1. Two chemical tests are carried out on an aqueous solution of an aromatic organic compound **Y**.

The results of the tests are shown below.

Test	$Br_2(aq)$	$Na_2CO_3(aq)$
Observation	decolourised	effervescence

What is the minimum number of C atoms in **Y**?

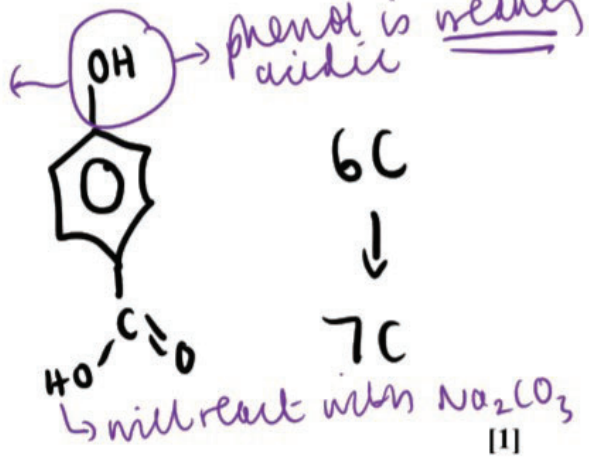
A 6

B 7

C 8

D 9

Your answer **B**



[1]

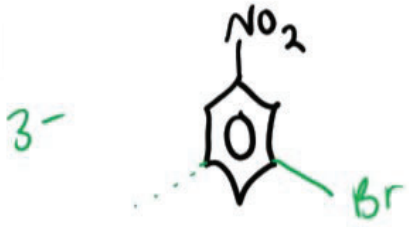
2. Bromine is reacted separately with nitrobenzene and phenylamine.

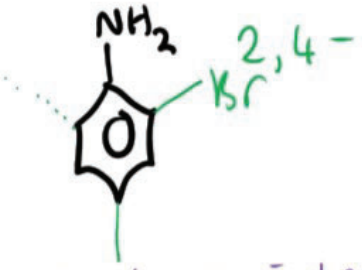
electrophilic substitution

Which organic products are likely to form?

	Product from nitrobenzene	Product from phenylamine
A	2-bromonitrobenzene	2-bromophenylamine
B	2-bromonitrobenzene	3-bromophenylamine
C	3-bromonitrobenzene	2-bromophenylamine
D	3-bromonitrobenzene	3-bromophenylamine

Your answer **C** [1]

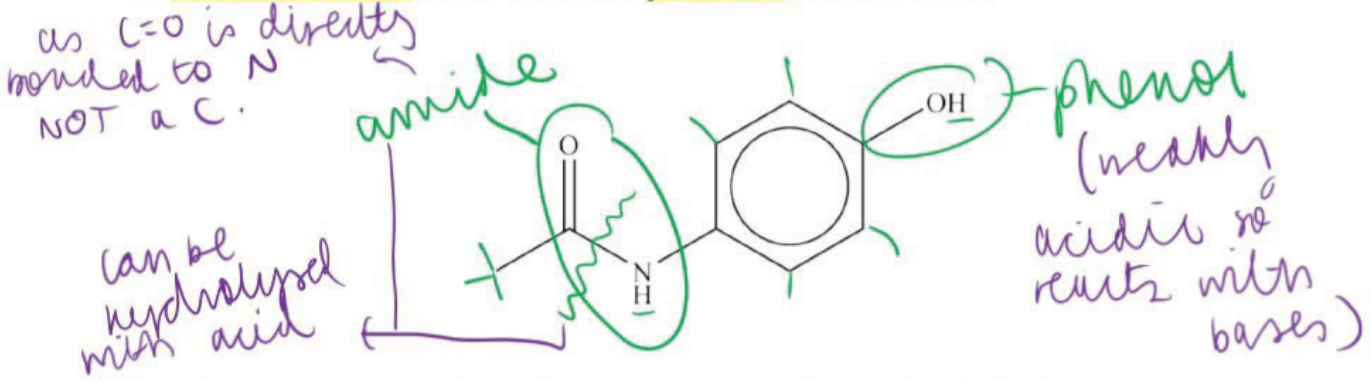




$-NO_2$ is an e^- withdrawing group so deactivates ring ∴ is 3- directing

$-NH_2$ is an e^- donating group so activates the ring ∴ is 2-, 4- (+-6.) directing

3. The structure of a molecule that is used as a pain reliever is shown below.



Which statement about this molecule is **not** true?

$C_8H_9NO_2$

A It has the molecular formula $C_8H_9NO_2$.

B It reacts with bases to form salts.

