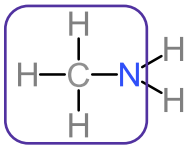
Organic Nitrogen Compounds

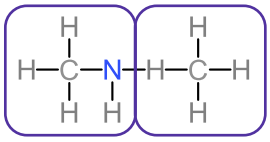
A. AMINES

- Amines are compounds that contain the amine functional group ($-NH_2$)

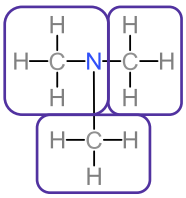
- Classes of Amines
  1. **Primary**
     One alkyl attached to Nitrogen atom



  2. **Secondary**
     Two alkyl attached to Nitrogen atom



  3. **Tertiary**
     Three alkyl attached to Nitrogen atom

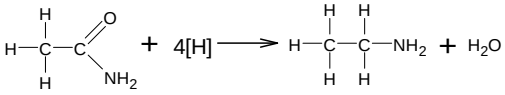


B. PRODUCTION OF AMINES

- Nucleophilic Substitution of Halogen
  There are two kind substitutes for this reaction
  1. **With Ammonia**
     $CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$
     Condition : Heated
     Solvent : Ethanol
  2. **With Primary Amine**
     $CH3CH2Cl + CH3CH2NH2 \rightarrow CH3CH2NH\ CH2\ CH3 + HCl$
     Condition: Heated in Sealed Tube
     Solvent : Ethanol

  Each substitutes have nitrogen atom and act as the nucleophile which replace the halogen atom in the halogenoalkane compound

- Reduction of Amides
  Amine could be produced from reduction of amides by $LiAlH_4$ in dry ether. The product of the reaction **depends on the classes of amides**



  Reducing agent: $LiAlH_4$

- Reduction of Nitriles
  Nitriles contain $-CN$ functional group and could be reduced to $-NH_2$ functional group by using reduction agent such as $LiAlH_4$ or hydrogen with Ni catalyst
  1. **With $LiAlH_4$**
     $CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2$
  2. **With H_2 Using Ni as a Catalyst**
     $CH_3CN + H_2 \rightarrow CH_3CH_2NH_2$

C. BASICITY OF AMINES

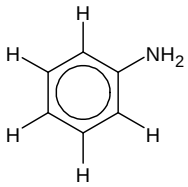
- Amines could act as a base in aqueous solutions by donating its lone pair of electrons to a proton (H^+) to make dative bond

- The more readily the lone pair is available, the stronger basicity of the amines

- There are also some factors that may affect the basicity of amines
  1. **Positive Inductive Effect**
     Groups like alkyl group **give electron density to the nitrogen atom** and make the lone pair electron become more available, so that, the basicity of the amines increases
  2. **Delocalisation**
     Delocalisation makes the lone pair electron of atom N become less available to form dative bond because it is withdrawn into the benzene ring and thus, it decreases the basicity of amines

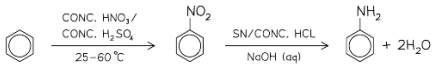
D. PRODUCTION AND REACTION OF PHENYLAMINE

- Phenylamine is an organic compound that contain benzene and amine functional group



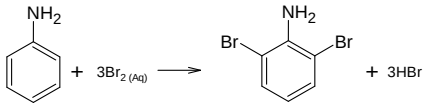
- Phenylamine is produced by three-steps synthesis followed by the separation of phenylamine from the mixture using steam distillation
  1. **Nitration**
     Benzene undergoes **nitration** with concentrated nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4) with **temperature at 25 to 60 °C** to form nitrobenzene

2. **Reduction of Nitrobenzene**
   Nitrobenzene is reduced with hot tin (Sn) and concentrated hydrochloric acid (HCl) under reflux to form an acidic mixture that contains the organic product $C_6H_5N^+H_3$
3. **Deprotonation**
   Sodium hydroxide (NaOH) is added to the acidic reaction mixture to form phenylamine
4. **Separation**
   The phenylamine is separated from the reaction mixture by steam distillation



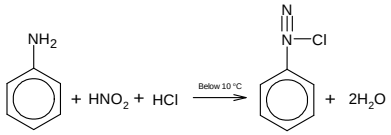
- Both benzene ring and amine functional group can take part in chemical reaction

1. **Bromination of Phenylamine**



2. **Formation of Diazonium Salt**
   Diazonium compounds are very reactive compounds containing an $-N_2^+$ group. The amine ($-NH_2$) group of phenylamines will react with nitric (III) acid (HNO_3) at a temperature below 10 °C to form diazonium salts.

