ANSWERS TO PRACTICE QUESTIONS

Q5
Order of increasing basicity: **(d) < (a) < (e) < (b) < (c).**

The basicity of each given compound depends on the availability of the lone pair of electrons on the nitrogen atom to form a dative covalent bond with a proton. The greater this availability, the greater the basicity of the compound**.**

(d) is an amide and is the least basic (effectively neutral) because the orbital containing the lone pair of electrons on the nitrogen atom overlaps with the π electron cloud of both the benzene ring and the C=O bond. As such, the lone pair is delocalised and is the least available to form a dative covalent bond with a proton**.**

The aromatic amines, **(a)** and **(e)**, are less basic than the aliphatic amines, **(b)** and **(c)**, because of the delocalisation of the lone pair of electrons on the nitrogen atom into the benzene ring**.**

(a) is less basic than **(e)** because the electron-withdrawing $-NO_2$ group further decreases the electron density at the nitrogen atom and hence further reduces the availability of the nitrogen lone pair to form a dative covalent bond with a proton**.**

The aliphatic amines, **(b)** and **(c)**, are stronger bases because the alkyl groups bonded to the nitrogen atom are electron-donating and this increases the electron density at the nitrogen atom, making the lone pair of electrons on the nitrogen atom much more readily available to form a dative covalent bond with a proton**.**

(c) is a stronger base than **(b)** since there are two electron-donating alkyl groups bonded to the nitrogen atom in **(c)** compared to only one in **(b)**.

Q6a phenylamine and (phenylmethyl)amine

Test	Add a few drops of Br_2(aq) to each sample in a test tube at room temperature.
Observations	For phenylamine, there would be decolourisation of orange Br_2(aq) and the formation of a white precipitate. For (phenylmethyl)amine, there would be no decolourisation of orange Br_2(aq) nor formation of a white precipitate.

Q6b $CH_3CH_2CH_2NH_3^+Cl^-$ and $(CH_3)_4N^+Cl^-$

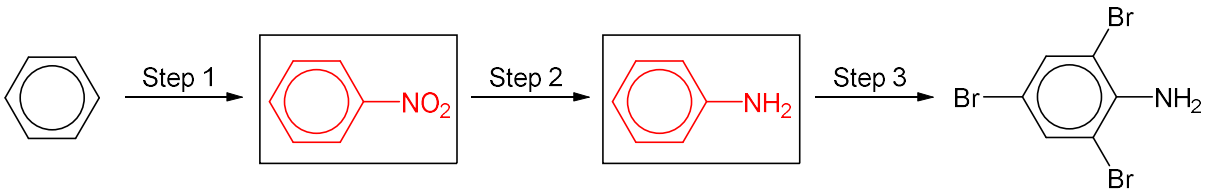
Test	Add NaOH(aq) to each sample in a test tube and warm/heat each mixture gently.
Observations	For $CH_3CH_2CH_2NH_3^+Cl^-$, a pungent gas ($CH_3CH_2CH_2NH_2$) which turns moist red litmus paper blue will be evolved on warming. For $(CH_3)_4N^+Cl^-$, there will not be any gas evolved upon warming.

Q6c CH_3CONH_2 and $CH_3COO^-NH_4^+$

Test	Add NaOH(aq) to each sample in a test tube and warm each mixture.
Observations	For $CH_3COO^-NH_4^+$, NH_3 gas which turns moist red litmus paper blue, would be evolved almost immediately upon warming. For CH_3CONH_2, there would not be any NH_3 gas evolved upon gentle heating. The NH_3 gas would only evolve after strong heating for some time.

