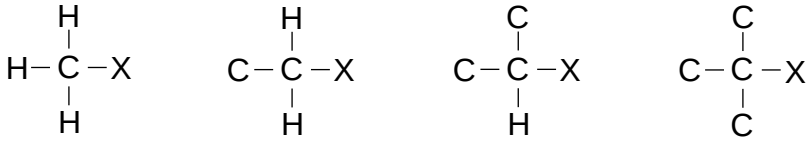
HALOALKANES

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

Types **Haloalkanes** - halogen is attached to an aliphatic skeleton - alkyl group
Haloarenes - halogen is attached **directly** to a benzene *(aromatic)* ring - aryl group

Classification Haloalkanes are classified according to what is attached to the C-X functional group.



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

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

$CH_3CH_2CH_2Cl$	1-chloropropane	$CH_3CHClCH_3$	2-chloropropane
$CH_2ClCHClCH_3$	1,2-dichloropropane	$CH_3CBr(CH_3)CH_3$	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

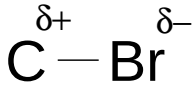
Boiling pts
- **boiling point increases with mass**
- for isomeric compounds the greater the degree of branching, the lower the boiling point

Solubility
- haloalkanes 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



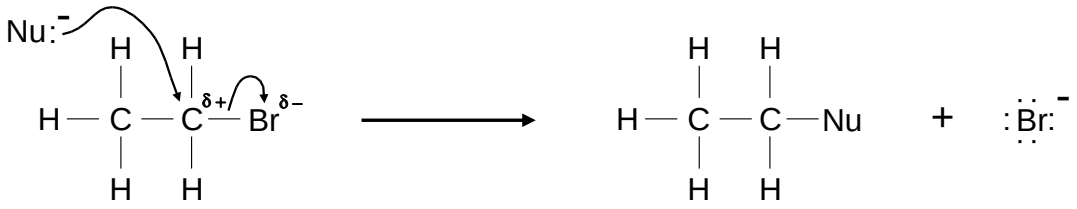
polarity in a C-Br bond

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
- the halogen is displaced as an ion as carbon can only have 8 electrons in its outer shell
- 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-Cl .....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.

1. NaOH

Reagent Aqueous sodium (or potassium) hydroxide

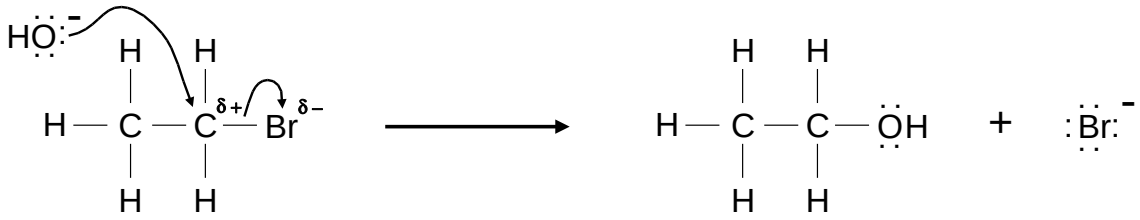
Conditions Reflux in **aqueous** solution (SOLVENT IS IMPORTANT)

Product Alcohol

Nucleophile hydroxide ion (OH^-)

Equation *e.g.* $C_2H_5Br_{(l)} + NaOH_{(aq)} \longrightarrow C_2H_5OH_{(l)} + NaBr_{(aq)}$

Mechanism



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

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

2. KCN

Reagent Aqueous, alcoholic potassium (or sodium) cyanide

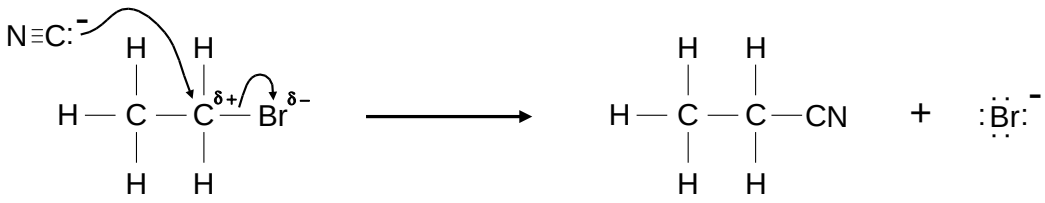
Conditions Reflux in aqueous, alcoholic solution

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 $C_2H_5CN + 4[H] \longrightarrow C_2H_5CH_2NH_2$

3. NH_3

Reagent Aqueous, alcoholic ammonia

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)

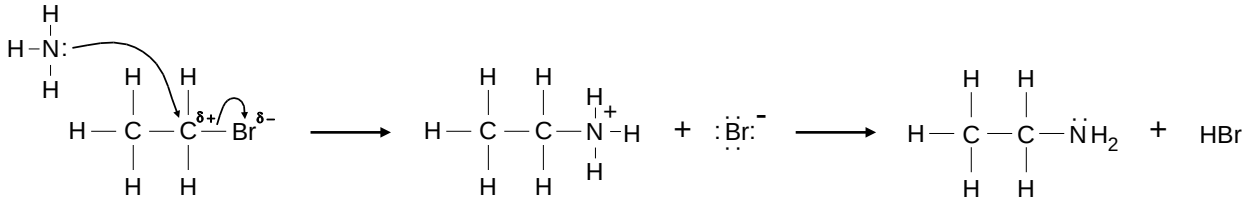
Equation

$$\mathbf{C_2H_5Br + NH_{3\,(aq\,/\,alc)} \longrightarrow C_2H_5NH_2 + HBr}$$

$$\mathbf{HBr + NH_{3\,(aq\,/\,alc)} \longrightarrow NH_4Br}$$

$$\mathbf{C_2H_5Br + 2NH_{3\,(aq\,/\,alc)} \longrightarrow C_2H_5NH_2 + NH_4Br}$$

Mechanism



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.

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

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

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

4. 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.* $\mathbf{C_2H_5Br_{(l)} + H_2O_{(l)} \longrightarrow C_2H_5OH_{(l)} + HBr_{(aq)}}$

ELIMINATION REACTIONS OF HALOALKANES

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

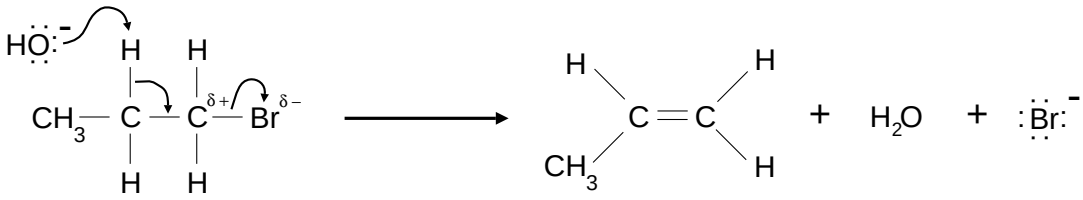
Solvent	Product	Action of OH^-	Mechanism
WATER	ALCOHOL	NUCLEOPHILE	SUBSTITUTION
ALCOHOL	ALKENE	BASE	ELIMINATION

Reaction

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

Equation $\mathbf{C_3H_7Br + NaOH_{(alc)} \longrightarrow C_3H_6 + H_2O + NaBr}$

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 halogen is displaced
- overall there is **ELIMINATION** of HBr.

Q.5 *What organic products are formed when concurrent substitution and elimantion 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-Halogen bond, 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.6 *What organic products do you get with alcoholic NaOH and $CH_3CHBrCH_2CH_3$? Explain your answers with a mechanism.*