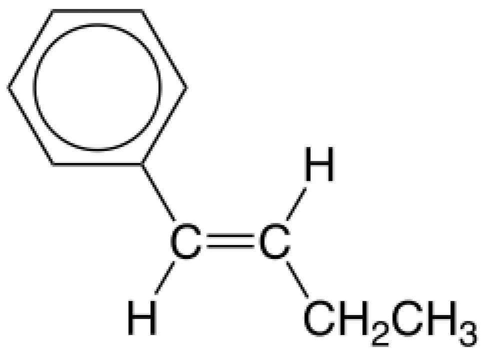
(a)



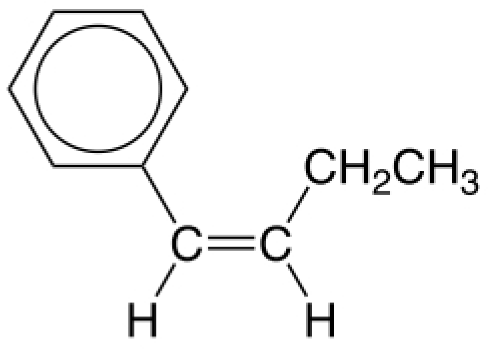
etc

(b)(i) $CH_3CH_2CHClCH_3$

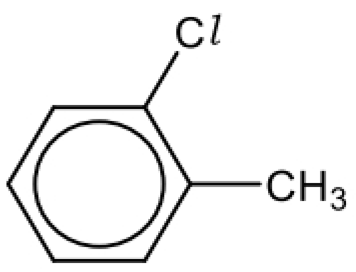
(ii)



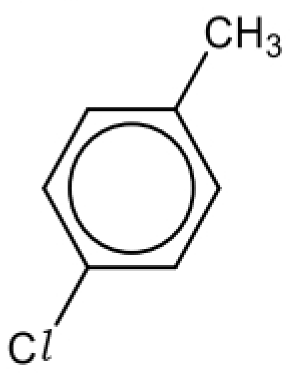
OR



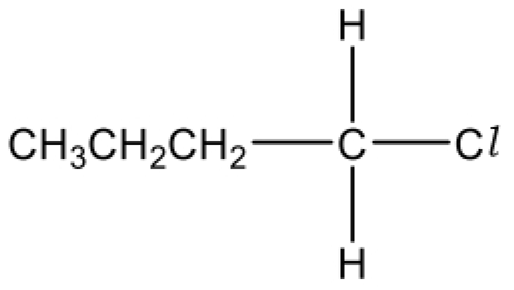
(iii)



(iv)

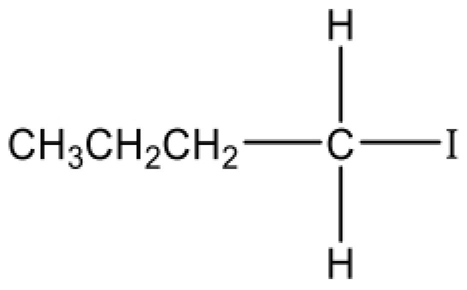


(c)(i)



$CH_3CH_2CH_2CH_2Cl$

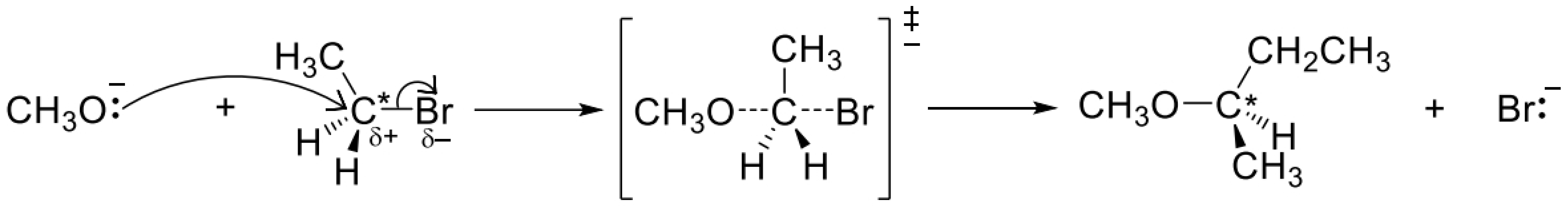
(ii)



