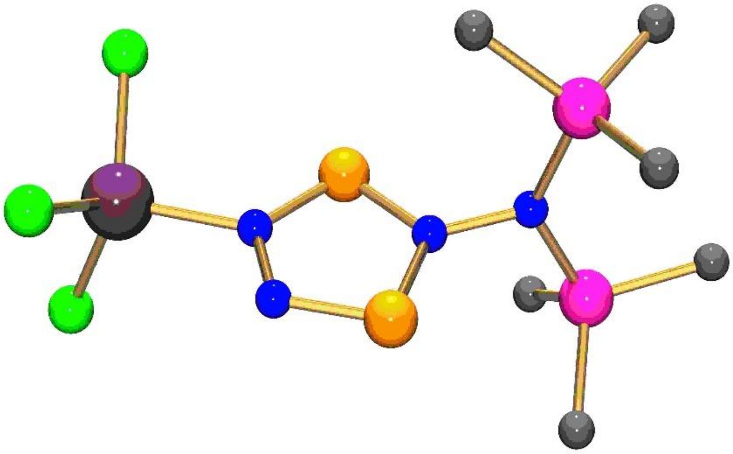
A2 Level

Chemistry

CODE: (9701)

Chapter 27

Organic nitrogen compounds



Amines

Classes of amines

There are three classes of amine: primary, secondary and tertiary

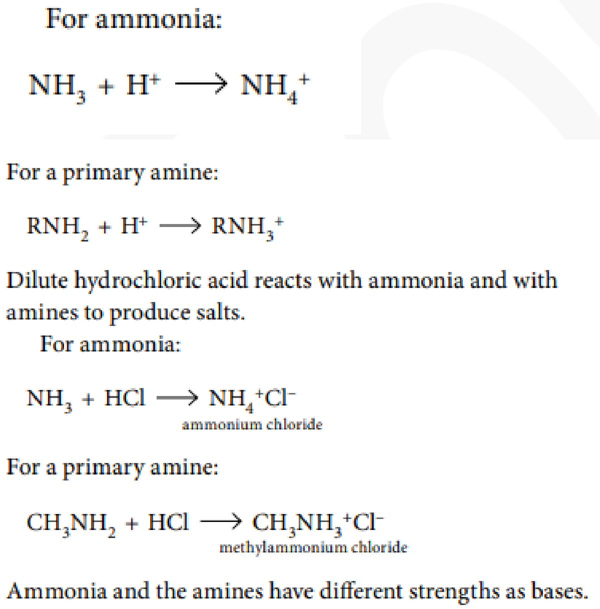
■ Primary amines have an NH2 group bonded to an alkyl or aryl group, like ethylamine or phenylamine. Some amines do not have an NH_2 group at the end, referred to as the 'amino' group.

■ Secondary amines have two alkyl or aryl groups attached to an NH group, e.g. dimethylamine, $(CH_3)_2NH$ (Figure 27.3).

■ Tertiary amines have three alkyl or aryl groups attached to the same nitrogen atom

The basicity of amines

Amines are substituted ammonia molecules, such as primary amines, which act as bases due to the lone pair of electrons on the nitrogen atom, forming a co-ordinate (dative) bond with an H+ ion.



For ammonia:

$$NH_3 + H^+ \longrightarrow NH_4^+$$

For a primary amine:

$$RNH_2 + H^+ \longrightarrow RNH_3^+$$

Dilute hydrochloric acid reacts with ammonia and with amines to produce salts.

For ammonia:

$$NH_3 + HCl \longrightarrow \underset{\text{ammonium chloride}}{NH_4^+Cl^-}$$

For a primary amine:

$$CH_3NH_2 + HCl \longrightarrow \underset{\text{methylammonium chloride}}{CH_3NH_3^+Cl^-}$$

Ammonia and the amines have different strengths as bases.

Ethylamine is a stronger base than ammonia due to its electron-donating nature, allowing a lone pair to bond more readily with an H+ ion.