C It has a ketone functional group.

D It can be hydrolysed with aqueous acid.

Your answer C

[1]

both are planar

4. Which of the following support(s) the delocalised model for benzenе rather than the Kekulé model?

1: Benzene is less reactive than cyclohexene ✓  + Br_2

2: A benzene molecule has a planar, hexagonal structure ✗

3: The enthalpy change of hydrogenation of benzene is more exothermic than predicted from the Kekulé structure ✗

A 1, 2 and 3

B Only 1 and 2

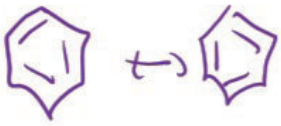
C Only 2 and 3

D Only 1

Your answer D

[1]

Delocalised: 

Kekulé: 

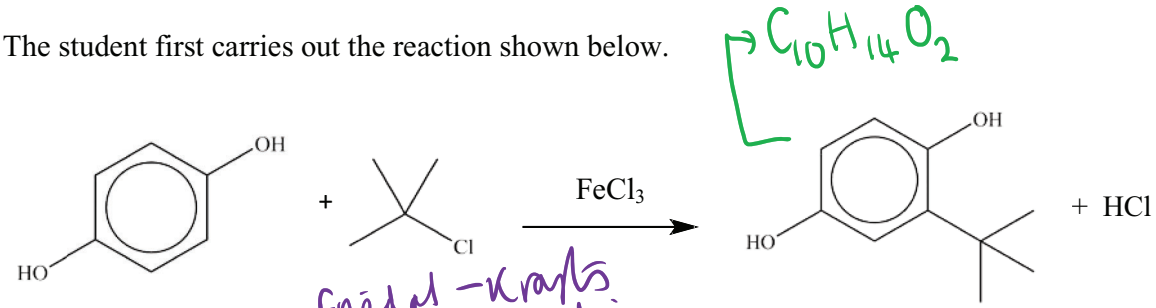
+ Br_2 , $AlBr_3$

↳ less e^- dense so needs halogen carrier / catalyst to react

↳ it's less exo than predicted due to extra stability from the delocalised π e^- ring.

5. A student investigates reactions of aromatic compounds.

The student first carries out the reaction shown below.



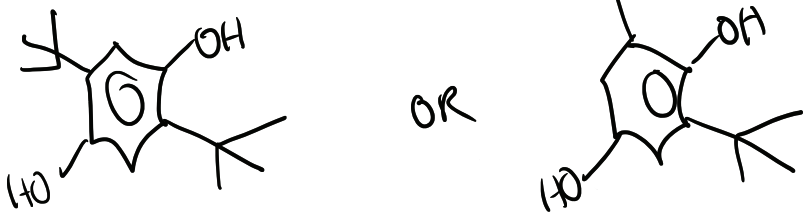
quinol **Compound E**

Friedel-Crafts reaction

$C_{10}H_{14}O_2$

The student obtains a very low yield of compound **E**.
The student obtains a much higher yield of a different organic product with molecular formula $C_{14}H_{22}O_2$.

Suggest an identity for the organic product $C_{14}H_{22}O_2$ and draw its structure below.



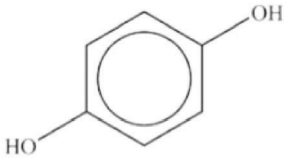
Multiple substitutions → worked out from the difference in molecular formulae.

[1]

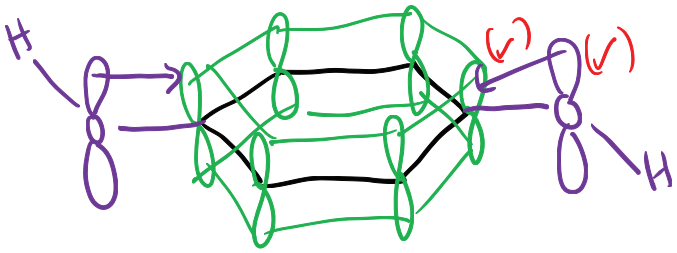
The student is told by a friend that the $FeCl_3$ catalyst is not needed because quinol is more reactive than benzene.

Explain why the student's friend is correct.

You may draw a diagram to support your answer.

