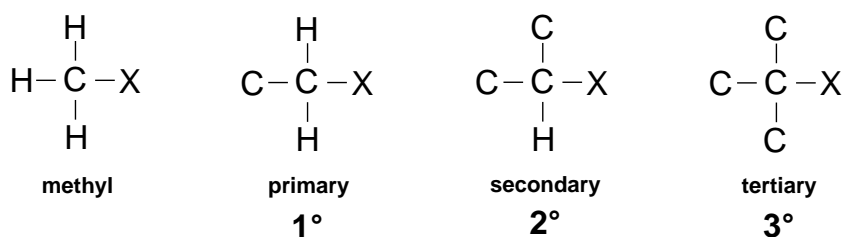


HALOALKANES (HALOGENOALKANES)

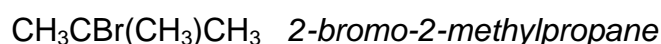
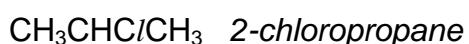
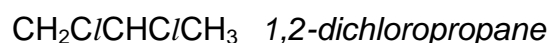
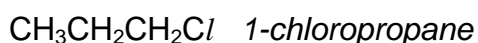
Structure Contain the functional group C-X where X is a halogen (F, Cl, Br or I)

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

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



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



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° , 2° or 3° .

Physical properties

Boiling points

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

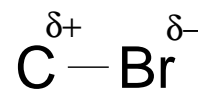
Solubility

- haloalkanes are soluble in organic solvents but insoluble in water - they are not polar enough and don't exhibit hydrogen bonding.

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

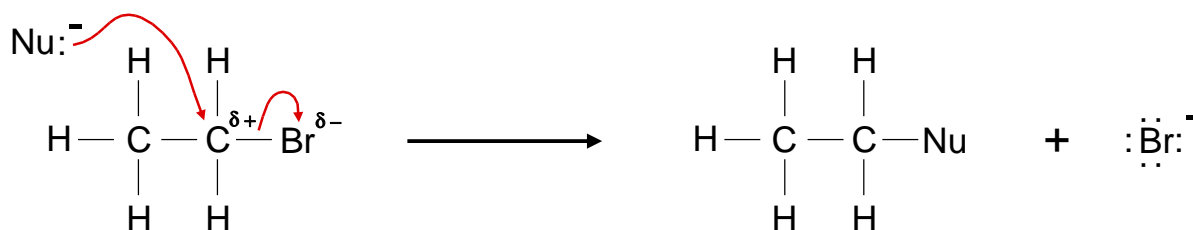
Nucleophiles

- 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** not the polarity of the C-X bond

C-I	238	kJmol^{-1}	least polar
C-Br	276	kJmol^{-1}	
C-Cl	338	kJmol^{-1}	
C-F	484	kJmol^{-1}	most polar

WEAKEST BOND EASIEST TO BREAK FASTEST REACTION

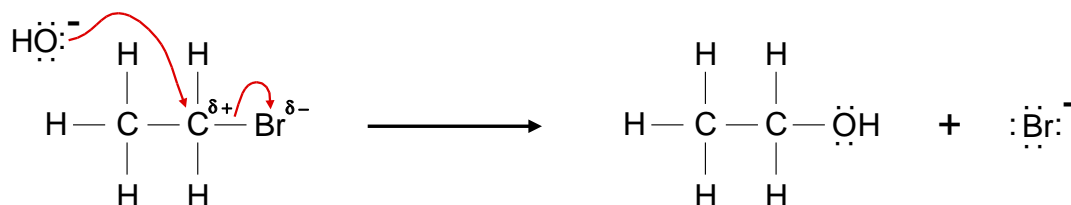
Practical investigation

The time taken for a precipitate of silver halide is measured. The faster the precipitate forms, the faster the hydrolysis and the weaker the C-X bond.

