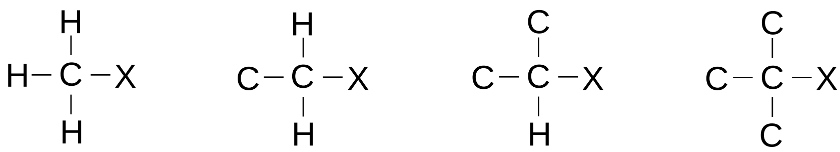
HALOGENOALKANES (HALOALKANES)

Structure Contain the functional group C-X where X is a halogen (F, C*l*, Br or I)

Types **Halogenoalkanes** - halogen is attached to an aliphatic skeleton - alkyl group

Haloarenes - halogen is attached **directly** to a benzene *(aromatic)* ring

Classification Classified according to what is attached to the functional group.



methyl | **primary 1°** | **secondary 2°** | **tertiary 3°**

Names Based on the original alkane with a prefix indicating halogens and their position.

$CH_3CH_2CH_2Cl$ *1-chloropropane* $CH_2ClCHClCH_3$ *1,2-dichloropropane*

$CH_3CHClCH_3$ *2-chloropropane* $CH_3CBr(CH_3)CH_3$ *2-bromo-2-methylpropane*

Q.1 *Draw and name all the structural isomers of $C_3H_6Br_2$, C_4H_9Cl and $C_5H_{11}Br$.*

Q.2 *Classify the structural isomers of C_4H_9Cl and $C_5H_{11}Br$ as 1°, 2° or 3°.*

Physical properties

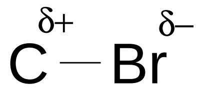
Boiling points
- **boiling point increases with mass**
- for isomeric compounds the greater the branching, the lower the boiling point

Solubility
- halogenoalkanes are soluble in organic solvents but insoluble in water

NUCLEOPHILIC SUBSTITUTION REACTIONS

Theory

- halogens have a **greater electronegativity** than carbon
- a **dipole is induced** in the C-X bond and it becomes **polar**
- the carbon is thus open to attack by nucleophiles



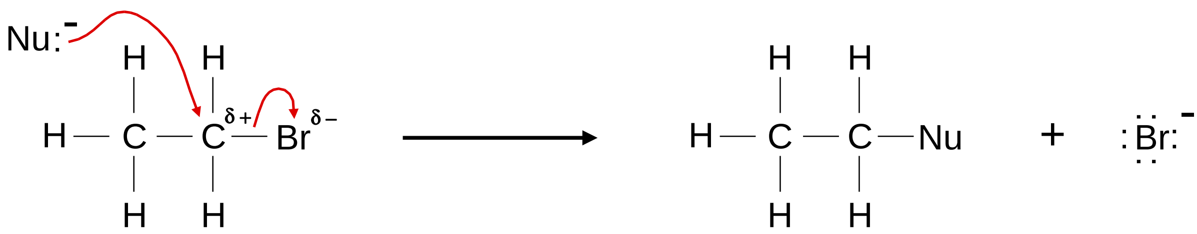
polarity in a C-Br bond

Nucleophiles

- examples are **OH^-**, **CN^-**, **NH_3** and **H_2O**
- possess **at least one LONE PAIR** of electrons
- are **attracted to the slightly positive** (electron deficient) **carbon**

Basic mechanism

- the **nucleophile** uses its lone pair to provide the electrons for a new bond
- as carbon can only have 8 electrons in its outer shell a **halide ion is displaced**
- the result is **substitution** following attack by a nucleophile
- the mechanism is therefore known as - **NUCLEOPHILIC SUBSTITUTION**



Rate of reaction

- the rate of reaction depends on the strength of the C-X bond

C-I ..238..... **kJmol^{-1}**
C-Br ..276..... **kJmol^{-1}**
C-C*l* ..338..... **kJmol^{-1}**
C-F ..484..... **kJmol^{-1}**

WEAKEST BOND
EASIEST TO BREAK
FASTEST REACTION

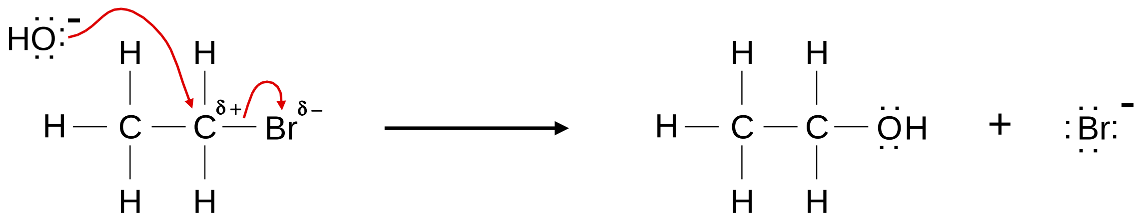
Advanced work

This form of nucleophilic substitution is known as S_N2; it is a bimolecular process. An alternative method involves the initial breaking of the C-X bond to form a carbocation, or carbonium ion, (a unimolecular process - S_N1 mechanism), which is then attacked by the nucleophile. S_N1 is favoured for tertiary haloalkanes where there is steric hindrance to the attack and a more stable tertiary, 3°, carbocation intermediate is formed.

