

32.2 PHENOL

Learning outcomes

Candidates should be able to:

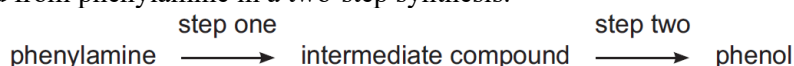
- recall the reactions (reagents and conditions) by which phenol can be produced:
 - reaction of phenylamine with HNO_2 or NaNO_2 and dilute acid below 10°C to produce the diazonium salt; further warming of the diazonium salt with H_2O to give phenol
- recall the chemistry of phenol, as exemplified by the following reactions:
 - with bases, for example NaOH(aq) to produce sodium phenoxide
 - with Na(s) to produce sodium phenoxide and $\text{H}_2\text{(g)}$
 - in NaOH(aq) with diazonium salts, to give azo compounds
 - nitration of the aromatic ring with dilute $\text{HNO}_3\text{(aq)}$ at room temperature to give a mixture of 2-nitrophenol and 4-nitrophenol
 - bromination of the aromatic ring with $\text{Br}_2\text{(aq)}$ to form 2,4,6-tribromophenol
- explain the acidity of phenol
- describe and explain the relative acidities of water, phenol, and ethanol
- explain why the reagents and conditions for the nitration and bromination of phenol are different from those for benzene
- recall that the hydroxyl group of a phenol directs to the 2-, 4-, and 6-positions
- apply knowledge of the reactions of phenol to those of other phenolic compounds, e.g., naphthol

Preparation from phenylamine

- Phenol, $\text{C}_6\text{H}_5\text{OH}$, is a weak acid.
 - Phenol can be made from phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$.
Give the reagents and conditions for this reaction.

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

- Phenol can be produced from phenylamine in a two-step synthesis.



Describe the reagents and conditions needed in each step.

step one:

reagents

conditions

step two:

reagents

conditions

[2]

3. 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.

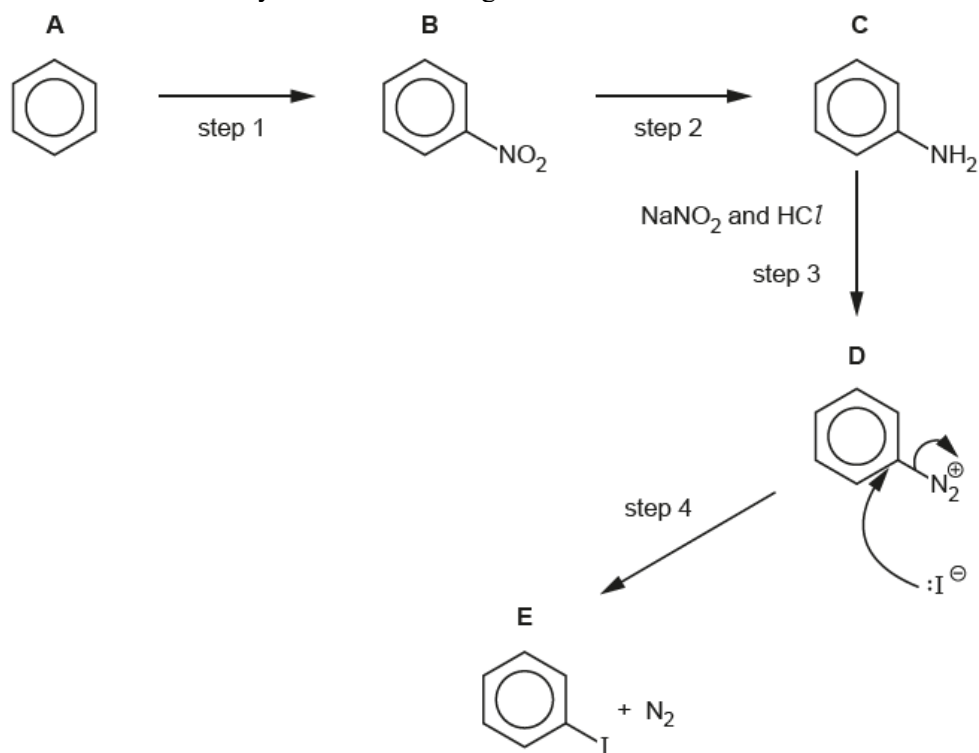


Fig. 1.1

- (i) Identify the reagents required for steps 1 and 2.

