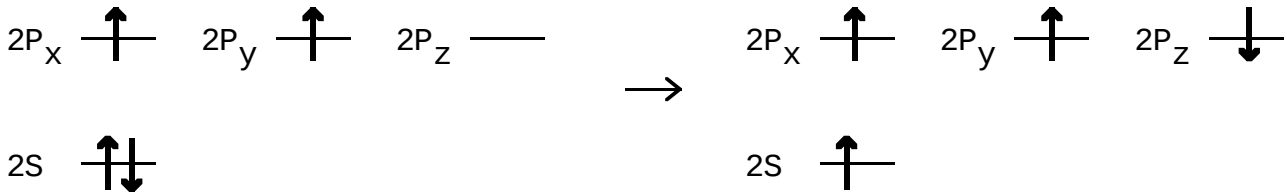
ORGANIC CHEMISTRY

Bonding

In order to form the maximum number of bonds, all atoms maximise their number of unpaired electrons by entering an excited state, known as the valence state, just before they bond with another atom.

Carbon does this by promoting a 2S electron into a 2P orbital:



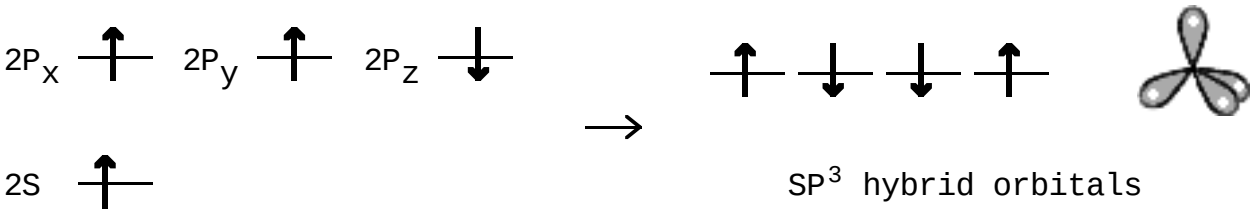
The valency of Carbon is therefore **FOUR**.

The excited state depicted above, however, is unstable. The electrons are too close to each other. They can move further apart by a procedure known as **hybridisation**. This involves mixing atomic orbitals to generate a set of new atomic orbitals called hybrid orbitals.

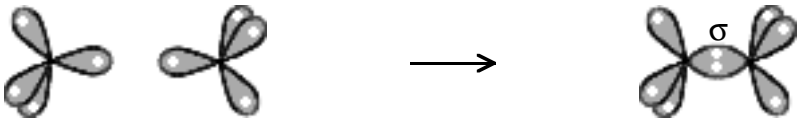
Carbon can form hybrid orbitals in three distinct ways:

SP^3 Hybridisation

The mixing of the 2S and all three 2P orbitals:



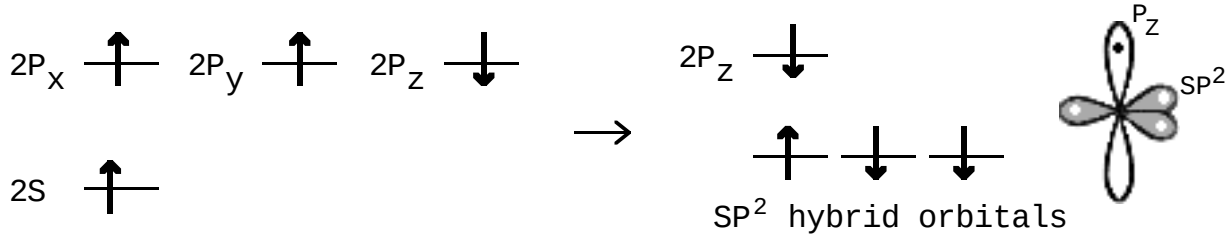
C-C bonds are formed by end-on overlap of two SP^3 hybrid orbitals lying along the axis of the bond:



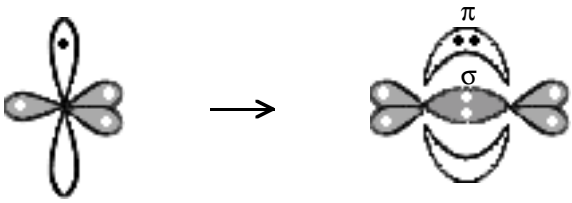
This is known as sigma σ bonding.

SP^2 Hybridisation

The mixing of the 2S and two of the 2P orbitals:

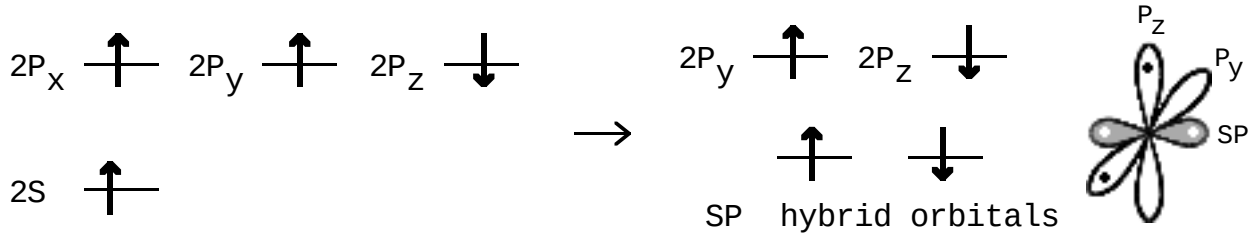


C=C bonds are formed by σ bonding between two SP^2 hybrid orbitals and by sideways overlap (pi π bonding) of two of the P_z orbitals:

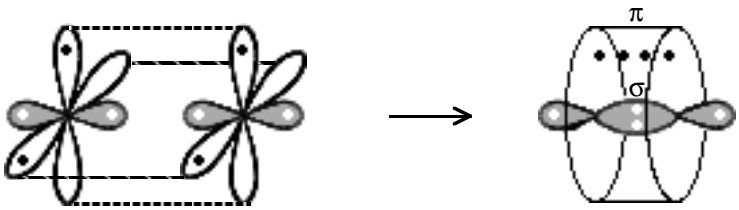


SP Hybridisation

The mixing of the 2S and one of the 2P orbitals:

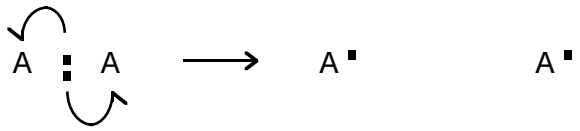


C≡C bonds are formed by σ bonding between two SP hybrid orbitals and by π bonding between four of the P_z orbitals:



Alkanes

Alkanes consist entirely of non-polar bonds. When a non-polar bond breaks, since both atoms have equal electronegativities, the two electrons are shared, one to each atom, forming free radicals (particles containing unpaired electrons) i.e.



↶ Denotes the movement of **ONE** electron.
Bond breaking of this type is known as **homolytic fission**.

The free radicals will then combine with colliding free radicals.

e.g. the chain reaction of Methane with Chlorine.

CH_4 + Cl_2 -> CH_3Cl + HCl

Mechanism :

Initiation	Cl_2	$\xrightarrow{\text{UV or heat}}$		$Cl^{\bullet}$	$Cl^{\bullet}$
Propagation	CH_4	$Cl^{\bullet}$	->	$CH_3^{\bullet}$	HCl
	$CH_3^{\bullet}$	Cl_2	->	CH_3Cl	$Cl^{\bullet}$
Termination	$Cl^{\bullet}$	$Cl^{\bullet}$	->	Cl_2	
	$CH_3^{\bullet}$	$CH_3^{\bullet}$	->	CH_3-CH_3	
	$CH_3^{\bullet}$	$Cl^{\bullet}$	->	CH_3Cl	

Once the initiation step has produced a few Cl• free radicals by homolysis of Cl_2 the reaction will continue in the absence of heat or UV ; although the free radicals are consumed by one of the propagation steps they are regenerated by the other.

The propagation cycle can continue about 5000 times before Cl• are wiped out in termination steps.

Alkanes also undergo substitution reactions with Bromine by a similar mechanism.

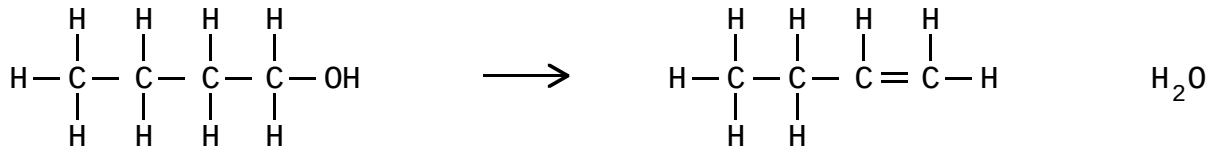
Alkenes

Alkenes contain at least one C=C bond.

Alkenes can be prepared by dehydration of alcohols:

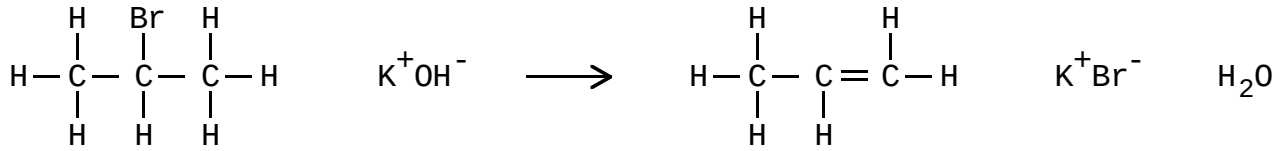
- pass alcohol vapour over heated Aluminium oxide catalyst
- heat a mixture of alcohol and a dehydrating agent
  e.g. concentrated Sulphuric acid or concentrated Phosphoric acid

e.g. dehydration of Butan-1-ol



Butan-1-ol But-1-ene

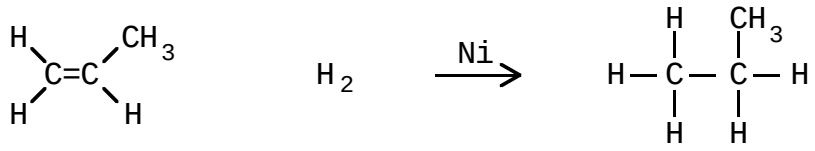
Alkenes can also be prepared by elimination of hydrogen halides from haloalkanes. The haloalkane is heated with a solution of Potassium hydroxide in Ethanol solvent e.g.