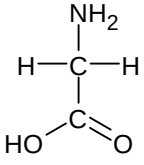
$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$



This salt is unstable so they will upon further warming with water to form phenol

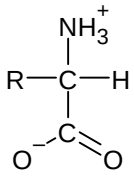
E. AMINO ACID AND THE REACTION

- Amino acid is an organic compound that contain amine ($-NH_2$) and carboxylic acid ($-COOH$) functional group



- Properties of Amino Acid

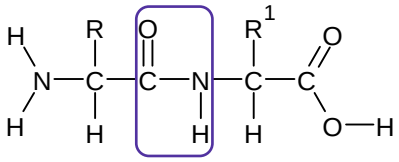
1. **Amphoteric Compound**
   Amino acid contain amine ($-NH_2$) and carboxylic acid ($-COOH$) functional group so they can act as a base and an acid
2. **Form Zwitterion**
   They could form zwitterion by interact intramolecularly. Zwitterion is an ion with both a positive ($-NH_3^+$) and a negative ($-COO^-$) charge



F. PEPTIDE

- The amine functional group of an amino acid could react with the carboxylic functional group of another amino acid to make dipeptide. This reaction is called **condensation** and it makes any small molecules like H_2O in this case is eliminated

- The new amine bond between these two amino acids is called **peptide link / bond**

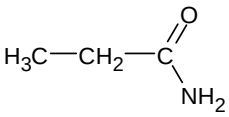


- Dipeptide could make tripeptide since it still has amine and carboxylic functional group at each end of the molecule and tripeptide could make a bigger molecule called “Polypeptide”

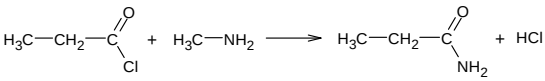
- Polypeptide is formed when there are **many amino acids join together** to form a long chain of molecules

C. REACTION OF AMIDES

- Amides are organic compounds that contain $-CONR_2$ functional group



- Amides could be produced by condensation reaction of acids or acid halides with ammonia or amine



If the nucleophile is a primary or secondary amine, the product will give a substitute amide while an acyl halide will give a non-substitute amide

- Amides could also be produced with carboxylic acids and ammonia or amine but, this reaction is slower since **carboxylic acids is less reactive than acids or acid halides** and the reaction does not go to completion

- Amides are neutral compounds because the **presence of electron acceptor species**, oxygen atom in the amide group causing the **lone pair on the nitrogen atom** of an amide **is not available to donate to electron donor species** such as H^+ so that, amides are mostly less reactive and are the least reactive from the entire carboxylic acid derivative

H. ELECTROPHORESIS

- Electrophoresis is an **analytical technique to separates ions** by placing them in an electrical field. It can also be used to identify and purify proteins

- A sample of amino acid is placed on absorbent paper or a gel supported on a glass plate. A buffer solution carries the ions all along

- When the sample is placed between two oppositely charged electrodes, the positively charged ions will move towards the negatively charged electrode and vice versa

- The rate (how fast) at which the ions move towards the electrodes depends on
  1. **The size of the ions**
     The larger ions, the move will more slowly and vice versa
  2. **The charge of the ions**
     The higher charged ions, the ions move more quickly and vice versa

- After electrophoresis occurred, you will get a series of lines or bands. This series called "electropherogram"

I. EXERCISE

1. Methyl iodide can be heated with ammonia. Which options describes the products of this reaction?
   - **(A)** Methylamine
   - **(B)** Dimethylamine
   - **(C)** Trimethylamine
   - **(D)** All of the above

Solution

The reaction ammonia with methyl iodide is nucleophilic substitution. The ammonia will act as the nucleophile and attack the iodide which substitute it to give amines product.

$$CH_3I \xrightarrow{NH_3\ /\ Heat} CH_3NH_2$$

The product contains amine. Then, we can react the previous product with CH_3I because the iodine could be substituted with the amine functional group

$$CH_3NH_2 \xrightarrow{CH_3I} CH_3CH_2NH_2$$
$$CH_3CH_2NH_2 \xrightarrow{CH_3I} CH_3CH_2CH_2NH_2$$

We can conclude that all (A), (B) and (C) options are correct and thus, the most correct option is **(D)**

2. CH_3CH_2Cl reacts with an excess of ethanolic NH_3. Which compound is the main organic product?
   - **(A)** $(CH_3CH_2)_3N$
   - **(B)** $(CH_3CH_2)_2NH$
   - **(C)** $CH_3CH_2NH_2$
   - **(D)** $(CH_3CH_2)_4N^+$