step 1

step 2

[2]

- (ii) 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**, $\text{C}_6\text{H}_5\text{N}_2^+$.

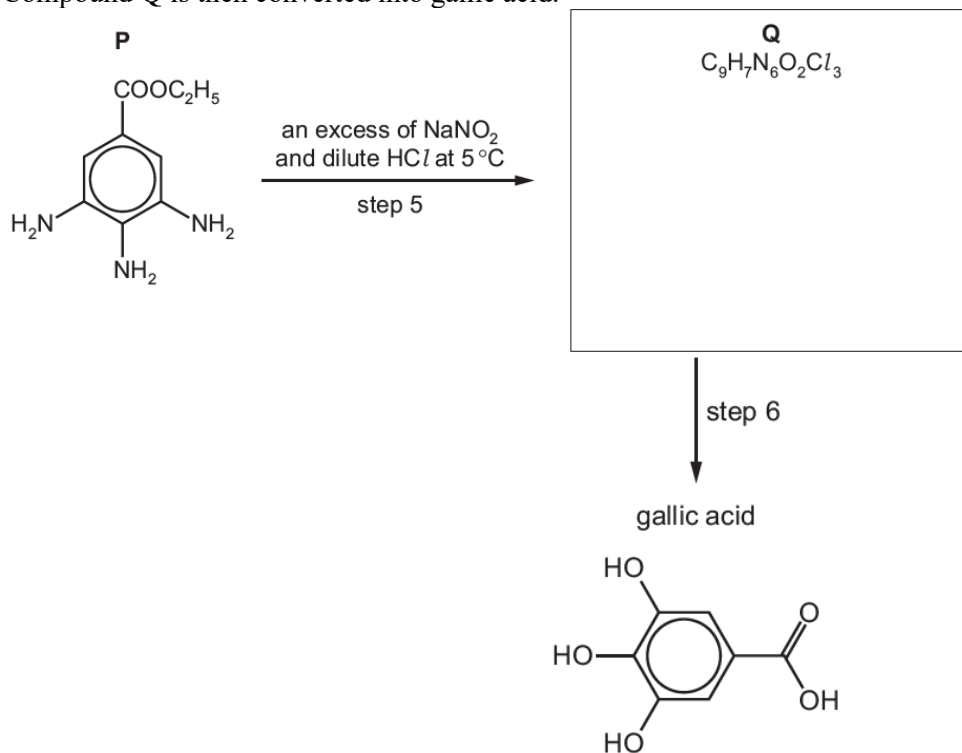
Complete the equations for stage I and for stage II.

stage I $\text{NaNO}_2 + \text{HCl}$

stage II

[2]

4. **P** reacts with an excess of sodium nitrite, NaNO_2 , and dilute HCl at 5°C to form compound **Q**, $\text{C}_9\text{H}_7\text{N}_6\text{O}_2\text{Cl}_3$. Compound **Q** is then converted into gallic acid.



(v) Suggest the structure of compound **Q** in the box provided.

[2]

(vi) State the reagents and conditions for step 6.

[1]

Reaction with Na

Acids react with the more reactive metals to give hydrogen gas. Phenol is no exception - the only difference is the slow reaction because phenol is such a weak acid.