2-Bromopropane Propene

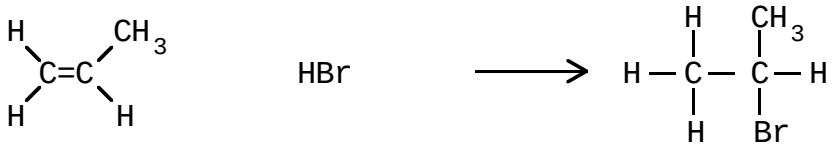
Alkenes undergo addition reactions:

Addition of Hydrogen using Nickel catalyst e.g.



Propene Propane

Addition of Hydrogen halides e.g.



Propene 2-Bromopropane

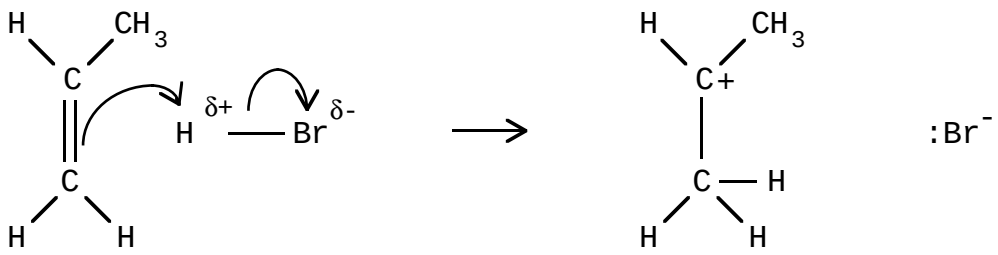
MECHANISM (TWO steps):

STEP 1:

HBr is polar. The $H^{\delta+}$ attracts a pair of electrons from the double bond.

HBr is an **electrophile** - a negative seeking reagent.

The alkene is a **nucleophile** - a postive seeking reagent.

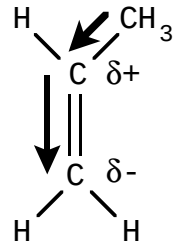


carbocation intermediate

Denotes the movement of **TWO** electrons.
Bond breaking of this type is known as **heterolytic fission**.

Why does the H atom prefer to bond to the bottom Carbon atom? This is because of the **inductive** effect of the CH_3 group.

The CH_3 group repels electrons in the C-C and C=C bonds. The bottom Carbon thus becomes δ- and thus more likely to be the nucleophilic source.

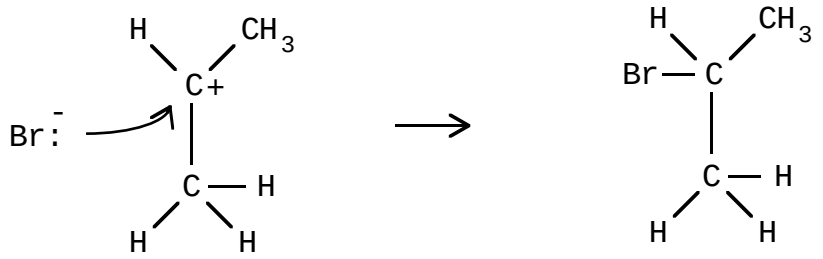


Markownikoff's rule can be used to predict which of the two Carbon atoms is most nucleophilic:

The Hydrogen atom bonds to the Carbon atom that already has the most Hydrogen atoms bonded to it.

STEP 2:

The Br^- ion does a nucleophilic attack at the carbocation intermediate:

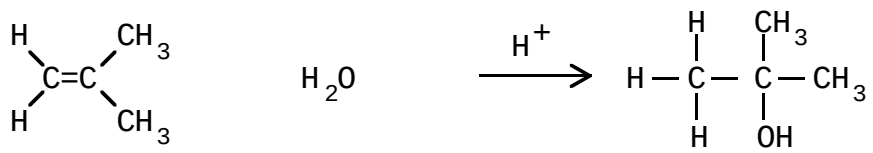


Acid catalysed addition of Water

Alkenes react with Water in the presence of H^+ catalyst.
Hydration of Ethene, with Phosphoric acid catalyst, is used in the industrial preparation of Ethanol:

C_2H_4 + H_2O -> C_2H_5OH

Hydration of alkenes also follows Markownikoff's Rule e.g.

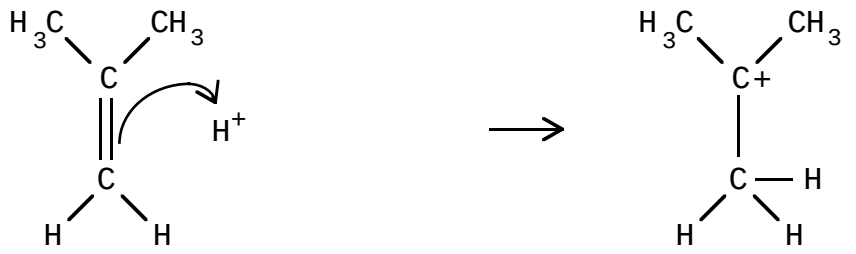


Methylpropene Methylpropan-2-ol

MECHANISM (THREE steps):

STEP 1:

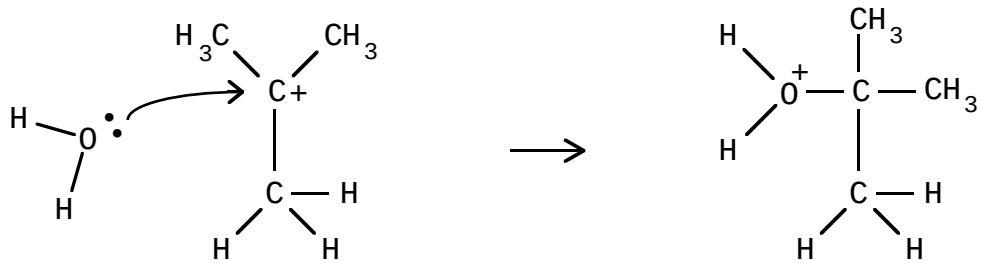
Nucleophilic attack by the alkene at the H^+ catalyst:



carbocation intermediate

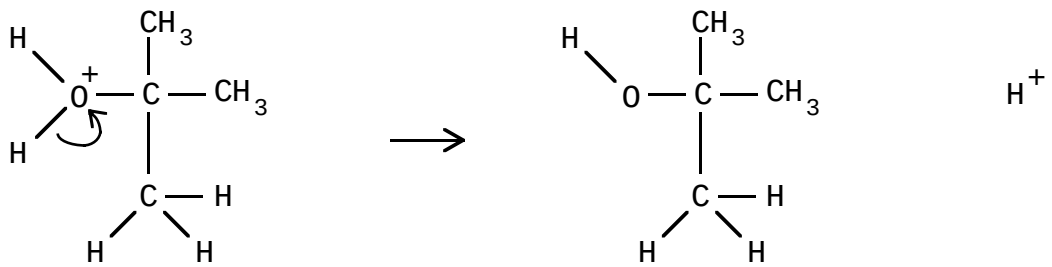
STEP 2:

The H_2O does a nucleophilic attack at the carbocation intermediate:

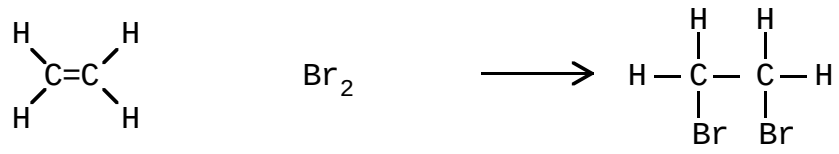


STEP 3:

Regeneration of the H^+ catalyst:



Addition of Halogens e.g.

