

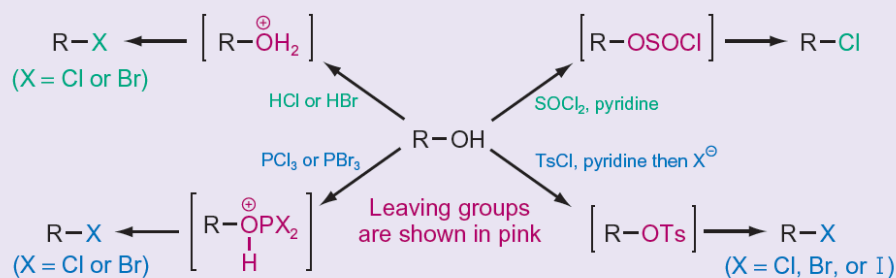
Halogenoalkanes: substitution and elimination reactions

20.1 Structure and reactivity of halogenoalkanes

- As the halogen atom (X) increases in size, from fluorine to iodine, the C–X bond length increases and the C–X bond enthalpy decreases, that is, the bond becomes weaker.
- C–X bonds, apart from C–I, are polar with the electrons in the bonds displaced toward fluorine, bromine, or chlorine.
- The C–I bond is non-polar but has a high polarizability.
- Halogenoalkanes undergo nucleophilic substitution reactions and elimination reactions.

20.2 Preparation of halogenoalkanes

- Radical substitution reactions of alkanes (using Cl₂ or Br₂) produce chloro- or bromoalkanes.
- Radical bromination of alkanes is more selective than chlorination.
- The relative order of reactivity of C–H bonds toward radical halogenation is tertiary C–H > secondary C–H > primary C–H > methyl C–H.
- Halogenoalkanes are formed from alcohols using reagents that convert the –OH group into a good leaving group. Good leaving groups are neutral molecules or stable anions that are weak bases. A halogen atom then displaces the leaving group in a nucleophilic substitution reaction.



- Halogenoalkanes are formed on addition of HCl, HBr, HI, or Br₂ to alkenes.



For practice questions on this topic, see questions 1 and 7 at the end of this chapter (pp.958–959).

20.3 The mechanisms of nucleophilic substitution reactions

<ul style="list-style-type: none"> • S_N2 reaction <p>One-step mechanism</p> <p>Second-order kinetics (rate = $k[\text{RX}][\text{Nu}]$)</p> <p>Rate-determining step is bimolecular</p> <p>Chiral centres undergo inversion</p> <p>Reactivity of RX:</p> <p style="padding-left: 20px;">$\text{CH}_3\text{X} > \text{RCH}_2\text{X} > \text{R}_2\text{CHX} \gg \text{R}_3\text{CX}$</p> <p>Rate governed by steric effects</p> <p>Favoured in polar aprotic solvents</p> <p>Requires a good nucleophile</p> <p>Requires a good leaving group:</p> <p style="padding-left: 20px;">$\text{RI} > \text{RBr} > \text{RCI} \gg \text{RF}$</p>	<ul style="list-style-type: none"> • S_N1 reaction <p>Two-step mechanism</p> <p>First-order kinetics (rate = $k[\text{RX}]$)</p> <p>Rate-determining step is unimolecular</p> <p>Chiral centres undergo racemization</p> <p>Reactivity of RX:</p> <p style="padding-left: 20px;">$\text{R}_3\text{CX} > \text{R}_2\text{CHX} \gg \text{RCH}_2\text{X} > \text{CH}_3\text{X}$</p> <p>Rate governed by carbocation stability</p> <p>Favoured in polar protic solvents</p> <p>Any nucleophile will do</p> <p>Requires a good leaving group:</p> <p style="padding-left: 20px;">$\text{RI} > \text{RBr} > \text{RCI} \gg \text{RF}$</p>
<ul style="list-style-type: none"> • S_N1 reactions that do not lead to complete racemization can be explained by the formation of intermediate tight (intimate) ion pairs. These are S_Ni reactions. 	

 For practice questions on these topics, see questions 2–6 at the end of this chapter (pp.957–958).

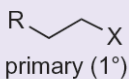
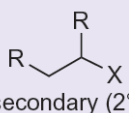
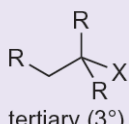
20.4 The mechanisms of elimination reactions

<p>E2 reaction</p> <p>One-step mechanism</p> <p>Second-order kinetics (rate = $k[\text{RX}][\text{B}]$)</p> <p>Rate-determining step is bimolecular</p> <p>Anti-periplanar conformation required</p> <p>Reactivity of RX:</p> <p style="padding-left: 20px;">$\text{R}_3\text{CX} > \text{R}_2\text{CHX} > \text{RCH}_2\text{X}$</p> <p>Saytzev or Hofmann elimination</p> <p>Favoured by polar aprotic solvents</p> <p>Requires a strong base (e.g. RO⁻)</p> <p>Requires a good leaving group:</p> <p style="padding-left: 20px;">$\text{RI} > \text{RBr} > \text{RCI} \gg \text{RF}$</p>	<p>E1 reaction</p> <p>Two-step mechanism</p> <p>First-order kinetics (rate = $k[\text{RX}]$)</p> <p>Rate-determining step is unimolecular</p> <p>No specific conformation of RX required →</p> <p>Reactivity of RX:</p> <p style="padding-left: 20px;">$\text{R}_3\text{CX} > \text{R}_2\text{CHX} \gg \text{RCH}_2\text{X}$</p> <p>Most stable alkene formed</p> <p>Favoured by polar protic solvents</p> <p>Any base will do (usually weak, e.g. ROH)</p> <p>Requires a good leaving group:</p> <p style="padding-left: 20px;">$\text{RI} > \text{RBr} > \text{RCI} \gg \text{RF}$</p>
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 For practice questions on these topics, see questions 4, 6, and 7 at the end of this chapter (pp.957–959).


20.5 Substitution versus elimination reactions

- The following table summarizes the favoured substitution and elimination mechanisms undergone by primary, secondary, and tertiary halogenoalkanes.

Halogenoalkane	Favoured substitution and elimination mechanisms
 primary (1°)	S _N 2 E2
 secondary (2°)	S _N 1 S _N 2 E1 E2
 tertiary (3°)	S _N 1 E1 E2

Favoured when using a strong nucleophile

Favoured when using a strong base

-  For practice questions on these topics, see questions 4, 6, and 7 at the end of this chapter (pp.957–959).

» Concept review

By the end of this chapter you should be able to do the following.

- Understand why different carbon–halogen bonds in halogenoalkanes react differently from one another.
- Describe how halogenoalkanes can be prepared from alkanes, alcohols, and alkenes.
- Understand how halogenoalkanes react in S_N2 reactions.
- Understand how halogenoalkanes react in S_N1 reactions.
- Recognize the importance of tight ion pairs in some S_N1 reactions.
- Understand how halogenoalkanes react in E2 reactions.
- Understand how halogenoalkanes react in E1 reactions.
- Understand the factors that affect S_N2 versus S_N1 reactions.
- Understand the factors that affect E2 versus E1 reactions.
- Understand the factors that influence substitution versus elimination reactions.