5. Samples of phenol, $\text{C}_6\text{H}_5\text{OH}$, are reacted separately with sodium and with dilute nitric acid.

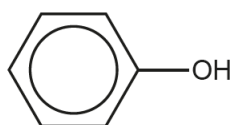


Fig. 9.1

(i) Write the equation for the reaction of $\text{C}_6\text{H}_5\text{OH}$ with Na.

..... [1]

6. A sample of 2-nitrophenol is reacted with sodium.
Complete the equation in Fig. 6.2 for the reaction of 2-nitrophenol with sodium.

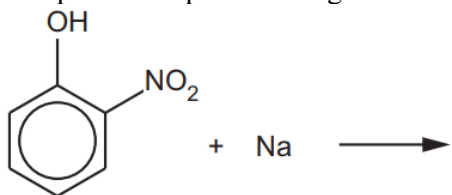
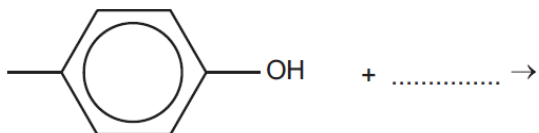


Fig. 6.2

[1]

7. 4-methylphenol reacts readily with sodium.
Complete the equation for this reaction.



[1]

Reaction with NaOH

8. Write an equation for a neutralisation reaction in which phenol behaves as an acid.

..... [1]

Reaction with Diazonium salts

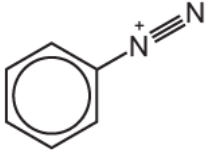
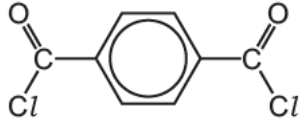
9. Phenylamine reacts with $\text{HNO}_2(\text{aq})$ at 4°C to form compound **P**. Compound **P** reacts with phenol under alkaline conditions at 4°C . The product of this reaction is acidified, forming azo compound **Q**.
 Draw the structure of compound **Q**.
 Circle the azo group on your structure.
 State one use of an azo compound such as **Q**.
 compound **Q**:

An azo compound can be used

[2]

10. Complete the table to show the structure of the organic product from each reaction of phenol, $\text{C}_6\text{H}_5\text{OH}$.

[4]

reaction	reaction mixture	structure of organic product
1	phenol + $\text{NaOH}(\text{aq})$	
2	phenol + $\text{Na}(\text{s})$	
3	phenol +  (aq) + NaOH , at 4°C	
4	an excess of phenol + 	

- (i) Identify **two** reactions from the table in which ethanol would behave in a similar way to phenol.

..... [1]

11. Fig. 7.1 shows some reactions of phenol.

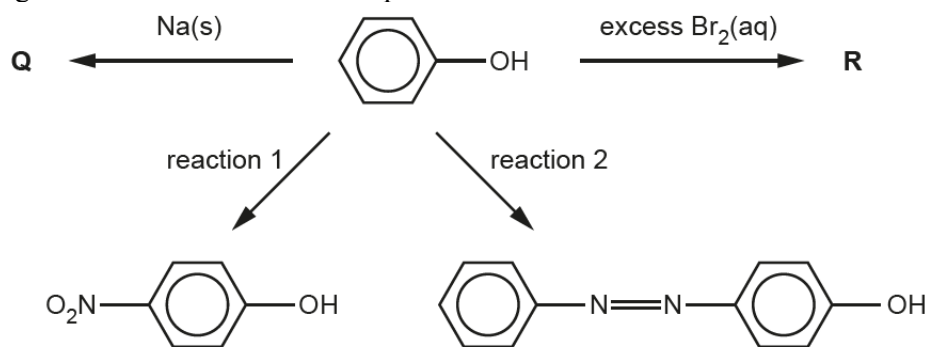


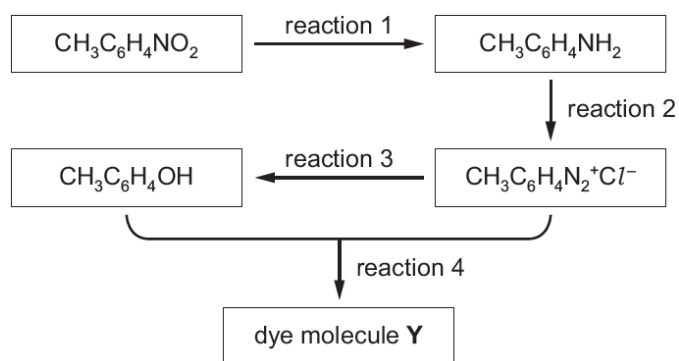
Fig. 7.1

(i) State the reagents and conditions for reaction 1 and reaction 2 in Fig. 7.1.

reaction 1

reaction 2 [2]

12. A reaction scheme is shown in Fig. 7.2.



(i) Describe the reagents and conditions to produce $\text{CH}_3\text{C}_6\text{H}_4\text{N}_2^+\text{Cl}^-$ from $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ in reaction 2.

reagents

conditions [1]

(ii) Describe how $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$ can be produced from $\text{CH}_3\text{C}_6\text{H}_4\text{N}_2^+\text{Cl}^-$ in reaction 3.

..... [1]

(iii) Draw the structure of the dye molecule Y formed when $\text{CH}_3\text{C}_6\text{H}_4\text{N}_2^+\text{Cl}^-$ and $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$ react together in reaction 4. Describe the conditions for this reaction.

Structure

conditions [2]

13. Fig. 4.2 shows some reactions of phenylamine.

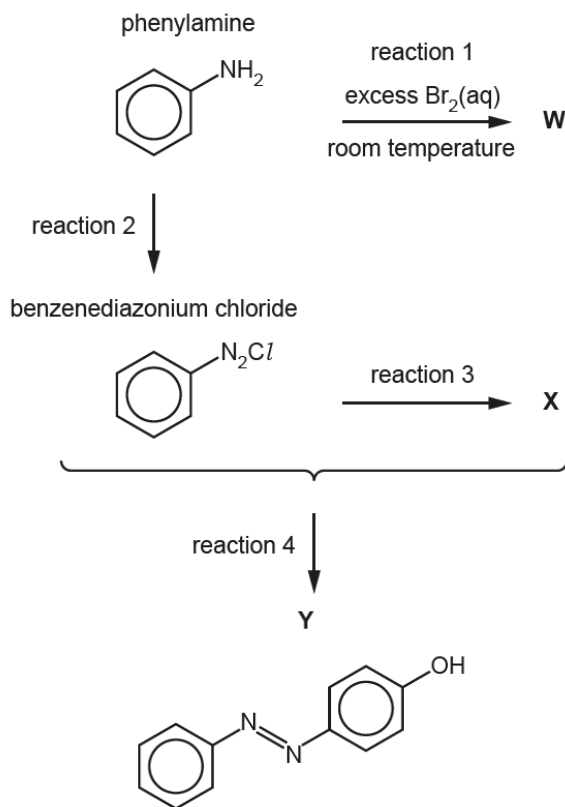


Fig. 4.2

(a) State the reagents used in reaction 2.

..... [1]

(b) Benzenediazonium chloride, $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$, and X react together in reaction 4 to form Y, an azo compound.

(i) Name X, the organic product of reaction 3.

..... [1]

(ii) State the necessary conditions for reaction 4 to occur.

..... [1]

(iii) Suggest a use for Y.

..... [1]

14. Fig. 5.4 shows two reactions of phenol

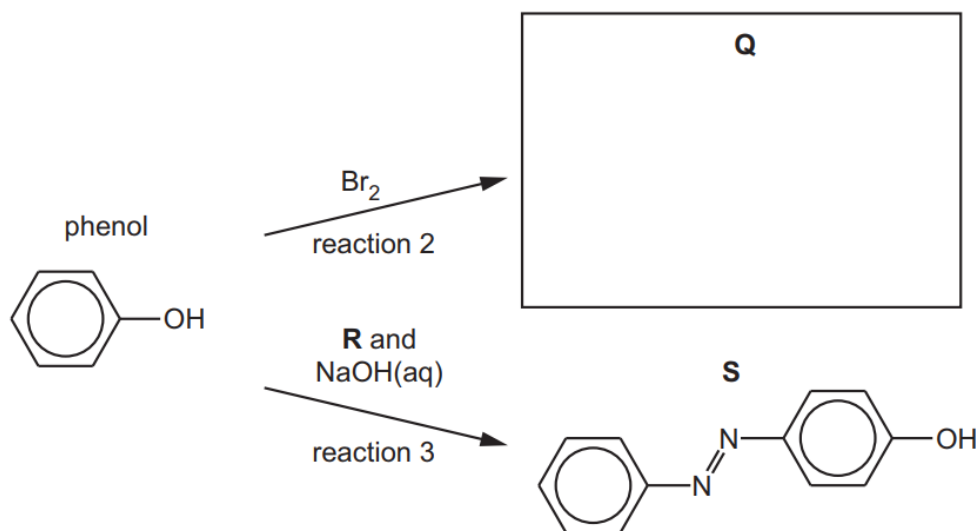


Fig. 5.4

(i) State the conditions for the bromination of phenol in reaction 2.
Explain why these conditions are different from those for the bromination of benzene.

conditions

explanation

.....

.....

.....

..... [4]

(ii) Draw the structure of organic compound Q in Fig. 5.4.

[1]

(iii) Identify organic reagent R.

[1]

(iv) Name the functional group that is formed in reaction 3.

..... [1]

explanation

.....

..... [2]

15. Salbutamol is a pharmaceutical drug that contains a phenol functional group.

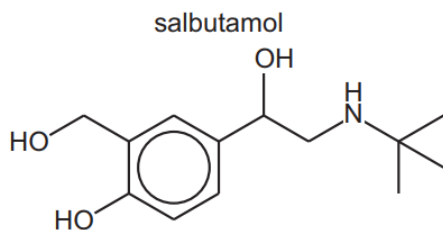


Fig. 6.4

- (ii) Salbutamol reacts with $\text{Br}_2(\text{aq})$ to form organic product X.
Draw the structure of X.

[1]

- (iii) Salbutamol reacts with an excess of SOCl_2 to form organic product Y.
The molecular formula of Y is $\text{C}_{13}\text{H}_{19}\text{Cl}_2\text{NO}$.
Draw the structure of Y.

[1]

16. Phenol and benzene both react with nitric acid, as shown in Fig. 4.5.

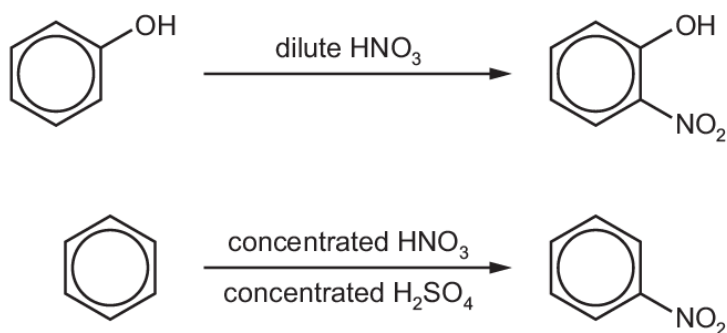


Fig. 4.5

Explain why the reagents and conditions for these two reactions are different.

.....

.....

.....

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

17. Suggest why bromination of phenol occurs more readily than bromination of benzene.

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

18. Explain why phenol is brominated much more easily than benzene is.

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

19. Suggest why bromination of phenol occurs more readily than bromination of benzene.

[2]

20. Phenol can be nitrated with dilute nitric acid.

Explain why the nitration of phenol occurs under milder conditions than the nitration of benzene.