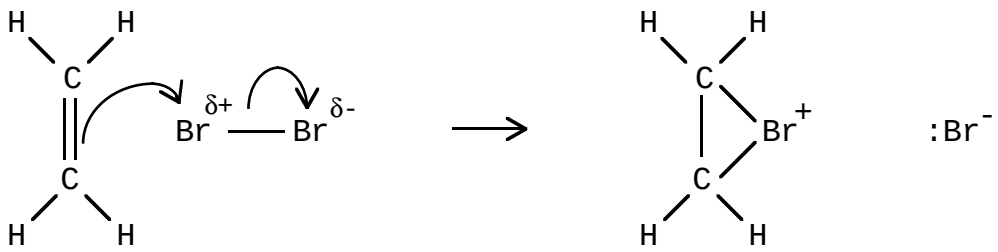


Ethene 1,2-Dibromoethane

MECHANISM (TWO steps):

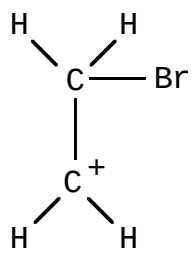
STEP 1:

As Br_2 approaches the double bond, electrons in the Br-Br bond are repelled by the double bond electrons causing a δ+ charge to develop on the Br nearest the double bond. Thus the Bromine becomes electrophilic. It draws an electron pair from the double bond:

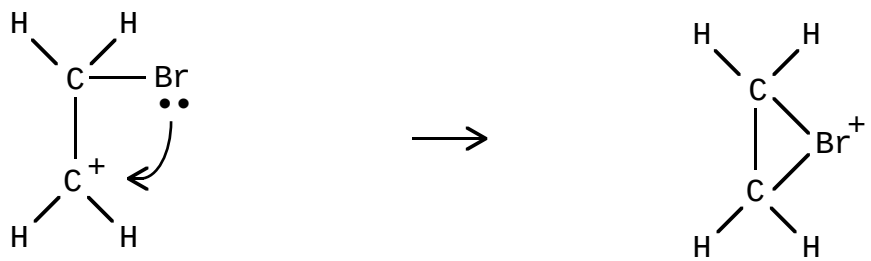


cyclic ion intermediate

Why do we get a cyclic ion intermediate? Why not just the carbocation:

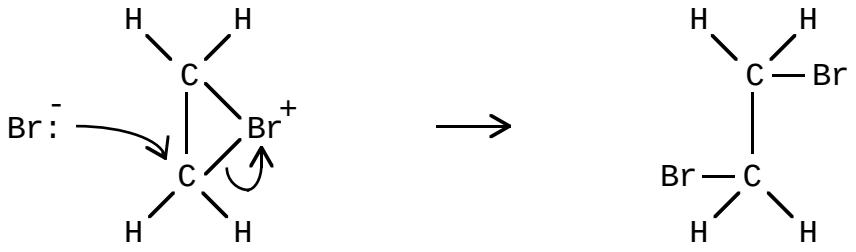


Br is nucleophilic: it contains an electron pair which can be donated to C^+ thus closing the ring:



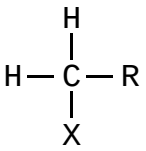
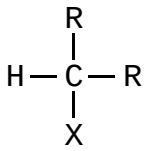
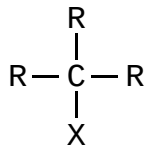
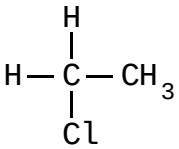
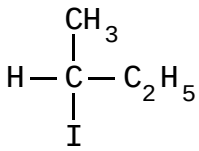
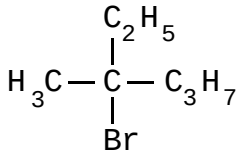
STEP 2:

The Br^- ion does a nucleophilic attack at the cyclic ion intermediate:



Haloalkanes

Haloalkanes are classified according to the number of alkyl groups (R) bonded to the Carbon atom containing the halogen atom (X):

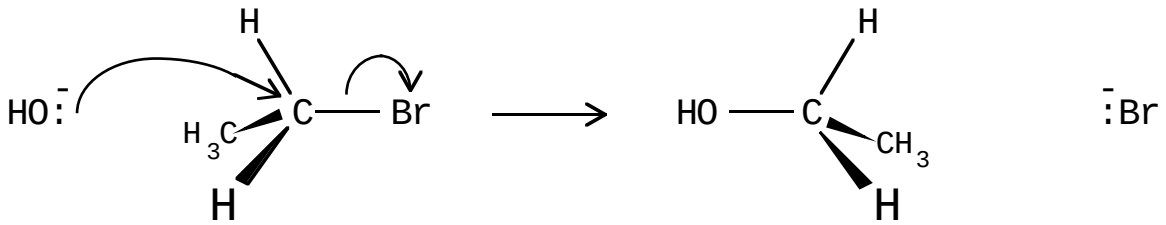
	PRIMARY	SECONDARY	TERTIARY
			
e.g.			
	Chloroethane	2-Iodobutane	3-Bromo 3-methylhexane

The $C^{\delta+}$ - $X^{\delta-}$ bond is polar ; the positively charged Carbon atom is **electrophilic** and is therefore attacked by **nucleophiles**.

Haloalkanes undergo nucleophilic **substitution** reactions.

Reaction with hydroxide ion ^-OH to form alcohols

e.g. the reaction of Bromoethane with hydroxide ion.
The reaction occurs in one step: HO^- attacks the $C^{\delta+}$ forcing electrons in the C-Br bond on to the Br.



Bromoethane Ethanol

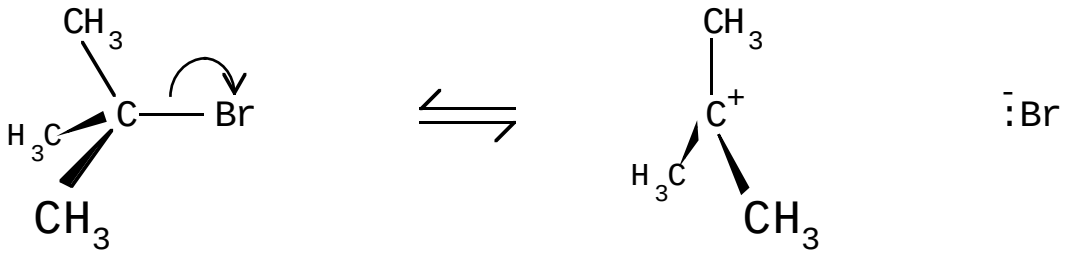
The above mechanism is described as **SN2**:

Substitution of Br by the
Nucleophile HO^- with
2 particles (HO^- and C_2H_5Br) taking part in the rate determining step

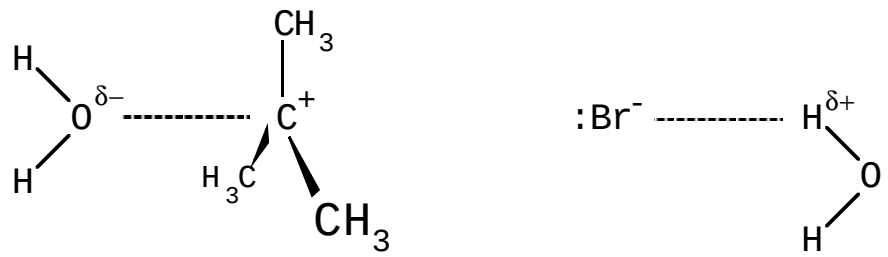
An alternative mechanism, favoured by **tertiary** and, to some extent, secondary haloalkanes in **polar solvents** is described as **SN1**:

The SN1 reaction occurs in two steps:

STEP 1 - the slow, rate determining step.

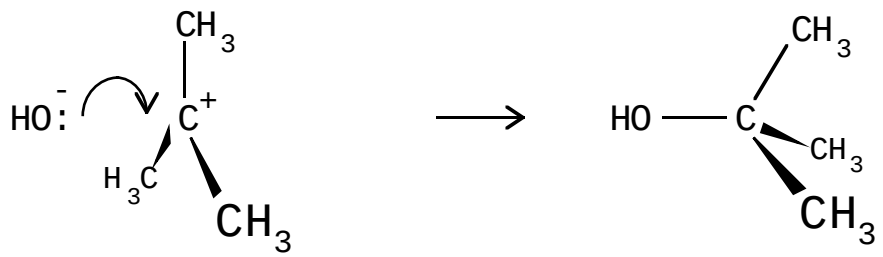


Polar solvents like Water bond to these ions and prevent reversal:



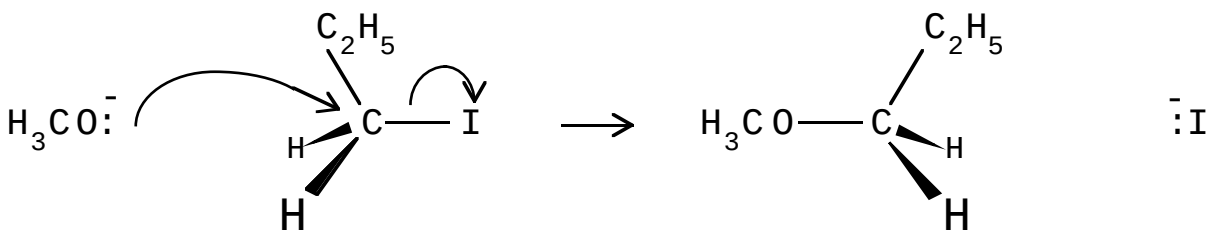
The inductive effect of the alkyl groups in the carbocation, forcing electrons on to C^+, reduces the positive charge and makes reversal less likely. The more alkyl groups, the more stable the carbocation and the more likely it is to survive and be able to take part in step 2.

STEP 2 - a fast step.



We will assume the SN2 mechanism in all further examples since they involve primary haloalkanes.

Reaction with alkoxide ions $^-$OR to form ethers e.g.

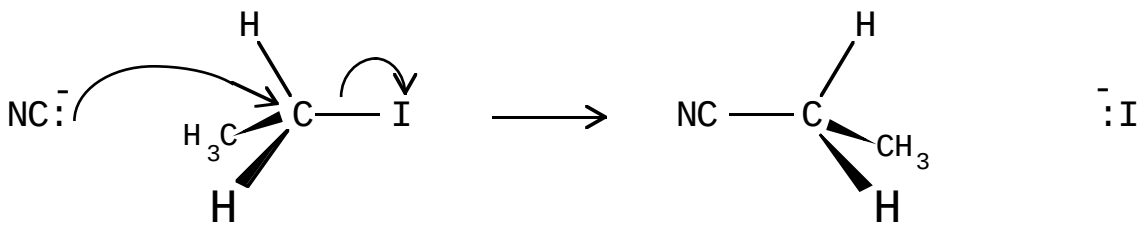


1-Iodopropane Methoxypropane

The alkoxide ion is produced by reaction of the appropriate alcohol with Sodium e.g. the methoxide ion above is produced by reaction of Methanol with Sodium:

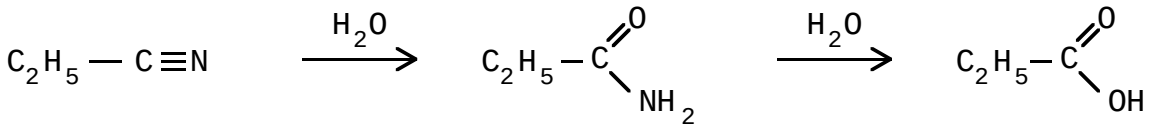
CH_3OH + Na -> $CH_3O^-Na^+$ + H_2

Reaction with cyanide ion $^-$CN (in Ethanol solvent) to form nitriles e.g.



