

34.2 PHENYL AMINES AND AZO COMPOUNDS

Learning outcomes

Candidates should be able to:

1. describe the preparation of phenylamine via the nitration of benzene to form nitrobenzene, followed by reduction with hot Sn/concentrated HCl followed by NaOH(aq)
2. describe:
 - (a) the reaction of phenylamine with Br₂(aq) at room temperature
 - (b) the reaction of phenylamine with HNO₂ or NaNO₂ and dilute acid below 10°C to produce the diazonium salt; further warming of the diazonium salt with H₂O to give phenol
3. describe and explain the relative basicities of aqueous ammonia, ethylamine, and phenylamine
4. recall the following about azo compounds:
 - (a) describe the coupling of benzenediazonium chloride with phenol in NaOH(aq) to form an azo compound
 - (b) identify the azo group
 - (c) state that azo compounds are often used as dyes
 - (d) that other azo dyes can be formed via a similar route

Reduction of nitrobenzene

<https://www.youtube.com/watch?v=nKWOZajmAQo>

<https://www.youtube.com/watch?v=4fmIqhkGmKk>

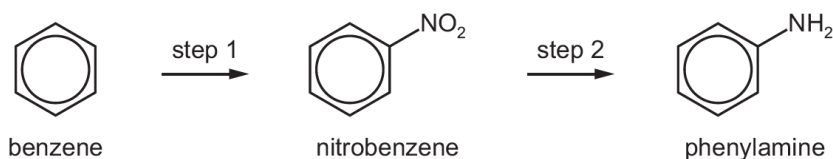
1. Pure phenylamine, C₆H₅NH₂, can be prepared from benzene in two steps.

Draw the structure of the intermediate compound.

Suggest reagents and conditions for each step.

.....
.....
.....
.....
..... [3]

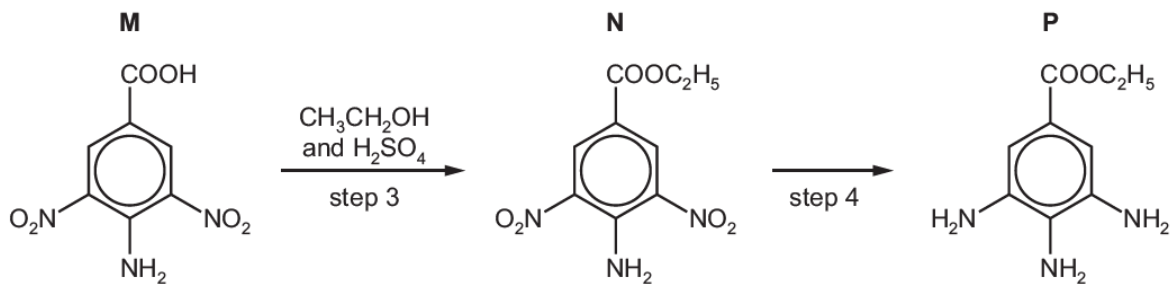
2. Benzene can be used as a starting material to produce phenylamine by a two-step synthesis.



Give reagents and conditions for the production of phenylamine from nitrobenzene in step 2.

.....
..... [2]

3. Compound **M** is converted into compound **P** as shown.



State the reagents and conditions for step 4.

..... [2]

4. 2-nitrophenol can undergo different reactions as shown in Fig. 6.3

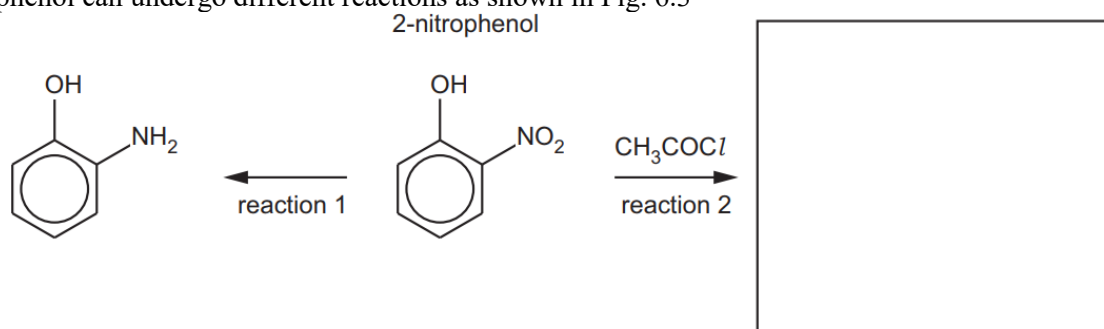


Fig. 6.3

- (i) Suggest reagents and conditions for reaction 1.

..... [1]

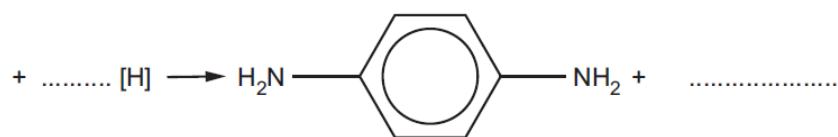
- (ii) Name the type of reaction for reaction 1.

..... [1]

5. Benzene-1,4-diamine can be formed by reduction of 1,4-dinitrobenzene.

Complete the equation for this reduction.

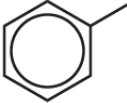
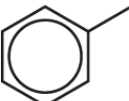
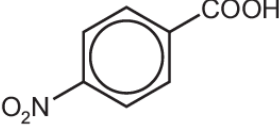
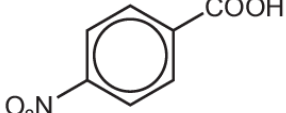
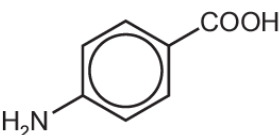
[H] represents one atom of hydrogen from a reducing agent.



