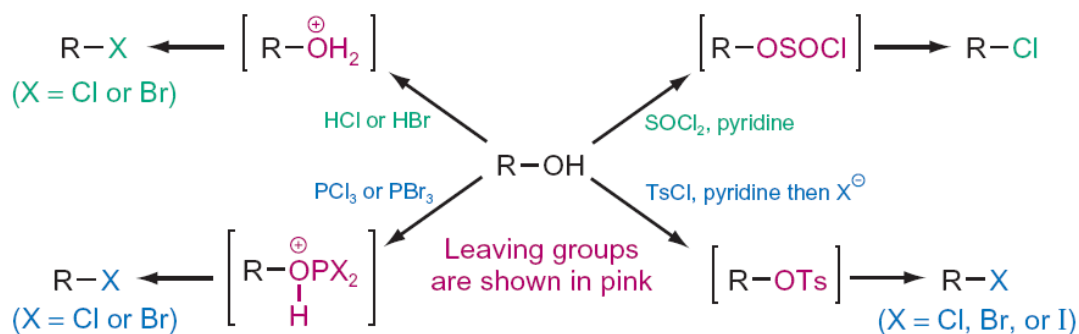

Halogenoalkanes: substitution and elimination reactions

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.
- 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 nonpolar but has a high polarizability.
- Halogenoalkanes undergo nucleophilic substitution and elimination reactions.

20.2 Preparation of halogenoalkanes

- Radical substitution reactions of alkanes (using Cl_2 or Br_2) 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 replaces the leaving group in a nucleophilic substitution reaction.



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

20.3 The mechanisms of nucleophilic substitution reactions

S_N2 reaction

One-step mechanism

Second-order (rate = $k[\text{RX}][\text{Nu}]$)

Chiral centres undergo inversion

Reactivity of RX:

$\text{CH}_3\text{X} > \text{RCH}_2\text{X} > \text{R}_2\text{CHX} \gg \text{R}_3\text{CX}$

Rate governed by steric effects

Favoured in polar aprotic solvents

Requires a good nucleophile

Requires a good leaving group:

$\text{RI} > \text{RBr} > \text{RCl} \gg \text{RF}$

S_N1 reaction

Two-step mechanism

First-order (rate = $k[\text{RX}]$)

Chiral centres undergo racemisation

Reactivity of RX:

$\text{R}_3\text{CX} > \text{R}_2\text{CHX} \gg \text{RCH}_2\text{X} > \text{CH}_3\text{X}$

Rate governed by carbocation stability

Favoured in polar protic solvents

Any nucleophile will do

Requires a good leaving group:

$\text{RI} > \text{RBr} > \text{RCl} \gg \text{RF}$

- 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.

20.4 The mechanisms of elimination reactions

E2 reaction

One-step mechanism

Second-order (rate = $k[\text{RX}][\text{B}]$)

Anti-periplanar conformation required

Reactivity of RX:



Saytzev or Hofmann elimination

Favoured by polar aprotic solvents

Requires a strong base (e.g. RO^-)

Requires a good leaving group:



E1 reaction

Two-step mechanism

First-order (rate = $k[\text{RX}]$)

No specific conformation of RX required

Reactivity of RX:



Most stable alkene formed

Favoured by polar protic solvents

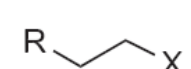


Any base will do (usually weak, e.g. ROH)

Requires a good leaving group:



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°)	$\text{S}_{\text{N}}2$ $\text{E}2$	Favoured when using a strong nucleophile
 secondary (2°)	$\text{S}_{\text{N}}1$ $\text{S}_{\text{N}}2$ $\text{E}1$ $\text{E}2$	Favoured when using a strong base
 tertiary (3°)	$\text{S}_{\text{N}}1$ $\text{E}1$ $\text{E}2$	

Learning outcomes

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

- Understand why 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.