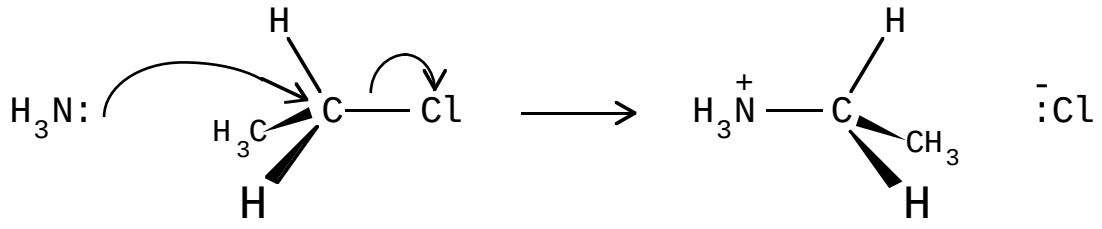
Iodoethane Propane nitrile

Nitriles can be hydrolysed to form amides and, subsequently, carboxylic acids e.g. hydrolysis of Propane nitrile:



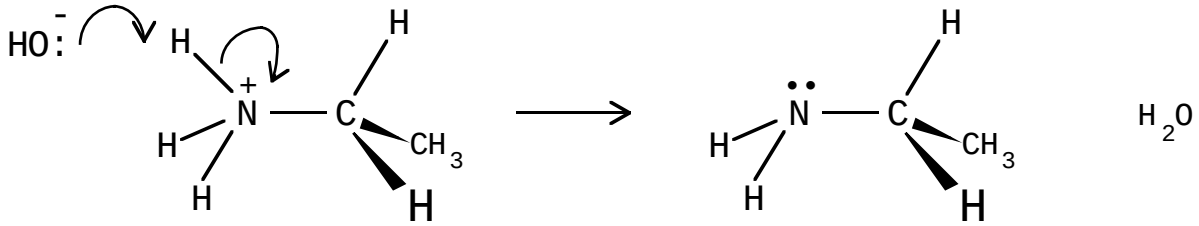
Propane nitrile Propanamide Propanoic acid

Reaction with Ammonia NH_3 to form alkyl ammonium salts e.g.



Chloroethane Ethyl ammonium chloride

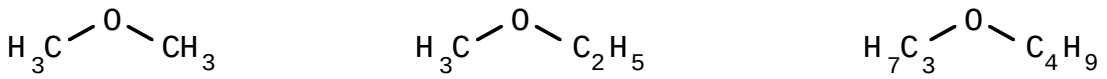
Reaction of the alkyl ammonium salt with alkali produces amines e.g.



Aminoethane

Ethers

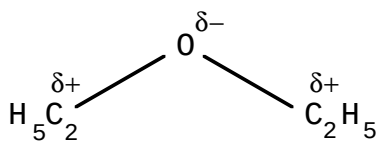
Ethers have the general formula R^1-O-R^2 where R^1 and R^2 are alkyl groups e.g.



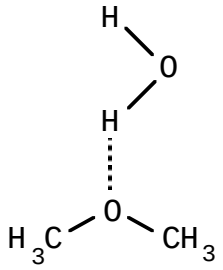
Methoxymethane (Dimethylether) Methoxyethane (Ethylmethylether) Propoxybutane (Butylpropylether)

Properties:

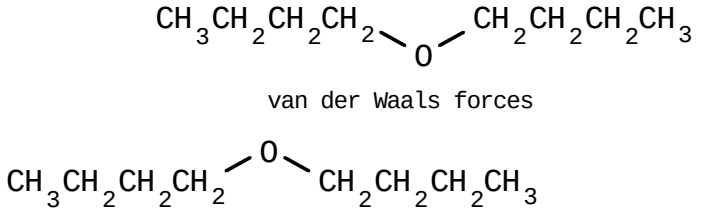
- They are fairly polar because of their non-linear shape e.g. Ethoxyethane (Diethylether):

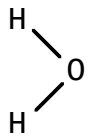


- Ethers of very low formula mass dissolve in water by hydrogen bonding e.g. Methoxymethane (Dimethylether) dissolves in water:



Higher members are less soluble in water. The increasing length of the alkyl group increases the strength of the van der Waals attraction between the ether molecules themselves. Water molecules are unable to break this attractive force. e.g. Butoxybutane (Dibutylether)





- They have low boiling points due to the lack of hydrogen bonding between the molecules.

- They are generally unreactive but:-

  (1) they are highly flammable

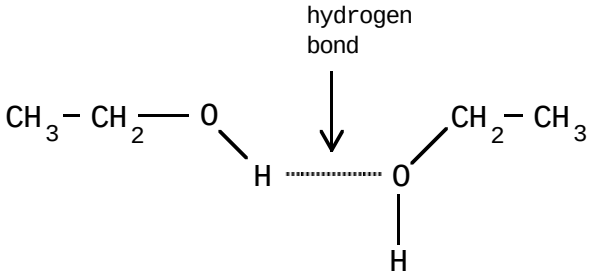
  (2) they slowly react with the Oxygen in the air forming explosive peroxides (-O-O-)

Ethers make good solvents because of their polarity, low boiling points and low reactivities.

Alcohols

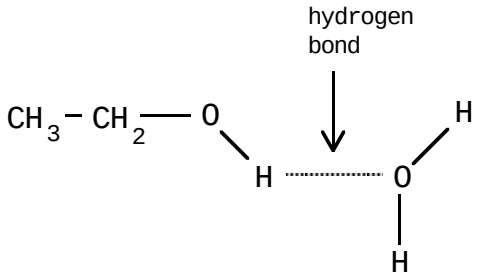
The presence of the OH group enables alcohols to form hydrogen bonds.

Hydrogen bonding occurs between molecules in liquid and solid alcohols e.g. in Ethanol

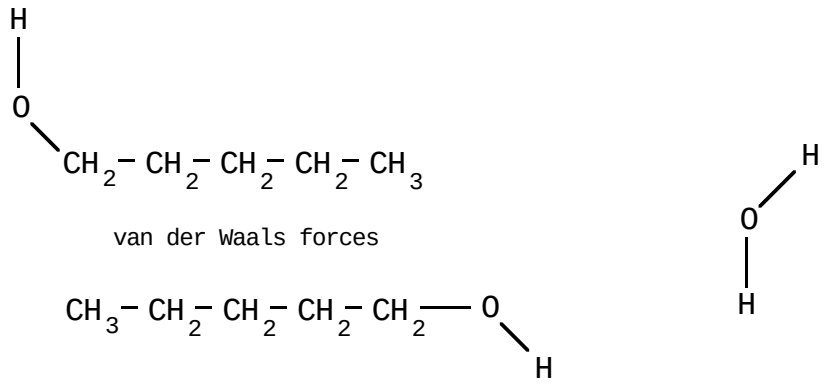


Alcohols thus have higher melting points and boiling points than other organic compounds of comparable formula mass and shape e.g. BP of Ethanol is 78 ^{0}C; BP of isomeric Dimethylether is -24 ^{0}C.

Hydrogen bonding is also responsible for the solubility of the lower alcohols in water e.g. Ethanol



Higher members are less soluble in water. The increasing length of the alkyl group increases the strength of the van der Waals attraction between the alcohol molecules themselves. Water molecules are unable to break this attractive force e.g. Pentan-1-ol is only sparingly soluble in water



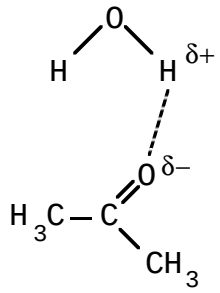
Aldehydes and Ketones

Examples:-

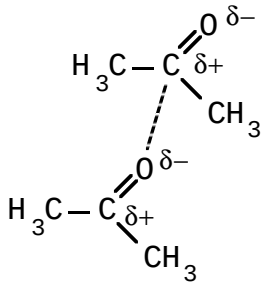
Pentanal (Aldehyde) Pentan-2-one (Ketone)

Both aldehydes and ketones contain the highly polar carbonyl group $C^{\delta+}=O^{\delta-}$.

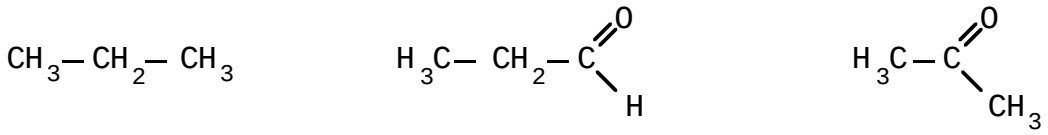
Lower members dissolve in water by hydrogen bonding e.g. Propanone



Inter-molecular bonding in solids and liquids is by attraction between the polar bonds e.g. Propanone

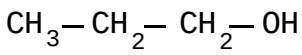


Aldehydes and ketones are more polar and therefore have higher boiling points than the parent alkanes:



Propane	Propanal	Propanone
BP -42 ^{0}C	BP 49 ^{0}C	BP 56 ^{0}C

Aldehydes and ketones cannot form inter-molecular hydrogen bonds and therefore have lower boiling points than the corresponding alcohol.