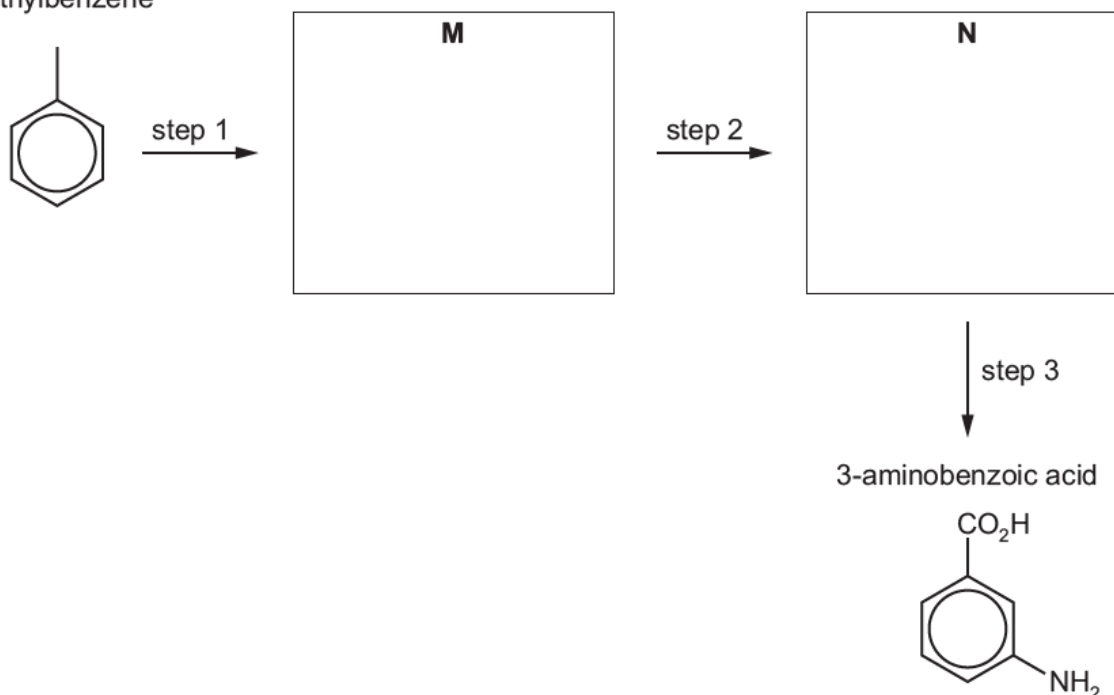
[1]

6. A student proposes a multi-step synthesis of F from benzene, as shown in Table 4.1. Complete Table 4.1 by providing relevant details of the reagents and conditions for steps 1 and 4, and the structure of product D.

Table 4.1

step	organic reactant	reagent(s) and conditions	organic product
1			
2		concentrated HNO_3 and concentrated H_2SO_4	D
3	D	hot alkaline KMnO_4 then dilute H_2SO_4	E 
4			F 

7. 3-aminobenzoic acid can be synthesised from methylbenzene in three steps.
methylbenzene



(i) Draw the structures of M and N in the boxes.

[2]

(ii) Suggest reagents and conditions for each step of the synthesis.

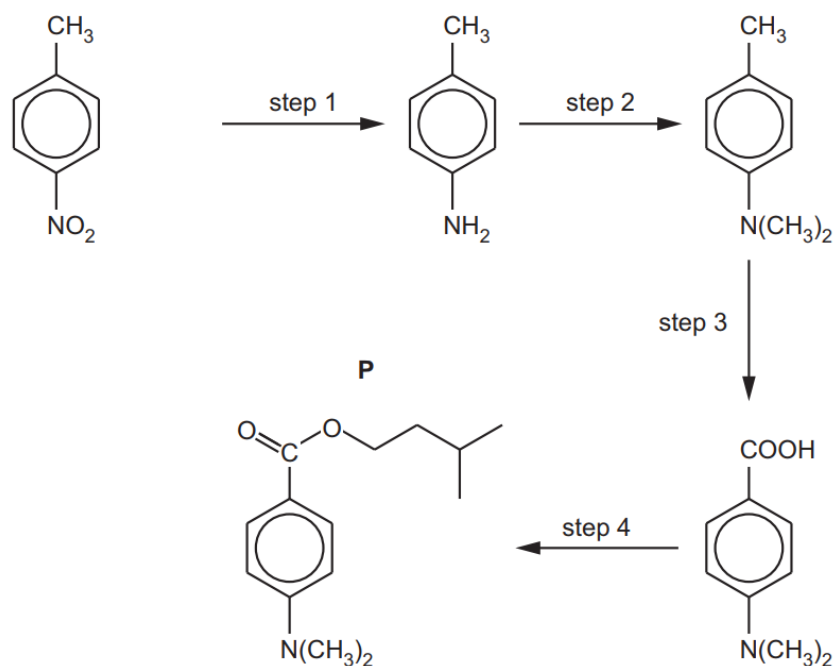
step 1

step 2

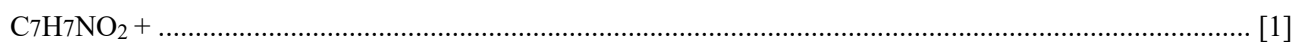
step 3

[3]

8. Compound P can be synthesised from 1-methyl-4-nitrobenzene by the route shown in Fig. 4.3.



- (i) Step 1 is a reduction reaction.
Complete the equation for this reaction. Use [H] to represent an atom of hydrogen from the reducing agent.



- (ii) Complete Table 4.1 to give details of each step of the synthesis shown in Fig. 4.3.

step	reagents and conditions	type of reaction
1		reduction
2		
3		
4		condensation

9. Compound X is made from benzene by the route shown in Fig. 9.1.

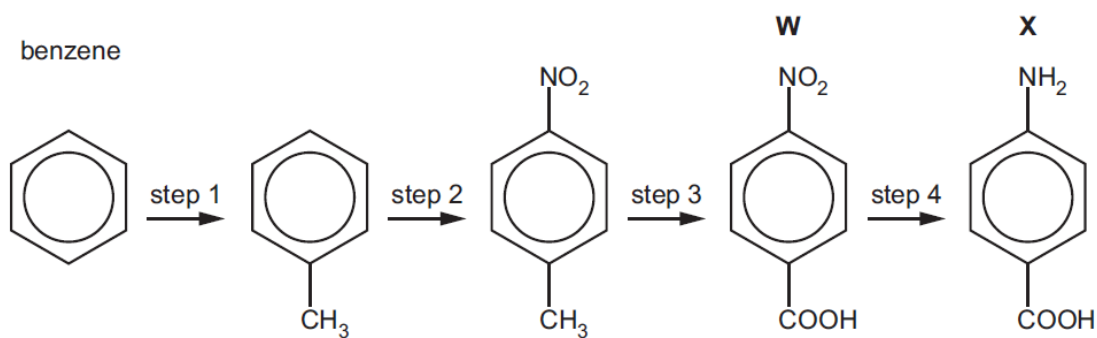


Fig. 9.1

(b) Describe the reagents and conditions required for step 1 in Fig. 9.1.

