



REACTIONS OF HALOGENOALKANES 1

NUCLEOPHILIC SUBSTITUTION

Halogenoalkanes are susceptible to attack by **nucleophiles** (lone pair donors) such as OH^- , CN^- and NH_3 .

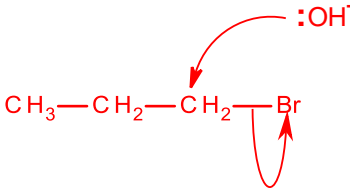
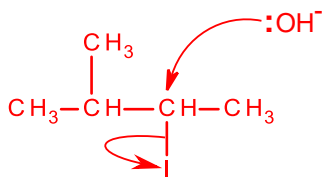
This is because the halogen atom is more electronegative than carbon atoms and so the C of the C-halogen bond is δ^+ .

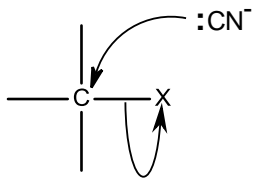
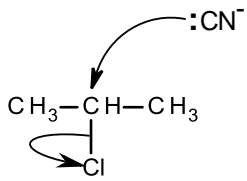
In a **substitution** reaction, the halogen atom is replaced by another atom/group.

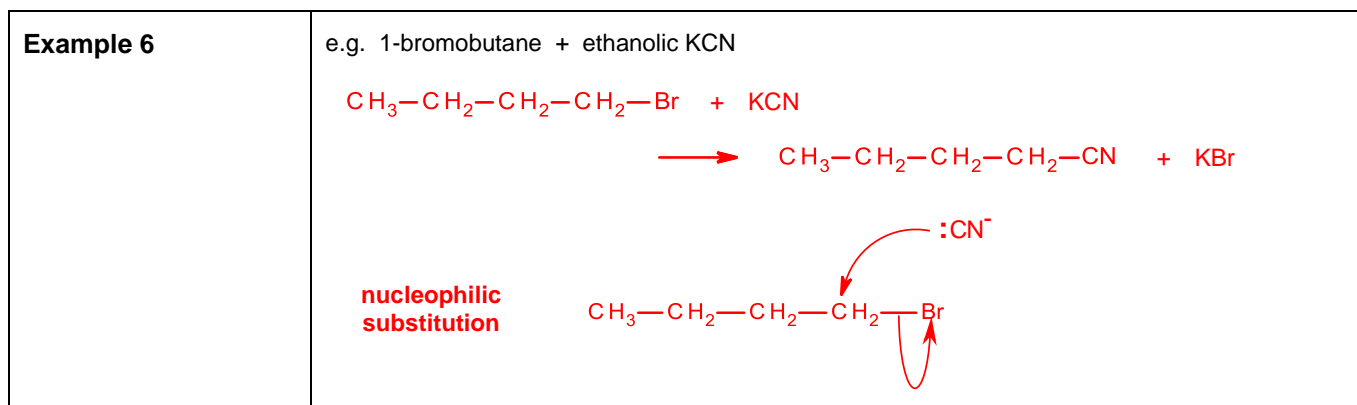
The rate of the reaction is partly affected by the strength of the C-halogen bond. The longer the bond, the weaker the bond, the more easily it breaks and the faster the reaction. Therefore, in terms of rate: $\text{C-I} > \text{C-Br} > \text{C-Cl} > \text{C-F}$.

NUCLEOPHILIC SUBSTITUTION 1 – reaction with warm, aqueous NaOH

Reagent	NaOH
Conditions	aqueous, warm
What happens	halogen atom is replaced by OH group
Overall equation	$\text{R-X} + \text{NaOH} \longrightarrow \text{R-OH} + \text{NaX}$
Mechanism	<p>nucleophilic substitution</p>
Example 1	<p>e.g. bromoethane + aqueous NaOH</p> $\text{CH}_3\text{-CH}_2\text{-Br} + \text{NaOH} \longrightarrow \text{CH}_3\text{-CH}_2\text{-OH} + \text{NaBr}$ <p>nucleophilic substitution</p>
Example 2	<p>e.g. 2-chloropropane + aqueous NaOH</p> $\begin{array}{c} \text{CH}_3\text{-CH-CH}_3 \\ \\ \text{Cl} \end{array} + \text{NaOH} \longrightarrow \begin{array}{c} \text{CH}_3\text{-CH-CH}_3 \\ \\ \text{OH} \end{array} + \text{NaCl}$ <p>nucleophilic substitution</p>

