33.1 CARBOXYLIC ACIDS

Learning outcomes

Candidates should be able to:

1. recall the reaction by which benzoic acid can be produced:

(a) reaction of an alkylbenzene with hot alkaline $KMnO_4$ and then dilute acid, exemplified by methylbenzene

2. describe the reaction of carboxylic acids with PCl_3 and heat, PCl_5 or $SOCl_2$ to form acyl chlorides

3. recognise that some carboxylic acids can be further oxidised:

(a) the oxidation of methanoic acid, HCOOH, with Fehling's reagent or Tollens' reagent or acidified $KMnO_4$ or acidified $K_2Cr_2O_7$ to carbon dioxide and water

(b) the oxidation of ethanedioic acid, HOOCCOOH, with warm acidified $KMnO_4$ to carbon dioxide

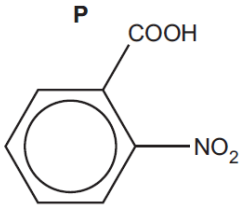
4. describe and explain the relative acidities of carboxylic acids, phenols and alcohols

5. describe and explain the relative acidities of chlorine-substituted carboxylic acids

Initial assessment

1. Write down the definition of a *Brønsted–Lowry acid* and *Brønsted–Lowry base*. Compare your definitions with those of another learner.

1. Give the systematic name of **P**.

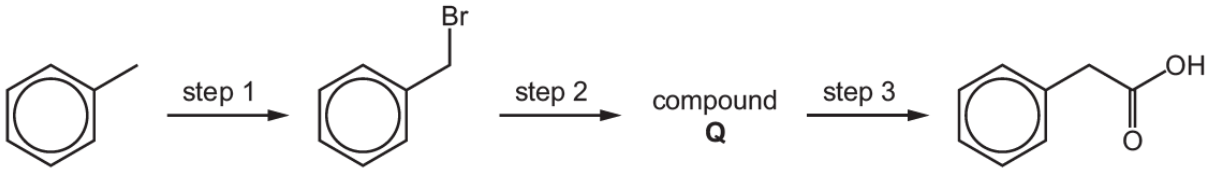


..... [1]

Preparation of benzoic acid

(Studied already at 30. Arenes)

2. A three-step synthesis of phenylethanoic acid from methylbenzene is shown.



(i) Suggest the structure of compound **Q**. [1]

(ii) State reagents and conditions for steps 2 and 3.

step 2 .....

step 3 ..... [2]

Reaction with PCl_3 PCl_5 and $SOCl_2$

Carboxylic acids react with phosphorus(V) chloride or sulfur dichloride oxide in exactly the same way as do alcohols. Acyl chlorides are produced.

3. **(i)** Benzoyl chloride, C_6H_5COCl, can be synthesised by the reaction of benzoic acid with either PCl_5 or $SOCl_2$. Complete the equations for these reactions.

   reaction 1 $C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl +$ ..... + ...

   reaction 2 $C_6H_5COOH + SOCl_2 \rightarrow C_6H_5COCl +$ ..... + ... [1]

   (ii) Use your answer to **(i)** to suggest why it is easier to isolate, in a pure form, the C_6H_5COCl from reaction 2 compared to reaction 1.

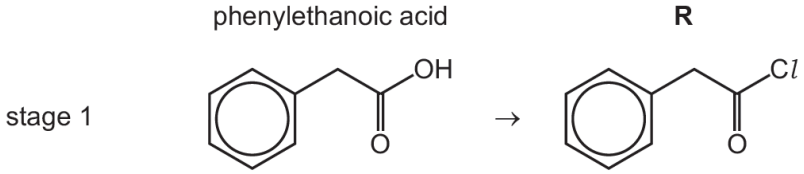
   .....

   ..... [1]

4. Acyl chlorides are formed by reacting carboxylic acids with thionyl chloride, $SOCl_2$.
   Ethanedioyl chloride, $(COCl)_2$, can be prepared by reacting ethanedioic acid, $(COOH)_2$, with an excess of $SOCl_2$.
   Write an equation for this reaction.

   ..... [1]

5. Compound **T** is made by a three-stage synthesis.
   In stage 1, phenylethanoic acid reacts with a suitable reagent to form compound **R**.



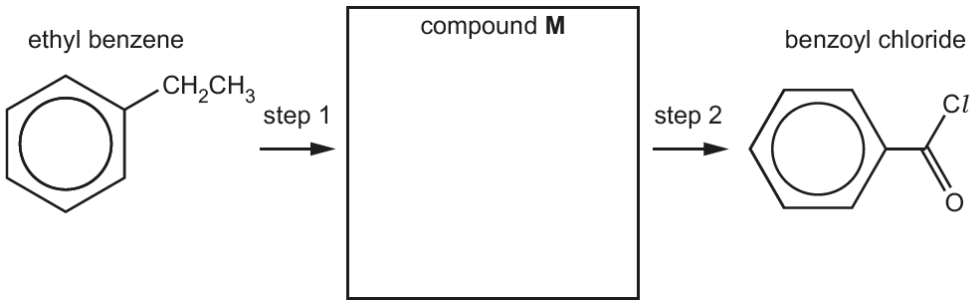
   Suggest a suitable reagent for stage 1.

   ..... [1]

6. Acyl bromides, RCOBr, can be synthesised by the reaction of a carboxylic acid and $SOBr_2$.
   This is a similar reaction to the synthesis of acyl chlorides using $SOCl_2$.
   Give an equation for the reaction between ethanoic acid and $SOBr_2$.

   ..... [1]

7. Benzoyl chloride, C_6H_5COCl, can be made from ethyl benzene in a two-step process.
   A reaction scheme is shown.



   (i) Draw the intermediate organic compound M in the box. [1]

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

   step 1 .....

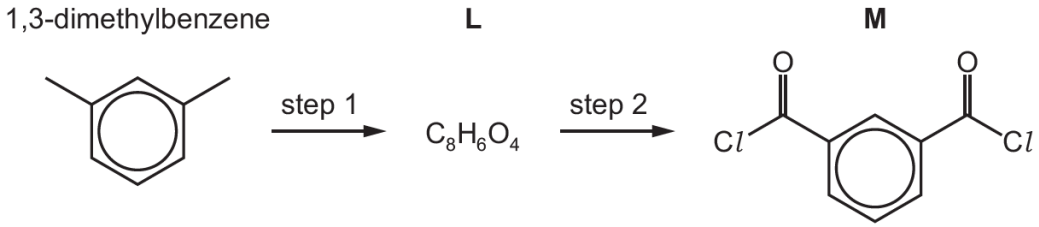
   step 2 ..... [2]

   (iii) Identify the type of reaction in step 1 and step 2.

   step 1 .....

   step 2 ..... [2]

8. Compound **M** is made from 1,3-dimethylbenzene in a two-step synthesis.



(i) Draw the structure of L. [1]

(ii) Suggest reactants and conditions for each step of this synthesis.

step 1 .....

step 2 ..... [2]

(iii) Write an equation for step 2.

..... [1]

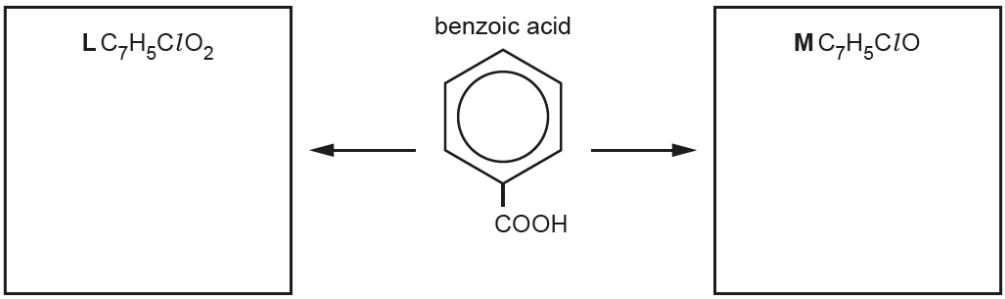
(iv) A student investigates a possible synthesis of M directly from benzene using $COCl_2$ in the presence of an $AlCl_3$ catalyst.
Benzene initially reacts with $COCl_2$ as shown.

reaction 1 $COCl_2 + AlCl_3 \rightarrow AlCl_4^- + Cl{-}\overset{+}{C}{=}O$

reaction 2 $C_6H_6 + Cl{-}\overset{+}{C}{=}O \rightarrow C_6H_5COCl + H^+$

Reaction 2 is the electrophilic substitution of $Cl{-}\overset{+}{C}{=}O$ for H^+ in benzene.
Suggest a mechanism for reaction 2. [3]

9. When treated with a chlorine-containing reagent under suitable conditions, benzoic acid forms compound L.
When treated with a different chlorine-containing reagent under different conditions, benzoic acid forms compound M.
Suggest and draw structures of compounds L and M in the boxes. The molecular formula of each product is given.



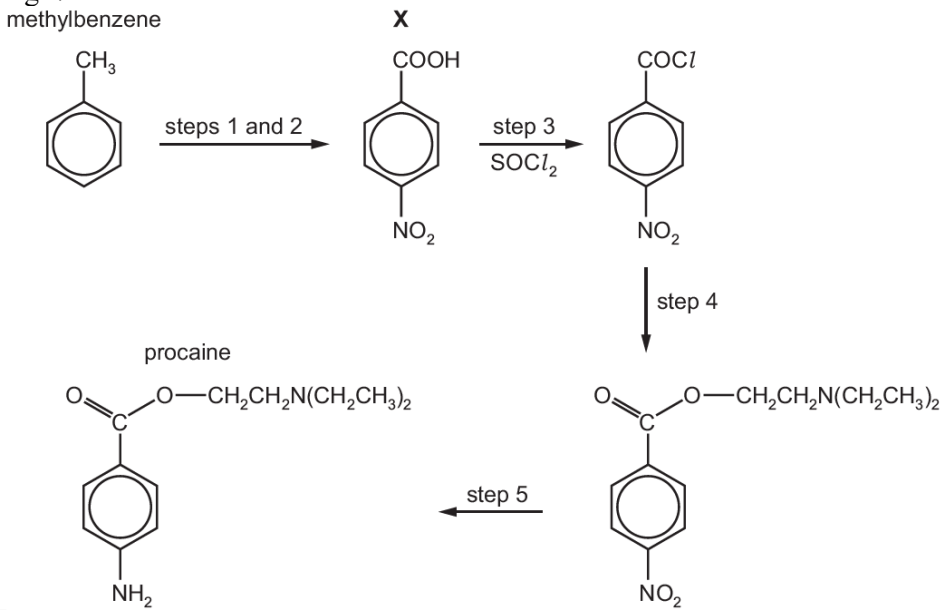
State the reagents and conditions to form compound M from benzoic acid.

..... [3]

10. Propanedioic acid, $HOOCCH_2COOH$, is treated with an excess of thionyl chloride, $SOCl_2$.
Propanedioyl chloride, $ClOCCH_2COCl$, is formed.
(i) Write an equation for this reaction.

..... [1]

11. Procaine is used as an anaesthetic in medicine. It can be synthesised from methylbenzene in five steps as shown in Fig. 7.1.



Procaine is synthesised in three steps from X.
Suggest the reagents and conditions for step 4 and for step 5 in Fig. 7.1.

step 4 .....

step 5 ..... [3]

The oxidation of Methanoic acid, HCOOH

Unlike other aliphatic carboxylic acids, **methanoic acid** does not contain an alkyl chain attached to the $-CO_2H$ group. Instead, the $H-CO$ group, consisting of a hydrogen atom attached to a carbonyl group, has some reactions in common with aldehydes. In particular, it undergoes oxidation with common oxidants such as acidified dichromate(VI).

$3H-CO_2H(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3CO_2(g) + 7H_2O(l)$

It also reacts with both Fehling's solution and Tollens' reagent.

$H-CO_2H(aq) + 2Cu^{2+}(aq) + 6OH^-(aq) \rightarrow CO_3^{2-}(aq) + Cu_2O(s) + 4H_2O(l)$

Oxidation of Ethanedioic acid with alkaline $KMnO_4$

Ethanedioic acid contains two adjacent carbonyl groups. The proximity of two $\delta+$ carbon atoms weakens the C−C bond sufficiently for the molecule to be readily oxidised by warm acidified manganate(VII).

$5HO_2C-CO_2H(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

12. An excess of ethanedioic acid, HOOCCOOH(aq), is reacted with warm acidified $KMnO_4(aq)$.
    State the type of reaction undergone by ethanedioic acid.
    Describe what you would observe.
    Write an equation for this reaction.
    Your equation can use [O] or [H] as necessary.

    type of reaction .....

    observations .....

    equation ..... [2]

13. Fig. 6.1 shows two reactions of ethanedioic acid, HOOCCOOH.

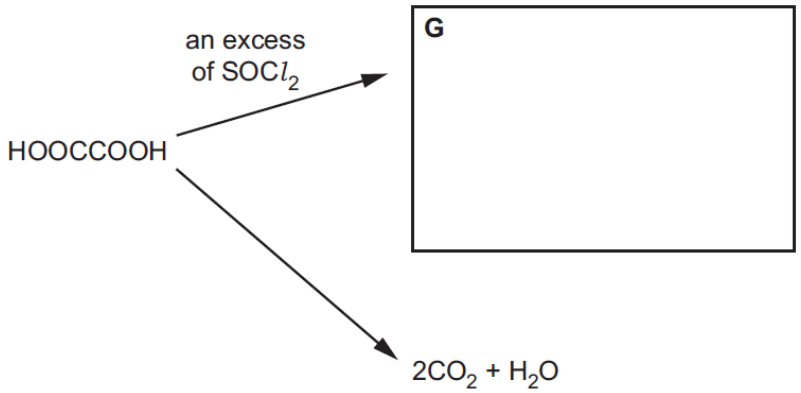


Fig. 6.1

(i) Draw the organic product G in the box in Fig. 6.1. [1]

(ii) In Fig. 6.1, $SOCl_2$ is given as the reagent that reacts with HOOCCOOH to produce G.
Identify a different reagent that also reacts with HOOCCOOH to produce G.

..... [1]

(b) Identify two different reagents that oxidise HOOCCOOH to form carbon dioxide and water.

.....

..... [2]

14. Methanoic acid, HCO_2H, and ethanedioic acid, HO_2CCO_2H, are two other carboxylic acids.
(i) State which, if any, of ethanoic acid, methanoic acid, and ethanedioic acid will react with Fehling's reagent.

..... [1]

(ii) State which, if any, of ethanoic acid, methanoic acid, and ethanedioic acid will react with warm acidified manganate(VII) ions.

..... [1]

15. Three carboxylic acids, methanoic acid, HCO_2H, ethanedioic acid, HO_2CCO_2H, and butanedioic acid, $HO_2CCH_2CH_2CO_2H$, are compared. Two tests were carried out on separate samples of each organic acid, as shown. The following results were obtained. √ = observed change X = no observed reaction

test	reagents and conditions	HCO_2H	HO_2CCO_2H	$HO_2CCH_2CH_2CO_2H$	observed change
1		✓	✗	✗	
2		✓	✓	✗	

Complete the table with the reagents and conditions and the observed change for a positive test.
Assume these organic acids all have a similar acid strength. [3]

16. Three tests were carried out on separate samples of the organic acids shown in the table.
The following results were obtained.
√ = observed change
X = no observed reaction

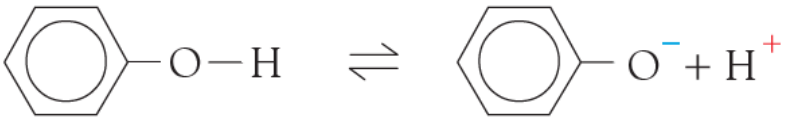
test	reagent(s) and conditions	HCO_2H	CH_3COCO_2H	HO_2CCO_2H	observed change
1	....	✓	✗	✗	
2	....	✗	✓	✗	
3	....	✓	✗	✓	

Complete the table with the reagent(s) and conditions and the observed change for each test.
Assume these organic acids all have a similar acid strength. [5]

Acidity of Phenols

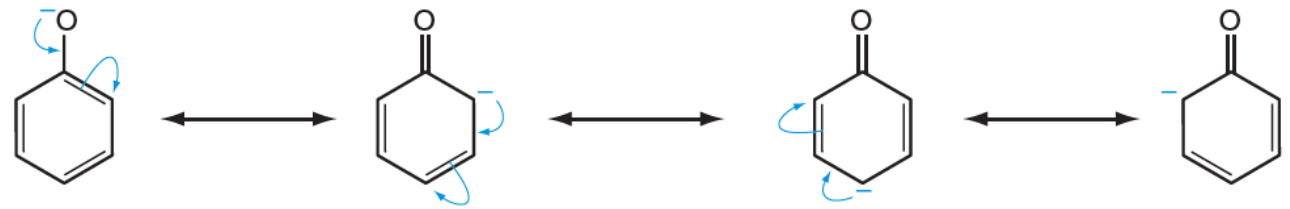
Phenols are more acidic than alcohols:

$$R{-}O{-}H \rightleftharpoons RO^- + H^+ \qquad K_a = 1.0 \times 10^{-16}\ \text{mol dm}^{-3}$$



$$K_a = 1.3 \times 10^{-10}\ \text{mol dm}^{-3}$$

Alcohols are less acidic than water because the electron-donating alkyl group destabilises the anion, RO^-, compared to the alcohol ROH, so the $[RO^-]/[ROH]$ ratio is smaller than the $[OH^-]/[H_2O]$ ratio in water. In phenol, on the other hand, the negative charge of the anion can be delocalised over the benzene ring. This allows the $[PhO^-]/[PhOH]$ ratio to be larger than the $[OH^-]/[H_2O]$ ratio in water. Figure 27.22 shows various ways in which this can be represented.



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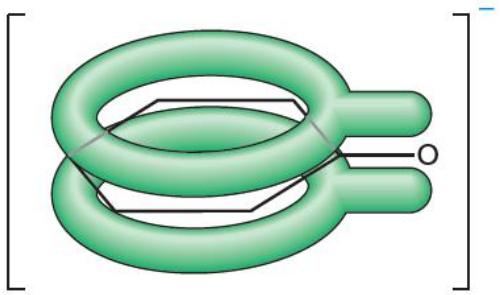

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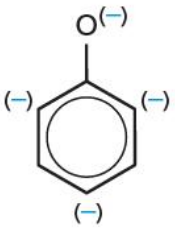
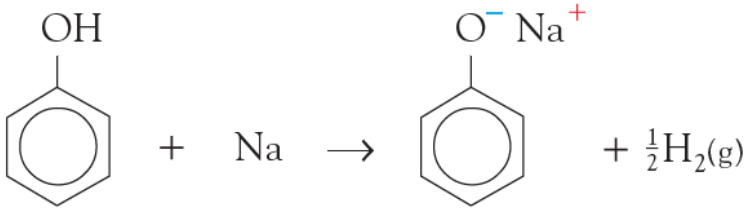
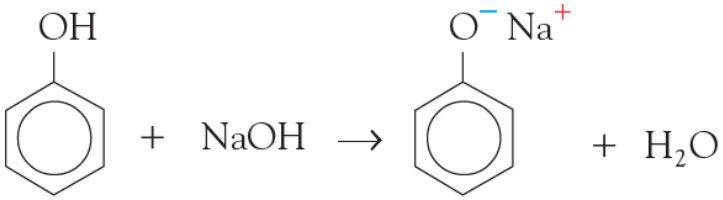


Consequently, phenol not only reacts with sodium metal, giving off hydrogen gas:



sodium phenoxide
(a white solid)

but, unlike alcohols, it also dissolves in aqueous sodium hydroxide:



Phenol is visibly acidic: the pH of a 0.1 mol dm−3 solution in water is 5.4, so it will turn the universal indicator solution yellow. However, it is not acidic enough to give off bubbles of $CO_2(g)$ with aqueous sodium carbonate (unlike carboxylic acids).

The order of acidity is therefore $RCO_2H > C_6H_5OH > H_2O > C_2H_5OH$.

17. Water, phenol, and ethanol can all behave as acids.
Place these three compounds in order of acidity, starting with the most acidic.
Explain your answer.

..... > ..... > .....
most acidic least acidic [3]

[MS=

phenol>water>ethanol [1]

• (phenol:) lone pair on oxygen is delocalised into the benzene ring

• (ethanol:) positive inductive effect / electron donating effect of alkyl / ethyl group

• correct statement about stabilisation of anion/ conjugate base **OR** weakening of O-H bonds once *in the context of phenol / ethanol*

• correct statement about ease of proton/H+ donation *in the context of phenol / ethanol* [2]

Two correct statements = 1 mark]

18. An aqueous solution of phenol, C_6H_5OH, is acidic at 298 K.
Explain why phenol is more acidic than water.

.....

.....

..... [2]

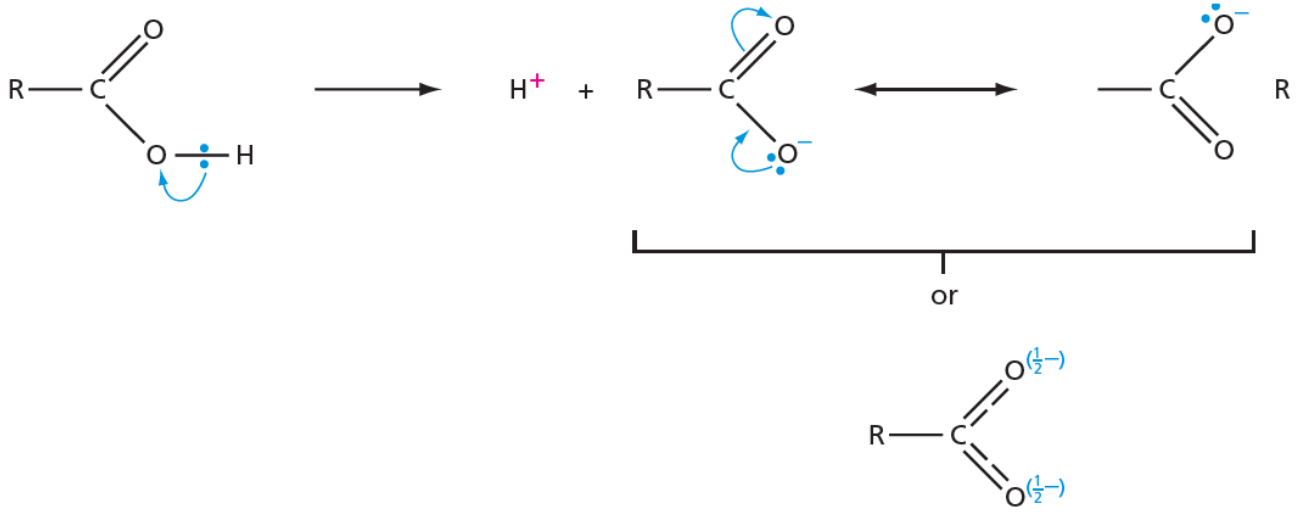
Acidity of carboxylic acids

In terms of the Brønsted–Lowry theory. Acids are proton donors, and bases are proton acceptors.

Carboxylic acids are weak acids and dissociate to a small extent when in aqueous solution:

$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H+$

They are more acidic than alcohols because the negative charge on the anion can be delocalised over two electronegative oxygen atoms.



The increasing acidities of alcohols, phenols, and carboxylic acids are explained by the increasing ability of the molecular structures to delocalise the negative charge in the alkoxide, phenoxide, and carboxylate anions. Their relative acidities are demonstrated by their different reactions with sodium, sodium hydroxide, and sodium carbonate

Reagent	Observation with		
	Hexanol	Phenol	Hexanoic acid
Na(s)	$H_2(g)$ evolved	$H_2(g)$ evolved	$H_2(g)$ evolved
NaOH(aq)	no reaction	dissolves	dissolves
$Na_2CO_3(aq)$	no reaction	no reaction	$CO_2(g)$ evolved

19. A series of nine separate experiments is carried out as shown in Table 5.1.
Complete the table by placing a tick (✓) in the relevant box if a reaction occurs. Place a cross (✗) in the box if no reaction occurs. [3]

Table 5.1

	benzoic acid	phenylmethanol	Phenol
Na(s)			
NaOH(aq)			
$Na_2CO_3(aq)$			

20. State the relative acidities of benzoic acid, $C_6H5COOH$, ethanol, CH_3CH_2OH, and phenol, C_6H5OH, in aqueous solution. Explain your answer.

....
most acidic least acidic

……

.....

.....

.....

..... [3]

21. Compare the relative acidities of benzoic acid (C_6H_5COOH), phenylmethanol ($C_6H_5CH_2OH$), and phenol (C_6H_5OH). Explain your reasoning.

..... > ..... > .....
most acidic least acidic

.....

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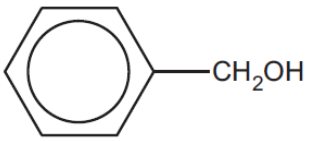
.....

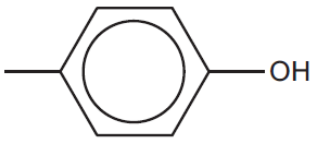
..... [3]

22. Phenylmethanol and 4-methylphenol are isomers.

phenylmethanol



4-methylphenol



(a) Complete Table 7.1 to show the relative acidities of benzoic acid (C_6H_5COOH), phenylmethanol, 4-methylphenol and water.
Explain your answer.

Table 7.1

	name of compound
most acidic ↓	
least acidic	

explanation .....

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.....

.....

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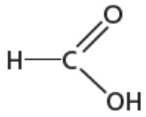
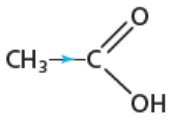
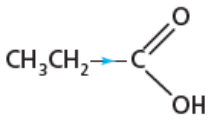
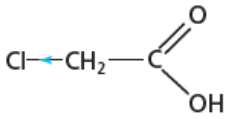
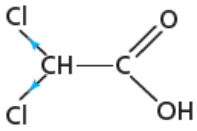
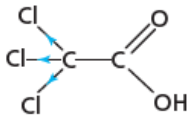
.....

..... [4]

Atoms or groups that draw electrons away from the $-CO_2^-$ group will help the anion to form, and this causes the acid to be more dissociated (that is, to become a stronger acid).

On the other hand, groups that donate electrons to the $-CO_2^-$ group will cause the acid to become weaker

Formula of acid	pK_a	Percentage dissociation in 1.0 mol dm^{-3} aqueous solution
	3.75	1.3%
	4.76	0.42%
	4.87	0.36%
	2.87	3.7%
	1.26	21%
	0.66	59%

Electron-donating groups decrease the acid strength of carboxylic acids, whereas electron-withdrawing groups increase their acid strength.

23. Explain why trichloroethanoic acid, CCl_3COOH, is more acidic than ethanoic acid, CH_3COOH.

.....

.....

..... [1]

24. Compare and explain the relative acidities of butanoic acid, ethanol, ethanoic acid and water.

..... > ..... > ..... > .....
most acidic least acidic

.....

.....

.....

.....

.....

..... [4]

25. CH_3CH_2COOH, CH_3CCl_2COOH and H_2SO_4 are all acidic.
Suggest the trend in the relative acid strength of these three compounds.
Explain your answer.

....
strongest acid weakest acid

explanation .....

…….....

…….....

…….....

……..... [3]

26. Compare the relative acidities of ethanol, ethanoic acid, chloroethanoic acid, and phenol.
Explain your reasoning.

..... > ..... > ..... > .....
most acidic least acidic

.....

.....

.....

.....

.....

..... [4]

(a) State the relative acidities of bromoethanoic acid, $BrCH_2COOH$, chloroethanoic acid, $Cl\ CH_2COOH$, ethanoic acid, $CH3COOH$ and ethanol, $CH3CH_2OH$.
Explain your answer.

....
most acidic least acidic

.....

.....

.....

.....

.....

.....

..... [4]

27. HOOCCOOH ionises as shown.
HOOCCOOH ⇌ $HOOCCOO^-$ + H^+
HOOCCOOH is a much stronger acid than methanoic acid, HCOOH.
Suggest an explanation for this difference in acidity.

.....

.....

..... [2]

28. Compare and explain the relative acidities of 2-chloropropanoic acid, 3-chloropropanoic acid, and propanoic acid.
Explain your answer.

..... > ..... > .....
most acidic least acidic

explanation .....

.....

.....

.....

.....

..... [3]

29. The NO_2 group in 2-nitrophenol is electron-withdrawing.
Suggest the relative acidities of ethanol, 2-nitrophenol, phenol, and water.
Explain your answer.

....
most acidic least acidic

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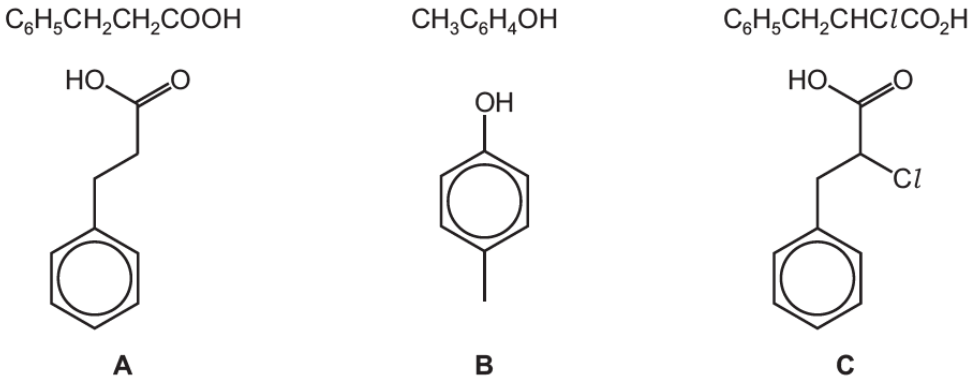
..... [4]

30. The structural and displayed formulae of three aromatic compounds, A, B, and C, are shown in Fig. 7.1.



Compare the relative acidities of A, B, and C.

..... > ..... > .....
most acidic least acidic

Explain your answer.

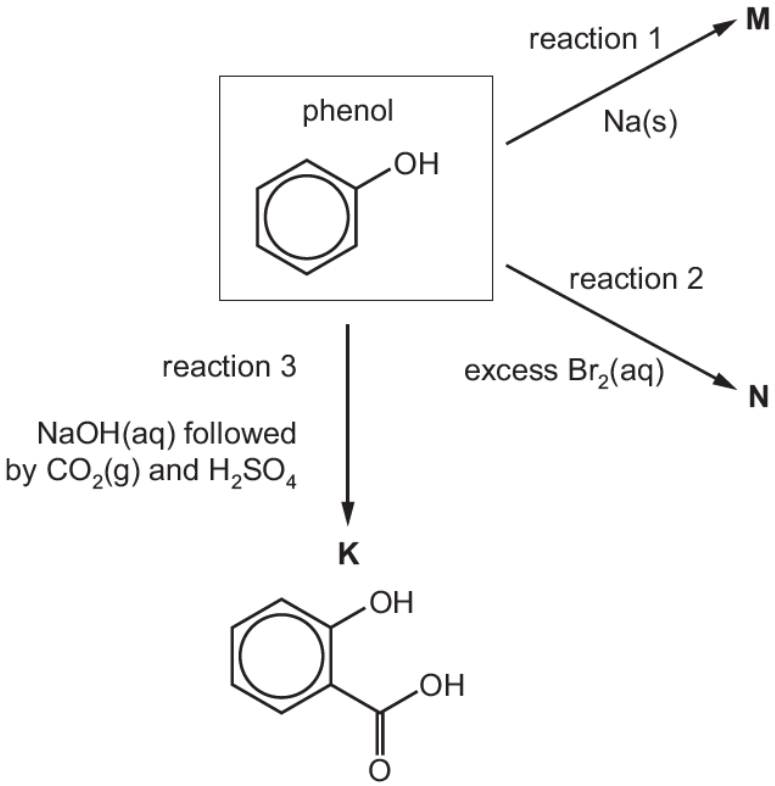
.....

.....

.....

..... [3]

31. **K** can also be synthesised from phenol, C_6H5OH.
Fig. 4.4 shows several reactions of phenol.



(i) Write an equation for the formation of **M** in reaction 1.

..... [1]

(ii) Draw **N**, the product of reaction 2.

[1]

(iii) Explain why phenol is a weaker acid than **K**.

.....

.....

.....

..... [2]

32. 2-Chloropropanoic acid, $CH_3CHCl\ COOH$, is used in many chemical syntheses.
(a) (i) An equilibrium is set up when $CH_3CHCl\ COOH$ is added to water.
Write the equation for this equilibrium.

..... [1]

(ii) 0.150 mol of $CH_3CHCl\ COOH$ dissolves in 250 cm^3 of distilled water to produce a solution of pH 1.51.
Calculate the p*K*a of $CH_3CHCl\ COOH$.

p*K*a = ... [2]

(iii) An equal concentration of aqueous propanoic acid has pH 2.55.
Explain the difference in the pH of solutions of equal concentration of $CH_3CHCl\ COOH$ and propanoic acid.

.....

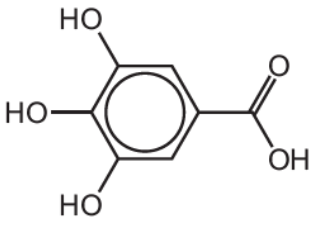
.....

.....

..... [2]

33. Gallic acid, $C_7H_6O_5$, is a naturally occurring aromatic molecule.

gallic acid



(a) Gallic acid contains the carboxylic acid and phenol functional groups.
State and explain the relative acid strength of these two functional groups.

.....

.....

.....

..... [2]

(b) A buffer solution was prepared by dissolving 2.04 g of gallic acid in 250 cm3 of a solution containing 0.0600 mol dm–3 of gallate ions, $C_7H_5O_5^-$.

$C_7H_6O_5 \rightleftharpoons C_7H_5O_5^- + H^+$ $K_a = 3.89 \times 10^{-5}$ mol dm–3 at 298 K

(i) Define the term *buffer solution*.

.....

.....

..... [2]

(ii) Calculate the pH of this buffer solution.

pH = ... [3]

(iii) Write **two** equations to show how a solution containing gallic acid, $C_7H_6O_5$, and gallate ions, $C_7H_5O_5^-$, acts as a buffer.

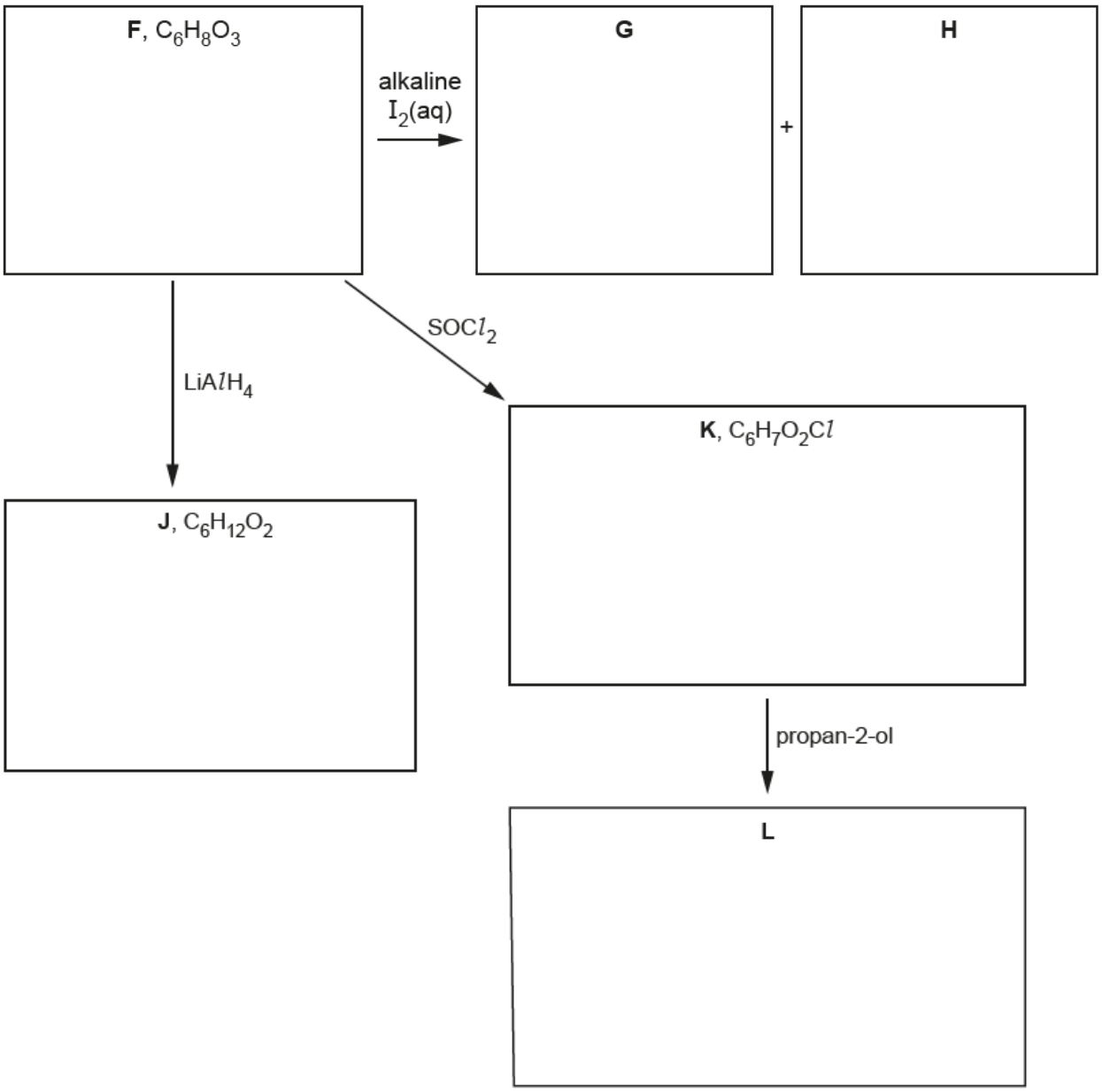
.....

.....

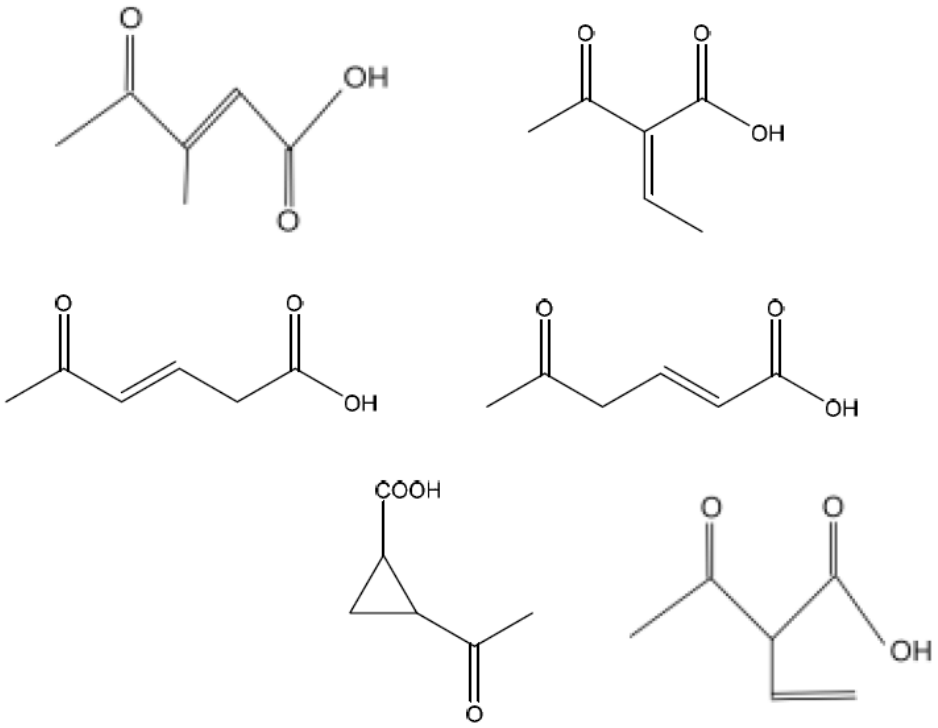
.....

..... [2]

34. Compound **F**, $C_6H_8O_3$, shows stereoisomerism and effervesces with $Na_2CO_3(aq)$.
Compound **F** reacts with alkaline $I_2(aq)$ to form yellow precipitate **G** and compound **H**.
Compound **F** reacts with $LiAlH_4$ to form compound **J**, $C_6H_{12}O_2$.
Compound **F** reacts with $SOCl_2$ to form compound **K**, $C_6H_7O_2Cl$.
Compound **K** reacts with propan-2-ol to form compound **L**.
Draw the structures of compounds **F**, **G**, **H**, **J**, **K,** and **L** in the boxes in Fig. 7.3. [6]



six alternatives for **F**



35. **P** can be synthesised as shown in Fig. 7.2.

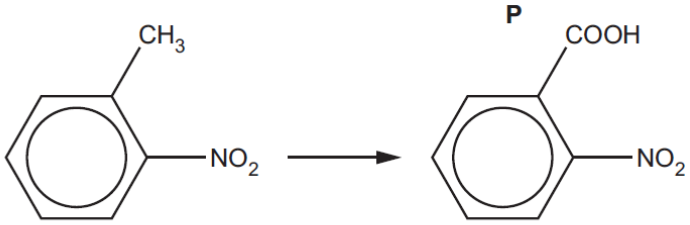


Fig. 7.2

(i) Suggest reagents and conditions for this reaction.

..... [1]

(ii) A student attempts to synthesise P by an alternative route, as shown in Fig. 7.3. Compound T is the major product in this reaction rather than P.

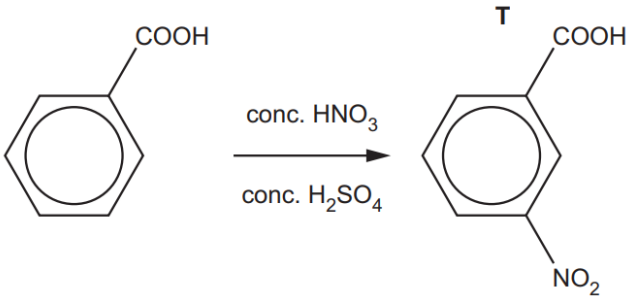


Fig. 7.3

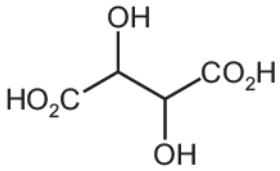
Explain why **T** is the major product in this reaction.

.....

..... [1]

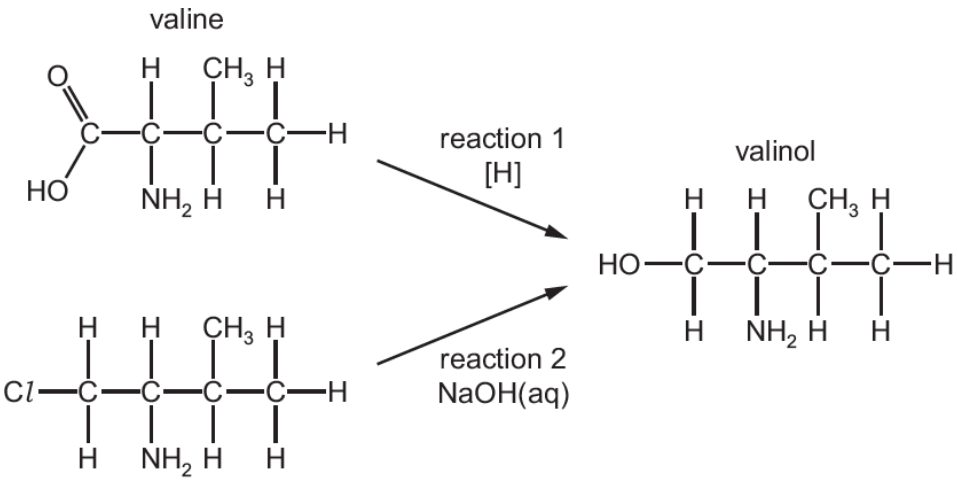
36. Complete the following table to show the structures of the organic products formed when tartaric acid reacts separately with each reagent. Identify each type of reaction.

tartaric acid



reagent	structure of organic product	type of reaction
an excess of $LiAlH_4$		
an excess of CH_3COCl		

37. Valinol can be synthesised by the following reactions. Reaction 1 uses valine as the starting material.



(i) Write an equation for reaction 1, using [H] to represent the reducing agent.

..... [1]

(ii) Suggest a suitable reagent for reaction 1.

..... [1]

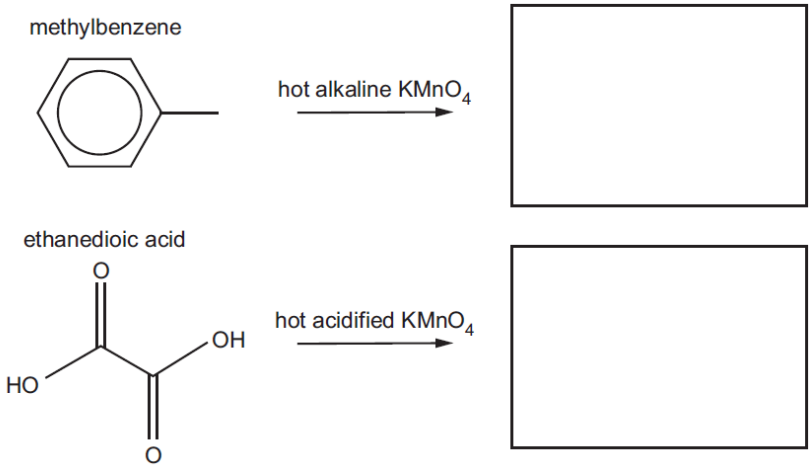
(iii) Name the mechanism for reaction 2.

..... [1]

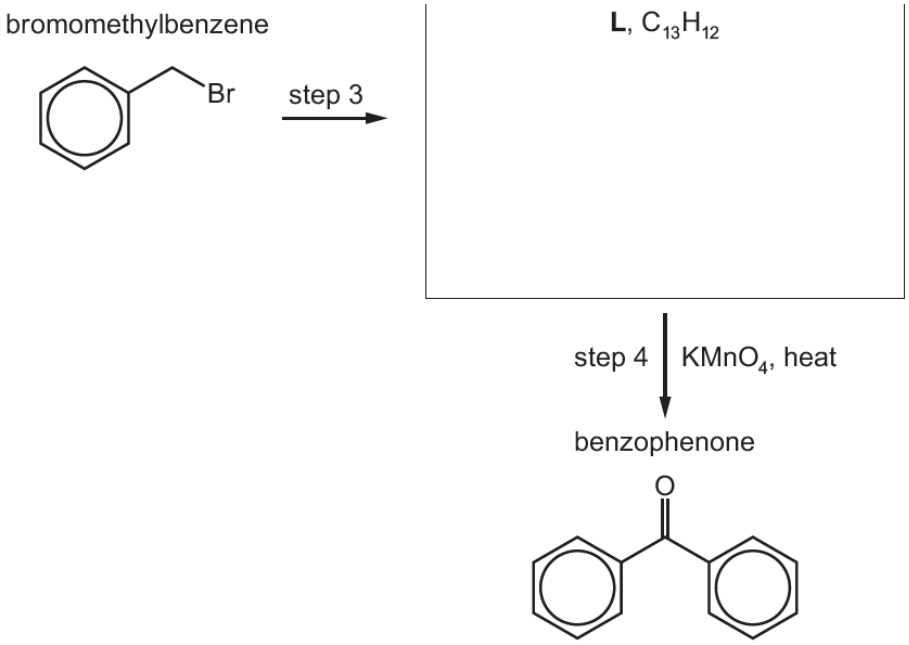
38. A list of tests for different organic groups is given in Table 6.1.
Complete Table 6.1 to identify an organic functional group, in aliphatic compounds, that produces a positive result in each test. [4]

test					
sodium metal	$Na_2CO_3(aq)$	2,4-DNPH	$I_2(aq)$ + $OH^-(aq)$	warm with Fehling's reagent	$Br_2(aq)$

39. Fig. 7.1 shows the reaction of methylbenzene and ethanedioic acid with KMnO4.
Predict the major carbon-containing product for each of these reactions.



40. Benzophenone can also be synthesised in two steps from bromomethylbenzene.



(i) Deduce the identity of compound **L** and draw its structure in the box. [1]

(ii) Name the mechanism of step 3 and suggest reagents and conditions for step 3.