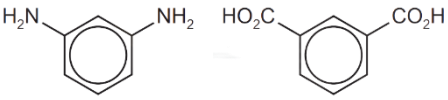
Solution

The reaction between halogenoalkanes and ammonia is called nucleophilic substitution. The ammonia act as the nucleophile and attack the chloride which substitute it to give amines product

$$CH_3CH_2Cl \xrightarrow{NH_3\ /\ Heat} CH_3CH_2NH_2$$

Thus, the correct option is **(C)**

3. *Nomex* is a polymeric material with excellent flame-resistant properties. It contains a polymer made from the two monomers shown below

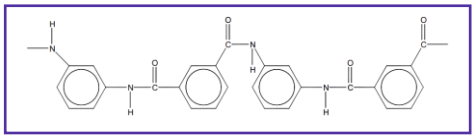


Draw the structure of the polymer showing two repeat units and the linkage between monomer unit should be shown fully displayed and name the linkage formed from the polymer!

Solution

Here, we are instructed to draw the structure of the polymer showing two repeat units with fully displayed linkage that is formed.

Before drawing, we have to know how they are bonded together. Each monomer has amine and carboxylic function and they could react together since the amine is bases while carboxylic is acid thus, forming an amine linkage with formula –CO–NH–



This new amine bond or the linkage between two monomers are called peptide link or bond

4. The analysis of a protein may be carried out by breaking it down into its amino acid. These can then be separated by a process called electrophoresis

The structure of glycine, lysine, and glutamic acid at pH 7 are shown

Glycine	$H_3N^+CH_2CO_2^-$
Lysine	$H_3N^+CH(CH_2CH_2CH_2CH_2NH_3^+)CO_2^-$
Glutamic	$H_3N^+CH(CH_2CH_2\ CO_2^-)CO_2^-$

Draw and label three circles on the chart below to indicate the likely position of each of these amino acids after electrophoresis of a solution containing these amino acids in a buffer at pH 7!

Start Point

Solution

To determine whether the compound move toward the negatively or positively charged electrode, we could count the amount charge of each compound

Glycine $H_3N^+CH_2CO_2^-$

Glycine has one positive charge at NH_3^+ and one negative charge at CO_2^-. The total charge of this compound is zero

Lysine $H_3N^+CH(CH_2CH_2CH_2CH_2NH_3^+)CO_2^-$

Lysine has two positive charges at NH_3^+ attached to CH and another NH_3^+ attached to $CH_2CH_2CH_2CH_2$. It also has one negative charge at CO_2^-. The total charge of this compound is one positive charge

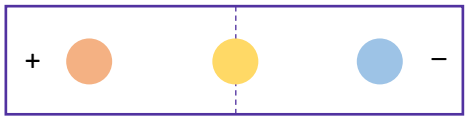
Glutamic $H_3N^+CH(CH_2CH_2\ CO_2^-)CO_2^-$

Glutamic has one positive charge at NH_3^+ and two negative charges at CO_2^- and another CO_2^- attached to CH_2CH_2. The total charge of this compound is one negative charge

From here, it can be concluded that

a. The compound with the total charge of zero charge will probably very close to the start point
b. The compound with the total charge of one positive charge will probably move toward the negatively charged
c. The compound with the total charge of one negative charge will probably move toward the positively charged

And thus, the result after the process of electrophoresis occurred will probably like this

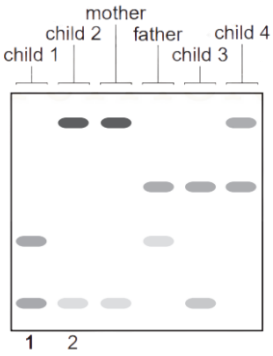


Start Point

Red = Glutamic
Yellow = Glycine
Blue = Lysine

5. **[Trivia Question]**

The following DNA fingerprints were taken from a family of mother, father and four children. This DNA fingerprints were electrophoresed and the result is shown below



Are all the children related to the mother? And which child is unlikely to be related to the father? State the evidence!

Solution

To determine whether the children are related or not, we can see the position of the band. If it has the same position with the parent's band, then the children are related to them

For the first question, the answer is yes, all the children are related to the mother. This is because we can see that all of them shared one or some band with the mother's

For the second question, the answer is it might be likely the child 2 because the child shares none of the band of father's DNA

Note:

For the fifth question, this may not appear at Cambridge Chemistry A – Level Exam because the writer intended to show that electrophoresis could help to identify the paternity of children