NaOH

Reagent	**AQUEOUS** sodium (or potassium) hydroxide
Conditions	Reflux in **aqueous** solution (SOLVENT IS IMPORTANT)
Product	Alcohol
Nucleophile	hydroxide ion (OH^-)

Equation *e.g.* $C_2H_5Br(l) + NaOH(aq) \longrightarrow C_2H_5OH(l) + NaBr(aq)$



WARNING It is **important to quote the solvent** when answering questions. **Elimination** takes place when ethanol is the solvent - SEE LATER

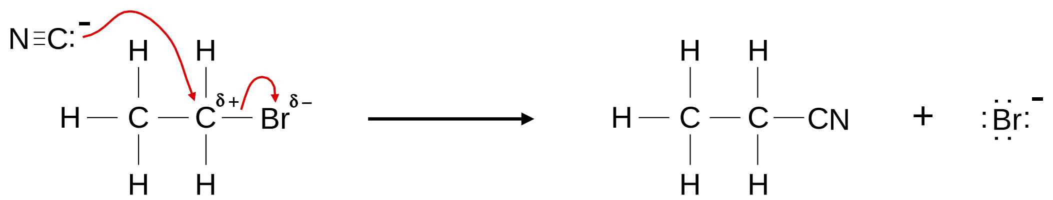
This reaction (and the one with water) is sometimes known as **HYDROLYSIS**

KCN

Reagent	Aqueous, alcoholic potassium (or sodium) cyanide
Conditions	Reflux in aqueous, alcoholic solution
Product	Nitrile (cyanide)
Nucleophile	cyanide ion (CN^-)

Equation $C_2H_5Br + KCN(aq/alc) \longrightarrow C_2H_5CN + KBr$

Mechanism



Importance reaction is that it extends the carbon chain by one carbon atom
The CN group can then be converted to carboxylic acids or amines.

Hydrolysis $C_2H_5CN + 2H_2O \longrightarrow C_2H_5COOH + NH_3$

Reduction $C_2H_5CN + 4[H] \longrightarrow C_2H_5CH_2NH_2$

NH_3

Reagent	Aqueous, alcoholic ammonia (in EXCESS)
Conditions	Reflux in aqueous, alcoholic solution under pressure
Product	Amine (or its salt due to a reaction with the acid produced)
Nucleophile	Ammonia (NH_3)

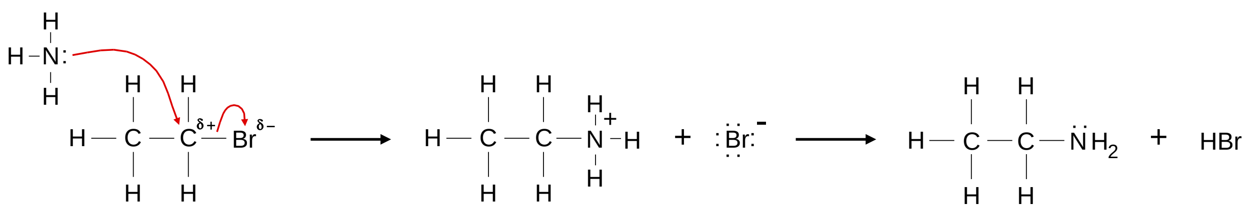
Equation

$$C_2H_5Br + NH_3\,(aq/alc) \longrightarrow C_2H_5NH_2 + HBr$$

$$HBr + NH_3(aq/alc) \longrightarrow NH_4Br$$

$$C_2H_5Br + 2NH_3(aq/alc) \longrightarrow C_2H_5NH_2 + NH_4Br$$

Mechanism



Why excess ammonia?

The second ammonia molecule ensures the removal of HBr which would lead to the formation of a salt.

A large excess of ammonia ensures further substitution doesn't take place

Problem The **amine produced is also a nucleophile** (lone pair on the N) and can attack another molecule of haloalkane to produce a 2° amine. This in turn is a nucleophile and can react further producing a 3° amine and, eventually an ionic quarternary ammonium salt.

