

Chemguide – answers

PHENYLAMINE: AS A PRIMARY AMINE

1. Amines and ammonia are bases because the lone pair on the nitrogen atom can pick up hydrogen ions. In phenylamine, the lone pair becomes delocalised to some extent with the ring electrons, and that makes it less attractive to hydrogen ions.

Delocalisation also makes a molecule more energetically stable. If the lone pair reacts with a hydrogen ion, the small amount of extra delocalisation has to be broken, and that needs some energy.

2. a) Any *named* acid – for example, dilute hydrochloric acid or dilute sulphuric acid (but not nitric acid because it reacts with the ring).
b) Any named strong base – for example, sodium hydroxide solution.
c) You can use ethanoyl chloride, CH_3COCl , or ethanoic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$. If you use the anhydride, the reaction needs to be heated. The ethanoyl chloride reaction is vigorous in the cold.
d) Bromoethane, $\text{CH}_3\text{CH}_2\text{Br}$. Heat.
e) This reaction happens because the lone pair on the phenylamine attacks the bromoethane pushing the bromine off and forming a new bond with the ethyl group. The product molecule also has a lone pair on a nitrogen and can do the same thing, giving a tertiary amine (which still has a lone pair on the nitrogen), which can go on to produce a quaternary ammonium salt.

(I am leaving out the formation of the salts of the amines which are produced as well to try to keep the whole thing more manageable. Check to see exactly what your examiners want, and be sure to learn it in enough detail for them. You may well find that they don't want anything beyond the formation of the secondary amine shown in the flow scheme.)