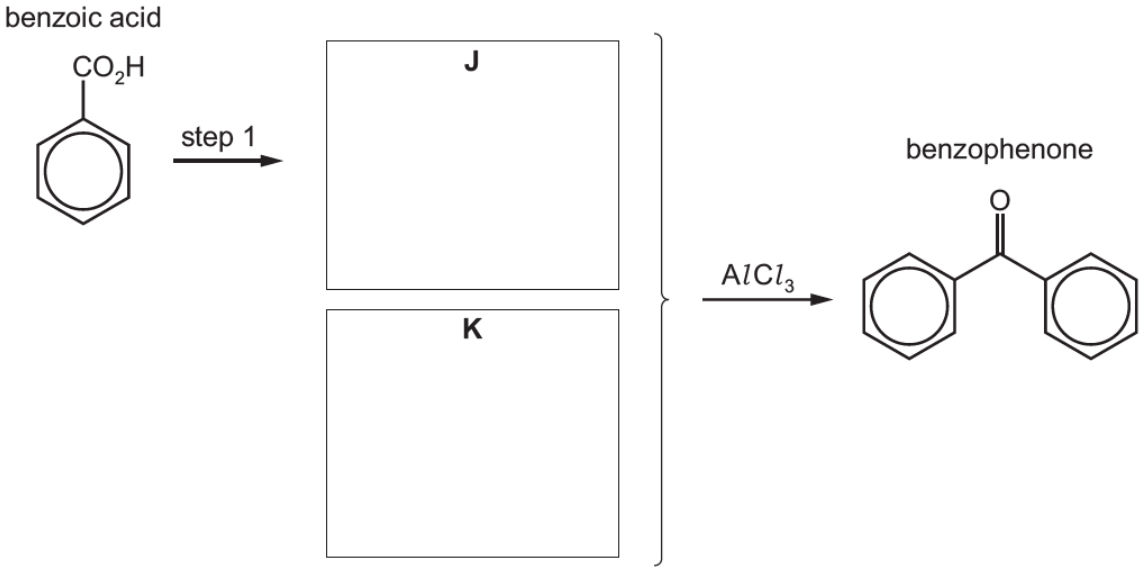
mechanism of step 3 .....

reagents and conditions ..... [2]

(iii) Deduce the *type of reaction* in step 4.

..... [1]

41. Benzophenone can be synthesised from benzoic acid in two steps, as shown.
In step 1, compound **J**, a reactive intermediate, is formed.
Compound **J** then reacts with an organic compound, **K**, to form benzophenone.

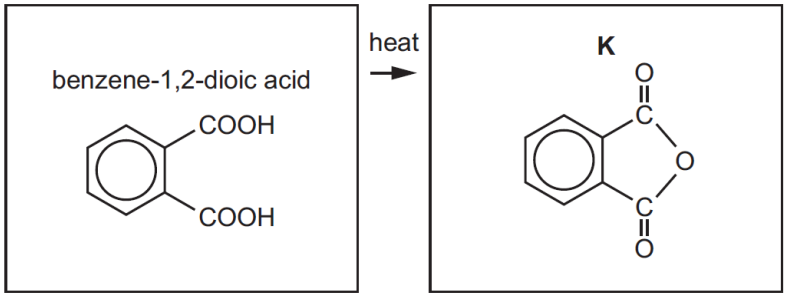


(i) Deduce the identities of organic compounds **J** and **K** and draw their structures in the boxes. [2]

(ii) Suggest reagents and conditions for step 1.

..... [1]

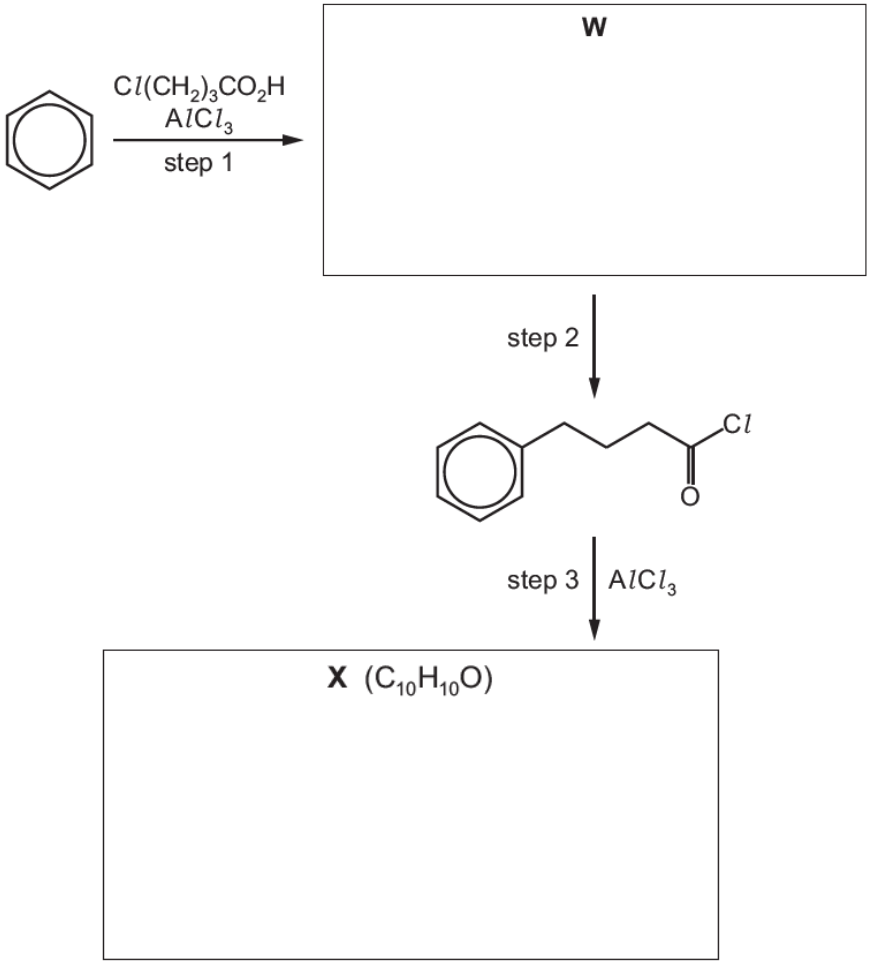
42. Benzene-1,2-dioic acid can be used to produce K.



Suggest the name of this type of reaction.

..... [1]

43. A three-step synthesis of X ($C_{10}H_{10}O$) from benzene is suggested as shown.



(i) Step 1 is the alkylation of benzene by electrophilic substitution.
Use R–C*l* to represent C*l* $(CH_2)_3CO_2H$.
Write an equation for the formation of an electrophile from R–C*l* and A*l*C*l*$_3$.

..... [1]

(ii) Deduce and draw the structures of W and X in the boxes. [2]

(iii) Suggest the reagents and conditions for step 2.

..... [1]

44. P, Q, R, S, T, U, and V are the seven structural isomers with molecular formula C5H10O that have a carbonyl group.

P CH3(CH2)3CHO	Q CH3CH2CH(CH3)CHO	R (CH3)2CHCH2CHO
S (CH3)3CCHO	T CH3CH2CH2COCH3	U CH3CH2COCH2CH3
V (CH3)2CHCOCH3		

P, Q, R, S, T, U, and V are treated separately with alkaline I_2(aq) and the product mixture is acidified.
(i) Identify the two compounds that give a positive result with alkaline I_2(aq).

..... and ..... [1]
(ii) Describe the observations when one of the compounds you have identified in (b)(i) is treated with alkaline I_2(aq) and give the structural formulae of the two carbon-containing products of this reaction.

observations .....

two carbon-containing products .....

and ..... [2]

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