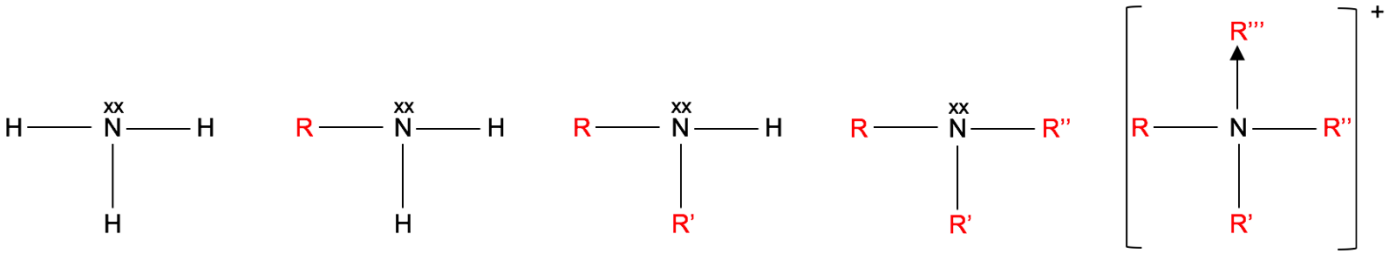
3.11 Amines

Introduction to amines:

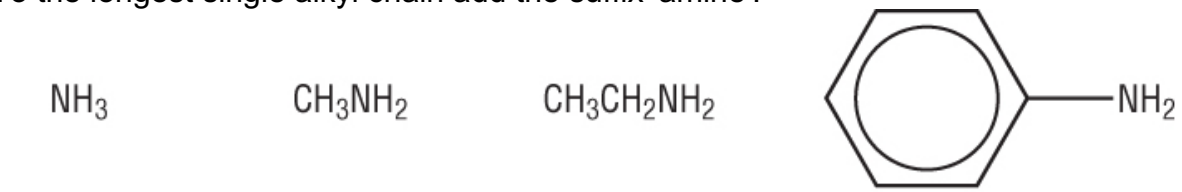
- Have an **NH_2**, attached to an alkyl group.
- Amines are derivatives of ammonia where at least 1 H has been replaced with an R group:



Ammonia	Primary amine 1 C attached to N	Secondary amine 2 C attached to N	Tertiary amine 3 C attached to N	Quaternary ammonium ion 4 C attached to N

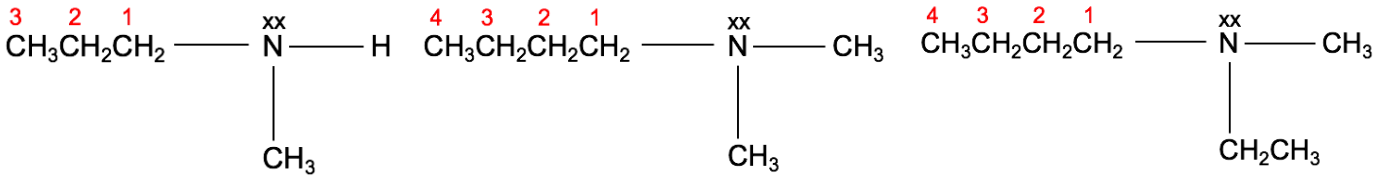
Naming amines:

- To the longest single alkyl chain add the suffix 'amine':



Ammonia	Methylamine	Ethylamine	Phenylamine

- If there are 2 or more alkyl groups on the nitrogen:



N – methyl propylamine	N,N – dimethyl butylamine	N,N – Ethyl methyl butylamine

Naming amines

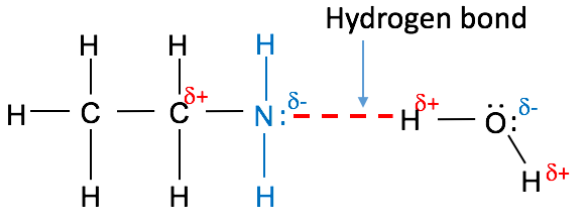
- Give the IUPAC name of the following and classify the amine:

Structure	IUPAC name
$CH_3CH_2CH_2CH_2CH_2NH_2$	
$CH_3CH_2CH_2NHCH_2CH_3$	
$CH_3CH_2CH_2CH_2N(CH_3)CH_2CH_3$	
$[CH_3CH_2CH_2CH_2N(CH_3)_3]^+$	

- Draw the structure of the following and classify the amine:

Amine	Structural formula	Skeletal formula
Hexylamine		
N – ethyl pentylamine		
N,N – ethyl methyl pentlylamine		
N – methyl Phenylamine		

Solubility



- The amines form hydrogen bonds with water (and themselves).
- The solubility decreases with the increase in the alkyl chain (as with alcohols / carboxylic acids)

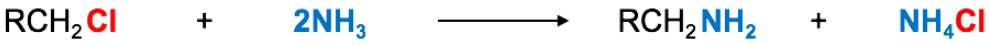
Preparation of amines:

- These are done in one of 3 ways:

1) From halogenoalkanes (AS)
2) Reduction of nitrated benzene
3) Reduction of nitriles

1) Preparation of amines from halogenoalkanes (AS):

