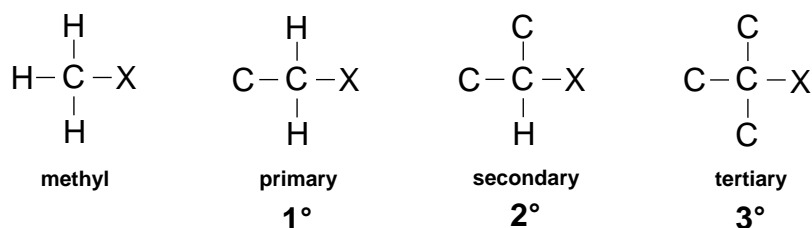


## HALOGENOALKANES (HALOALKANES)

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

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

**Classification** Halogenoalkanes are classified according to what is attached to the functional group.



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

$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  1-chloropropane

$\text{CH}_3\text{CHClCH}_3$  2-chloropropane

$\text{CH}_2\text{ClCHClCH}_3$  1,2-dichloropropane

$\text{CH}_3\text{CBr}(\text{CH}_3)\text{CH}_3$  2-bromo-2-methylpropane

**Q.1** Draw and name all the structural isomers of  $\text{C}_3\text{H}_6\text{Br}_2$ ,  $\text{C}_4\text{H}_9\text{Cl}$  and  $\text{C}_5\text{H}_{11}\text{Br}$ .

**Q.2** Classify the structural isomers of  $\text{C}_4\text{H}_9\text{Cl}$  and  $\text{C}_5\text{H}_{11}\text{Br}$  as  $1^\circ$ ,  $2^\circ$  or  $3^\circ$ .

### Physical properties

**Boiling pts**

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

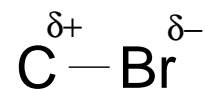
**Solubility**

- 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

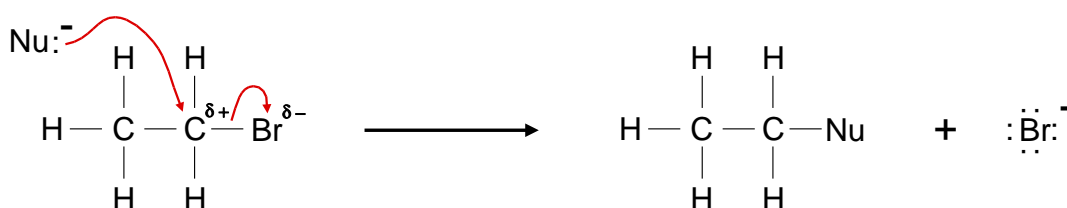
### Nucleophiles

- examples are OH<sup>-</sup>, CN<sup>-</sup>, NH<sub>3</sub> and H<sub>2</sub>O
- 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 <sup>-1</sup>
C-Br	..... 276	kJmol <sup>-1</sup>
C-Cl	..... 338	kJmol <sup>-1</sup>
C-F	..... 484	kJmol <sup>-1</sup>

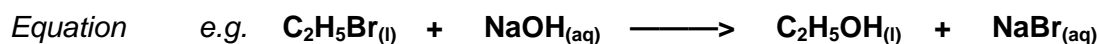
*WEAKEST BOND*  
**EASIEST TO BREAK**  
**FASTEST REACTION**

### Advanced work

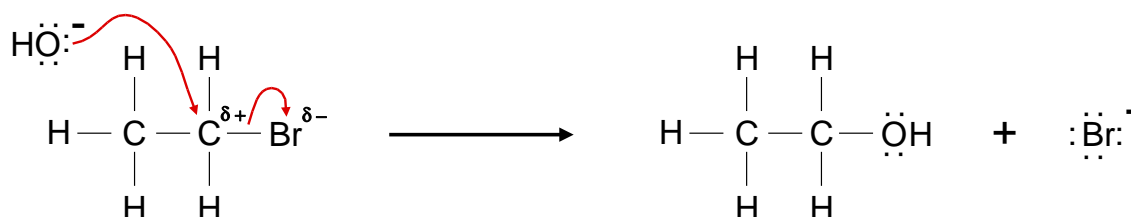
This form of nucleophilic substitution is known as S<sub>N</sub>2; it is a bimolecular process. An alternative method involves the initial breaking of the C-X bond to form a carbocation, or carbonium ion, (a unimolecular process - S<sub>N</sub>1 mechanism), which is then attacked by the nucleophile. S<sub>N</sub>1 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**

<i>Reagent</i>	Aqueous sodium (or potassium) hydroxide
<i>Conditions</i>	Reflux in <b>aqueous</b> solution (SOLVENT IS IMPORTANT)
<i>Product</i>	Alcohol
<i>Nucleophile</i>	hydroxide ion (OH <sup>-</sup> )



*Mechanism*



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

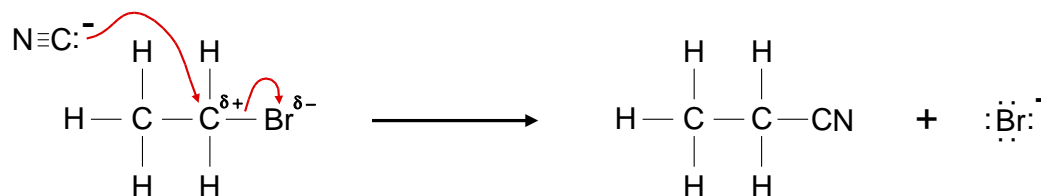
The reaction (and the one with water) is sometimes known as **HYDROLYSIS**

**2. KCN**

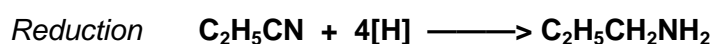
<i>Reagent</i>	Aqueous, alcoholic potassium (or sodium) cyanide
<i>Conditions</i>	Reflux in aqueous, alcoholic solution
<i>Product</i>	Nitrile (cyanide)
<i>Nucleophile</i>	cyanide ion (CN <sup>-</sup> )



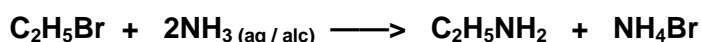
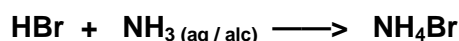
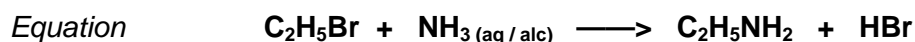
*Mechanism*



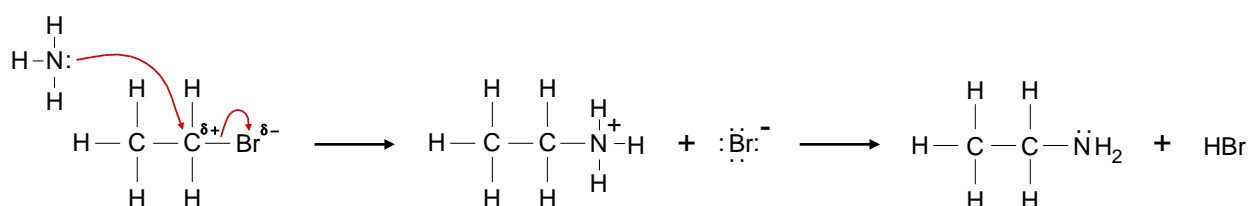
*Importance* reaction is that it extends the carbon chain by one carbon atom  
 The CN group can then be converted to carboxylic acids or amines.



3. NH <sub>3</sub>	<i>Reagent</i>	Aqueous, alcoholic ammonia (in EXCESS)
	<i>Conditions</i>	Reflux in aqueous, alcoholic solution under pressure
	<i>Product</i>	Amine (or its salt due to a reaction with the acid produced)
	<i>Nucleophile</i>	Ammonia (NH <sub>3</sub> )



### 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 ammonia ensures that further substitution doesn't take place - see *below*

### Problem

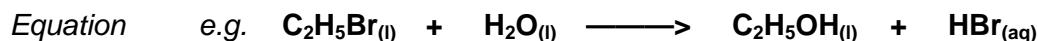
The **amine produced is also a nucleophile** (lone pair on the N) and can attack another molecule of haloalkane to produce a 2° amine. This in turn is a nucleophile and can react further producing a 3° amine and, eventually an ionic quaternary ammonium salt.



### 4. H<sub>2</sub>O

A similar reaction to that with OH<sup>-</sup> takes place with water.

It is **slower** as water is a **poor nucleophile**.

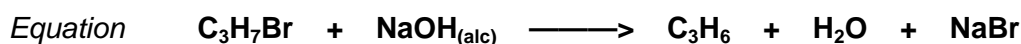


## ELIMINATION REACTIONS OF HALOALKANES

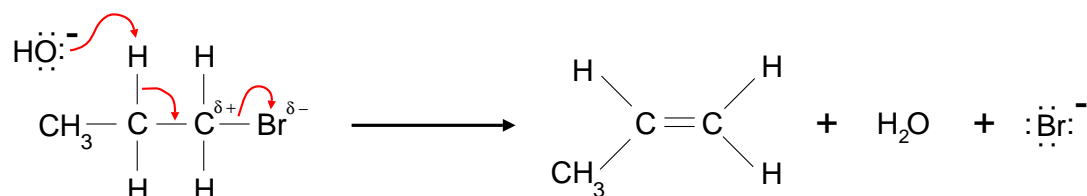
**Problem** The products of reactions between haloalkanes and  $\text{OH}^-$  are influenced by the solvent. Both mechanisms take place simultaneously but the choice of solvent favours one route.

Solvent	Product	Action of $\text{OH}^-$	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



**Mechanism**



- the  $\text{OH}^-$  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  $\text{HBr}$ .

**Q.3** What organic products are formed when concurrent substitution and elimination takes place with  $\text{CH}_3\text{CHBrCH}_3$  ?

**Complication** The  $\text{OH}^-$  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.4** What organic products do you get with alcoholic  $\text{NaOH}$  and  $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$  ? 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  
tetrafluoroethene

*Polymers*

poly(chloroethene)	PVC	$-(\text{CH}_2-\text{CHCl})_n-$	packaging
poly(tetrafluoroethene)	PTFE	$-(\text{CF}_2-\text{CF}_2)_n-$	non-stick surfaces

*CFC's*

dichlorofluoromethane	$\text{CHFCl}_2$	refrigerant, aerosol propellant, blowing agent
trichlorofluoromethane	$\text{CF}_3\text{Cl}$	refrigerant, aerosol propellant, blowing agent
bromochlorodifluoromethane	$\text{CBrClF}_2$	fire extinguishers
	$\text{CCl}_2\text{FCClF}_2$	dry cleaning solvent, degreasing agent

## PROBLEMS WITH CFC'S

*Ozone layer*

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



- the free radicals catalyse the breaking up of ozone



*Solution*

- CFC's were designed by chemists to help people
- chemists are now having to synthesise alternatives to CFC's to protect the environment
- this will allow the reversal of the ozone layer problem

## Preparation of halogenoalkanes - Summary *(details can be found in other sections)*

<i>From alkanes</i>	$\text{CH}_4 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{HCl}$	Free radical substitution / UV light
<i>alkenes</i>	$\text{C}_2\text{H}_4 + \text{HBr} \longrightarrow \text{C}_2\text{H}_5\text{Br}$	Electrophilic addition / no catalyst or light
<i>alcohols</i>	$\text{C}_2\text{H}_5\text{OH} + \text{HBr} \longrightarrow \text{C}_2\text{H}_5\text{Br} + \text{H}_2\text{O}$	Protonation of alcohol with an acid catalyst