$C_2H_5NH_2 + C_2H_5Br \longrightarrow HBr + (C_2H_5)_2NH$ diethylamine, a 2° amine

$(C_2H_5)_2NH + C_2H_5Br \longrightarrow HBr + (C_2H_5)_3N$ triethylamine, a 3° amine

$(C_2H_5)_3N + C_2H_5Br \longrightarrow (C_2H_5)_4N^+ Br^-$ tetraethylammonium bromide, (a 4° salt)

H_2O A similar reaction to that with OH^- takes place with water.
It is **slower** as water is a **poor nucleophile.**

Equation *e.g.* $C_2H_5Br(l) + H_2O(l) \longrightarrow C_2H_5OH(aq/alc) + HBr(aq)$

ELIMINATION REACTIONS OF HALOGENOALKANES

Problem The products of reactions between halogenoalkanes and OH^- are influenced by the solvent. Both mechanisms take place simultaneously but the choice of solvent favours one route.

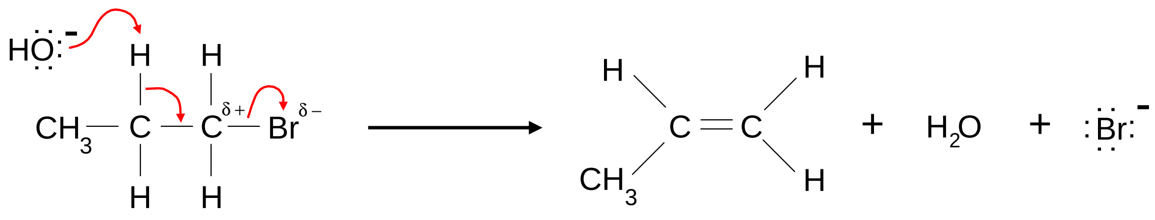
Solvent	Product	Action of OH^-	Mechanism
WATER	ALCOHOL	NUCLEOPHILE	SUBSTITUTION
ALCOHOL	ALKENE	BASE	ELIMINATION

Reaction

Reagent **Alcoholic** sodium (or potassium) hydroxide
Conditions Reflux in alcoholic solution
Product Alkene
Mechanism Elimination

Equation C_3H_7Br + $NaOH(alc)$ ——> C_3H_6 + H_2O + $NaBr$

Mechanism



- the OH^- ion acts as a base and picks up a proton
- the proton comes from a carbon atom next to the one bonded to the halogen
- the electron pair left moves to form a second bond between the carbon atoms
- the halide ion is displaced
- overall there is **ELIMINATION** of HBr.

Q.3 *What organic products are formed when concurrent substitution and elimination takes place with $CH_3CHBrCH_3$?*

Complication The OH^- removes a proton from a carbon atom adjacent the C bearing the halogen. If there had been another carbon atom on the other side of the C-X, its hydrogen(s) would also be open to attack. **If the haloalkane is unsymmetrical** (e.g. 2-bromobutane) a **mixture of isomeric alkene products** is obtained.

Q.4 *What organic products do you get with alcoholic NaOH and $CH_3CHBrCH_2CH_3$? Explain your answers with a mechanism.*

USES OF HALOGENOALKANES

Synthetic The reactivity of the C-X bond means that halogenoalkanes play an important part in synthetic organic chemistry. The halogen can be replaced by a variety of groups via a nucleophilic substitution mechanism.

During the **manufacture of ibuprofen**, substitution of a bromine atom takes place.

Monomers **chloroethene** $CH_2 = CHCl$ **tetrafluoroethene** $CF_2 = CF_2$

Polymers

	poly(chloroethene)	PVC	$—(CH_2 — CHCl)_n—$	packaging
	poly(tetrafluoroethene)	PTFE	$—(CF_2 — CF_2)_n—$	non-stick surfaces

CFC's

	dichlorofluoromethane	$CHFCl_2$	refrigerant
	trichlorofluoromethane	CF_3Cl	aerosol propellant blowing agent
	bromochlorodifluoromethane	$CBrClF_2$	fire extinguishers
		CCl_2FCClF_2	dry cleaning solvent degreasing agent

All the above were chosen because of their..
- low reactivity
- volatility
- non-toxicity

PROBLEMS WITH CFC's

Ozone layer
- CFC's have been blamed for environmental damage by thinning the ozone layer
- Ozone absorbs a lot of harmful UV radiation
- CFC's break up in the atmosphere to form free radicals

$$\mathbf{CF_2Cl_2 \longrightarrow CF_2Cl• + Cl•}$$

- the free radicals catalyse the breaking up of ozone

$$\mathbf{2O_3 \longrightarrow 3O_2}$$

Solution
- CFC's were designed by chemists to help people
- chemists now synthesise **alternatives** to CFC's to protect the environment such as **hydrocarbons** and **HCFC's**
- **CO_2** can be use as an **alternative blowing agent**
- this will allow the reversal of the ozone layer problem