Q7

(a)



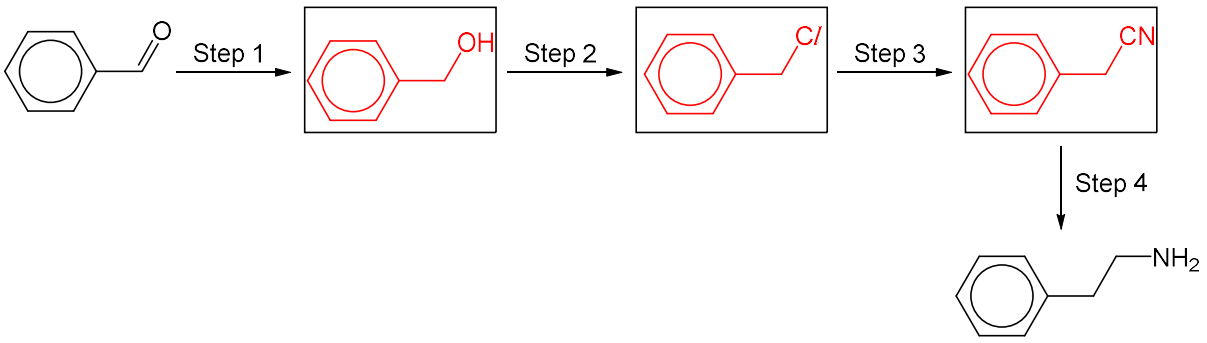
Reagents and conditions

Step 1: conc HNO_3, conc H_2SO_4, heat (or 55 °C)

Step 2: Sn, conc HC*l*, heat (under reflux), followed by NaOH(aq)

Step 3: Br_2(aq)

(b)



Reagents and conditions

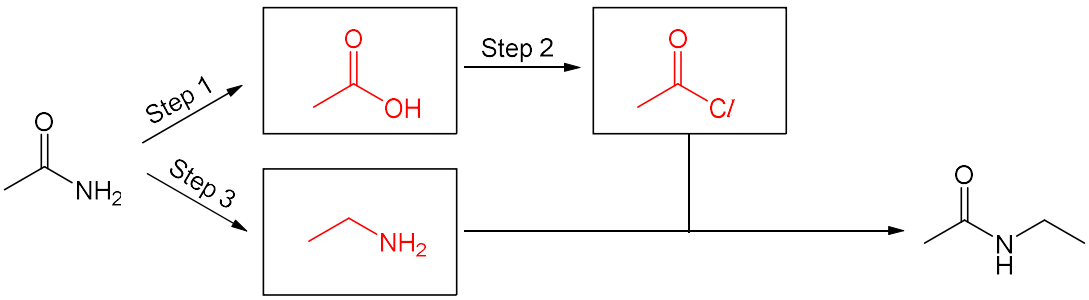
Step 1: $LiAlH_4$ in dry ether OR $NaBH_4$ OR H_2, Ni, heat

Step 2: $SOCl_2$ OR PCl_5 OR PCl_3

Step 3: KCN in ethanol, heat (under reflux)

Step 4: $LiAlH_4$ in dry ether OR H_2, Ni, heat

(c)