.....
 [1]

(c) In step 1 of Fig. 9.1 benzene reacts with $^+\text{CH}_3$.

Complete Fig. 9.2 to show the mechanism for this reaction, including:

- the movement of electron pairs using curly arrows
- the structure of the intermediate involved.

[3]

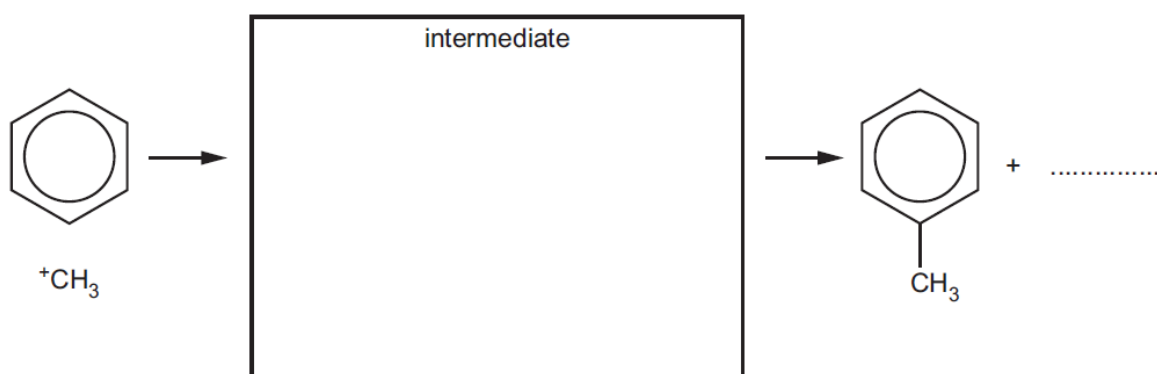


Fig. 9.2

(d) Describe the reagents and conditions required for step 2 of Fig. 9.1.

.....
 [2]

(e) Identify the reagents required for step 3 of Fig. 9.1. Compound W is the product of this step.

..... [1]

(f) Name compound W.

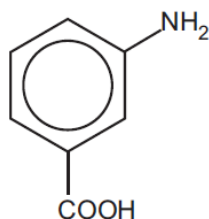
..... [1]

(g) The reagents commonly used for step 4 will not reduce the $-\text{COOH}$ group.

Identify the reagents and conditions required for step 4 of Fig. 9.1.

..... [1]

- (h) Benzene can also be used as a starting material to make compound Y.
 compound Y



Describe how the route described in Fig. 9.1 (repeated below) can be changed to give compound Y instead of compound X.
 Explain your answer.

.....

 [2]

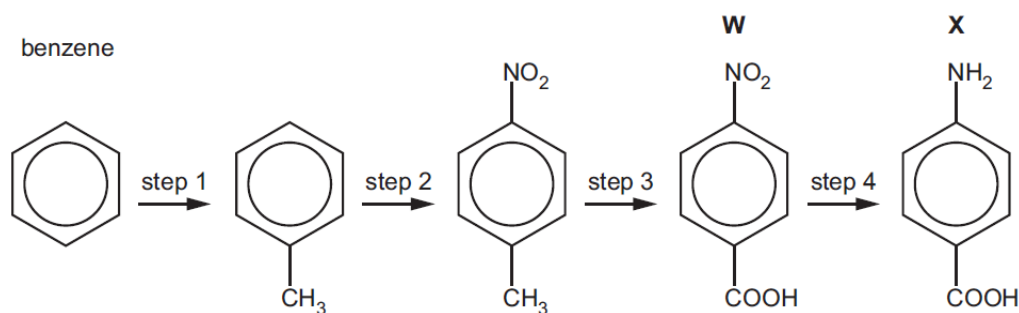
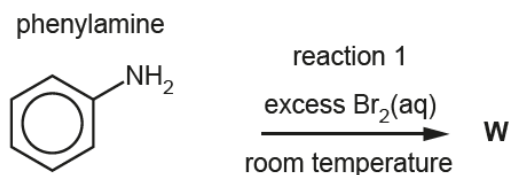


Fig. 9.1

Reaction with aqueous bromine

10. Draw the structure of W, the organic product of reaction 1.

[1]



11. Phenylamine, $C_6H_5NH_2$, and ethylamine, $C_2H_5NH_2$, can be distinguished by adding aqueous bromine.
 (a) State what is seen when aqueous bromine is added to phenylamine.

.....
 [2]

- (b) Suggest what is seen when aqueous bromine is added to ethylamine.

..... [1]

(c) Draw the structure of the organic product formed when an excess of aqueous bromine is added to phenylamine. [1]

(d) Name the product you have drawn in (c).

..... [1]

12. a) Phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, and propylamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, can be produced by different reduction reactions.

(i) Identify an organic compound that can be converted into $\text{C}_6\text{H}_5\text{NH}_2$ by a reduction reaction. State the reagents and conditions for this reaction.

organic compound

reagents

conditions[2]

(iii) Identify a single test that will distinguish between $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ by producing a white precipitate with only one of these amines.

Draw the structure of the compound that is precipitated.

testing reagent

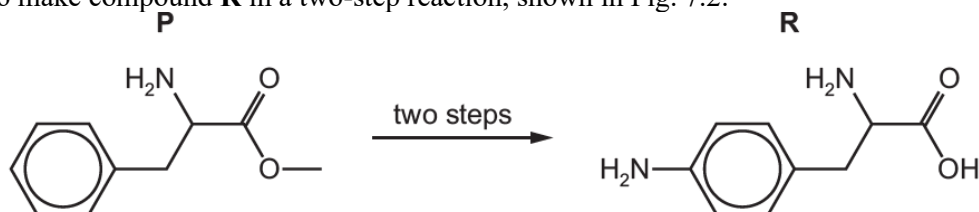
amine that gives a precipitate

structure of the compound that is precipitated:

[2]

<https://www.youtube.com/watch?v=101sftzNnck>

13. **P** can be used to make compound **R** in a two-step reaction, shown in Fig. 7.2.