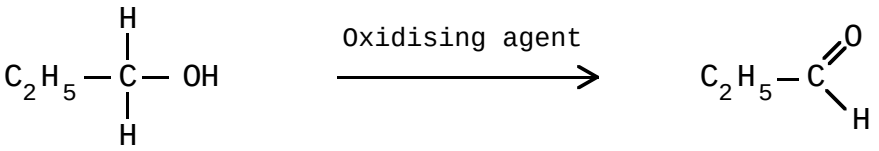
Propan-1-ol

BP 97 ^{0}C

Reactions of Aldehydes and Ketones

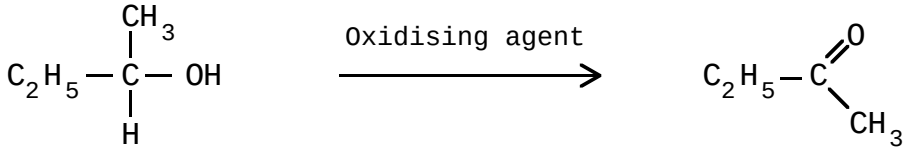
1. Reduction

Aldehydes are prepared by oxidation of primary alcohols e.g.



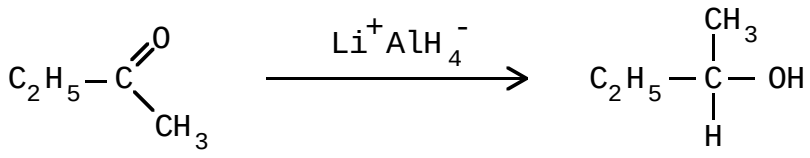
Propan-1-ol Propanal

Ketones are prepared by oxidation of secondary alcohols e.g.



Butan-2-ol Butanone

Since oxidation involves LOSS OF HYDROGEN, both aldehydes and ketones can be converted back to their parent alcohols by **reduction** (GAIN OF HYDROGEN). This is done using a solution of Lithium aluminium hydride in Ethoxyethane solvent e.g.



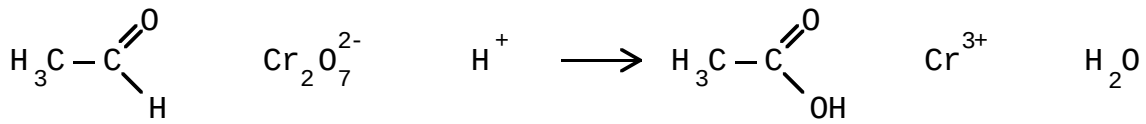
Butanone Butan-2-ol

2. Oxidation

Aldehydes can be oxidised to carboxylic acids by a variety of oxidising agents.

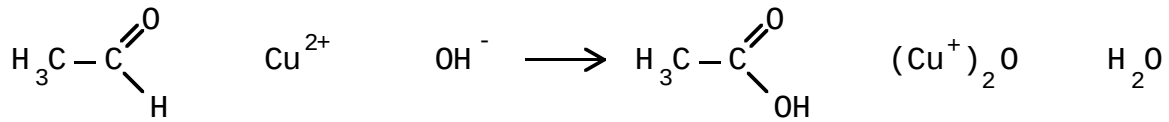
e.g. the oxidation of Propanal to Propanoic acid

(1) With acidified Potassium dichromate.



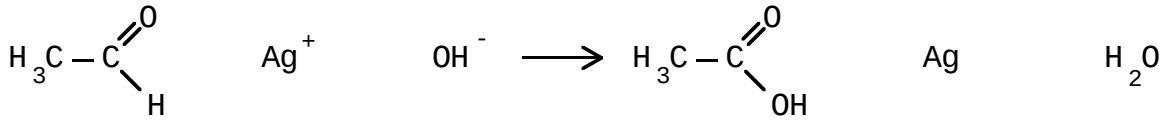
orange green

(2) With Benedict's solution - a solution containing OH^- and Cu^{2+}. Cu^{2+} is complexed with the citrate ion to prevent the reaction between Cu^{2+} and OH-.



blue brick-red

(3) With ammoniacal Silver(I) nitrate (Tollen's reagent) - a solution containing OH^- and Ag^+. Ag^+ is complexed with Ammonia to prevent the reaction between Ag^+ and OH^-.

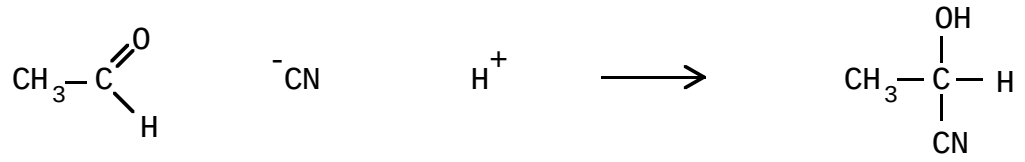


colourless silver mirror

Ketones CANNOT BE OXIDISED and therefore do not undergo the above three reactions. Since these reactions all involve colour changes they can be used to easily distinguish between aldehydes and ketones.

3. Addition

Both aldehydes and ketones undergo nucleophilic addition reactions.
e.g. reaction of Ethanal with acidified Sodium cyanide.

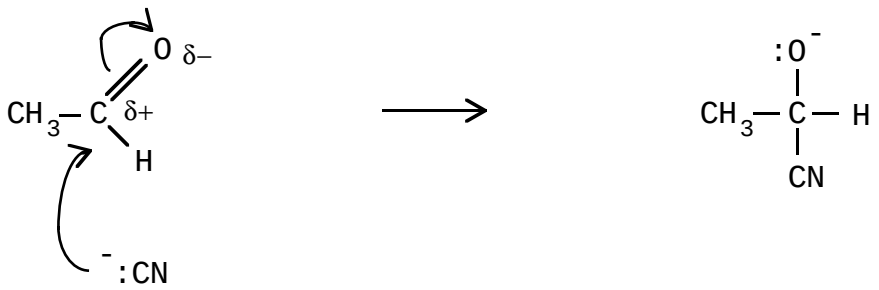


Ethanal Ethanal cyanohydrin

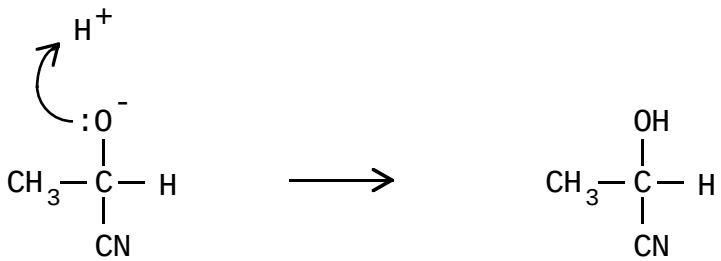
Mechanism (two steps)

STEP 1:

Nucleophilic attack by the cyanide ion at the $C^{\delta+}$ of the C=O group:



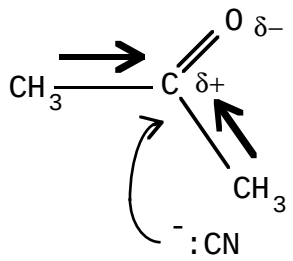
STEP 2:



Ketones undergo nucleophilic addition more slowly.

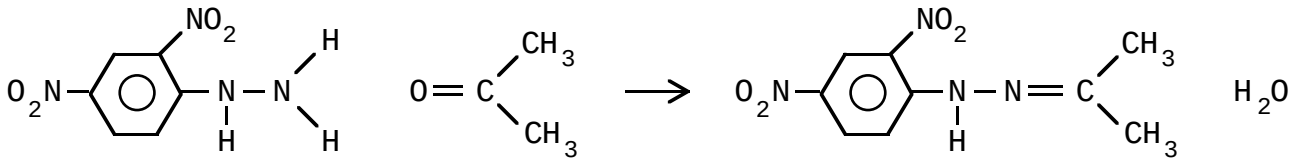
The presence of **TWO** alkyl groups:

- hinders attack by the nucleophile
- reduces the δ+ charge on the carbonyl Carbon atom due to the alkyl group's inductive effect



4. Condensation

Both aldehydes and ketones undergo condensation reactions. e.g. reaction of Propanone with 2,4-Dinitrophenylhydrazine.