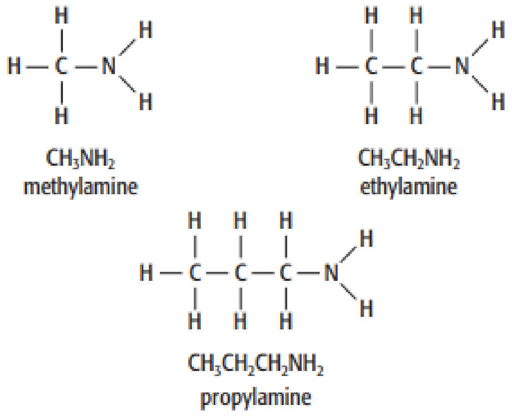


Figure 27.2 Three primary amines.

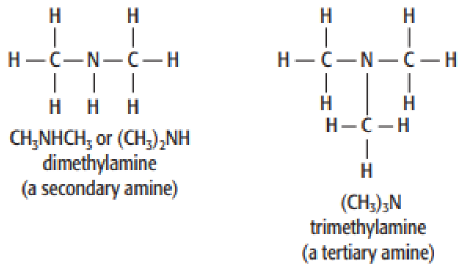
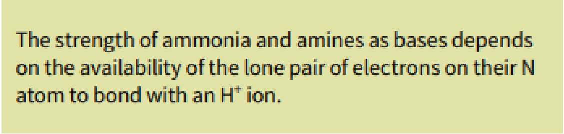
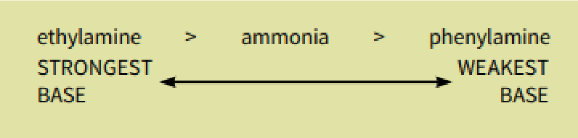


Figure 27.3 A secondary amine and a tertiary amine.

- Tertiary amines have three alkyl or aryl groups attached to the same nitrogen atom, e.g. trimethylamine, $(CH_3)_3N$ (shown in Figure 27.3).



The strength of ammonia and amines as bases depends on the availability of the lone pair of electrons on their N atom to bond with an H^+ ion.



ethylamine > ammonia > phenylamine

STRONGEST BASE ⟷ WEAKEST BASE

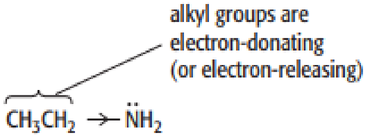
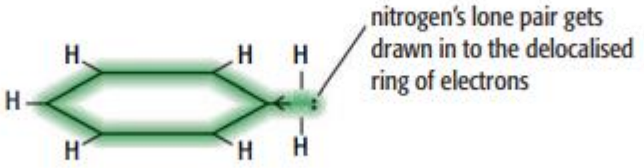


Figure 27.4 Ethylamine is a stronger base than ammonia.

Formation of amines



nitrogen's lone pair gets drawn in to the delocalised ring of electrons

Figure 27.5 Phenylamine is a very weak base.

Making ethylamine

1. Chapter 16 explains bromoethane's nucleophilic substitution with ammonia to create amine mixtures, using excess hot ethanolic ammonia to prepare ethylamine without secondary and tertiary amines and ammonium salts.

$$CH_3CH_2Br + NH_3 \longrightarrow \underset{\text{ethylamine}}{CH_3CH_2NH_2} + HBr$$

2. Chapter 16 explains the formation of nitriles by reacting a halogenoalkane with the CN– ion, using a potassium cyanide solution in ethanol under reflux.