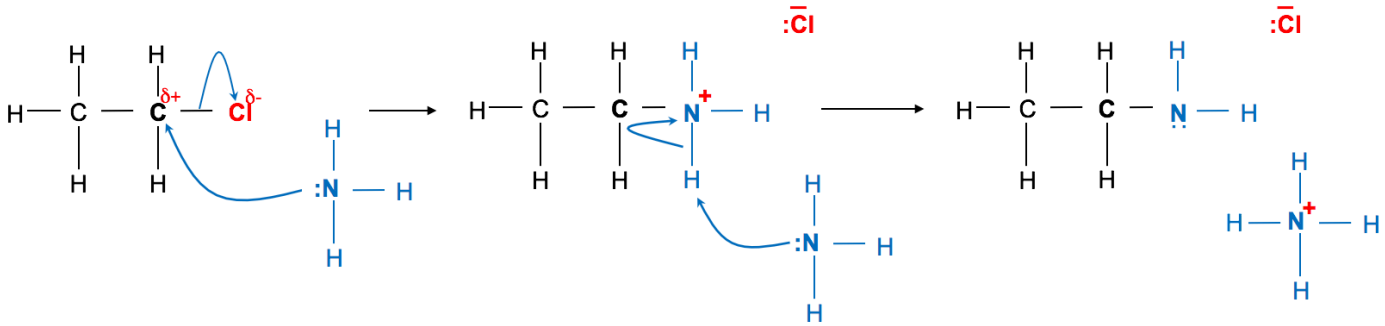
- This reaction converts a halogenoalkane to amines



Reagents: Excess ethanolic ammonia

Conditions: Reflux

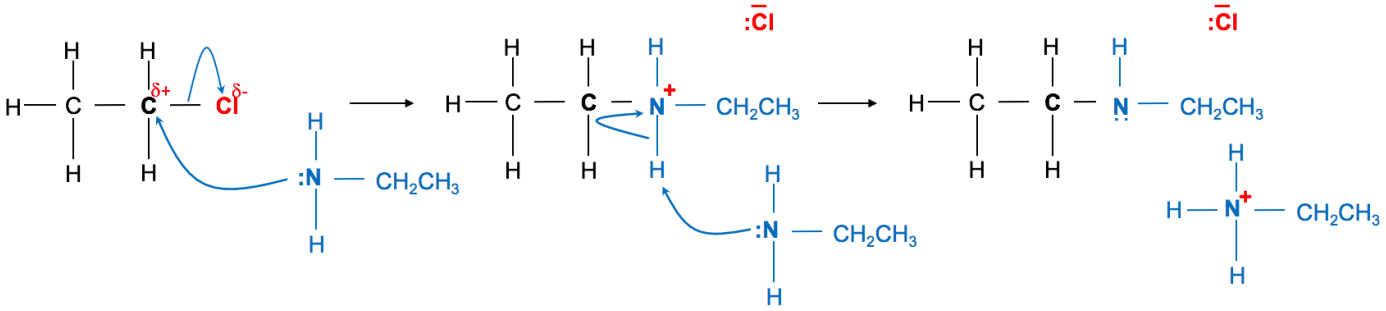
The Mechanism – Nucleophilic substitution



Further reactions of the halogenoalkanes secondary / tertiary aliphatic amines:

- Ethylamine can react further (like the ammonia) with more chloroethane:

$$CH_3CH_2Cl + 2CH_3CH_2NH_2 \rightarrow (CH_3CH_2)_2NH + CH_3CH_2NH_3Cl$$



- And diethylamine can react even further again:

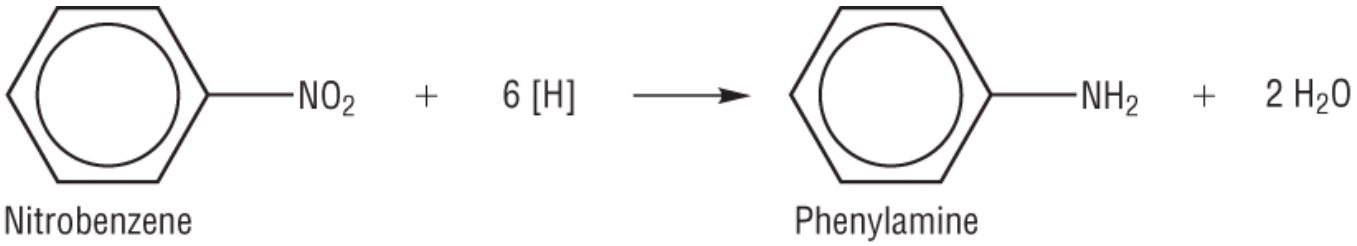
$$CH_3CH_2Cl + (CH_3CH_2)_2NH \rightarrow (CH_3CH_2)_3N + HCl$$

- Multiple substitution is avoided by having ammonia in excess.
- This minimises the 'chance' of further substitution.

2) Reduction of nitrobenzene to aromatic amines:

Reagents: 1) Sn and concentrated HCl 2) NaOH

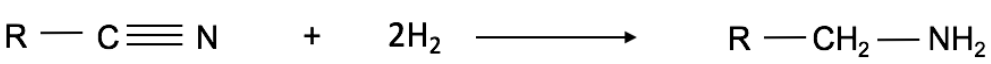
Conditions: Reflux



- NaOH is added to release phenylamine from its salt (with the HCl)
- This is an important reaction as it is used in the manufacture of dyes.

