Answer all the questions below as fully as you can then check your answers

1. Draw the structure of a primary, secondary and tertiary amine all of which have the formula of $CH_3CH_2CH_2NH_2$.

b. The amine $CH_3CH_2CH_2NH_2$ can be prepared by two different routes.

Route 1 starts from CH_3CH_2Br

Route 2 starts from $CH_3CH_2CH_2Br$

i. Identify the reagents and reactions taking place in each of these two routes.

2. Draw a mechanism and write an equation to show how the reaction of bromoethane with an excess of ammonia is likely to proceed.

a. Why is an excess of ammonia used in this reaction?

b. This reaction is likely to produce a number of unwanted by products. Name these by products and explain why they are formed.

c. Suggest a more efficient way to produce ethylamine which does not involve the formation of unwanted by products.

3. Name the following reagents and conditions needed to carry out the following reactions:

a. 2-bromopropane to propylamine

b. ethylamine to diethylamine

c. nitrobenzene to phenylamine.

4. Amines have a fishy and generally unpleasant smell, however with the addition of hydrochloric acid this smell disappears.

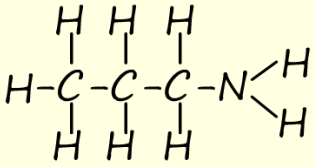
a. Write an equation to show why the unpleasant ammonia smell from ethylamine disappears when an excess of dilute hydrochloric acid is added to it.

b. Why does this strongly unpleasant ammonia smell then return when an excess of sodium hydroxide is added? Write an equation to show the reaction involved here.

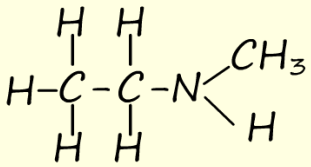
5. Explain how phenylamine can be made from benzene. Identify all reagents and the type of reactions taking place.

Answers

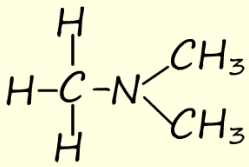
1. Draw the structure of a primary, secondary and tertiary amine all of which have the formula of $CH_3CH_2CH_2NH_2$.



primary amine
propylamine



secondary amine
N-methylethylamine



tertiary amine
N,N-dimethylmethylamine

b. The amine $CH_3CH_2CH_2NH_2$ can be prepared by two different routes.

Route 1 starts from CH_3CH_2Br

Route 2 starts from $CH_3CH_2CH_2Br$

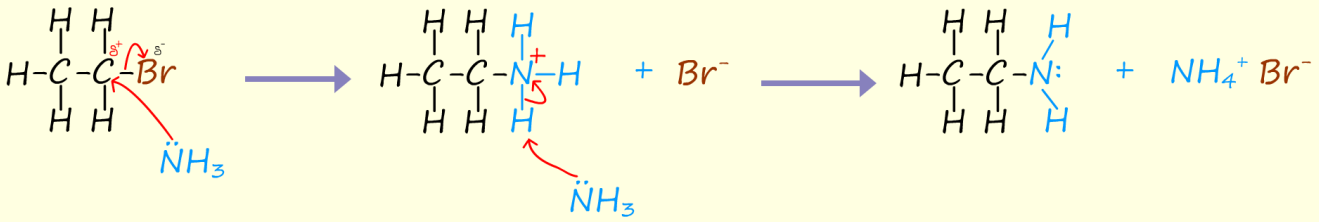
i. Identify the reagents and reactions taking place in each of these two routes.

Route 1 – the product of the reaction, propylamine contains 3 carbon atoms, but the starting material, bromoethane only contains 2 carbon atoms, so we need to add an extra carbon atom. So need to add sodium/potassium cyanide in alcoholic sodium/potassium hydroxide under reflux conditions. The product of the reaction will be propanenitrile which will need to be reduced using either Ni or Pt catalysts in the presence of hydrogen, or use a strong reducing agent such as $LiAlH_4$ in dry ether followed by hydrolysis using water to form the propylamine.