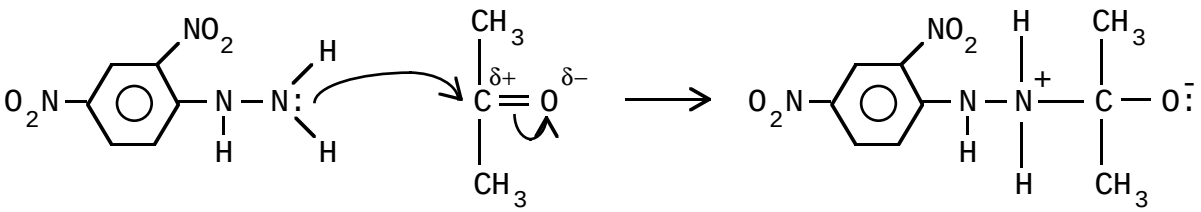


Propanone 2,4-dinitrophenylhydrazone

Mechanism (three steps)

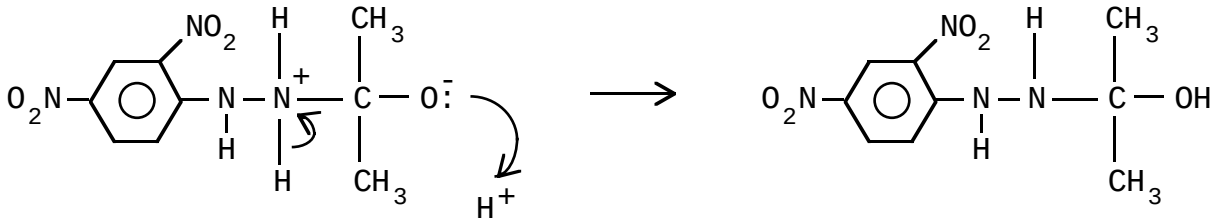
STEP 1:

Nucleophilic attack by 2,4-Dinitrophenylhydrazine at the $C^{\delta+}$ of the C=O group:



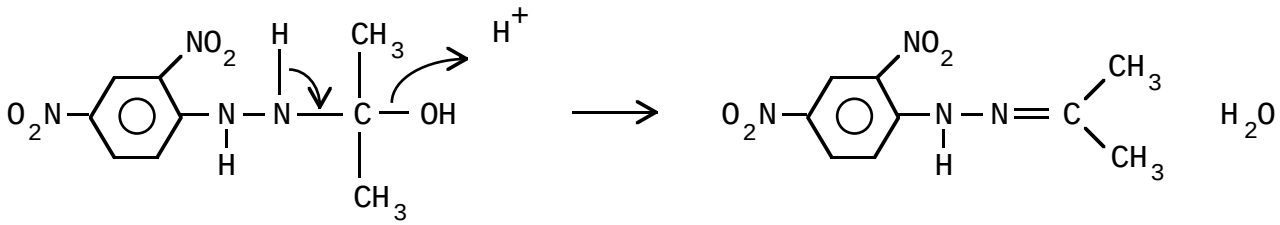
STEP 2:

Proton transfer:



STEP 3:

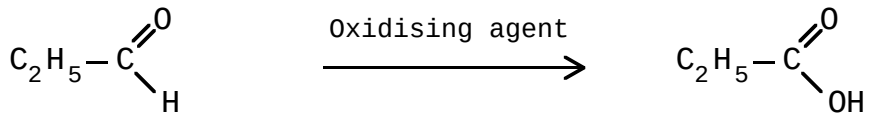
Proton transfer and subsequent elimination of water:



The melting points of the resulting 2,4-Dinitrophenylhydrazones are used to identify carbonyl compounds.

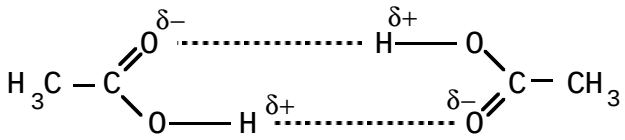
Carboxylic Acids

One method of preparing Carboxylic acids is by the oxidation of aldehydes e.g.

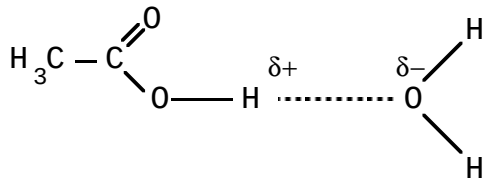


Propanal Propanoic acid

In pure carboxylic acids, hydrogen bonding produces dimers. The larger surface area of these dimers results in stronger van der Waals bonding between the dimers and high boiling points e.g. Ethanoic acid BP 118 ^{0}C.



Dimerisation does not occur in aqueous solution. Instead, hydrogen bonds form between the acid and water molecules thus explaining the appreciable solubility of the lower acids in water:

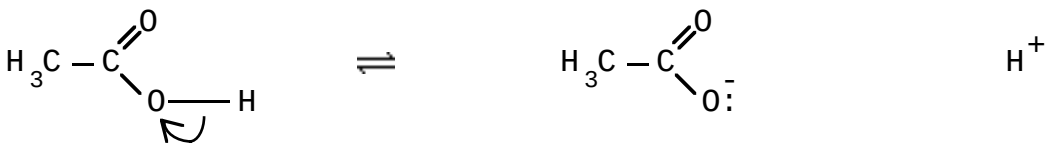


As the chain length increases water solubility decreases.

Reactions of Carboxylic Acids

1. Weak Acids

e.g. Ethanoic acid, $K_a = 1.7 \times 10^{-5}$ mol l^{-1}

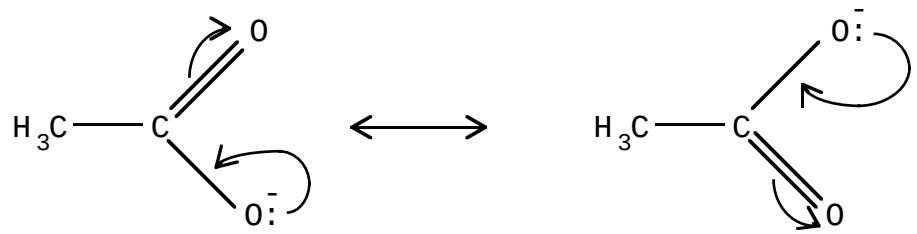


Ethanoate ion

Ionisation in carboxylic acids occurs more readily than ionisation in alcohols e.g. Ethanol K_a = ~ 1.0 x 10^{-16} mol l^{-1}

Ethoxide ion

Resonance in the ethanoate ion reduces the negative charge on O^-:



This renders O less attractive to attack by H^+ and thus reduces reversal. There is therefore a fairly high concentration of H^+ ions free in a solution of Ethanoic acid in water.

Resonance cannot occur in the ethoxide ion. Reversal is much more extensive and there are thus fewer H^+ ions in solution of Ethanol in water.

Carboxylic acids undergo the normal reactions of acids e.g.

(a) Reaction with metals

e.g. $CH_3COOH + Na \rightarrow CH_3COO^-Na^+ + H_2$

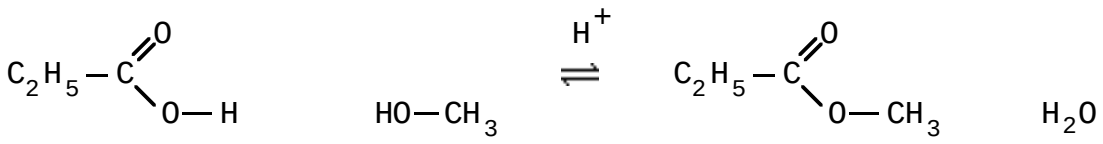
(b) Reaction with bases

e.g. $CH_3COOH + Na^+OH^- \rightarrow CH_3COO^-Na^+ + H_2O$

e.g. $CH_3COOH + Mg^{2+}CO_3^{2-} \rightarrow (CH_3COO^-)_2Mg^{2+} + CO_2 + H_2O$

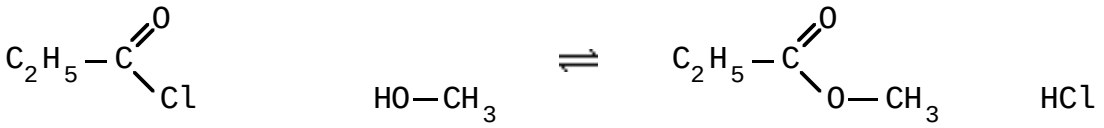
2. Reaction with Alcohols

Carboxylic acids undergo condensation reactions with alcohols, in the presence of concentrated Sulphuric acid catalyst, to form esters e.g.



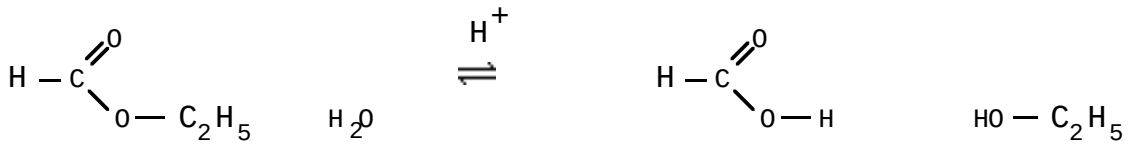
Propanoic acid Methanol Methyl propanoate

The reaction is slow. Esters are therefore often prepared by the much faster reaction between an alcohol and an acid chloride e.g.



Propanoyl chloride Methanol Methyl propanoate

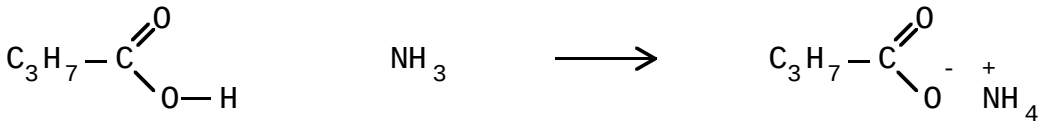
Since esterification is reversible carboxlic acids can be prepared by hydrolysis of the appropriate ester e.g.



Ethyl methanoate Methanoic acid

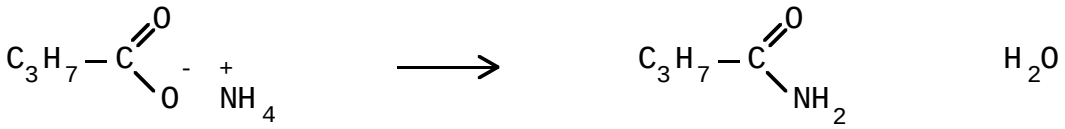
3. Reaction with Ammonia

Carboxylic acids react with Ammonia forming the ammonium salt e.g.



Butanoic acid Ammonium butanoate

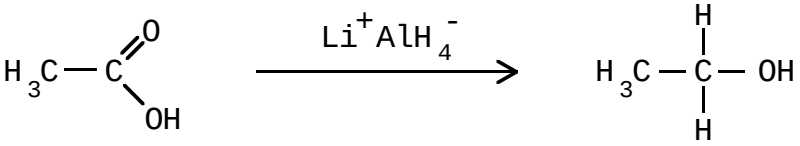
Subsequent heating of the ammonium salt produces an amide:



Butanamide

4. Reduction

Carboxylic acids can be reduced to the corresponding primary alcohol with a solution of Lithium aluminium hydride in Ethoxyethane solvent e.g.