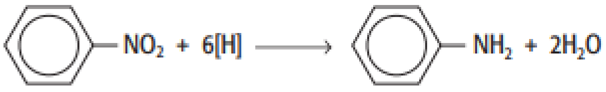
$$\underset{\text{bromomethane}}{CH_3Br} + CN^- \longrightarrow \underset{\text{ethanenitrile}}{CH_3CN} + Br^- \qquad CH_3CN + 4[H] \longrightarrow \underset{\text{ethylamine}}{CH_3CH_2NH_2}$$

3.We can also use $LiAlH_4$ in dry ether to reduce amides to amines. So ethanamide will be reduced ethylamine

$$\underset{\text{ethanamide}}{CH_3CONH_2} + 4[H] \longrightarrow \underset{\text{ethylamine}}{CH_3CH_2NH_2} + H_2O$$

Preparing phenylamine

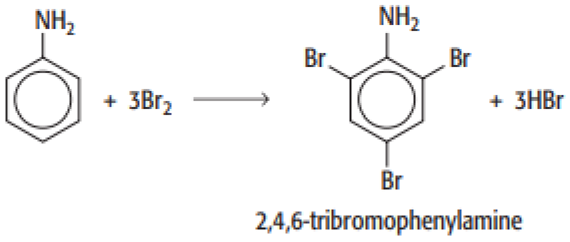
Phenylamine is made by reducing nitrobenzene. This reduction is carried out by heating nitrobenzene with tin (Sn) and concentrated hydrochloric acid



Reactions of phenylamine

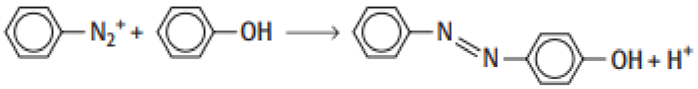
Phenylamine with aqueous bromine

The reaction between aqueous bromine and phenylamine produces a white precipitate, similar to the reaction with phenol. The NH_2 group in phenylamine has a lone pair of electrons, extending the π bonding system and making it more easily attacked by electrophiles.



This reaction is called **diazotisation.**

In the second step, the diazonium ion reacts with an alkaline solution of phenol in a **coupling** reaction:



The diazonium ion, acting as an electrontrophile, substitutes into phenol's benzene ring, forming an orange dye called an **azo dye**. The stable π bonding system extends between the rings, making it a good dye.

By using alternative aryl compounds to phenol, we can make a range of brightly coloured dyes. For example, Figure 27.8 shows a molecule of a compound used as a yellow dye.

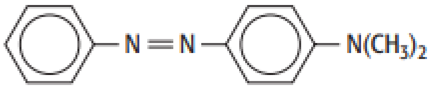


Figure 27.8 A molecule of a yellow azo dye. Instead of phenol, C_6H_5OH, the reactant used in the coupling reaction is $C_6H_5N(CH_3)_2$.

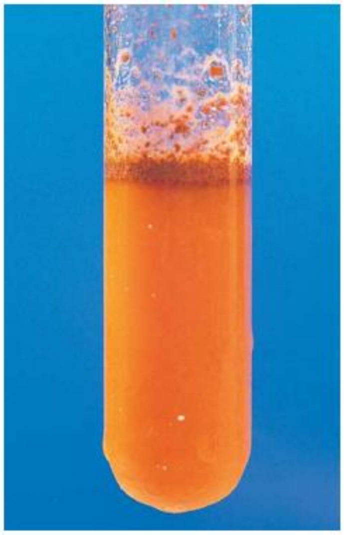
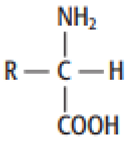


Figure 27.7 The azo dye (also called a diazonium dye) forms in a coupling reaction between the diazonium ion and an alkaline solution of phenol.

Amino acids

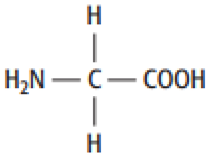
The general structure of a 2-amino-carboxylic acid molecule is shown in Figure 27.9



$$R-\overset{NH_2}{\underset{COOH}{C}}-H$$

Figure 27.9 The general structure of a 2-amino-carboxylic acid.