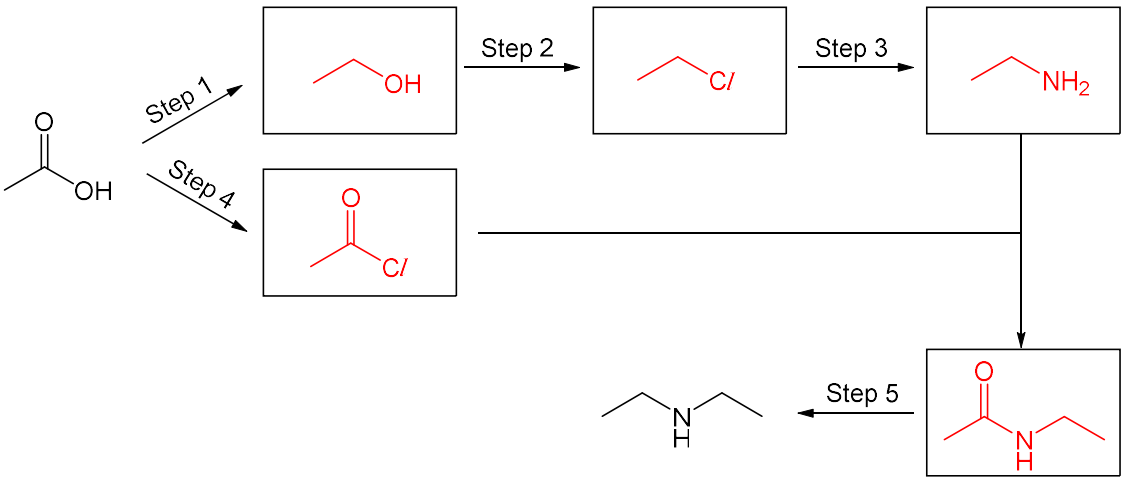
Reagents and conditions

Step 1: HC*l*(aq), heat (under reflux)

Step 2: $SOCl_2$ OR PCl_5 OR PCl_3

Step 3: $LiAlH_4$ in dry ether

(d)



Reagents and conditions

Step 1: $LiAlH_4$ in dry ether

Step 2: $SOCl_2$ OR PCl_5 OR PCl_3

Step 3: excess conc NH_3 in ethanol, heat in sealed tube

Step 4: $SOCl_2$ OR PCl_5 OR PCl_3

Step 5: $LiAlH_4$ in dry ether

Q8a

Functional groups present: 3° aromatic amine, 2° aliphatic amine and 2° amide

Q8b

The three nitrogen-containing groups can be arranged in the following order of increasing pK_b value:

(2) < (1) < (3).

The smaller the pK_b value, the larger is the K_b value and hence the stronger is the basicity of the nitrogen-containing group. In this case, the basicity is determined by the availability of the lone pair of electrons on the N atom to form a dative covalent bond with a proton. The greater this availability, the greater the basicity.

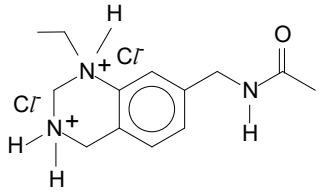
(2) is a secondary amine and is the strongest base here. The two electron-donating alkyl groups bonded to the N atom increases the electron density at the N atom and makes the lone pair of electrons at the N atom more available to form a dative covalent bond with a proton.

(1) is an aromatic amine. It is a weaker base than (2) because the lone pair of electrons on the N atom delocalises into the benzene ring and is less available to form a dative covalent bond with a proton.

(3) is an amide. It is the weakest base here because the orbital containing the lone pair of electrons on the N atom overlaps with the π electron cloud of the adjacent C=O group and the lone pair of electrons is delocalised, and hence not available to form a dative covalent bond with a proton.

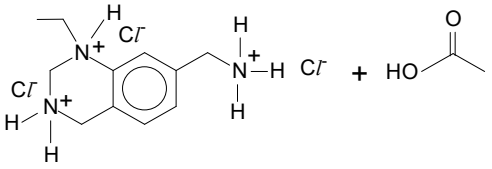
Q8c

(i)



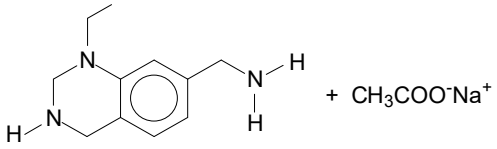
- acid-base reaction, amide is not protonated

(ii)



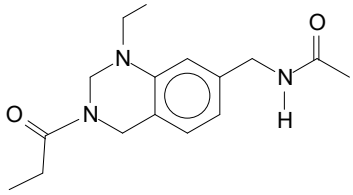
- acid-base reaction and amide undergoes acid hydrolysis

(iii)



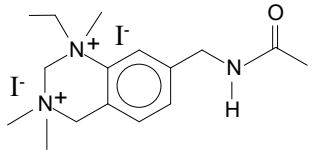
- amide undergoes base hydrolysis

(iv)



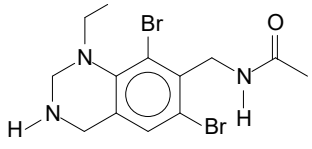
- N(2) undergoes condensation to form amide

(v)



- nucleophilic substitution occurs with N(1) and N(2) functioning as nucleophiles

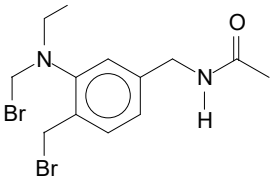
(vi)



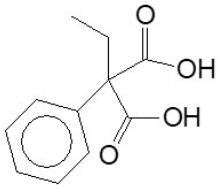
- benzene ring of aromatic amine undergoes electrophilic substitution (similar to phenylamine)

Q8d

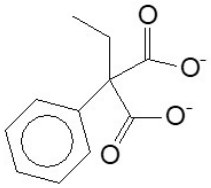
Type of reaction: nucleophilic substitution

X: 

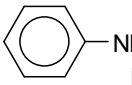
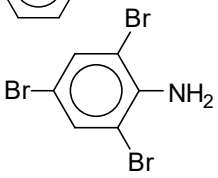
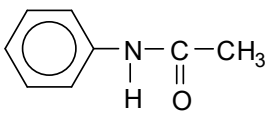
Q9a

 and CO_2 and NH_4^+

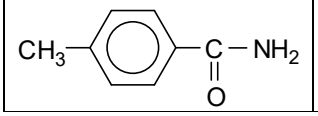
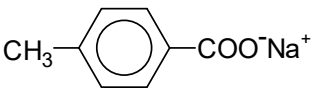
Q9b

 and CO_3^{2-} and NH_3

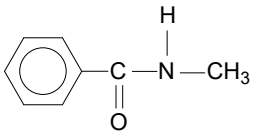
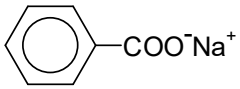
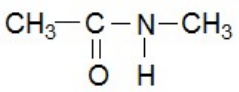
Q10(a) – Q, R, S and T

Information	Deduction / Explanation
Q has molecular formula, C_8H_9NO.	**Q** is likely to contain a benzene ring due to C:H ≈ 1:1.
Q, C_8H_9NO, is a neutral compound.	**Q** may contain an amide or –CN group.
Q on heating under reflux with NaOH(aq) yields a salt **R** and **S**.	Alkaline hydrolysis of **Q** occurred. **Q** contains the amide functional group. (Note to tutors: **Q** cannot be a nitrile because while the basic hydrolysis of a nitrile will yield a carboxylate salt, NH_3 (M_r = 17) will also be produced, which cannot be **S**. **R** is a carboxylate salt. **S** is an amine.
S (M_r = 93) reacts with Br_2(aq) to form **T**, $C_6H_4Br_3N$.	Electrophilic substitution of **S** occurred. **S** is an aromatic amine. **S** is  which has M_r = 93. **T** is 
Since the sum of carbon atoms in **R** and **S** is the same as that in **Q**, then the number of carbon atoms in **R** = 8 – 6 = 2. Hence **R** is $CH_3COO^-Na^+$. Hence **Q** is 	

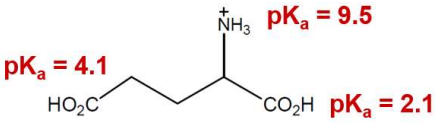
Q10(b) – U (C_8H_9NO) and V

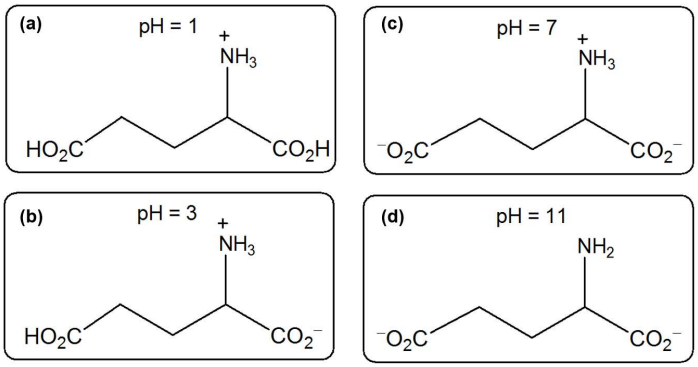
U	V
	

Q10(b) – W (C_8H_9NO), X, Y and Z

W	X	Y	Z
	CH_3NH_2		

Q11





Q12a

Proteins can be hydrolysed in the laboratory by **prolonged heating** with **aqueous HC*l* or H_2SO_4 of** higher concentration (e.g. 6 mol dm^{-3} HC*l*).

Q12b

Overlapping regions are **underlined**.

Chymotrypsin	Trypsin	Sequence of fragments in P
asp-lys-**gly-phe**	**gly-phe**-lys	asp-lys-**gly-phe**-lys
lys-**val-arg**	**val-arg**	lys-**val-arg**
val-phe	**val-phe**-asp-lys	**val-phe**-asp-lys

Based on sequences of fragments (last column), find overlapping regions again.

val-phe-asp-lys
asp-lys-**gly-phe**-lys
lys-**val-arg**

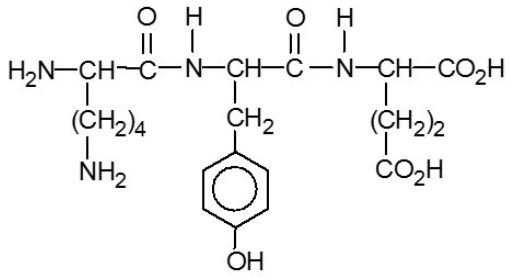
Sequence of amino acids in **P**: **val-phe-asp-lys-gly-phe-lys-val-arg**

Q13a

There are **6** ways of forming the tripeptide.
Note: Each tripeptide is formed from 3 different amino acids.

BCD CBD DBC
BDC CDB DCB

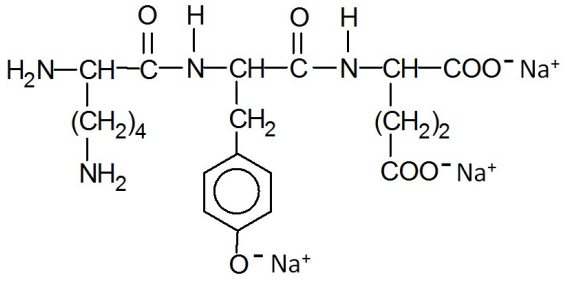
Q13b



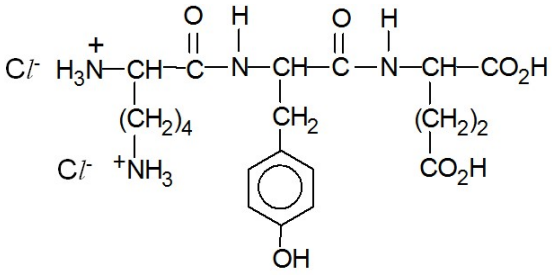
or the zwitterionic form

Q13c

(i) ***BCD*** *tripeptide in* ***(b)***
+ dilute aqueous sodium hydroxide



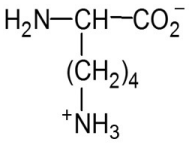
(ii) ***BCD*** *tripeptide in* ***(b)***
+ dilute hydrochloric acid



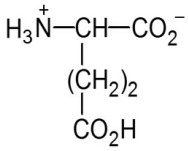
Q13d

A **zwitterion** is an electrically neutral molecule with oppositely charged ends.

Zwitterionic form of **B**



Zwitterionic form of **D**



Note to tutors:
Link back to **Q11** to explain why the CO_2H next to the amino group loses its proton more easily than the CO_2H on the side-chain.