Example 3	<p>e.g. 1-bromopropane + aqueous NaOH</p> $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br} + \text{NaOH} \longrightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH} + \text{NaBr}$ <p>nucleophilic substitution</p> 
Example 4	<p>e.g. 2-iodo-3-methylbutane + aqueous NaOH</p> $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-CH-CH-CH}_3 \\ \\ \text{I} \end{array} + \text{NaOH} \longrightarrow \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-CH-CH-CH}_3 \\ \\ \text{OH} \end{array} + \text{NaI}$ <p>nucleophilic substitution</p> 

NUCLEOPHILIC SUBSTITUTION 2 – reaction with KCN	
Reagent	KCN
Conditions	ethanolic, warm
What happens	halogen atom is replaced by CN group
Overall equation	$\text{R-X} + \text{KCN} \longrightarrow \text{R-CN} + \text{KX}$
Mechanism	<p>nucleophilic substitution</p> 
Example 5	<p>e.g. 2-chloropropane + ethanolic KCN</p> $\begin{array}{c} \text{CH}_3\text{-CH-CH}_3 \\ \\ \text{Cl} \end{array} + \text{KCN} \longrightarrow \begin{array}{c} \text{CH}_3\text{-CH-CH}_3 \\ \\ \text{CN} \end{array} + \text{KCl}$ <p>nucleophilic substitution</p> 



NUCLEOPHILIC SUBSTITUTION 3 – reaction with NH₃

Reagent	NH ₃
Conditions	Excess concentrated ammonia dissolved in ethanol at pressure in a sealed container
What happens	first molecule of NH ₃ : halogen atom is replaced by NH ₂ group second molecule of NH ₃ : leads to formation of NH ₄ X
Overall equation	$\text{R-X} + 2 \text{NH}_3 \longrightarrow \text{R-NH}_2 + \text{NH}_4\text{X}$
Mechanism	<p>nucleophilic substitution</p>
Example 7	<p>e.g. 2-chloropropane + excess conc NH₃</p> $\text{CH}_3\text{-CH(Cl)-CH}_3 + 2 \text{NH}_3 \longrightarrow \text{CH}_3\text{-CH(NH}_2\text{)-CH}_3 + \text{NH}_4\text{Cl}$ <p>nucleophilic substitution</p>
Example 8	<p>e.g. 2-bromo-3-methylbutane + excess conc NH₃</p> $\text{CH}_3\text{-CH(CH}_3\text{)-CH(Br)-CH}_3 + 2 \text{NH}_3 \longrightarrow \text{CH}_3\text{-CH(CH}_3\text{)-CH(NH}_2\text{)-CH}_3 + \text{NH}_4\text{Br}$ <p>nucleophilic substitution</p>

ELIMINATION	<p>When halogenoalkanes react with OH⁻ ions, an elimination reaction can compete with the nucleophilic substitution reaction.</p> <p>Elimination is favoured if hot, ethanolic KOH is used instead of warm, aqueous NaOH.</p> <p>In elimination, an H and X are removed from adjacent C atoms giving an alkene.</p> <p>In elimination, the OH⁻ ion acts as a base. In substitution, the OH⁻ ion acts as a nucleophile.</p>
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ELIMINATION – reaction with hot, ethanolic KOH

Reagent	KOH
Conditions	Ethanolic, hot
What happens	<p>The halogen atom and one H atom from an adjacent C atom is removed giving an alkene (note that elimination cannot happen if there is no H on an adjacent C atom).</p> <p>A mixture of alkenes could be formed depending on which of the adjacent C atoms the H is lost from.</p>
Overall equation	$ \begin{array}{c} & \\ -C & -C- \\ & \\ H & X \end{array} + KOH \longrightarrow \begin{array}{c} & \\ -C=C- \\ & \end{array} + KBr + H_2O $
Mechanism	<p style="text-align: center;">elimination</p>
Example 9	<p>e.g. 2-chloropropane + hot, ethanolic KOH</p> $ \begin{array}{c} CH_3-CH-CH_3 \\ \\ Cl \end{array} + KOH \longrightarrow CH_3-CH=CH_2 + KCl + H_2O $ <p style="text-align: center;">elimination</p>
Example 10	<p>e.g. 2-bromobutane + hot, ethanolic KOH (to give but-2-ene)</p> $ \begin{array}{c} CH_3-CH_2-CH-CH_3 \\ \\ Br \end{array} + KOH \longrightarrow CH_3-CH=CH-CH_3 + KBr + H_2O $ <p style="text-align: center;">elimination</p>