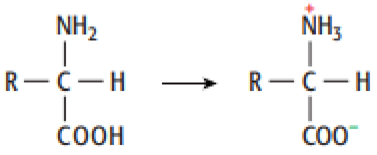
The R group is the part of the amino acid that can vary in different amino acids. The simplest amino acid is glycine (systematic name aminoethanoic acid) in which R is an H atom:



$$H_2N-\overset{H}{\underset{H}{C}}-COOH$$

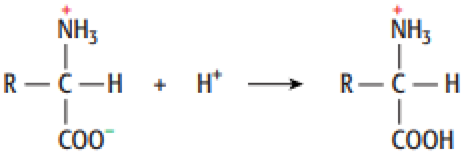
glycine (aminoethanoic acid)

Amino acids will undergo most reactions of amines and carboxylic acids. However, each molecule can interact within itself due to its basic ---NH₂ group and its acidic -----COOH group

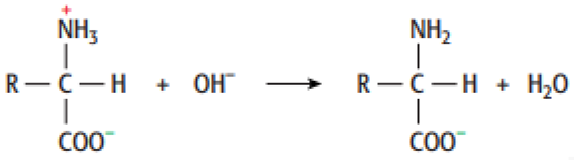


$$R-\overset{NH_2}{\underset{COOH}{C}}-H \longrightarrow R-\overset{\overset{+}{N}H_3}{\underset{COO^-}{C}}-H$$

If acid is added, the ---COO– part of the zwitterion will accept an H+ ion, re-forming the undissociated ---COOH group. This leaves a positively charged ion:

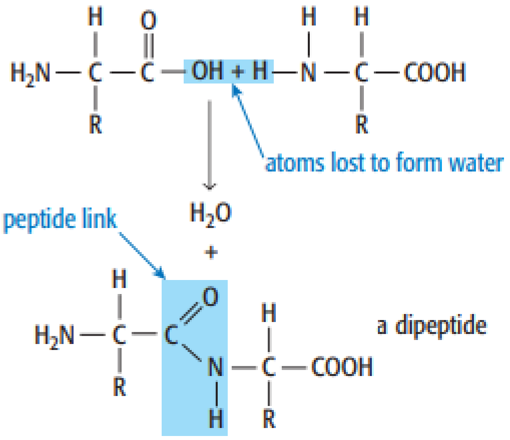


If alkali is added, the —NH_3^+ part of the zwitterion will donate an H+ ion to the hydroxide ion ($H^+ + OH^- \longrightarrow H_2O$), re-forming the amine —NH_2 group. This leaves a negatively charged ion:



Peptides

When two amino acids react together, the resulting molecule is called a **dipeptide:**

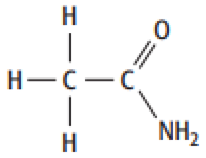


The reaction is a **condensation reaction** as a small molecule, in this case water, is eliminated when the reactant molecules join together.

The reaction can continue, to form a **tripeptide** initially, and then ever-longer chains of amino acids. The longer molecules become known as **polypeptides**, and then proteins as they get even longer sequences of amino acids.

Reactions of the amides

Unlike the basic amines met at the start of this chapter, the amides are neutral compounds. The presence of the electron-withdrawing oxygen atom in the amide group means that the lone pair on an amide's nitrogen atom is not available to donate to electron deficient species, such as H+ ions.



ethanamide

Making an amide

Ethanamide can be made by reacting ethanoyl chloride with concentrated ammonia solution:

$$CH_3COCl + NH_3 \longrightarrow CH_3CONH_2 + HCl$$

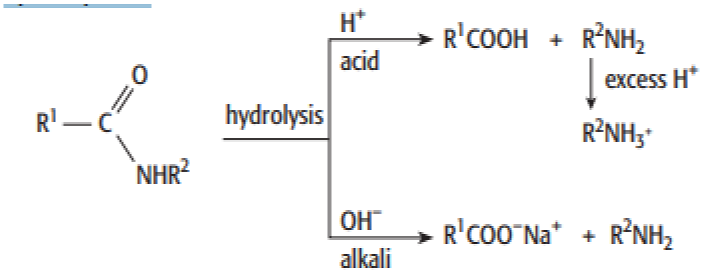
A primary amine, such as ethylamine, reacts with an acyl chloride to produce a substituted amide