3) Reduction of nitriles to amines:

- This reaction converts a nitrile to amines:



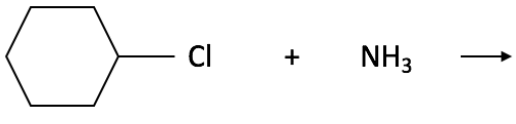
Reagents: H_2 and Ni

Conditions: High T and P

Questions:

1) Complete and balance the following reactions:

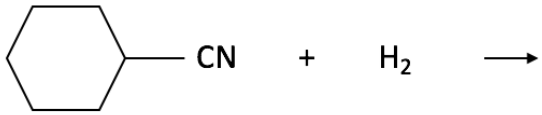
   a. $CH_3CH_2CH_2Cl$ + NH_3 →

   b.  + NH_3 →

   c. $ClCH_2CH_2CH_2CH_2Cl$ + NH_3 →

2) Complete and balance the following reactions forming amines:

   a. $CH_3CH_2CH_2CN$ + H_2 →

   b.  + H_2 →

   c. $NCCH_2CH_2CH_2CH_2CN$ + H_2 →

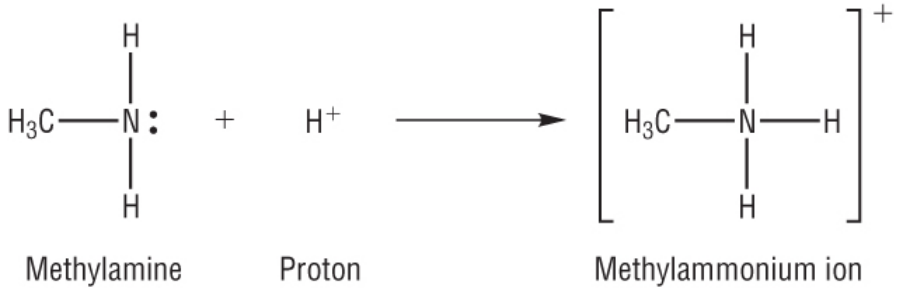
3) Outline, how you would make phenylamine from benzene (2 steps). In your answer include:
   - Balanced chemical equations
   - Any reagents and conditions
   - Types of reactions

Basicity in amines:

Definitions:

Base: ***Proton acceptor – accepts protons, H^+ ions when mixed with water***

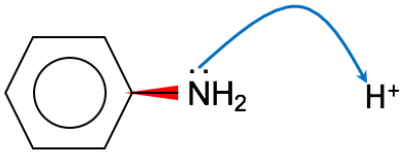
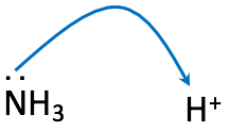
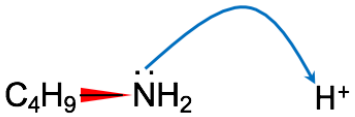
- Amines are weak bases.
- This is because they have a lone pair of electrons on the nitrogen available to donate when accepting a hydrogen ion:



Methylamine Proton Methylammonium ion

The basicity of the 1° amines: The inductive effect

- The strength of the basicity depends upon the availability of the nitrogen's lone pair electrons:

pH 8	pH 10	pH12
Phenylamine	Ammonia	Butylamine
		
➢ Negative inductive effect: ➢ Lone pair electrons on the nitrogen delocalise with the delocalised π electrons in benzene ➢ This decreases the electron density on the nitrogen. ➢ This makes it a weaker lone pair donor. ➢ Which makes it a weaker base.	Base line: No inductive effect	➢ Positive inductive effect: ➢ Alkyl groups give a small push of electrons towards the nitrogen. ➢ This increases the electron density on the nitrogen. ➢ This makes it a better lone pair donor. ➢ Which makes it a stronger base.

Base reactions of amines:

- Just as ammonia forms salts with acids so do amines:

Ammonia:

Base	+	Acid	→	Ammonia salts
NH_3	+	HCl	→	NH_4Cl

Amines:

Base	**+**	**Acid**	→	**Alkylammonium salts**
RNH_2	+	HCl	→	RNH_3Cl

Examples:

CH_3NH_2 Methylamine	+	HCl	→	CH_3NH_3Cl methylammonium chloride
CH_3NH_2 Methylamine	+	HNO_3	→	$CH_3NH_3^+NO_3^-$ methylammonium nitrate

- Either write in the charges of the salt or don't!

Phenylammonium nitrate

The amines can be recovered by adding NaOH (a stronger base):

$$CH_3NH_3Cl + NaOH \rightarrow CH_3NH_2 + NaCl + H_2O$$

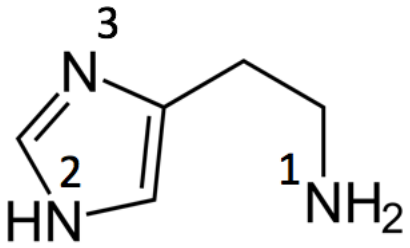
Questions:

1) Place the following molecules in order with the most basic first:

NH_3 CH_3NH_2 $C_6H_5NH_2$ $(CH_3)_2NH$ $(C_6H_5)_2NH$

2) Explain your answer to (1):

3) The molecule below is histamine. It has 3 amine groups present in the molecule. Place the 3 amine groups in order starting with the most basic, explain your answer:



4) Write the balanced chemical reaction for the following:
   a. Butylamine and hydrochloric acid

   b. Ethylamine and nitric acid

   c. Phenylamine and hydrobromic acid

   d. Propylamine and sulphuric acid (hard)

Nucleophilic properties of the amines:

- Remember, the amines are derivatives of ammonia. If you understand the reactions of ammonia, the amines will be similar:

***Nucleophile**: Donates a pair of electrons forming a dative covalent bond*

A) The reactions with the halogenoalkanes:

1) With ammonia, NH_3, to form 1° amines:

Recap: The nucleophilic substitution of the halogenoalkanes with ammonia:

- This reaction converts a halogenoalkane to amines

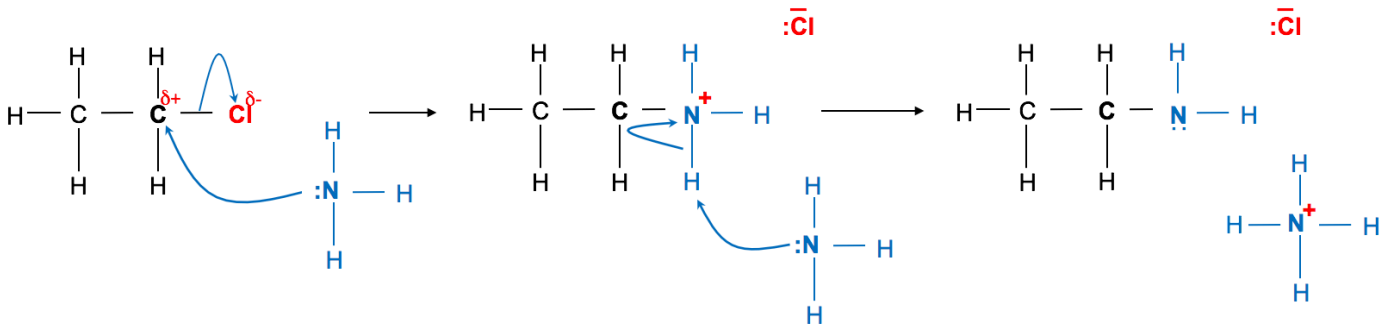
$$R^1X + 2NH_3 \rightarrow R^1NH_2 + NH_4^+ X^-$$

$$CH_3CH_2Cl + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4^+ Cl^-$$

Reagents: Excess ethanolic ammonia

Conditions: Reflux

The Mechanism



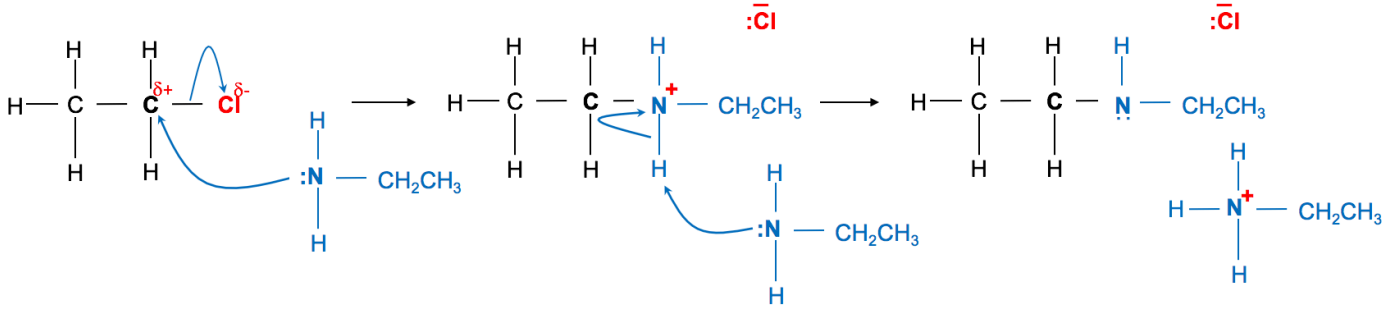
***Substitution**: When one atom or group of atoms are swapped with another atom or group of atoms*

2) With 1° amines, RNH_2, to form 2° amines, R_2NH:

$R^2X + 2R^1NH_2 \rightarrow R^2R^1NH + R^1NH_3^+ X^-$

$CH_3CH_2Cl + 2CH_3CH_2NH_2 \rightarrow (CH_3CH_2)_2NH + CH_3CH_2NH_3^+ Cl^-$

Mechanism:



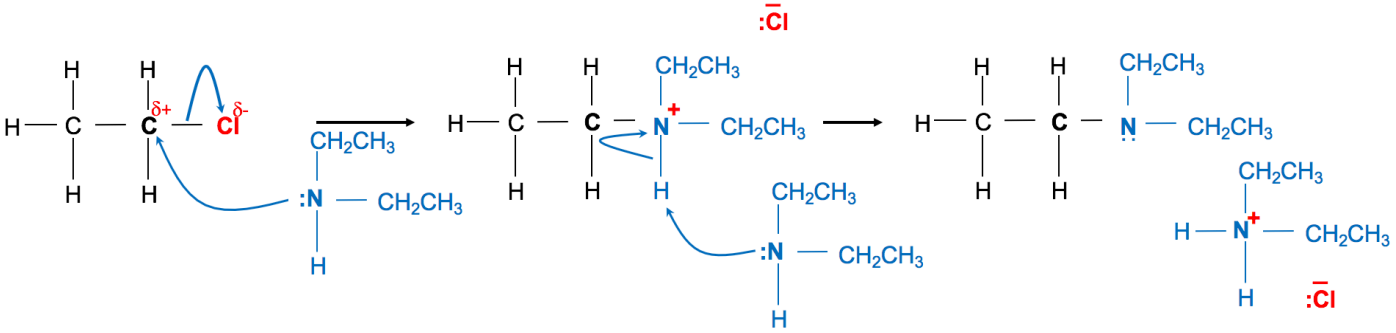
1° Amine — 2° Amine — Quaternary ammonium salt

