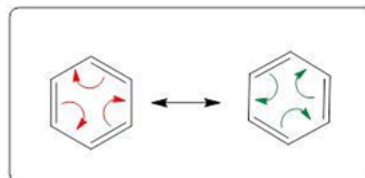
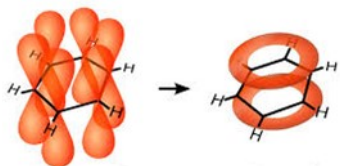
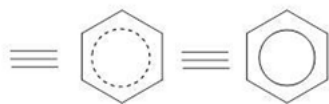


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Bond	Length/nm
C-C	0.154
C---C (in benzene)	0.140
C=C	0.134



Benzene 2 Resonance forms



Hybrid Forms

2. Benzene - Physical properties

Benzene was first isolated by Michael Faraday in 1825 and is now a major feedstock used in many industries:

- Polymers
- Pharmaceuticals
- Dyes
- Explosives.

Benzene itself is highly carcinogenic. It is the simplest arene with an empirical formula of CH and a molecular formula of C_6H_6 .

- The C-C bond length in benzene is an intermediate between a C-C single bond and a C=C double bond.
- Benzene is more stable than the hypothetical cyclohexa-1,3,5-triene because of electron delocalisation.
- Each C atom has three covalent bonds - one to a H atom and the other two to C atoms. The fourth electron of each C atom is in a p-orbital. The p-orbitals overlap and the electrons in them are delocalised. This forms an area of electron density above and below the ring to form a π cloud.
- Benzene is planar and the C-C bonds are equal in length.

2. Benzene - Reactivity

- Benzene combusts like other hydrocarbons and tends to produce very smoky flames. This is due to the high carbon:hydrogen ratio, this leaves a lot of carbon unburnt.
- Benzene has electrophilic substitution reactions in preference to addition reactions.
- Benzene does not discolour bromine water.

Electrophilic substitution - Nitration

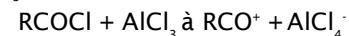
• The electrophile (NO_2^+) is made in the reaction mixture of concentrated nitric acid and concentrated sulfuric acid. The overall equation for the formation of the electrophile is:



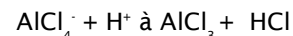
- The H^+ then reacts with the HSO_4^- to regenerate H_2SO_4 - the sulfuric acid is a catalyst.

Electrophilic substitution - Friedel-Crafts acylation

• It uses aluminium chloride as a catalyst. RCO substitutes for a hydrogen on the aromatic ring. • Acyl chlorides provide the RCO group, reacting with $AlCl_3$

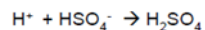
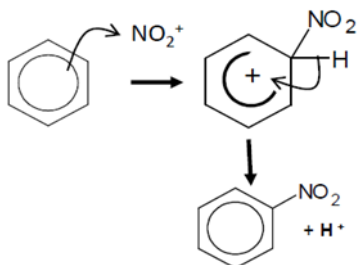


- The aluminium chloride is then reformed by reacting with H^+ from the benzene ring:



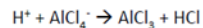
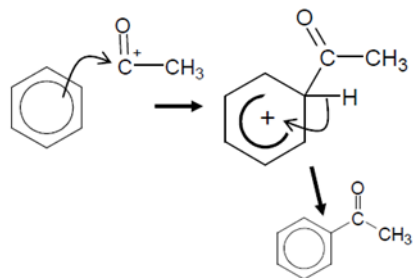
Electrophilic Substitution

Equation for Formation of electrophile
 $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

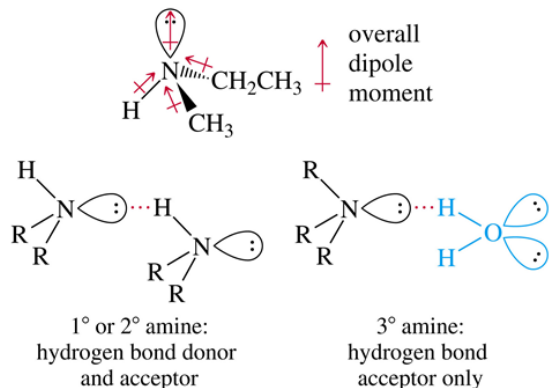


Electrophilic Substitution

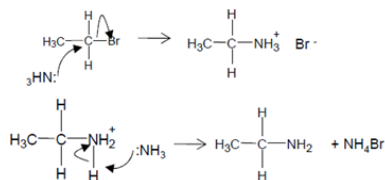
Equation for Formation of the electrophile.
 $AlCl_3 + CH_3COCl \rightarrow CH_3CO^+ + AlCl_4^-$



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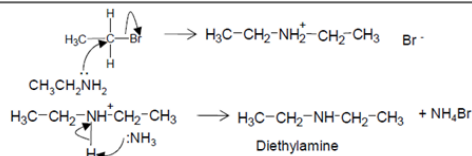


Reaction 1 with ammonia forming primary amine

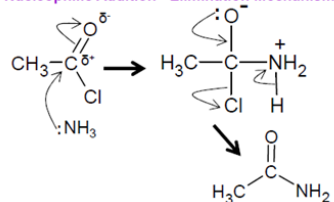


Reaction 2 forming secondary amine

The amine formed in the first reaction has a lone pair of electrons on the nitrogen and will react further with the haloalkane.



Nucleophilic Addition - Elimination Mechanism



1. Physical properties

- Amines are derivatives of ammonia, where one or more hydrogen atoms are replaced by alkyl or aryl groups.
- They are very reactive compounds

Nomenclature

- Amines are classified into primary secondary and tertiary based on the number of substituents bonded to the nitrogen.
- If there are more than one group attached to the amine we use N-R putting substituent in alphabetical order
- For secondary or tertiary amines each group from the amine group is named separately, the longest has the suffix -amine
- Amines are pyramidal molecules have all angles of approximately 107 degrees
- Short Amines are gases, longer ones are volatile liquids and have fishy smells.

2. Reactivity

Preparation :

- by reaction of ammonia with halogenoalkanes (Nucleophilic substitution)

The 1° amine can then act as a nucleophile and react with the halogenoalkane to produce a 2° amine, which can react to give a 3° amine, which in turn will react to make a 4° ammonium salt. This is not efficient.

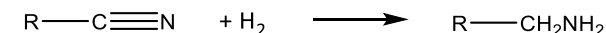
Preparation by reduction of nitriles:

Step 1: Halogenoalkanes react with a cyanide ion in aqueous ethanol. The ion replaces the halide ion by nucleophilic substitution to form a nitrile.



Step 2:

Nitriles can be reduced to primary amines with a nickel/hydrogen catalyst.



- Electrophilic substitution (nitration) of benzene. Nitrobenzene is then reduced to phenylamine using tin and HCl as the reducing agent:

Amines can act as bases

- Amines can accept a proton so they are weak Bronsted-Lowry bases:
- Alkyl groups release electrons towards the nitrogen atom, this is called inductive effect. The nitrogen is a stronger electron pair donor and so more attractive to protons.
- 1° alkylamines are stronger bases than ammonia because the inductive effect of the alkyl group increases the electron density on the N atom and makes it a better electron pair donor.
- 2° alkylamines have two inductive effects = stronger bases.
- 3° alkylamines = not strong because they are poorly soluble in water.
- Aryl groups withdraw electrons from the nitrogen atom. The nitrogen is a weaker electron pair donor and so less attractive to protons, so aryl amines are weaker bases than ammonia.