Route 2 – nucleophilic substitution using an excess of ammonia, reaction will need to be carried out in sealed containers.

2. Draw a mechanism and write an equation to show how the reaction of bromoethane with an excess of ammonia is likely to proceed.

reaction mechanism

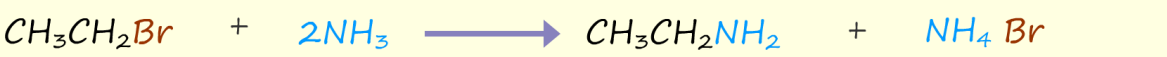


1. The C-Br bond is polar this means that the δ^+ carbon atom is readily attacked by nucleophiles, such as the ammonia molecule.

2. In the amine salt formed the nitrogen atom ends up with a positive charge, this will make the N-H bonds very polar. Another ammonia molecule now acts as a BASE and removes a hydrogen ion (H^+). This will reform the lone pair on the nitrogen atom.

3. The products of the reaction will be the primary amine, ethylamine and the amine salt ammonium bromide.

We can show the reaction as:



bromoethane + ammonia ⟶ ethylamine + ammonium bromide

a. Why is an excess of ammonia used in this reaction?

To try and limit the production of diethylamine, triethylamine and tetraethylammonium chloride.

b. This reaction is likely to produce a number of unwanted by products. Name these by products and explain why they are formed.

See answer to part A

c. Suggest a more efficient way to produce ethylamine which does not involve the formation of unwanted by products.

Start with bromoethane and convert to ethanenitrile by reaction with sodium cyanide in alcoholic sodium hydroxide, then reduce the ethanenitrile produced using either $LiAlH_4$ in dry ether followed by addition of water, or reduce with hydrogen and Pt or Ni catalyst

3. Name the following reagents and conditions needed to carry out the following reactions:

a. 2-bromopropane to propylamine

excess of ammonia in ethanol.

b. ethylamine to diethylamine

ammonia in ethanol

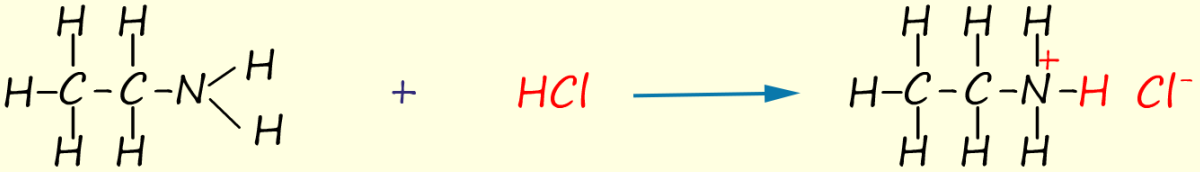
c. nitrobenzene to phenylamine.

Reflux conditions, Tin or iron in concentrated hydrochloric acid, followed by addition of sodium or potassium hydroxide to generate the amine from the salt.

4. Amines have a fishy and generally unpleasant smell, however with the addition of hydrochloric acid this smell disappears.

a. Write an equation to show why the unpleasant ammonia smell from ethylamine disappears when an excess of dilute hydrochloric acid is added to it.

The smell of the amine will disappear when it reacts with hydrochloric acid because it will undergo an acid base neutralisation reaction to form an amine salt, which being an ionic compound will not be volatile and will not smell.



$$C_2H_5NH_2 + HCl \longrightarrow C_2H_5NH_3^+ Cl^-$$

b. Why does this strongly unpleasant ammonia smell then return when an excess of sodium hydroxide is added? Write an equation to show the reaction involved here.

The smell of the amine returns because the sodium hydroxide will remove a proton (hydrogen ion, H^+) from the amine salt to reform the volatile ethylamine.

5. Explain how phenylamine can be made from benzene. Identify all reagents and the type of reactions taking place.

Aromatic amines are usually made by the reduction of the nitro group (NO_2) on an aromatic ring using iron or tin/conc hydrochloric acid followed by addition of a strong base to form the amine from the salt produced.