- warm equal amounts of each haloalkane in a water bath
- add a solution of ethanol, water and aqueous silver nitrate to each
- record the time it takes for a precipitate to appear

AgCl - white **AgBr** - cream **AgI** - yellow (AgF is soluble)

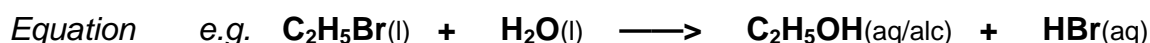
NaOH	<i>Reagent</i>	AQUEOUS sodium (or potassium) hydroxide
	<i>Conditions</i>	Reflux in aqueous solution (SOLVENT IS IMPORTANT)
	<i>Product</i>	Alcohol
	<i>Nucleophile</i>	hydroxide ion (OH ⁻)
<i>Equation</i>	e.g.	$\text{C}_2\text{H}_5\text{Br}(\text{l}) + \text{NaOH}(\text{aq}) \longrightarrow \text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{NaBr}(\text{aq})$

Mechanism

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

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

- H₂O**
- A similar reaction to the above but SLOWER because...
 - a) the liquids are **immiscible - less chance of molecules colliding**
 - b) water is a **poor nucleophile**
 - **faster** reaction in an **alcohol/water mixture**; miscible = more collisions



AgNO₃ (aq/alc) Used to identify the halide in a haloalkane - see above

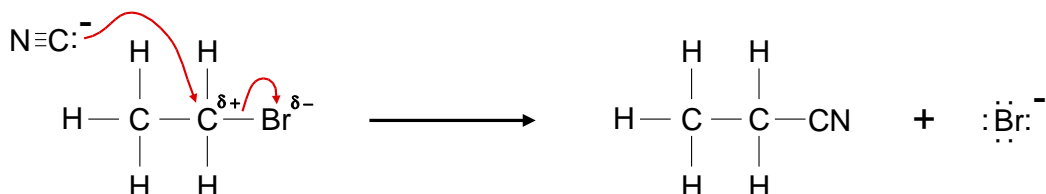
Q.3 Write equations for the reactions of hot, aqueous NaOH with...

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
- $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$
- $(\text{CH}_3)_3\text{CBr}$

Advanced work

This form of nucleophilic substitution discussed so far 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.

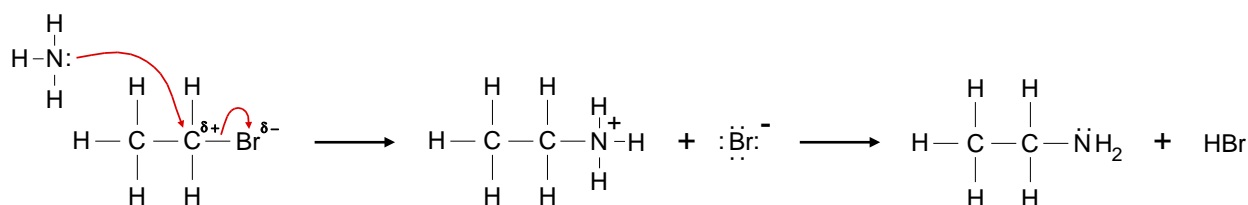
KCN	<i>Reagent</i>	Aqueous, alcoholic potassium (or sodium) cyanide
	<i>Conditions</i>	Reflux in aqueous, alcoholic solution
	<i>Product</i>	Nitrile (cyanide)
	<i>Nucleophile</i>	cyanide ion (CN ⁻)
	<i>Equation</i>	C₂H₅Br + KCN(aq/alc) → C₂H₅CN + KBr

Mechanism

Importance extends the carbon chain by one carbon atom as the CN group can then be converted to carboxylic acids or amines



NH₃	<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 ₃)
	<i>Equation</i>	C₂H₅Br + NH₃(aq/alc) → C₂H₅NH₂ + HBr
		HBr + NH₃(aq/alc) → NH₄Br
		<hr/>
		C₂H₅Br + 2NH₃(aq/alc) → C₂H₅NH₂ + NH₄Br

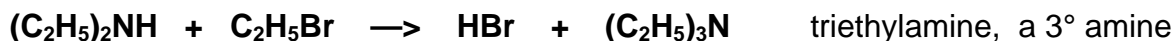
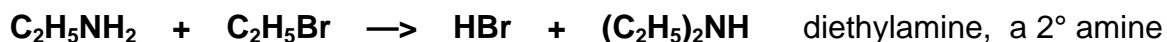
Mechanism

Why the 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 quaternary ammonium salt.