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

21. Compare the relative ease of nitration of benzene, benzoic acid and phenol.

Explain your reasoning; include reference to the structures of the three compounds in your answer.

..... > >

easiest least easy

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

[4]

22. Salicylic acid can be synthesised from phenol.

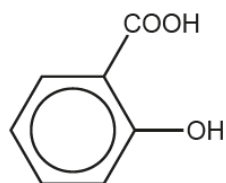


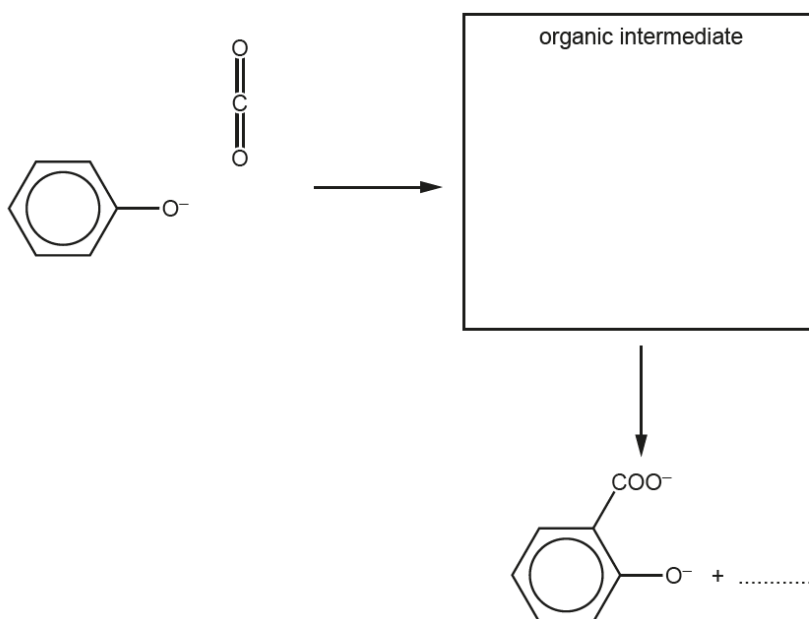
Fig. 9.2

One of the steps in this synthesis is the electrophilic substitution reaction of carbon dioxide with the phenoxide ion, $\text{C}_6\text{H}_5\text{O}^-$.

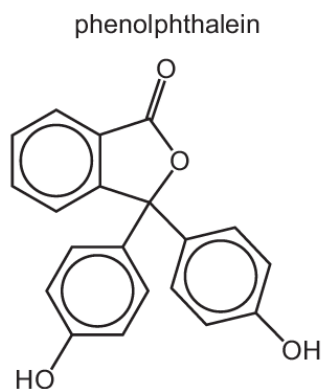
Complete the mechanism in Fig. 9.3 for the reaction of $\text{C}_6\text{H}_5\text{O}^-$ with CO_2 .

Include all relevant curly arrows, dipoles, and charges. Draw the structure of the organic intermediate.

[3]



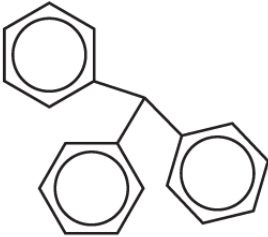
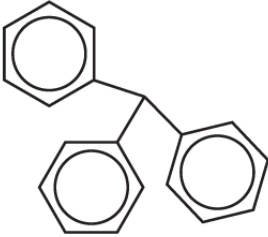
23. Phenolphthalein reacts separately with the two reagents shown in the table.



Complete the table by:

- drawing the structures of the organic products formed (part of the structure has been given for you)
- stating the types of reaction.

[4]

reagent	organic product structure	type of reaction
an excess of hot NaOH(aq)		
an excess of Br ₂ (aq)		

Relative acidities

(to be studied in 33.1 carboxylic acids)

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