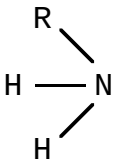
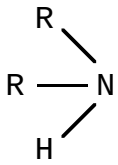
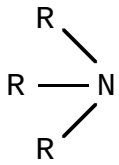
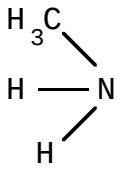
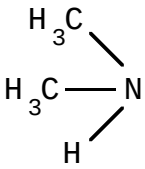
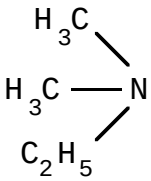


Ethanoic acid Ethanol

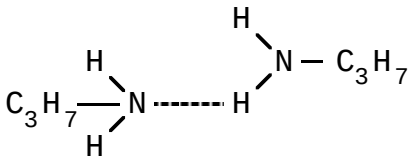
Amines

Amines are compounds of general formula NR_3 where R = alkyl or H.

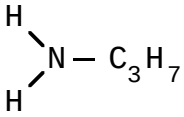
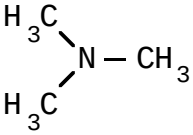
Amines are classified according to the number of alkyl groups (R) bonded to the Nitrogen atom:

PRIMARY	SECONDARY	TERTIARY
		
e.g. 		
Aminomethane (Methylamine)	N-Methyl aminomethane (Dimethylamine)	N,N-Dimethyl aminoethane (Ethyldimethylamine)

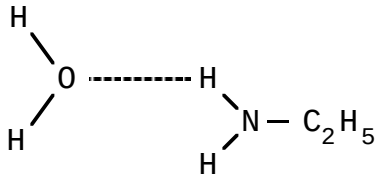
Primary and secondary amines, but not tertiary amines, associate by hydrogen bonding e.g. 1-Aminopropane



As a result, primary and secondary amines have higher boiling points than isomeric tertiary amines and alkanes with comaparable formula mass e.g.

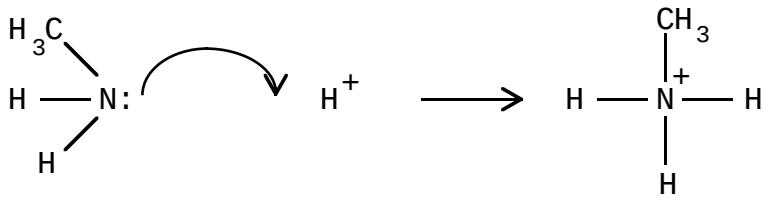
		C_4H_{10}
1-Aminopropane	N,N-Dimethylaminomethane	Butane
BP 49 ^0C	BP 7.5 ^0C	BP 0 ^0C

Amine molecules can hydrogen bond with water molecules thus explaining the appreciable solubility of the lower amines in water e.g. Aminoethane



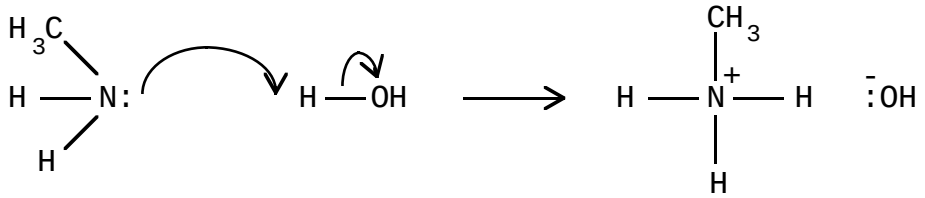
Reactions of Amines

The Nitrogen atom has a lone pair of electrons which can accept protons e.g.



Amines are thus weak **bases**.

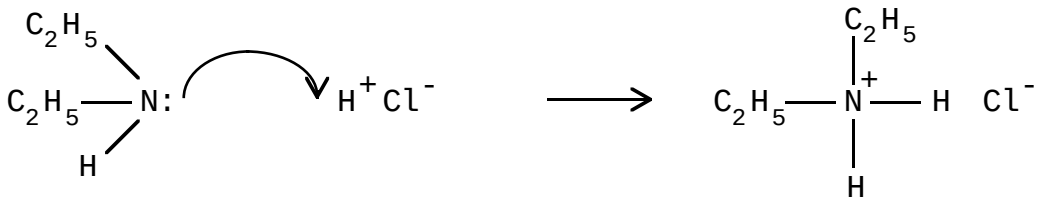
They react with Water to form alkaline solutions e.g.



They react with other acids to form salts.

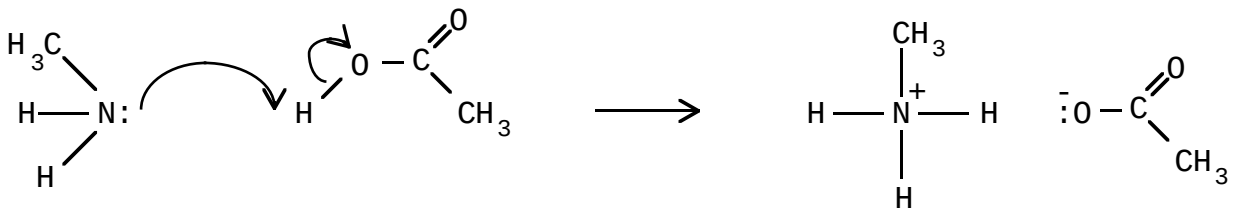
Example 1.

Reaction of N-Ethylaminoethane with dilute Hydrochloric acid:



Example 2.

Reaction of Aminomethane with Ethanoic acid:

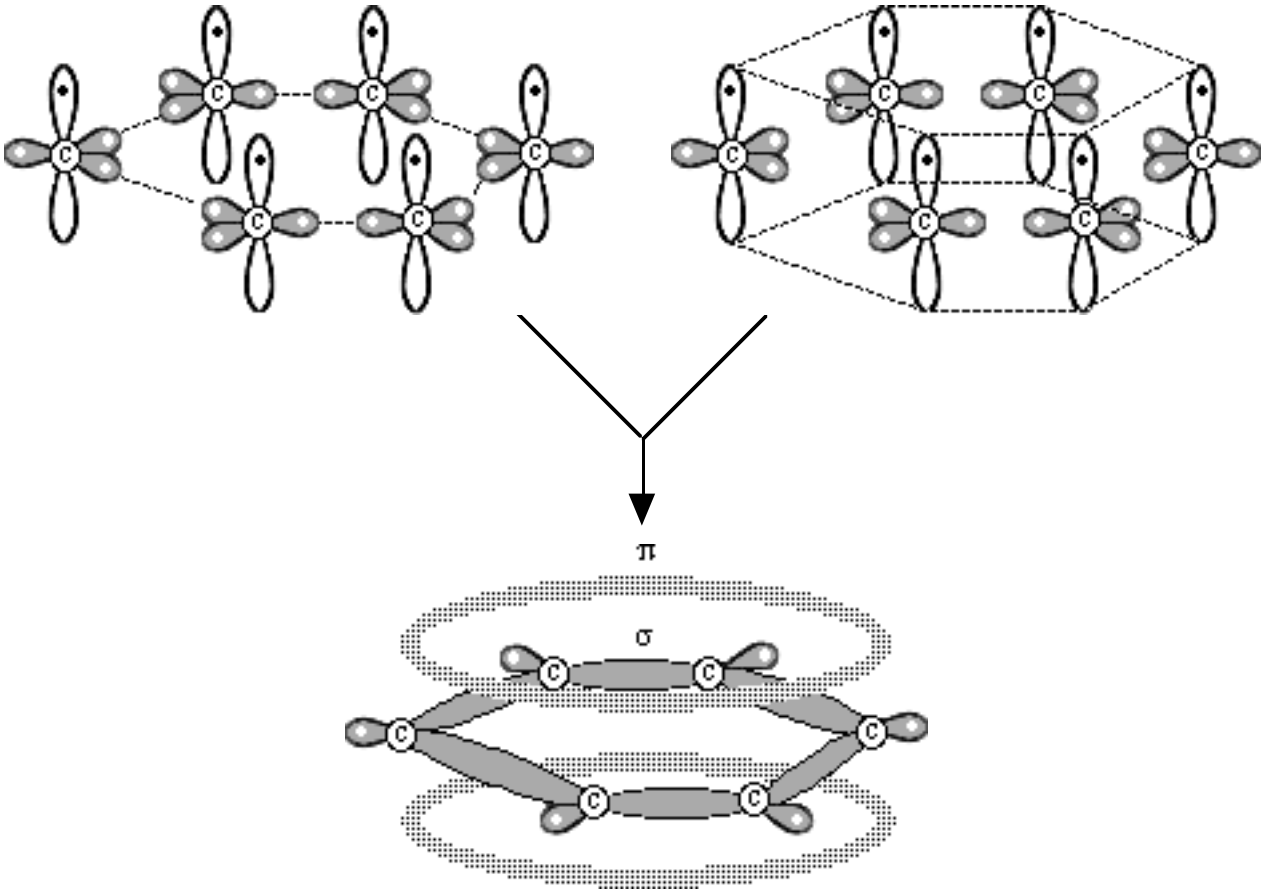


Aromatics

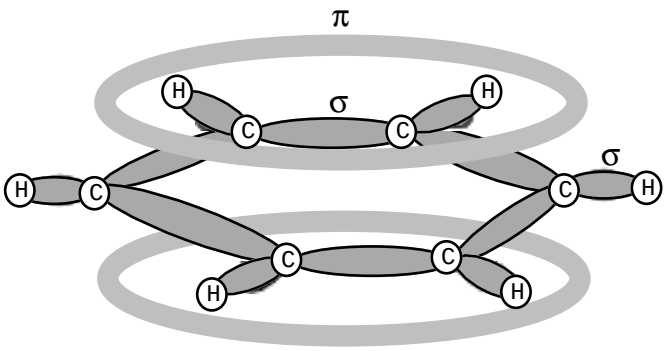
Compounds containing a benzene ring are described as **aromatic**; compounds which do not, are described as **aliphatic**.