OTHER REACTIONS OF HALOALKANES

Friedel Crafts

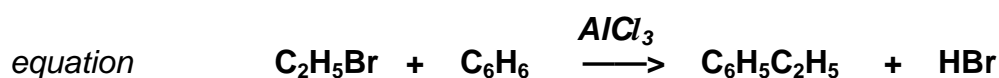
alkylation substitutes an alkyl (e.g. methyl, ethyl) group onto a benzene ring

reagents a haloalkane (RX) and anhydrous aluminium chloride AlCl_3

conditions room temperature; dry inert solvent (ether)

mechanism electrophilic substitution

electrophile a carbocation ion R^+ (e.g. CH_3^+)



see notes on benzene

Preparation of haloalkanes - Summary

(details can be found in other sections)

From

alkanes $\text{CH}_4 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{HCl}$ Free radical substitution / UV light

alkenes $\text{C}_2\text{H}_4 + \text{HBr} \longrightarrow \text{C}_2\text{H}_5\text{Br}$ Electrophilic addition / no catalyst or UV

alcohols $\text{C}_2\text{H}_5\text{OH} + \text{HBr} \longrightarrow \text{C}_2\text{H}_5\text{Br} + \text{H}_2\text{O}$ Protonation of alcohol with acid catalyst

USES OF HALOALKANES

Synthetic The reactivity of the C-X bond means that haloalkanes 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.

<i>Monomers</i>	chloroethene $\text{CH}_2 = \text{CHCl}$	tetrafluoroethene $\text{CF}_2 = \text{CF}_2$
<i>Polymers</i>	poly(chloroethene) PVC	$-(\text{CH}_2 - \text{CHCl})_n-$ packaging
	poly(tetrafluoroethene) PTFE	$-(\text{CF}_2 - \text{CF}_2)_n-$ non-stick surfaces
<i>CFC's</i>	dichlorofluoromethane CHFCl_2	refrigerant
	trichlorofluoromethane CF_3Cl	aerosol propellant blowing agent
	bromochlorodifluoromethane CBrClF_2	fire extinguishers
	$\text{CCl}_2\text{FCClF}_2$	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



• free radicals catalyse ozone decomposition e.g. $\bullet\text{Cl} + \text{O}_3 \longrightarrow \bullet\text{ClO} + \text{O}_2$

$$\bullet\text{ClO} + \text{O} \longrightarrow \bullet\text{Cl} + \text{O}_2$$

• overall $2\text{O}_3 \longrightarrow 3\text{O}_2$

Solution

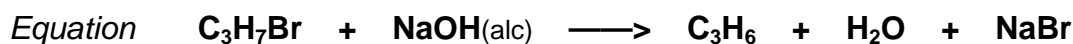
- CFC's were designed by chemists to help people
- chemists now synthesise **alternatives** to CFC's to protect the environment such as **hydrocarbons** and **HCFC's**
- **CO₂** can be use as an **alternative blowing agent**
- this will allow the reversal of the ozone layer problem

ELIMINATION REACTIONS OF HALOALKANES

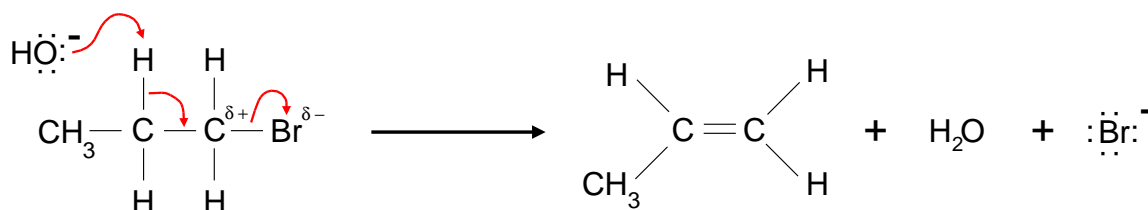
Problem The products of reactions between haloalkanes and OH^- are influenced by the solvent. Both mechanisms take place simultaneously but the choice of solvent favours one route.

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



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

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.5 What organic products do you get with alcoholic NaOH and $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$? Explain your answers with a mechanism.