Beckfoot

Subject: Chemistry | Topic: Amines 3.3.11 | Year Group: 13

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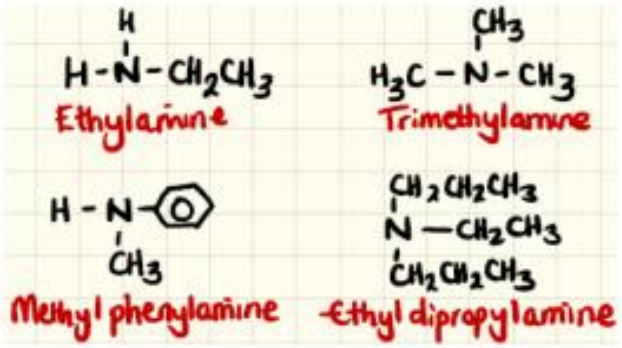
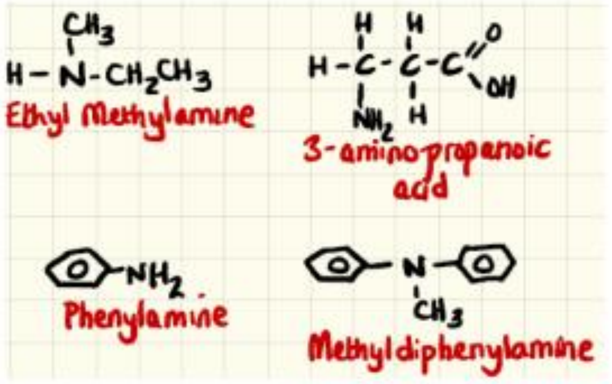
Structure / Classification

1	Functional group for primary amine: RNH_2
2	***Classification:*** Primary (RNH_2), Secondary (R_2NH), Tertiary (R_3N), Quaternary ammonium salts (R_4N^+)
3	*Amines are compounds derived from ammonia (the hydrogen atoms are replaced by aliphatic / aryl groups)*
4	**Nomenclature**: Named according to the alkyl or aryl chain followed by **–amine**. When naming amines, if you need to give the position of the carbon to which the NH_2 group is attached, use the '**amino**' prefix. For example, $CH_3CH(NH_2)\ CH_3$ is 2-aminopropane. See some named examples in separate box.
5	**Naming hierarchy**: order of priority of functional groups is listed here: 1. Carboxyl (-COOH) 2. Aldehyde (-CHO) 3. Ketone (-CO-) 4. Hydroxyl (-OH) 5. Amines (-NH2, -RNH, -R2N) 6. Alkene (-C=C-) The following groups are always named as prefixes in alphabetical order: alkyl (R-), phenyl (C_6H_5-), chloro (Cl-), bromo (Br-), iodo (I-), nitro ($-NO_2$)

Examples of amines & their names





Key Vocabulary

1	Alkyl group	Part of an aliphatic chain, e.g. CH_3-, CH_3CH_2-
2	Base	A species that can accept a hydrogen ion (a proton acceptor)
3	Nucleophile	A species with a lone pair of electrons that can attack an electron-deficient carbon atom
4	Substitution	A reaction in which an atom or group of atoms is replaced by a different atom or group of atoms
5	Surfactant	A surfactant is a compound which is partly soluble & partly insoluble in water
6	Cationic surfactant	A surfactant which is positively charged, e.g. quaternary ammonium salts
7	Amine	A molecule where one or more of the hydrogen atoms in ammonia have been replaced with an organic functional group, such as an alky or an aromatic group
8	Nucleophilic substitution	A reaction mechanism where a *nucleophile substitutes for an atom (or group of atoms) in a molecule*
9	Nucleophilic addition elimination	A reaction mechanism where a *nucleophile adds on to the delta plus carbon atom of a carbonyl group & another molecule is eliminated*

Base Properties – what you need to be able to do…

All amines have **a lone pair of electrons on the nitrogen atom** which gives them both NUCLEOPHILIC & BASE properties. A base accepts protons in water. You need to *write equations for the reaction of amines in water and with acids*. You also need to *explain the base strength of different amines by referring to how available the lone pair of electrons on the nitrogen atom is to accept protons*

Uses of quaternary ammonium salts

1	Synthesised **by nucleophilic substitution** using **excess haloalkane** to allow **further substitution** of the amine products.
2	Are **salts of a quaternary ammonium cation (NR_4^+) and an anion**, e.g. $(CH_3)_4N^+ Cl^-$ is tetramethyl ammonium chloride. They are used as cationic surfactants in products such as fabric conditioners & shampoo. Their purpose is **to smooth fabric or hair, making them softer**.

Preparation of primary aliphatic amines

	From halogenoalkanes	**From nitriles**
Reaction / Mechanism	**Nucleophilic substitution**	**Reduction**
Reagent(s)	**Ammonia**	**Hydrogen (& nickel catalyst) or $LiAlH_4$ (III) in dry ether**
Conditions	To make a higher amount of primary amine you need heat with excess NH_3 in a sealed tube under pressure. The primary amine product can *cause further substitution to get 2°& 3° amines* so a mixture of products is still likely to form. To promote formation of quaternary ammonium salts, you need to use excess haloalkane rather than excess ammonia.	**Nickel catalyst** if using hydrogen or **dry ether** is using lithium tetrahydridoaluminate (III).
General equation	**$R\text{-}X + 2\ NH_3 \rightarrow R\text{-}NH_2 + NH_4X$** **Example**: $CH_3CH_2Cl + 2\ NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Cl$	**$R\text{-}CN + 2H_2 \rightarrow R\text{-}CH_2NH_2$ or $R\text{-}CN + 4\ [H] \rightarrow R\text{-}CH_2NH_2$** **Example:** $CH_3CN + 2H_2 \rightarrow CH_3CH_2NH_2$
Advantages / Disadvantages	Produces a mixture of products so impure and therefore produces a lower yield of desired product.	Higher yield of desired product and pure as no other product formed. However, KCN is poisonous & H_2 is flammable

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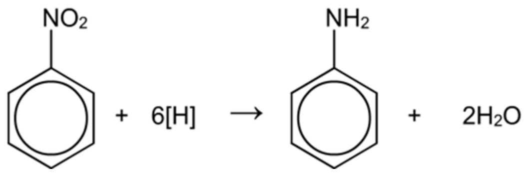
Preparation of aromatic amines

1	Type of reaction	Reduction of nitro compounds
2	General equation for reduction	**$RNO_2 + 6\,[H] \dashrightarrow RNH_2 + 2\,H_2O$**
3	Reagents & conditions	Heat under reflux with tin & excess concentrated HCl. The salt is initially formed so to liberate the free amine we need to add NaOH Alternative: use hydrogen and Nickel catalyst
4	Equation for making phenylamine using Sn & concentrated HCl	 To liberate the free amine from the salt formed: $C_6H_5NH_3^+ + OH^- \dashrightarrow C_6H_5NH_2 + H_2O$
5	Uses of aromatic amines	Used to make azo dyes for use in food & textiles

Base reactions of amines

1	With dilute **acids**	The lone pair of electrons on N atom can accept a proton from an acid or from water. Ammonia + acid → Ammonium salt Amine + acid -→ Alkyl ammonium salt e.g. $CH_3NH_2 + HCl \leftrightarrows CH_3NH_3^+Cl^-$ Addition of NaOH liberates the free base from its salt $CH_3NH_3^+Cl^- + NaOH \dashrightarrow CH_3NH_2 + H_2O + NaCl$ $2CH_3CH_2NH_2 + H_2SO_4 \leftrightarrows (CH_3CH_2NH_3)_2SO_4$
2	With **water**	Amines will accept a proton from water to produce an alkylammonium ion and hydroxide ions e.g. $CH_3NH_2 + H_2O \leftrightarrows CH_3NH_3^+ + OH^-$ A weakly basic solution is formed because the equilibrium lies well to the left since methylamine is only partly ionised, leading to a low $[OH^-\}$

Explaining differing base strength of amines

1	Base strength depends on the availability of the lone pair of electrons on the nitrogen atom
2	Aliphatic amines have at least one alkyl group attached to the nitrogen whereas aromatic amines contain a benzene ring directly attached to the NH_2 group
3	Alkyl groups have a **positive inductive effect**, this means they push electrons in the bond **towards the N atom** so that **the lone pair of electrons on the nitrogen is more readily available to accept a proton**. *This means an aliphatic amine is a stronger base than ammonia.* The more alkyl groups attached to the nitrogen on the amine group, the greater the positive indictive effect, hence *dimethylamine is a stronger base than methylamine*.
4	In an **aromatic amine**, the lone pair of electrons on the nitrogen is delocalized into the ring so that it is less available on the N atom to accept a proton. Hence, an aromatic amine with a NH_2 directly attached to the benzene ring is a *weaker base compared to ammonia*.

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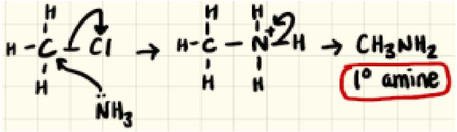
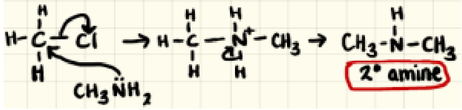
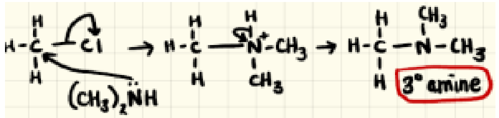
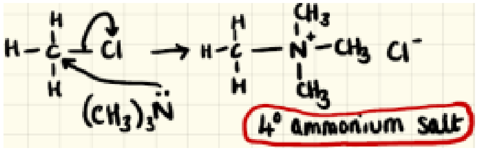
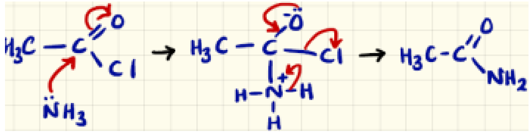
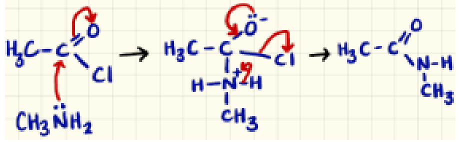
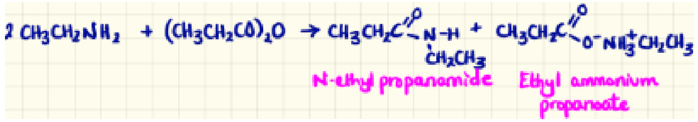
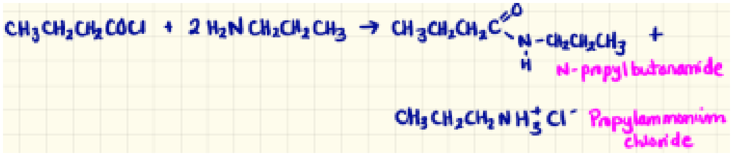
Nucleophilic properties: nucleophilic substitution

1	$CH_3Cl + 2NH_3 \rightarrow CH_3NH_2 + NH_4Cl$	
2	$CH_3Cl + CH_3NH_2 \rightarrow (CH_3)_2NH + NH_4Cl$	
3	$CH_3Cl + (CH_3)_2NH \rightarrow (CH_3)_3N + NH_4Cl$	
4	$CH_3Cl + (CH_3)_3N \rightarrow (CH_3)_4\overset{+}{N}\ Cl^-$	

Nucleophilic properties: nucleophilic addition-elimination

1	**Example mechanism of ammonia and ethanoyl chloride**	
2	**Example mechanism of methylamine and ethanoyl chloride**	
3	**Example equation of ethylamine and propanoic anhydride**	 $2CH_3CH_2NH_2 + (CH_3CH_2CO)_2O \rightarrow CH_3CH_2C(=O)NHCH_2CH_3 + CH_3CH_2C(=O)O^-NH_3^+CH_2CH_3$ N-ethyl propanamide Ethyl ammonium propanoate
4	**Example equation of propylamine and butanoyl chloride**	 $CH_3CH_2CH_2COCl + 2H_2NCH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2C(=O)NH-CH_2CH_2CH_3 + CH_3CH_2CH_2NH_3^+Cl^-$ N-propylbutanamide Propylammonium chloride