The Carbon atoms in Benzene are SP^2 hybridised.
Bonding within the ring is a combination of σ bonding between the SP^2 hybrid orbitals and π bonding between the P_z orbitals:

σ bonding π bonding



C-H bonds are formed by σ overlap:



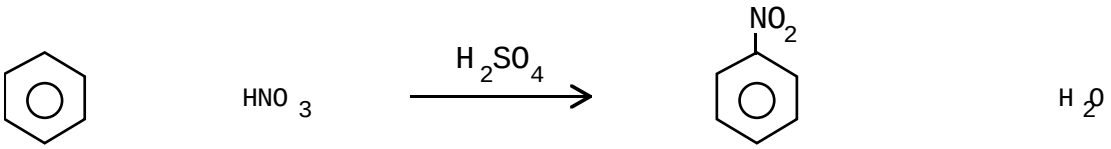
The 6 electrons in the π orbital move around the ring - they **delocalise**. Not confined to a single bond where they would be attracted by only two nuclei, these delocalised electrons are attracted by six nuclei and are therefore stabilised and strongly attracted to the ring. It is therefore paradoxical that it it these electrons which take part in the reactions of Benzene!

Reactions of Benzene

In most of the reactions of Benzene, the ring remains intact, held together by the delocalised electrons. Reactions usually involve **substitution of the Hydrogen atoms.**

Example

Reaction with concentrated Nitric acid using concentrated Sulphuric acid catalyst:



Nitrobenzene

The reaction is known as nitration.

Mechanism (three steps)

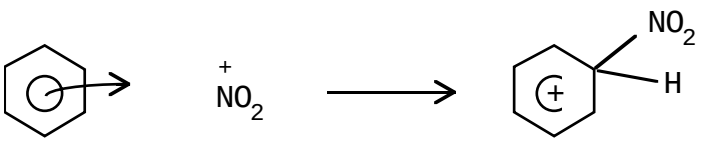
STEP 1:

Nitric acid and Sulphuric acid react:

$HNO_3 + H_2SO_4 \rightarrow HSO_4^- + H_2O + NO_2^+$

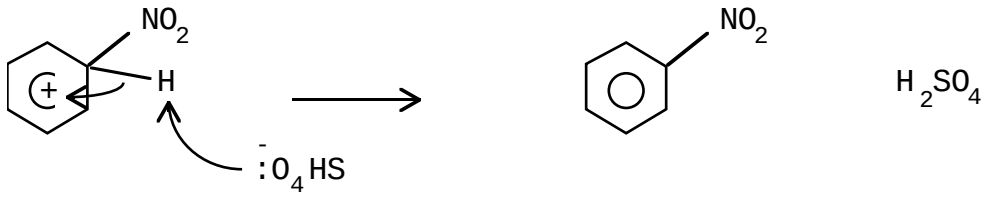
STEP 2:

The nitronium ion NO_2^+ is an electrophile. It attracts two of the delocalised electrons in the Benzene ring and bonds to one of the Carbon atoms:



STEP 3:

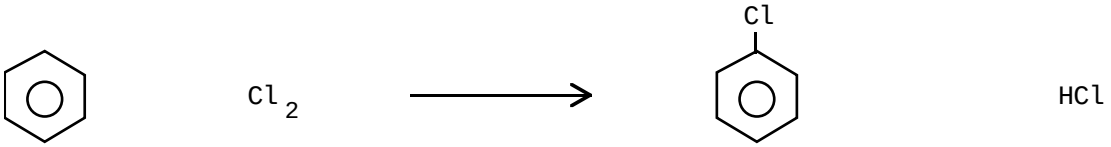
The delocalisation has been disrupted! Two electrons must re-enter the ring immediately! The HSO_4^- ion attacks:



This is substitution of Hydrogen by the electrophile NO_2^+ and is therefore known as **electrophilic substitution**.

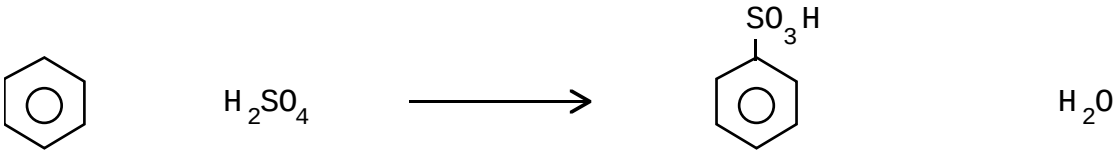
Other electrophilic substitution reactions of Benzene

With Chlorine or Bromine e.g.



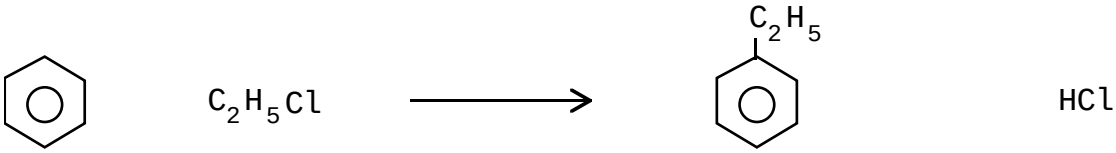
Chlorobenzene

With conc. Sulphuric acid, a reaction known as sulphonation:



Benzene sulphonic acid

With Chloroalkanes to form alkyl benzenes e.g.



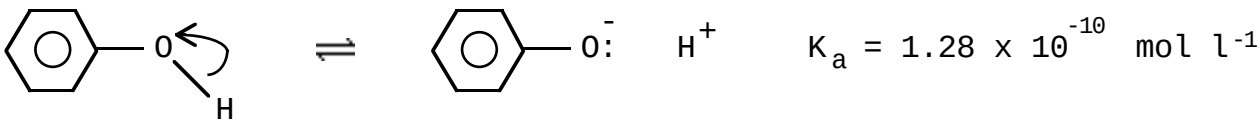
Ethyl benzene

Other Aromatic Compounds

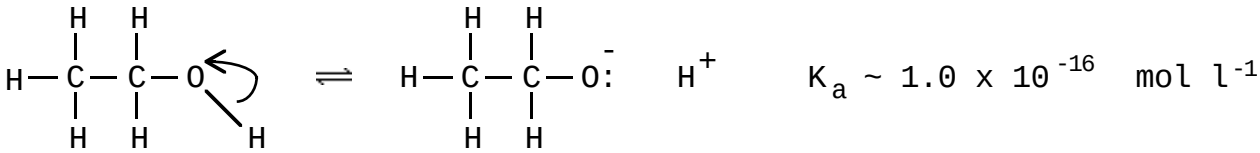
Hydroxybenzene (Phenol)

Phenol (K_a = 1.28 x 10^{-10} mol l^{-1}) is a stronger acid than aliphatic alcohols.

Ionisation in Phenol occurs more readily than ionisation in alcohols

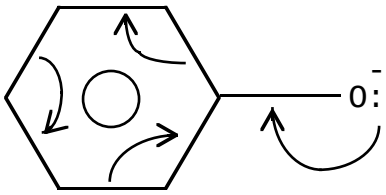


Phenol Phenoxide ion



Ethanol Ethoxide ion

Delocalisation of electrons into the Benzene ring in the phenoxide ion reduces the negative charge on O^-:



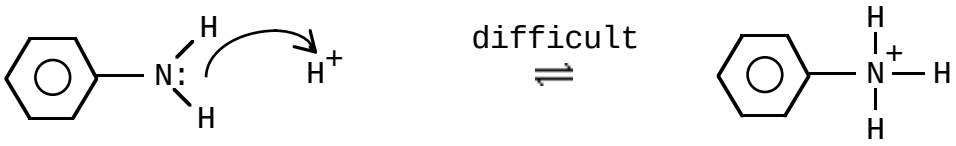
This renders O less attractive to attack by H^+ and thus reduces reversal. There is therefore a fairly high concentration of H^+ ions free in a solution of Phenol in water.

Delocalisation cannot occur in the ethoxide ion. Reversal is much more extensive and there are thus fewer H^+ ions in a solution of Ethanol in water.

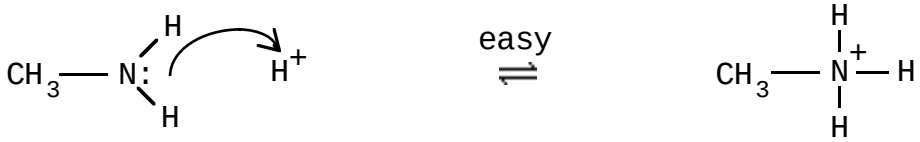
Aminobenzene (Aniline)

Aniline is a weaker base than aliphatic amines.

Donation of the lone pair is more difficult in Aniline:

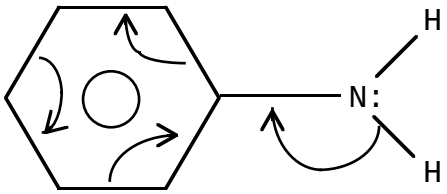


Aniline



Aminomethane

Delocalisation of the lone pair into the Benzene ring in Aniline makes donation of the lone pair to H^+ more difficult.



Delocalisation cannot occur in aliphatic amines. Donation of the lone pair to H^+ is therefore easier.