(i) Identify the reagents and conditions used for the two steps of the reaction.

step 1

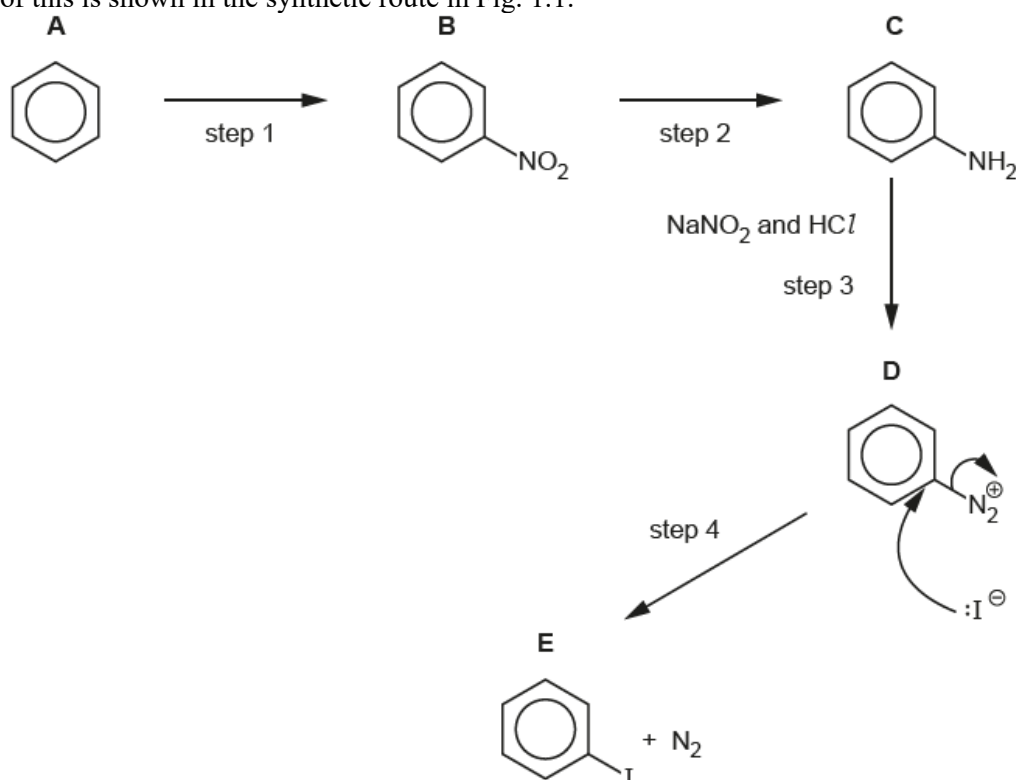
step 2 [2]

(ii) Complete Table 7.1 by drawing the structures of the organic products formed when **R** is treated separately with the reagents given. [2]

reagent	product
$\text{HNO}_2(\text{aq})$ at 4°C	
an excess of $\text{Br}_2(\text{aq})$ at room temperature	

14. KI is used as a source of I^- ions in organic synthesis.

One example of this is shown in the synthetic route in Fig. 1.1.



(ii) The I^- from KI reacts with **D** in step 4. The mechanism is shown in Fig. 1.1. Suggest the name for this mechanism. [1]

- (iii) Step 3 occurs in two stages. stage I NaNO_2 and HCl undergo an acid–base reaction to produce HNO_2 . stage II HNO_2 reacts with C, $\text{C}_6\text{H}_5\text{NH}_2$, to produce D, $\text{C}_6\text{H}_5\text{N}_2^+$. Complete the equations for stage I and for stage II. stage I $\text{NaNO}_2 + \text{HCl}$ stage II [2]

Azo dyes

<https://www.chemguide.co.uk/organicprops/aniline/propsdiaz.html#top>

15. Fig. 4.2 shows some reactions of phenylamine.

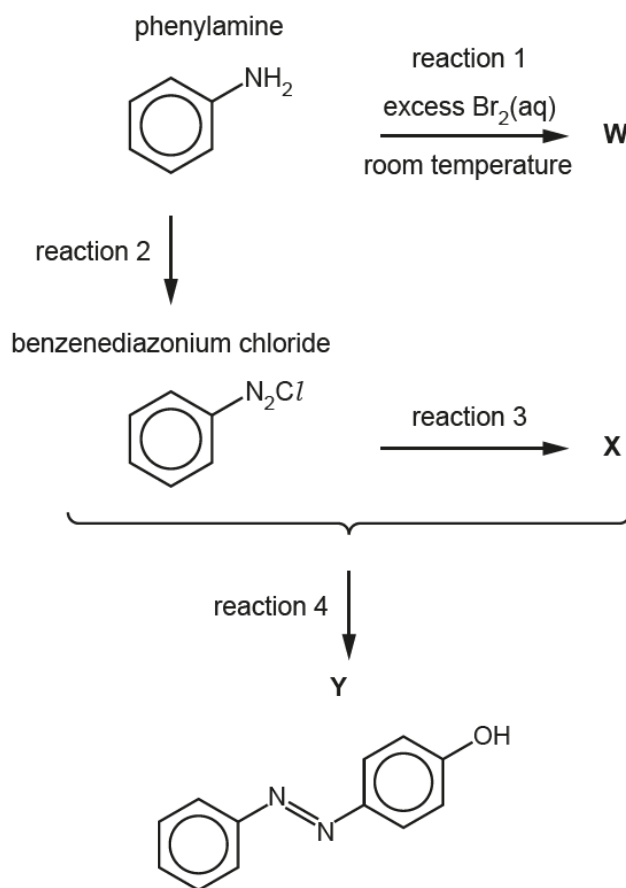
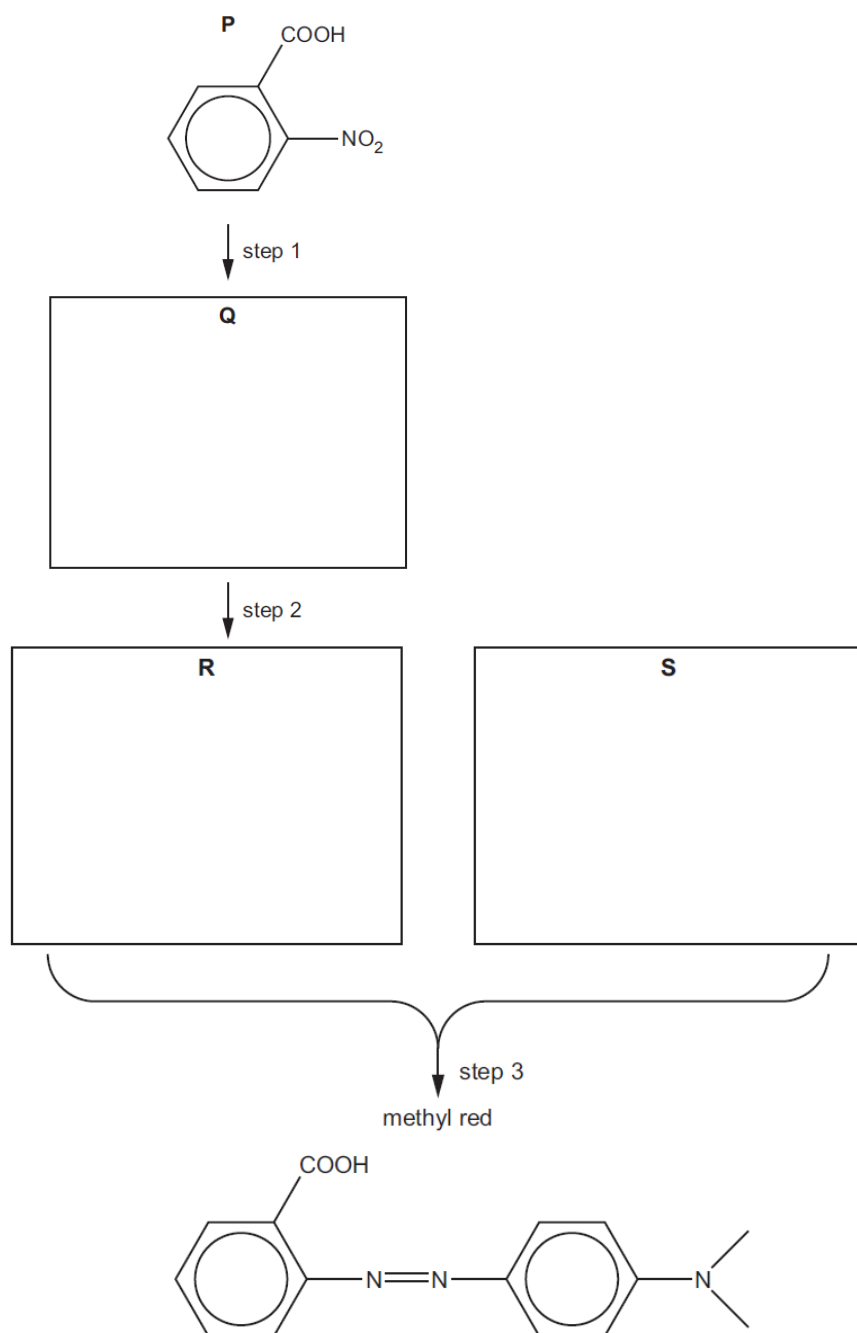


Fig. 4.2

16. Methyl red can be synthesised as shown in Fig. 7.1.



S reacts in a similar way to phenol in step 3.

(i) Draw the structures of **Q**, **R** and **S** in the boxes in Fig. 7.1.

[3]

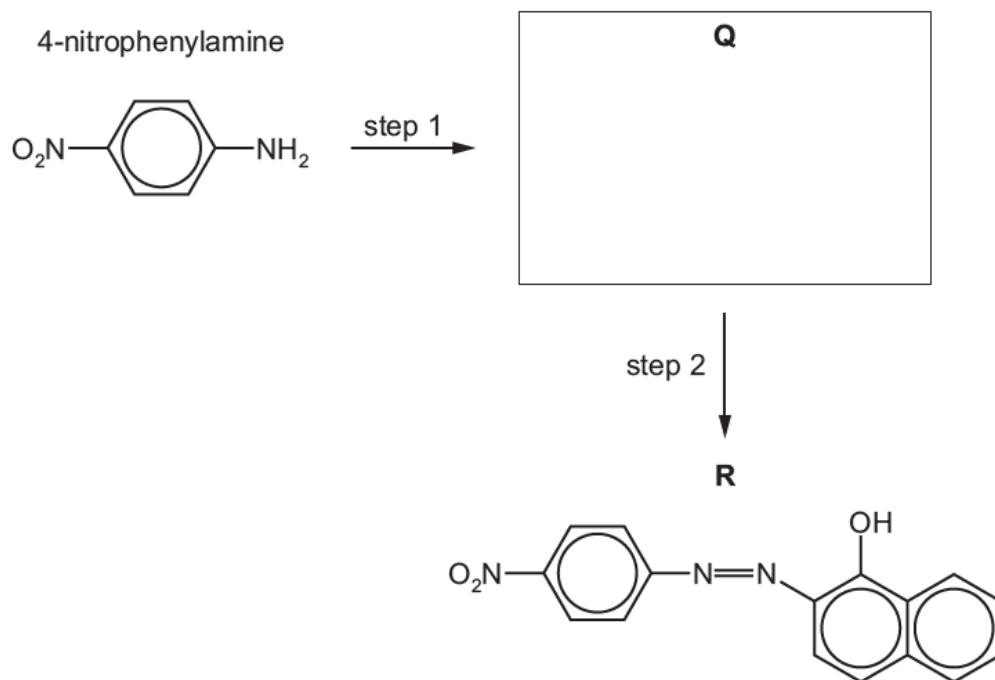
(ii) Suggest reagents and conditions for steps 1 and 2 in Fig. 7.1.

step 1

step 2

[3]

17. The dye R can be synthesised from 4-nitrophenylamine in two steps.



(i) Deduce and draw the structure of the organic salt Q in the box. [1]

(ii) Suggest reagents and conditions for step 1 and 2 in (b).

step 1

step 2

[2]

18. Fig. 7.2 shows the two-step synthesis of the azo compound W.

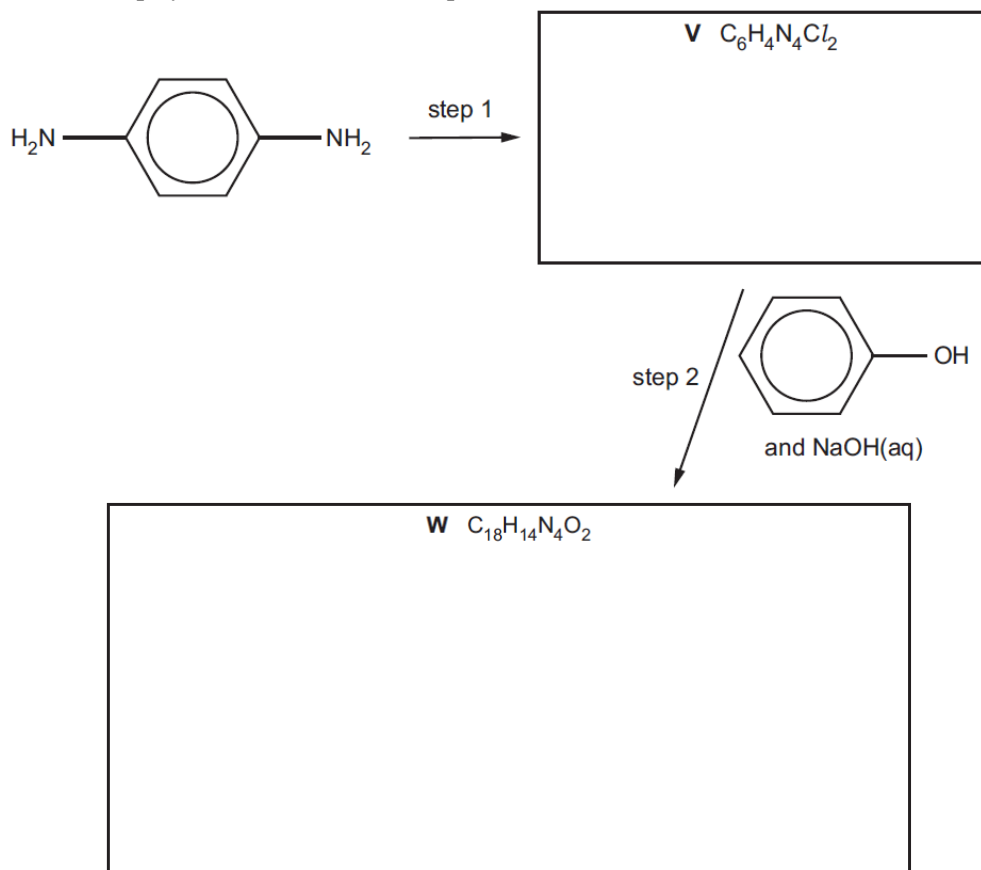


Fig. 7.2

(i) Suggest structures for compounds V and W and draw them in the boxes in Fig. 7.2. [2]

(ii) Give the reagents and conditions for step 1.

..... [1]

19. The azo compound Congo Red is used as an acid–base indicator and can be made by the route shown in Fig. 6.2. In step 3 of this synthesis, compound Y reacts with compound Z. Compound Z is made from compound X. Assume that the $\text{SO}_3^- \text{Na}^+$ groups do not react.

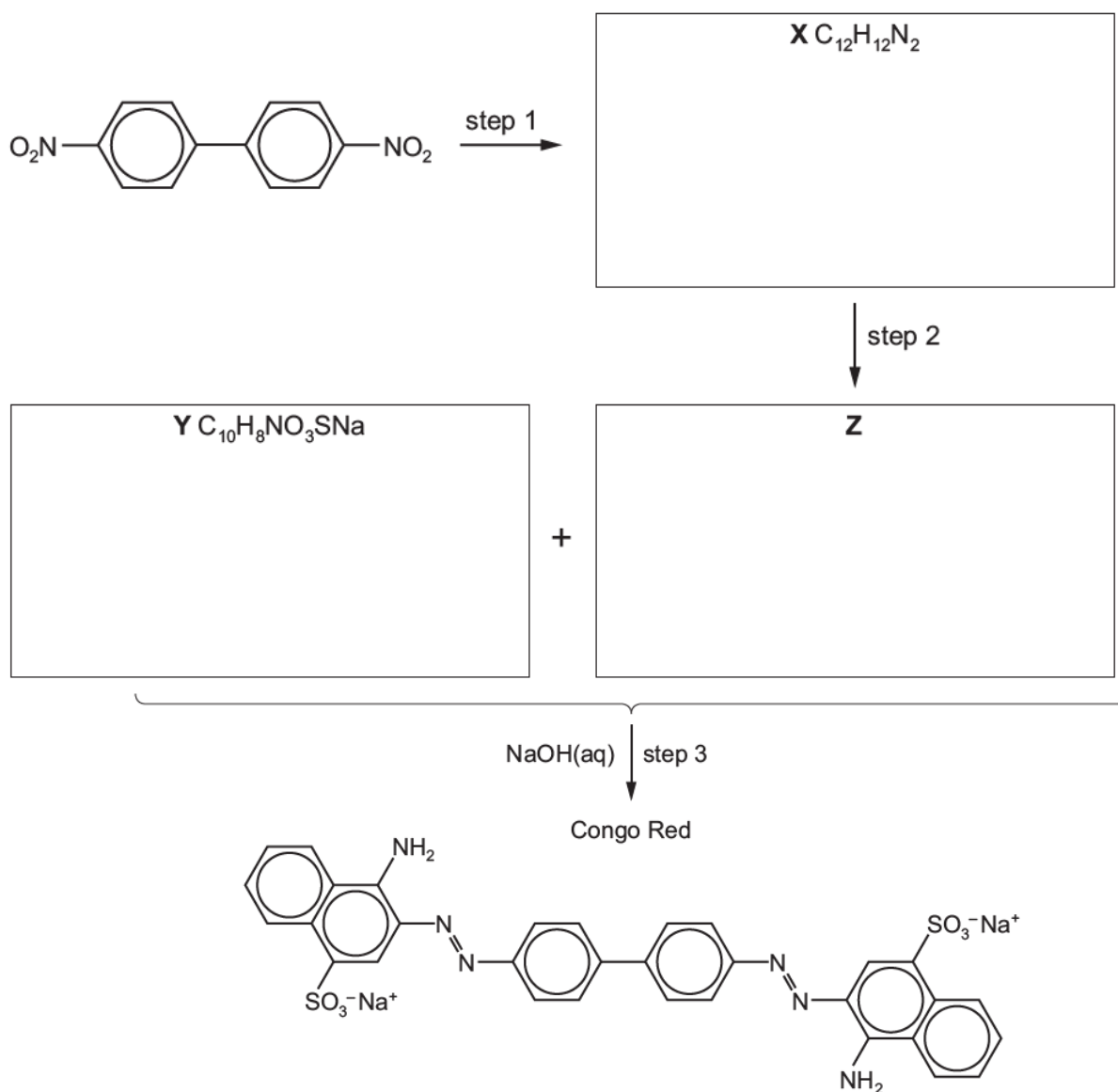


Fig. 6.2

(i) Suggest structures for compounds X, Y and Z and draw them in the boxes in Fig. 6.2. [3]

(ii) Give the reagents and conditions for step 1 and step 2.

step 1

step 2 [3]

20. Sunset Yellow is an additive used for colouring foods.

A synthetic route for making Sunset Yellow is shown.

Molecules E and G each contain one SO_3^- group. These groups are unchanged in the formation of Sunset Yellow.

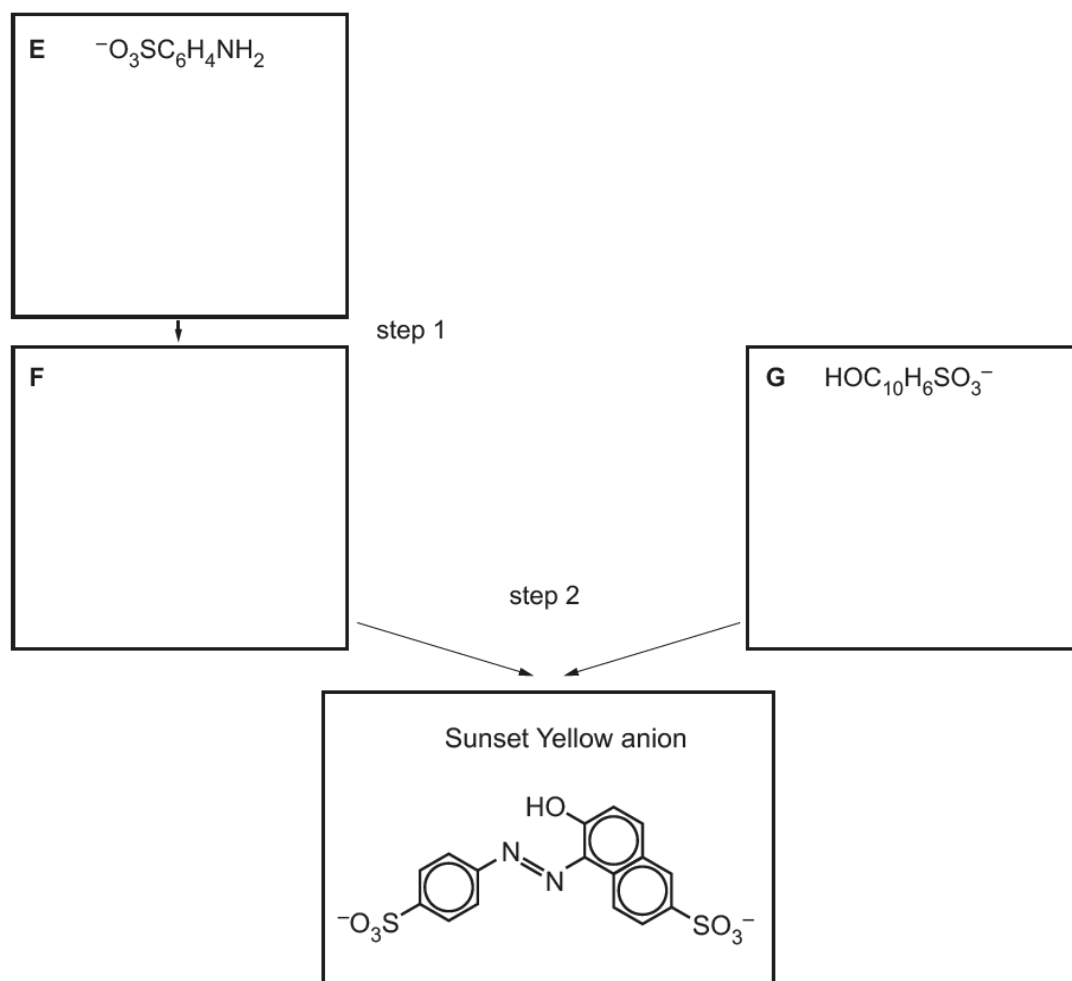


Fig. 7.1

(b) Deduce the structures of E, F and G and draw them in the boxes in Fig. 7.1.

[3]

(c) Suggest suitable reagents and conditions for step 1 and 2.

step 1

step 2

[3]

Basicity of amines

What is a Bronsted-Lowry acid?

What is a Bronsted-Lowry base?

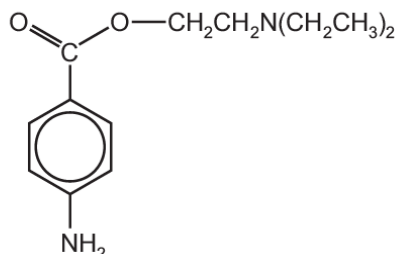
The strength of ammonia and amines as bases depends on the availability of the lone pair of electrons on their N atom to bond with an H^+ ion.

<https://www.chemguide.co.uk/basicorg/acidbase/bases.html>

21. $(\text{C}_2\text{H}_5)_2\text{NH}$ reacts with **Y** in reaction 2.
Explain why $(\text{C}_2\text{H}_5)_2\text{NH}$ can act as a nucleophile.

.....
 [1]

22. Procaine is used as an anaesthetic in medicine. It can be synthesised from methylbenzene in five steps



State why procaine can act as a base.

.....
 [1]

23. Explain why an aqueous solution of 2-aminobutane has a pH greater than 7.
Include an equation in your answer.

.....

 [2]

24. $(\text{CH}_3\text{CH}_2)_2\text{NH}$ reacts with ethanoic acid, CH_3COOH .
Complete the equation for this reaction.

$(\text{CH}_3\text{CH}_2)_2\text{NH} + \text{CH}_3\text{COOH} \dots\dots\dots$ [1]

25. A 0.10 mol dm^{-3} solution of diethylamine, $(\text{CH}_3\text{CH}_2)_2\text{NH}$, has a higher pH than a 0.10 mol dm^{-3} solution of 2-aminobutane, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_3$.
Suggest why.

.....

 [2]

26. Compare the basicities of $\text{C}_2\text{H}_5\text{NHCOCH}_3$, $\text{C}_2\text{H}_5\text{NHC}_2\text{H}_5$ and NH_3 .
Explain your answer.

..... most basic	 least basic
.....	
.....	
.....	
.....	
.....	
.....	

[4]

27. Ethylamine is a weak base.
State the relative basicities of ammonia, ethylamine and phenylamine.
Explain your answer.

..... < <

least basic

most basic

.....
.....
.....
.....
.....
.....
.....
.....

..... [4]

28. Compare and explain the relative basicities of ammonia, butylamine and phenylamine.

..... > >

most basic

least basic

.....
.....
.....
.....
.....
.....
..... [4]

29. Describe the relative basicities of $\text{C}_6\text{H}_5\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ and NH_3 .
Explain your answer.

[4]

30. Describe the relative basicities of ammonia, ethylamine and phenylamine, starting with the least basic.
Explain your answer in terms of their structures.

[3]

31. The structure of cyclohexylamine is shown in Fig. 9.1.

cyclohexylamine

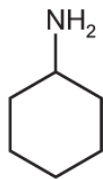


Fig. 9.1

Compare the relative basicities of ammonia, cyclohexylamine and phenylamine.
Explain your reasoning.

..... > >
 most basic least basic

.....

.....

.....

.....

..... [3]

32. State the relative basicities of phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, and ammonia, NH_3 , in aqueous solution. Explain your answer.

..... > >
 most basic least basic

.....

.....

.....

.....

..... [3]

33. Describe the relative basicities of diethylamine, phenylamine and ammonia in aqueous solution.
Explain your answer in terms of structure.

..... least basic most basic

explanation

.....

.....

.....

..... [3]

34. Describe and explain the relative basicities of phenylamine, ethylamine and 4-nitrophenylamine.

..... > >

most basic

least basic

.....
.....
.....
.....
..... [4]

Draw the amide showing all of the bonds and lone pairs of electrons.

Why is the basicity of the nitrogen atom in an amide greatly reduced compared to that of an amine.

35. Explain why benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$, is a much weaker base than ammonia, NH_3 .

.....
..... [1]

36. Explain why amides are much weaker bases than amines.

.....
.....
.....
..... [2]

37. Butanamide, $\text{C}_3\text{H}_7\text{CONH}_2$, is much less basic than butylamine. Explain why?

[1]

.....
.....

38. A student proposes a synthesis of hippuric acid by the reaction of benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$, and chloroethanoic acid, ClCH_2COOH .

The reaction does *not* work well because benzamide is a very weak base.

Explain why amides are weaker bases than amines.

[2]

39. State the difference in the basicities of ammonia, NH_3 , propanamide, $\text{CH}_3\text{CH}_2\text{CONH}_2$, and propylamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$.

Explain your answer.

..... < <

weakest base

strongest base

.....

.....
.....
.....
.....

- [4]
40. State the difference in the basicities of ammonia, NH_3 , propanamide, $\text{CH}_3\text{CH}_2\text{CONH}_2$, and propylamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$.
Explain your answer.

..... < <

weakest base

strongest base

.....
.....
.....
.....
.....
.....
.....

[4]

41. State the relative basicities of ethanamide, diethylamine and ethylamine in aqueous solution.
Explain your answer.

..... > >

most basic

least basic

.....
.....
.....
.....
.....
..... [4]

42. The molecular formulae of three nitrogen-containing compounds are given.

S $\text{C}_6\text{H}_5\text{CONH}_2$

T $\text{C}_6\text{H}_5\text{NH}_2$

U $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

Describe and explain the relative basicities of S, T and U.

..... > >

most basic least basic

.....
.....
.....

[3]

43. (a) The structure of compound **P** is shown in Fig. 7.1.

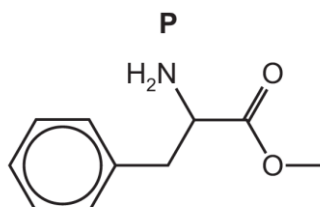
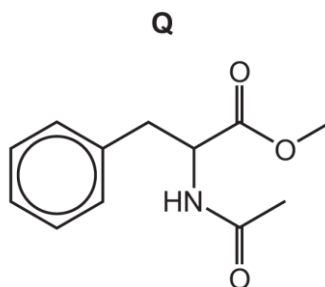


Fig. 7.1

P can be used to make compound **Q** in a single step reaction.



(ii) When an ester is treated with LiAlH_4 in dry ether the ester linkage is cleaved by the addition of four hydrogen atoms and two alcohols are produced.

Draw the structures of the compounds formed when **Q** is treated with an **excess** of LiAlH_4 in dry ether. [3]

(iii) Compare the relative basicities of compound **P**, compound **Q** and phenylamine.

..... < <

least basic

most basic

Explain your answer.

[3]

- < <
least acidic most acidic

.....

.....

.....

.....

.....

*****This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. *****