$$C_3H_7COCl + C_2H_5NH_2 \longrightarrow C_3H_7CONHC_2H_5 + HCl$$

Both these reactions occur at room temperature, releasing white fumes of hydrogen chloride as soon as the reactants are added together. If there is an excess of the amine, it will react with the HCl formed to make its salt

Hydrolysis of amides

The characteristic CONH— group in substituted amides links the two hydrocarbon sections of their molecules together. This link can be broken by hydrolysis with an acid or an alkali. The amide is refluxed with, for example, hydrochloric acid or sodium hydroxide solution, to hydrolyse it:



Hydrolysis of a substituted amide with acid produces carboxylic acid (R^1COOH) and primary amine (R^2NH_2). The amine reacts with excess acid to form ammonium salt. When alkali is used, the products are sodium salt of carboxylic acid and primary amine.

Electrophoresis

How electrophoresis works

Electrophoresis is used extensively in biochemical analysis. It can be used to separate, identify and purify proteins. We can use it with amino acids and peptides obtained when a protein is hydrolysed.

The sample is placed on absorbent paper or gel, and ions move towards an oppositely charged electrode. The ions' size and charge determine their movement. An **electropherogram** shows a series of lines or bands, sometimes with ultraviolet light. For example, a mixture of three amino acids undergoes separation, with amino acid A having a positively charged side-chain, amino acid B neutral, and amino acid C negatively charged.

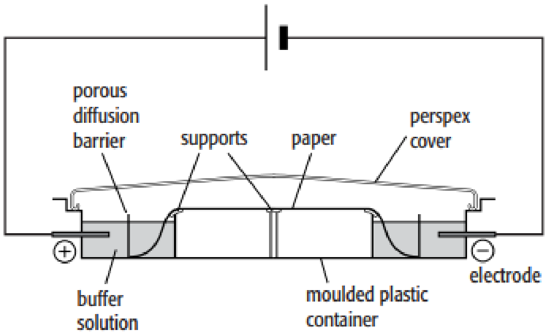


Figure 27.10 This apparatus shows how paper electrophoresis is carried out.

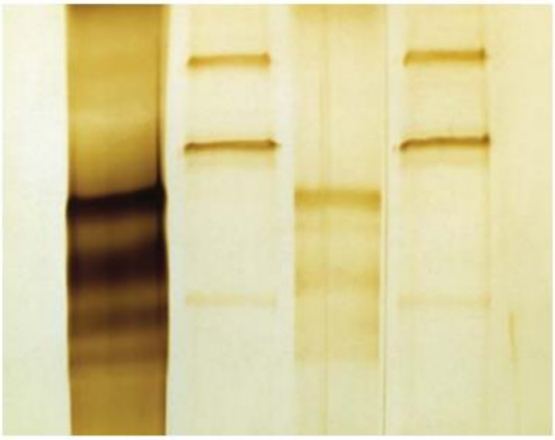


Figure 27.11 Comparing electropherograms.

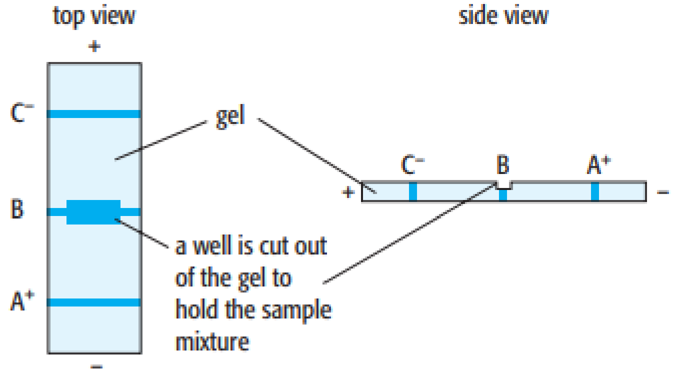


Figure 27.12 The principle of gel electrophoresis.

Figure 27.10 demonstrates the use of buffer solution in electrophoresis, emphasizing the importance of controlling pH in this process. The chemical structures in Figure 27.13 demonstrate how amino acids react in acidic and alkaline conditions, affecting ion movement.

At a pH of 7, the amino acid species present in samples of A, B and C are shown in Figure 27.13.

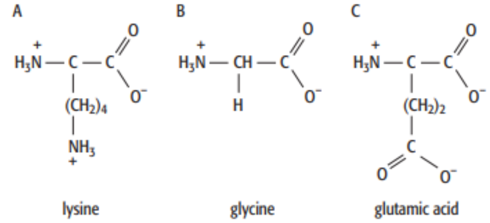


Figure 27.13 The charge on amino acids depends on the pH of the solution.

Revision questions

1)This question is about the reactions of some functional groups.

(a) (i) Draw the structural formula of an amide of your choice containing four carbon atoms.

(ii) What reagents and conditions are needed to hydrolyse this amide?

(iii) Write a balanced equation showing the hydrolysis of the amide whose structural formula you drew in part (i).

(b) (i) Draw the structural formula of an acyl chloride containing three carbon atoms.

(ii) What starting material and reagent are needed to form this acyl chloride?

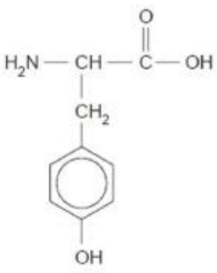
(iii) Write a balanced equation showing the formation of an ester containing five carbon atoms from the acyl chloride you drew in part (i).

2)The amino acids tyrosine, lysine and glycine are constituents of many proteins.

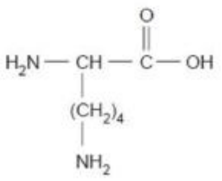
(a) State the reagents and conditions you could use to break proteins down into amino

(b) Draw a ring around each chiral centre in the above molecules.

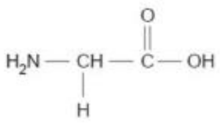
(c) In aqueous solution amino acids exist as zwitterions. Draw the zwitterionic structure of glycine.



tyrosine



lysine

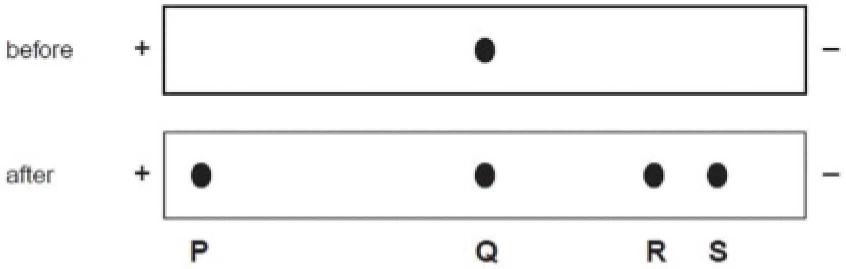


glycine

(d) For each of the following reactions, draw the structure of the organic compound formed.
(i) glycine + excess NaOH(aq)
(ii) tyrosine + excess NaOH(aq)

3)(a) Electrophoresis can be used to separate amino acids which are produced by the hydrolysis of a polypeptide. Using glycine as an example, explain why the result of electrophoresis depends on pH.

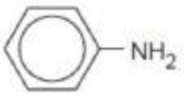
(b) The diagram below shows the results of electrophoresis in neutral solution. At the start of the experiment a spot of a solution containing a mixture of amino acids P, Q, R and S was placed in the middle of the plate. Following electrophoresis the amino acids had moved to the positions shown in the lower diagram.



(i) Which amino acid existed mainly as a zwitterion in the buffer solution? Explain your answer.
(ii) Assuming amino acids R and S carry the same charge when in this buffer solution, which is likely to be the larger molecule? Explain your answer.

(c) Amino acids may also be separated by using two-dimensional paper chromatography. This involves putting a spot of the mixture on the corner of a piece of chromatography paper and allowing a solvent to soak up the paper. The paper is then dried, turned through 90° and placed in a second solvent. This method gives better separation than a one solvent method.
(i) Paper chromatography relies on partition between the solvent applied and another phase.
What is this second phase?

4)Ethanolamine and phenylamine are two organic bases that are industrially important. Ethanolamine is a useful solvent with basic properties, whilst phenylamine is an important starting material in the manufacture of dyes and pharmaceuticals.
The following table lists some of their properties, together with those of propylamine.

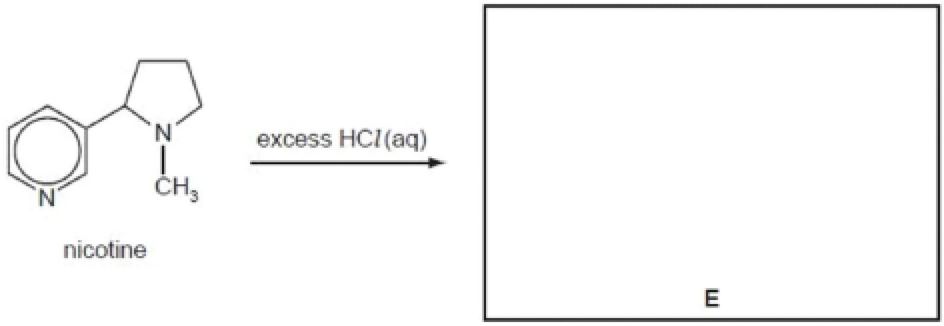
compound	formula	M_r	boiling point/ °C	solubility in water
propylamine	$CH_3CH_2CH_2NH_2$	59	48	fairly soluble
ethanolamine	$HOCH_2CH_2NH_2$	61	170	very soluble
phenylamine		93	184	sparingly soluble

(a) Suggest why the boiling point of ethanolamine is much higher than that of propylamine. Draw a diagram to illustrate your answer.

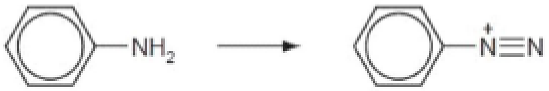
(b) Describe and explain the relative basicities of propylamine and phenylamine.
(c) Write an equation showing ethanolamine acting as a Brønsted-Lowry base.

5)Because of the lack of reactivity of the nitrogen molecule, extreme conditions need to be used to synthesise ammonia from nitrogen in the Haber process.
(a) Suggest an explanation for the lack of reactivity of the nitrogen molecule, N2
(b) Under conditions of high temperature, nitrogen and oxygen react together to give oxides of nitrogen.
(i) Write an equation for a possible reaction between nitrogen and oxygen.
(ii) State two situations, one natural and one as a result of human activities, in which nitrogen and oxygen react together.
(iii) What is the main environmental effect of the presence of nitrogen oxides in the atmosphere?
(c) Describe and explain how the basicities of ethylamine and phenylamine compare to that of ammonia.

6)(a) (1) Explain why ethylamine is basic.
(ii) Write an equation showing ethylamine acting as
a base,
a nucleophile.
(iii) Why is phenylamine less basic than ethylamine?
Alkaloids are naturally-occurring compounds that act as bases.
(iv) Suggest the structure of the product, E, of the reaction between the alkaloid nicotine and an excess of HCl(aq).



(b) Phenylamine, and substituted phenylamines, are used to make cloth dyes and food colourants.
The first step in this process is the production of a diazonium salt.



(i) State the reagents and conditions necessary for this reaction.