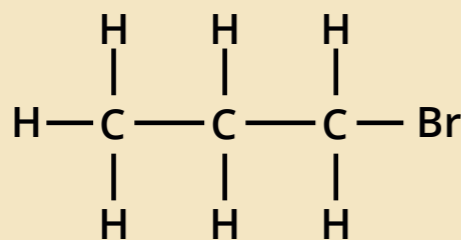


2.6 Halogenoalkanes

Halogenoalkanes can be divided into three types.

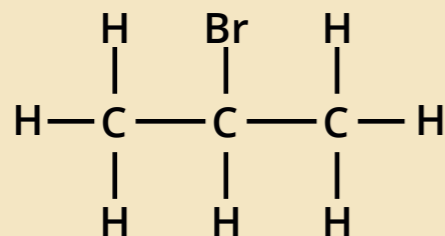
Primary

1-bromopropane



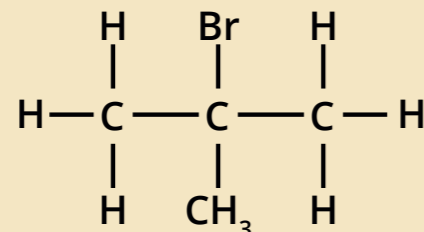
Secondary

2-bromopropane



Tertiary

2-bromomethylpropane

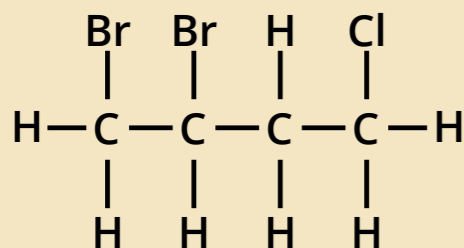


A primary halogenoalkane has a maximum of one alkyl group bonded to the carbon atom that is bonded to the halogen. A secondary has two and a tertiary three.

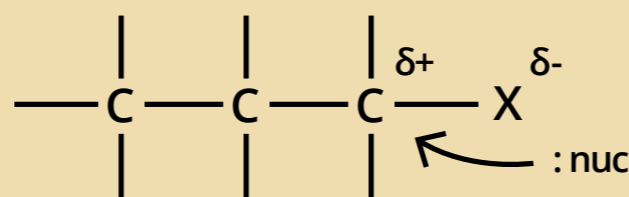
When naming a more complex halogenoalkane, the halogens are placed in alphabetical order.

bromo (Br) followed by chloro (Cl) followed by iodo (I)

e.g. 1,2-dibromo-4-chlorobutane



The halogens are more electronegative than carbon. The halogen attracts the bonding electrons more than carbon, causing the carbon to have a partial positive charge (δ^+). The carbon can then be attacked by nucleophiles.

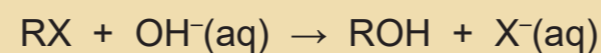
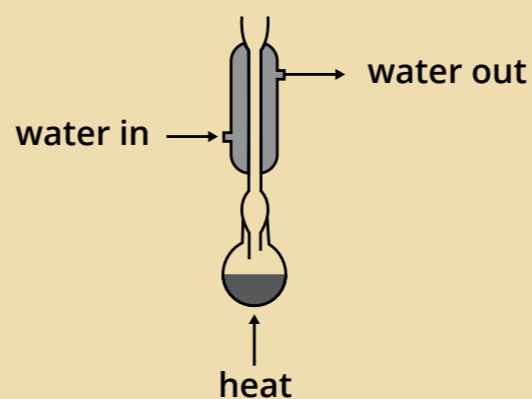


Nucleophiles are species which can donate an electron pair. They must have a lone pair. Examples of nucleophiles: H_2O , NH_3 , OH^-

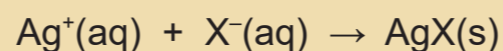
A substitution reaction occurs when a nucleophile replaces the halogen atom in a halogenoalkane.

The reaction of a halogenoalkane with an **aqueous** base, such as $\text{NaOH}(\text{aq})$, is called alkaline hydrolysis. The mixture must be heated under reflux.

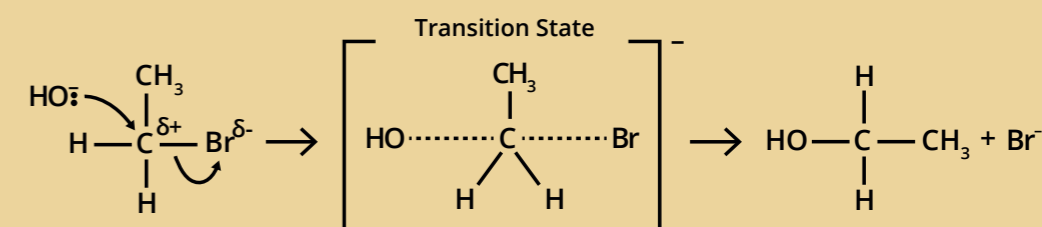
Many organic compounds are volatile and, when heated, would escape to the atmosphere before reaction is complete. Volatile products would also be lost. Reflux is used when heating a reaction mixture. By cooling the vapours from the mixture, the chemicals are contained within the reaction flask as they condense and run back.



A nucleophilic substitution reaction occurs. An alcohol and a halide ion are formed. The halide ion can be identified using nitric acid and silver nitrate solution.



Precipitate	Colour	Solubility in ammonia solution	
		dilute	concentrated
AgCl	white	soluble	soluble
AgBr	cream	insoluble	soluble
AgI	pale yellow	insoluble	insoluble



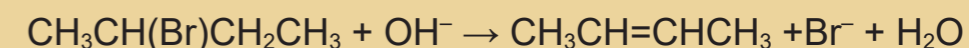
The lone pair of electrons on the nucleophile attacks the partial positive charge (δ^+) on the carbon. A bond forms between the oxygen and the carbon (left-hand dotted line) and the carbon–halogen bond breaks (right-hand dotted line).

The relative ease of hydrolysis of the halogenoalkanes can be explained by the bond strength of the carbon–halogen bond. The rate of hydrolysis increases as follows:

iodoalkanes > bromoalkanes > chloroalkanes

The C–I bond is the least polar and the weakest bond, so it is most easily broken and iodoalkanes are the most reactive.

Reaction with an **ethanolic** base, such as NaOH in ethanol, results in an elimination reaction. The mixture must be heated under reflux. An alkene, water and a halide ion are formed. An elimination reaction occurs.



Chlorofluorocarbons (CFCs) have been used as refrigerants and in aerosols, but their use has been banned because of their effect upon the ozone layer. CFCs are inert due to the high strength of the C–F and C–Cl bonds. In the upper atmosphere, above the ozone (O_3) layer, the CFCs are affected by UV radiation. UV has enough energy to break C–Cl bonds producing highly reactive chlorine radicals. The chlorine radicals react with and break down ozone molecules. The reaction can occur by a number of different mechanisms.