$CH_3CH_2CH_2CH_2I$

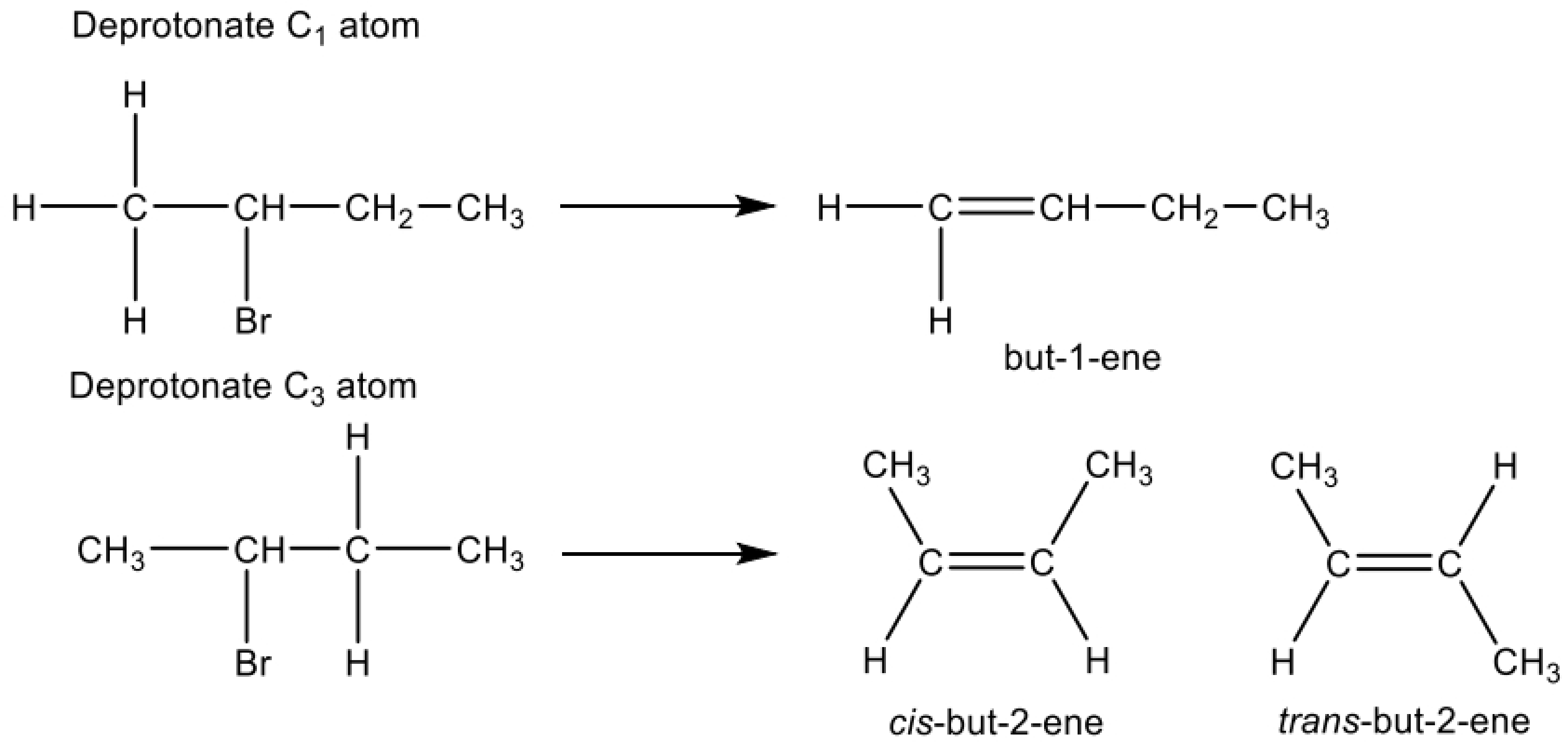
5A:

Name of mechanism: S_N2 nucleophilic substitution

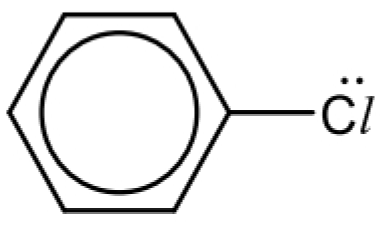
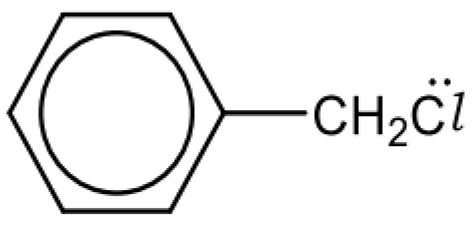


5B: D

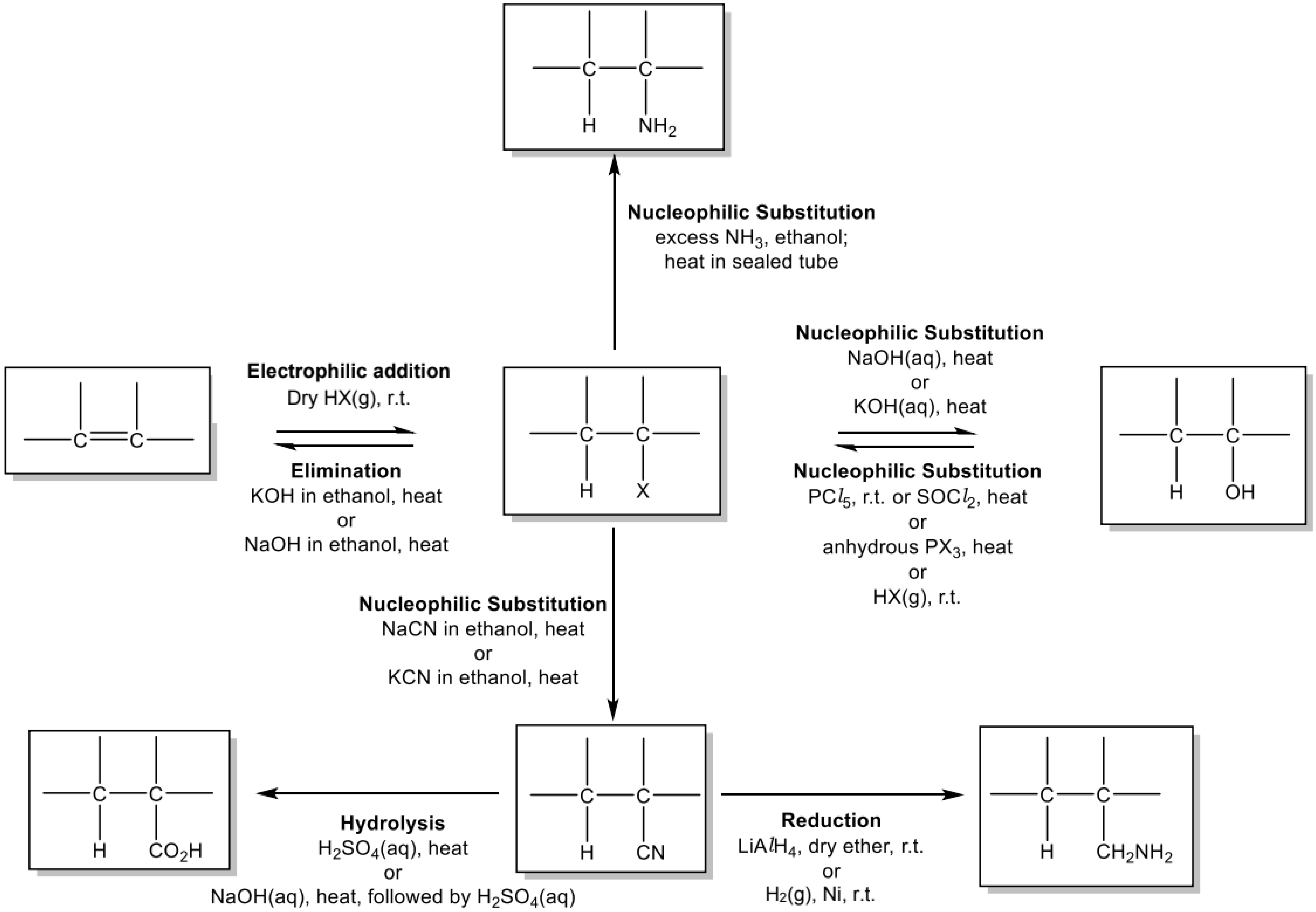
6A:



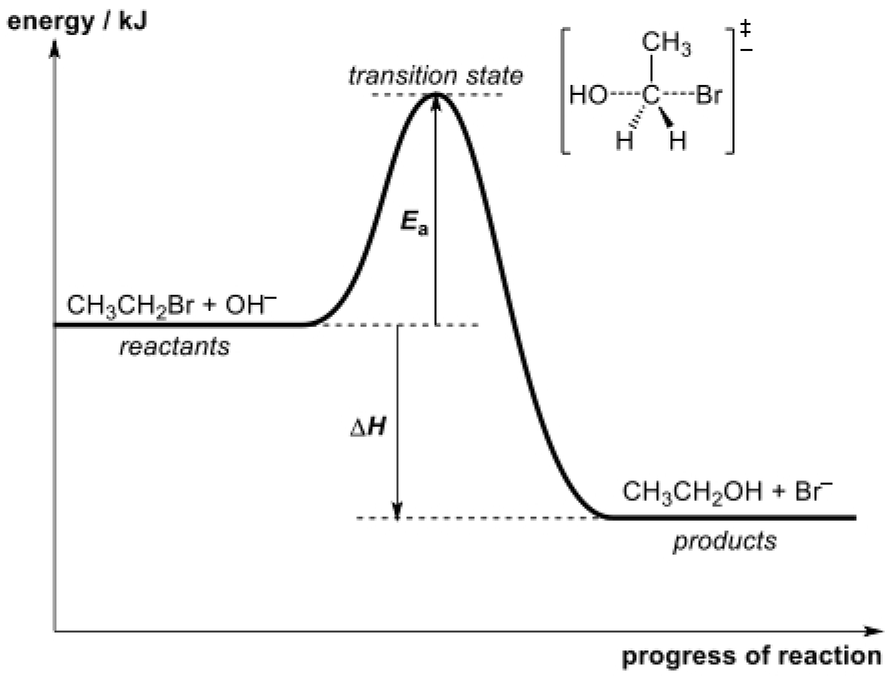
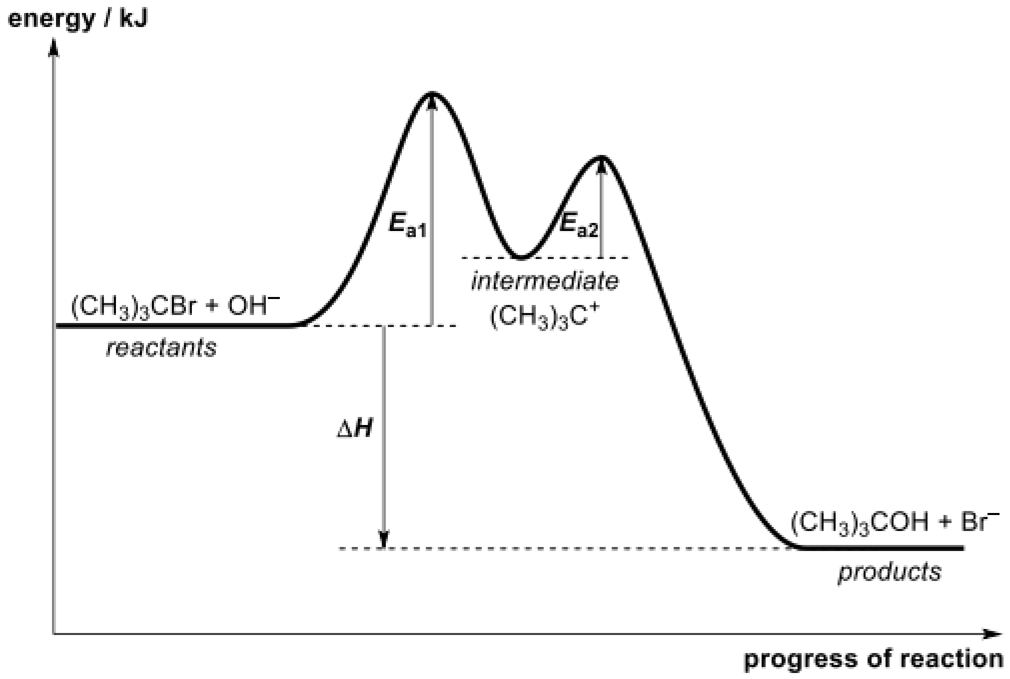
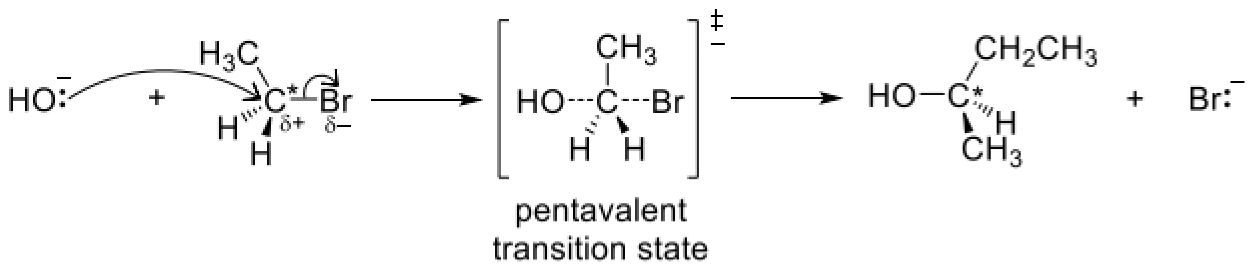
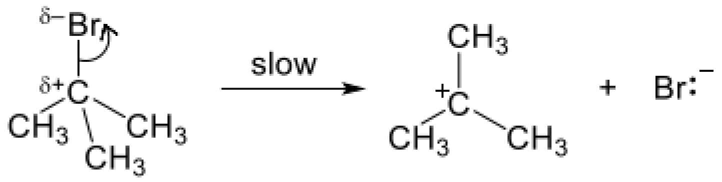
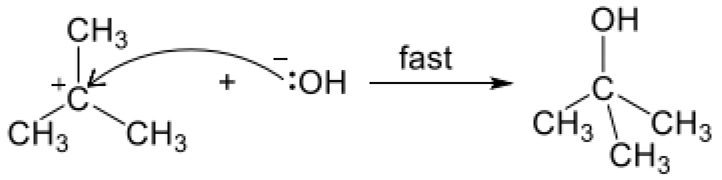
7A:

does the following compound exhibit the following properties or undergo the following reactions?	CH_3CH_2Cl		
delocalisation of electrons from chlorine	No	Yes	No
nucleophilic substitution	Yes	No	Yes
elimination	Yes	No	No
electrophilic substitution	No	Yes	Yes

Summary



C C H NH_2
Nucleophilic Substitution
excess NH_3, ethanol;
heat in sealed tube
C C
Electrophilic addition
Dry HX(g), r.t.
Elimination
KOH in ethanol, heat
or
NaOH in ethanol, heat
C C H X
Nucleophilic Substitution
NaOH(aq), heat
or
KOH(aq), heat
Nucleophilic Substitution
PCl_5, r.t. or $SOCl_2$, heat
or
anhydrous PX_3, heat
or
HX(g), r.t.
C C H OH
Nucleophilic Substitution
NaCN in ethanol, heat
or
KCN in ethanol, heat
C C H CO_2H
Hydrolysis
H_2SO_4(aq), heat
or
NaOH(aq), heat, followed by H_2SO_4(aq)
C C H CN
Reduction
$LiAlH_4$, dry ether, r.t.
or
H_2(g), Ni, r.t.
C C H CH_2NH_2

	S_N2	S_N1
rate equation	rate = k[halogenoalkane][nucleophile]	rate = k[halogenoalkane]
energy profile diagram		
mechanism		Step 1: C–X bond breaks to form the carbocation and halide ion  Step 2: Nucleophile attacks the carbocation to form the product 
type of RX	methyl, 1° or 2°	2° or 3°
factor that affects mechanism	steric hindrance	stability of carbocation intermediate
remarks	inversion of configuration about α-carbon	racemisation of chiral RX