3) With 2° amines, R_2NH, to form 3° amines, R_3N:

$R^3X + 2R^2R^1NH \rightarrow R^3R^2R^1N + R^2R^1NH_2^+ X^-$

$CH_3CH_2Cl + 2(CH_3CH_2)_2NH \rightarrow (CH_3CH_2)_3N + (CH_3CH_2)_2NH_2^+ Cl^-$

Mechanism:



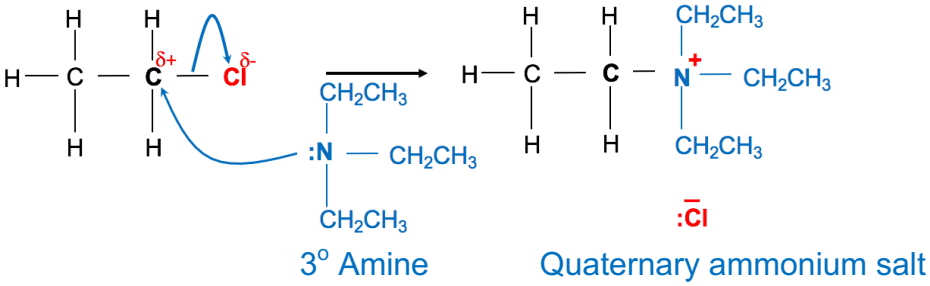
2° Amine ammonium salt — 3° Amine — quaternary

4) With 3° amines, R_3N, to form quartenary ammonium salt, R_4N^+:

R^4X + $R^3R^2R^1N$ → $R^4R^3R^2R^1N^+ X^-$

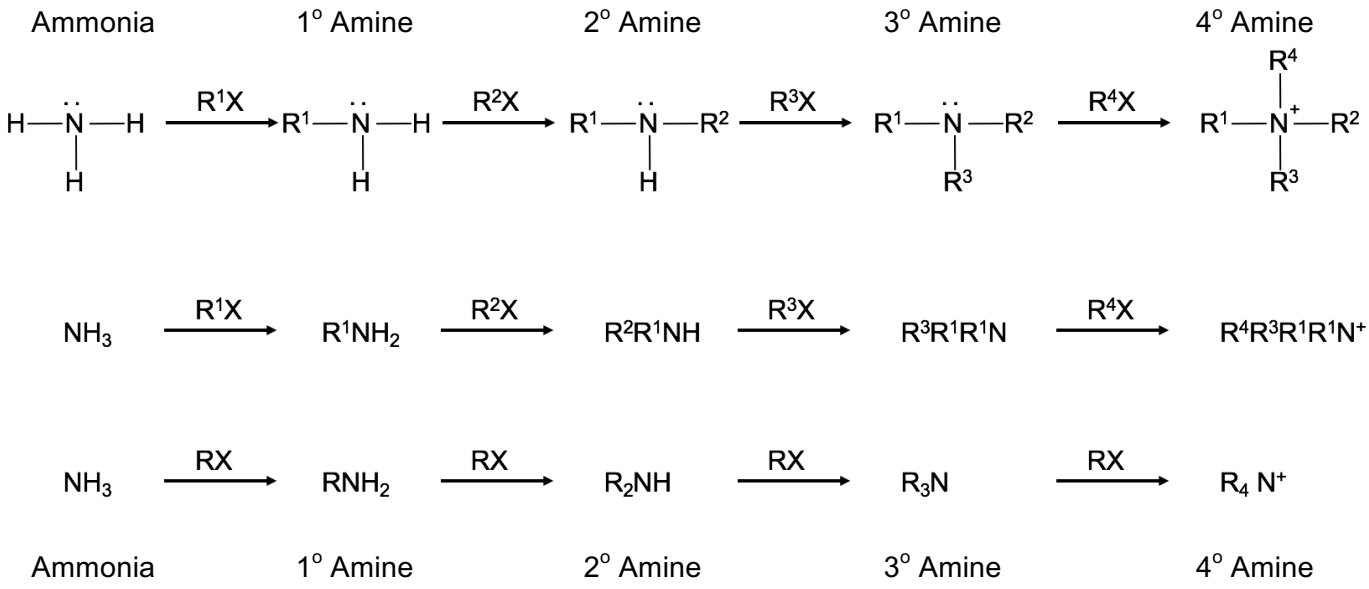
CH_3CH_2Cl + $(CH_3CH_2)_3N$ → $(CH_3CH_2)_4N^+ Cl^-$

Mechanism:



3° Amine Quaternary ammonium salt

Summary:

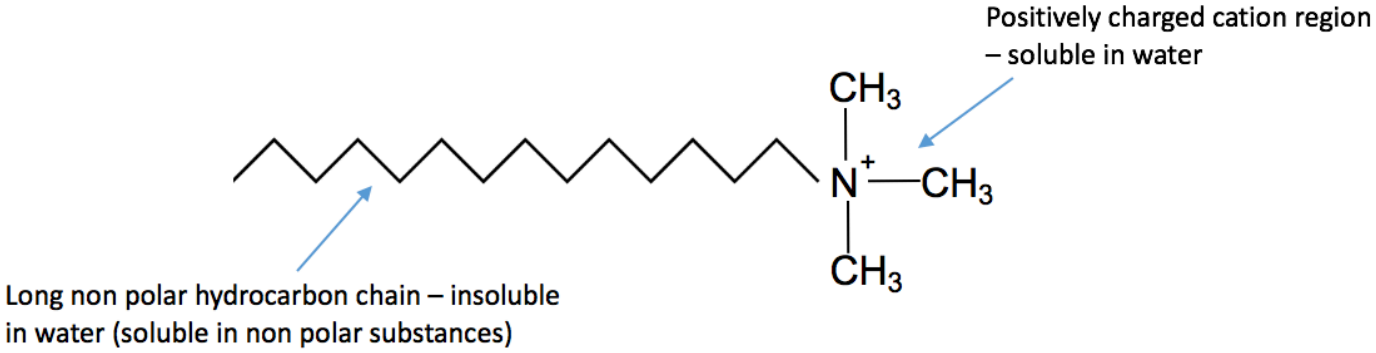


- Unless an amine is used in excess, further substitution can occur until a quaternary salt is made.

Cationic surfactants

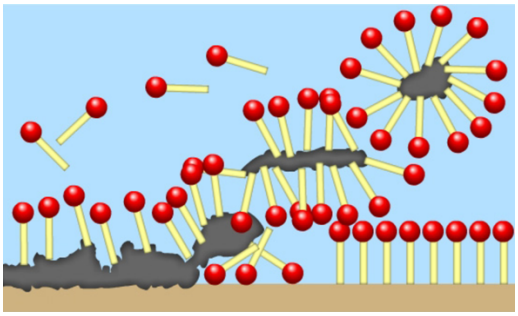
Surfactant: *A compound that is partly soluble and partly insoluble in water*

- Quartenary ammonium salts are one of these types of compounds:



As detergents:

- The non-polar hydrocarbon chain will dissolve in a non-polar substance (such as grease).
- The positively charged region will dissolve in water.
- This allows spots of grease to mix with water and therefore be washed away:



As conditioners:

- Wet hair and fabrics pick up negative charges.
- The wet hair / fabric attracts the positively charged region creating a coating.
- This prevents the build-up of further charges (static electricity) – smooth hair / soft fabric.

Questions:

1) Write balanced chemical equations for the following:
    a. Chloromethane and ammonia

    b. Chloroethane and ethylamine

    c. Chlorooethane and diethylamine

    d. Chloropropane and phenylamine

    e. Chlorododecane (12carbons) and trimethylamine

    f. Give a use of the product in (e). Explain how it works?

2) Write out the mechanisms for 1b:

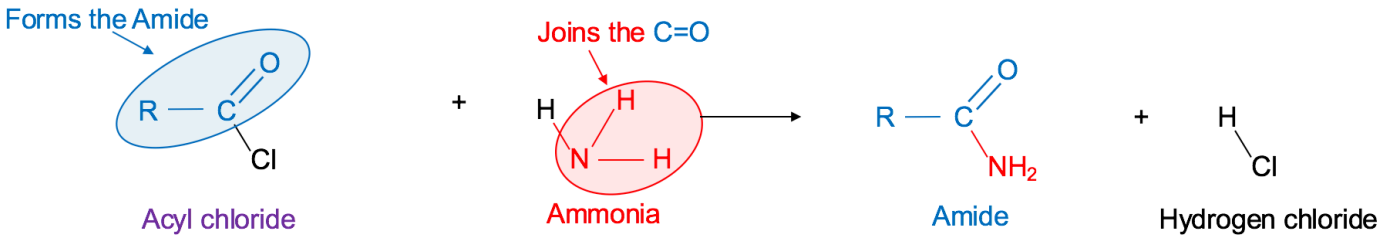
Nucleophilic addition – elimination reactions using amines as nucleophiles:

- ***Recap from 3.9 Carboxylic acids and derivatives:***

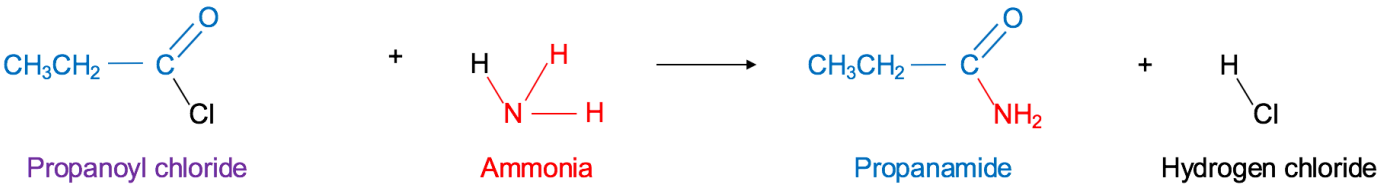
A) With acyl chlorides:

1) With ammonia:

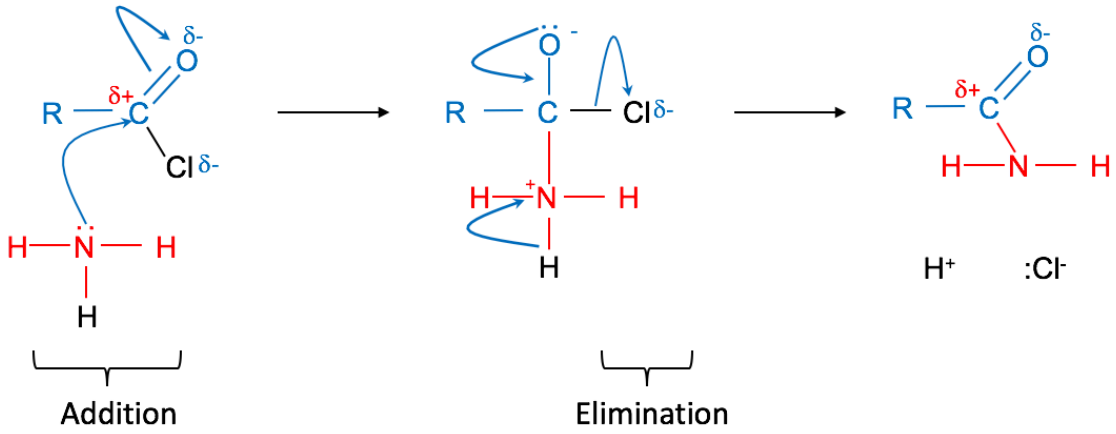
- The reaction with ammonia gives the amide:



Example:

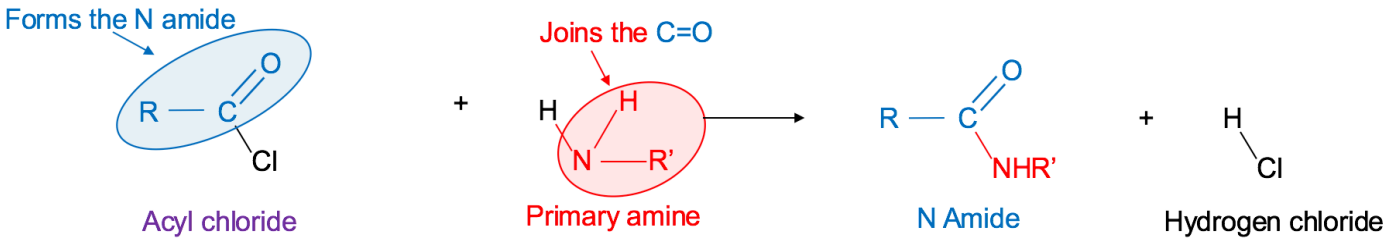


The mechanism:

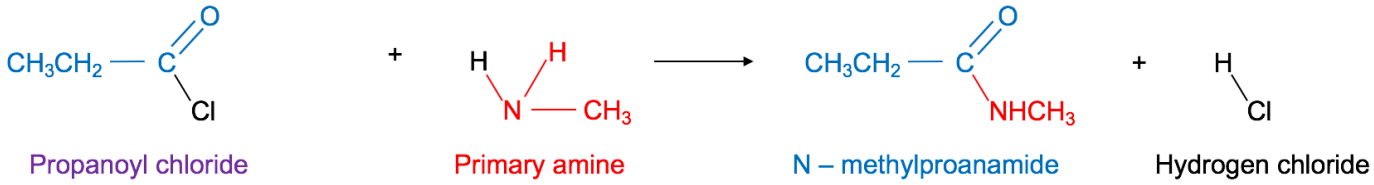


2) With primary amines:

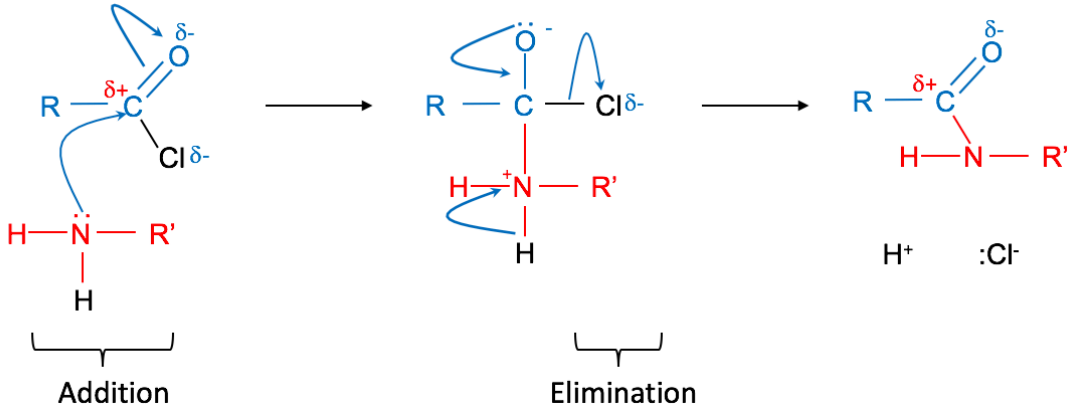
- The reaction with primary amines gives the N substituted amide:



Example:



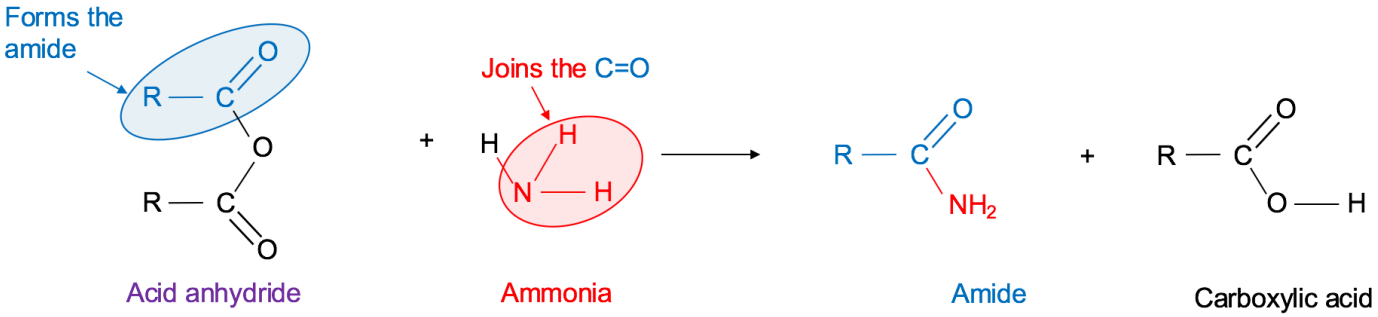
The mechanism:



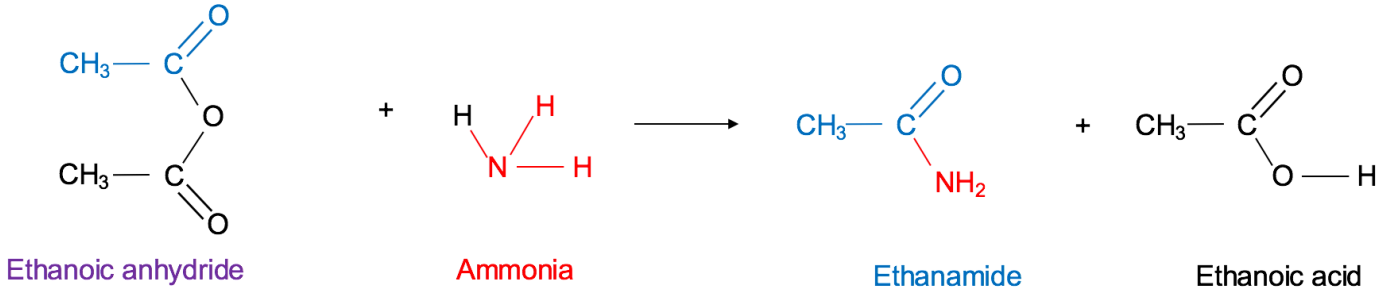
B) With acid anhydrides:

1) With ammonia:

- The reaction with ammonia gives the amide:

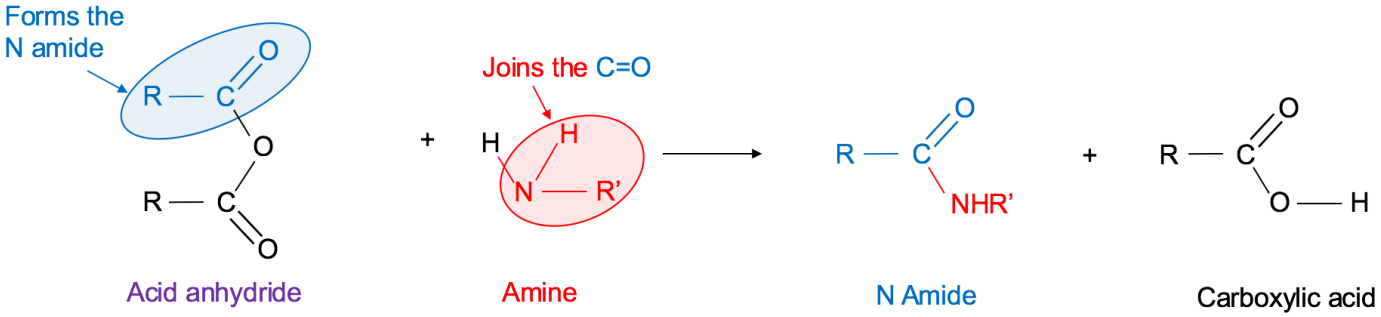


Example:

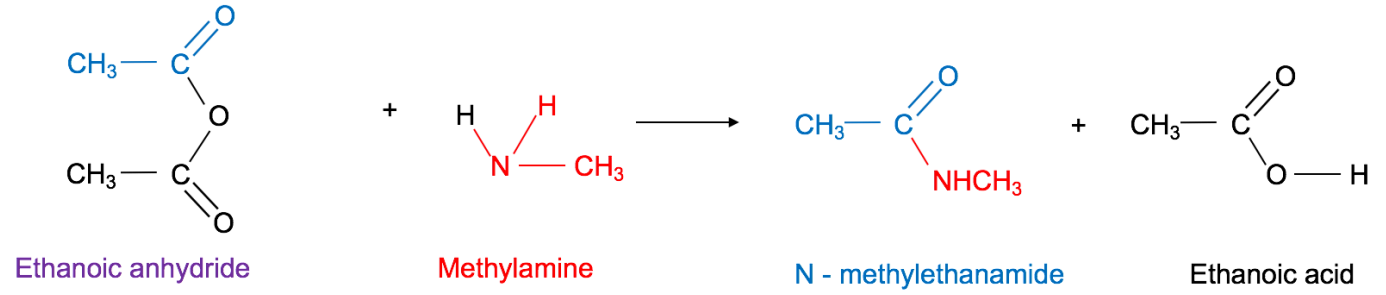


2) With primary amines:

- The reaction with primary amines gives the N substituted amide:



Example:



Questions:

1) Write balanced chemical equations for the following:
    a. Ethanoyl chloride and ammonia

    b. Ethanoyl chloride and methylamine

    c. Name the organic product formed for each of the reactions above

2) Write out the mechanisms for 1b:

3) Write balanced chemical equations for the following:
    a. Ethanoic anhydride and ammonia

    b. Ethanoic anhydride and methylamine

    c. Name the organic products formed for each of the reactions above

4) Have a go at the mechanism for 1b: