ChemFactsheet

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Organic Chemistry 5: Compounds Containing Nitrogen

To succeed in this topic you need to:-

- **Have a good knowledge and understanding of the organic chemistry covered so far (Factsheets 15, 16, 17, 27 31, 32 and 33);**
- **Be confident in using organic nomenclature and structural formulae.**

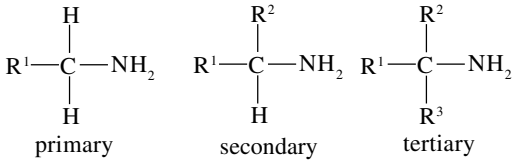
After working through this Factsheet you will:-

- **Know the functional groups of amines, amides, nitriles and amino acids;**
- **Have been given the required reaction types conditions and equations of the nitrogen containing compounds for the A2 exams.**

Amines

Functional group: $-\overset{|}{\underset{|}{C}}-\ddot{N}H_2$

Like alcohols, amines can be primary, secondary or tertiary:



The lone pair of electrons on the nitrogen atom makes the amine group both basic (an acceptor of protons, H^+) and a nucleophile (a donator of electrons).

Reactions of the amines.

1. Reaction of primary amines with aqueous hydrogen ions (acids).
Amines are **basic**, so react with acids to form salts.

$$CH_3CH_2NH_2 + HCl \rightleftharpoons CH_3CH_2NH_3^+Cl^-$$

Reaction type: addition
Conditions: acidic, aqueous
Mechanism: nucleophilic

2. Reaction of primary amines with acid chlorides.
Primary amines react quickly with acid chlorides to form substituted amides.

$$C_2H_5NH_2 + CH_3C(=O)Cl \rightleftharpoons CH_3C(=O)NHC_2H_5 + HCl$$

Recation type: substitution
Conditions: aqueous, room temperature
Mechanism: nucleophilic

Nitriles

Functional group: $-C\equiv N:$, which is also written as $-CN$

The lone pair on the electronegative nitrogen atom makes the nitrile group a strong nucleophile.

Nitriles can be prepared by reacting a haloalkane with KCN in aqueous ethanol (which increases the length of the carbon chain by one) - see Factsheet 16.

Reactions of the nitriles.

1. Hydrolysis of nitriles.
Nitriles can be hydrolysed by refluxing them with aqueous hydrochloric acid or aqueous sodium hydroxide.

(a) Hydrolysis with acid.

The carboxylic acid is formed (via the amide as an intermediate).

$$CH_3CH_2CN + HCl + 2H_2O \xrightarrow{heat} CH_3CH_2COOH + NH_4Cl$$

Reaction type: hydrolysis
Conditions: acidic, heat under reflux

(b) Hydrolysis with alkali.

The carboxylic acid salt is formed (again via the amide intermediate).

$$CH_3CH_2CN + NaOH + H_2O \xrightarrow{heat} CH_3CH_2COO^-Na^+ + NH_3$$

Reaction type: hydrolysis
Conditions: alkaline, heat under reflux

2. Reduction of nitriles

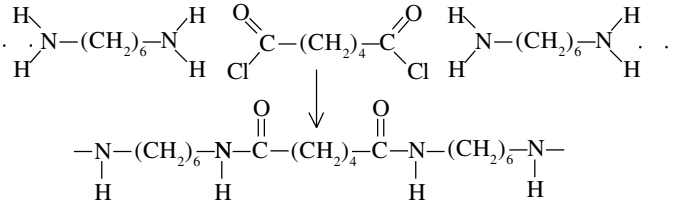
Nitriles are reduced to **amines** by $LiAlH_4$ dissolved in dry ether - a powerful reducing agent.

$$C_2H_5CN + 4[H] \xrightarrow{LiAlH_4} C_2H_5CH_2NH_2$$

Reaction type: reduction
Conditions: dry ether, followed by addition of dilute acid.

3. Formation of polyamides.
The above reaction between primary amines and acid chlorides can be used to form polymers if monomers are used with 2 amine groups and 2 acid chloride groups present.

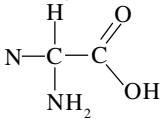
For example, the formation of nylon–6,6 – so called because both monomers contain 6 carbon atoms.



With HCl molecules being eliminated, this is a form of "elimination polymerisation".

Amino acids

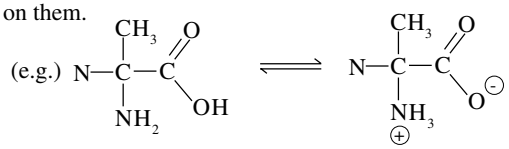
Functional group: Amino acids contain both -NH_2 and - COOH groups (usually bonded to the same carbon atom).

e.g.  glycine

Exam Hint *- Glycine is not a chiral molecule, but many amino acids are. Chirality will often figure in questions about amino acids, so ensure that you understand this form of isomerism - see Factsheet 27.*

Amino acids react as both acids and bases.
They are water soluble ionic solids because the molecules have ionic interactions.

They form **zwitterions**, ions having both positive and negative charges on them.

(e.g.) 

A "Zwitterion"

Reactions of amino acids

These reactions show that amino acids are **amphoteric**.

1. Reaction of amino acids with acids.

$NH_2CH_3CHCOOH + H^+ \rightarrow NH_3^+CH_3CHCOOH$

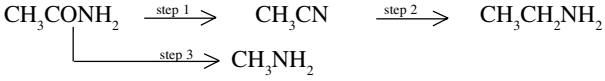
2. Reaction of amino acids with bases.

$NH_2CH_3CHCOOH + OH^- \rightarrow NH_2CH_3CHCOO^- + H_2O$

The amphoteric nature of amino acids goes some way towards explaining why these compounds are commonly used in buffer solutions.

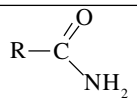
Questions

1. The amine functional group is both basic and a nucleophile. Explain why.
2. Draw structural formulae for the following:
   (a) Propanamine.
   (b) Propanamide.
   (c) Propanenitrile.
3. (a) Draw the structure of $NH_2CH_3CHCOOH$, indicating the position of the chiral centre.
   (b) Use equations to illustrate the amphoteric nature of $NH_2CH_3CHCOOH$.
4. The question refers to the following reaction scheme:



Give the reaction equations and conditions for:
(a) Step 1.
(b) Step 2.
(c) Step 3

Amides

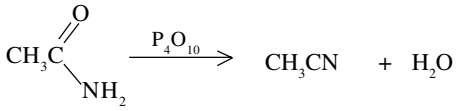
Functional group: 

The amides are carboxylic acid derivatives.
They are formed by reacting ammonia with acyl chloride - see Factsheet 32.

Reactions of the amides

1. Dehydration of amides using phosphorus (V) oxide.

Amides are dehydrated to **nitriles** on heating with P_4O_{10}.

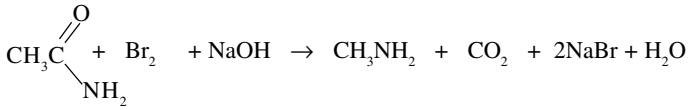


ethanamide ethanenitrile

Reaction type: dehydration (elimination)
Conditions: warm and distil off ethanenitrile

2. Hoffmann degradation reaction with bromine and aqueous alkali.

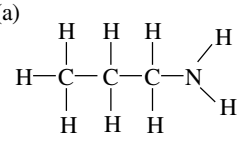
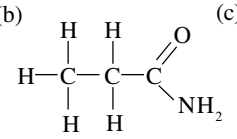
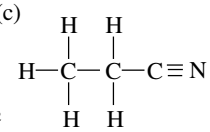
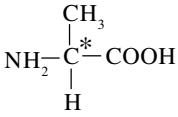
Amides react with bromine in a solution of sodium hydroxide to give amines.



Conditions: Add liquid bromine to amide at room temperature, then add concentrated sodium hydroxide solution and warm. The amine is then distilled off.

Note: The length of the carbon chain is decreased by one as CO_2 is given off.

Answers

1. The lone pair of electrons on the nitrogen atom allows the group to accept protons (H^+), hence it is basic, and also to donate electrons to form dative covalent bonds with electron deficient species (hence a nucleophile).
2. (a)  (b)  (c) 
3. (a)  * = chiral centre

   (b) As a base:
   $NH_2CH_3CHCOOH + H^+ \rightarrow NH_3^+CH_3CHCOOH$

   As an acid:
   $NH_2CH_3CHCOOH + OH^- \rightarrow NH2CH_3CHCOO^- + H_2O$
4. (a) $CH_3CONH_2 \rightarrow CH_3CN + H_2O$
   Conditions: P_4O_{10}, warm, and distil off ethanenitrile.

   (b) $CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2$
   Conditions: $LiAlH_4$ in dry ether, followed by addition of dilute acid.

   (c) $CH_3CONH_2 + Br_2 + 2NaOH \rightarrow CH_3NH_2 + CO_2 + 2NaBr + H_2O$
   Conditions: Add Br_2 at room temperature, then add concentrated sodium hydroxide solution and warm.

Acknowledgements: *This Factsheet was researched and written by Sam Goodman and Kieron Heath.* ***Curriculum Press, Unit 305B, The Big Peg, 120 Vyse Street, Birmingham, B18 6NF.***