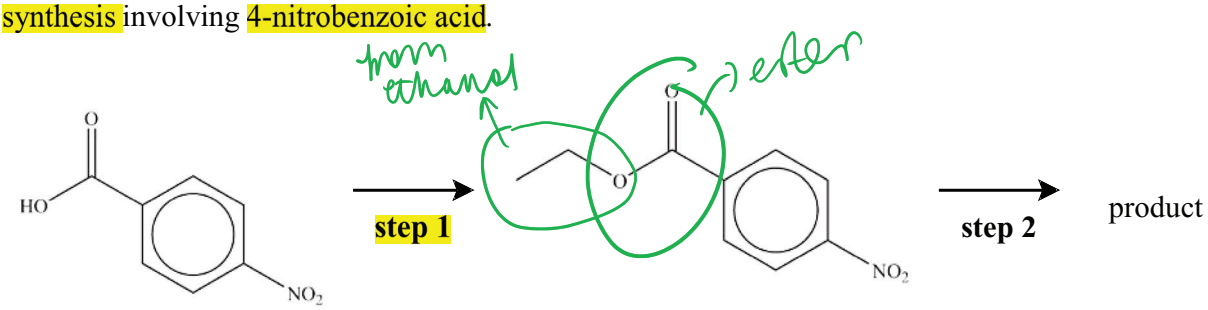


quinol



lone pairs of e⁻ on the oxygen (OH in quinol) → partially delocalise into the ring. Adding e⁻ density to the ring ∴ making it more reactive so no catalyst is needed ∴ quinol more susceptible to attack from an electrophile (⊕). **[3]**

4-Nitrobenzoic acid is an important compound in chemical synthesis. The flowchart below shows a synthesis involving 4-nitrobenzoic acid.



Compound F

State suitable reactant(s) and conditions for **step 1**.

- Esterification (carboxylic acid + alcohol.

conc H_2SO_4 , CH_3CH_2OH .

catalyst + reducing agent.

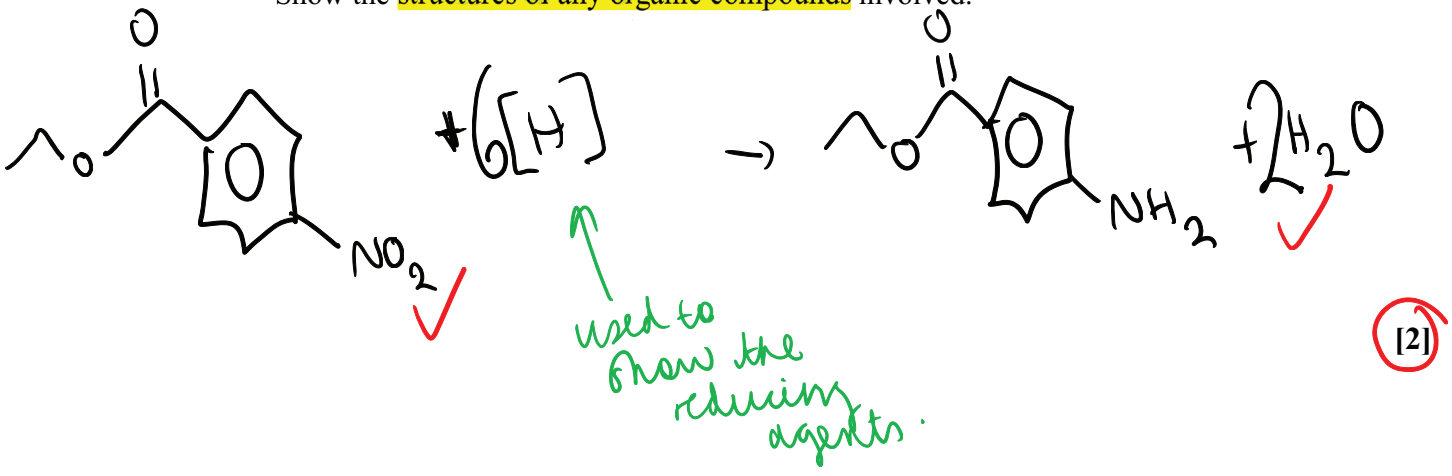
NH_2

[1]

In **step 2**, the $-NO_2$ group in compound **F** is reduced by tin and concentrated hydrochloric acid.

Write an equation for the reduction of compound **F**.

Show the structures of any organic compounds involved.

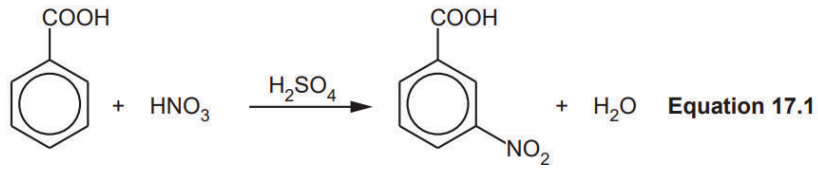


[2]

6. This question is about the chemistry of aromatic compounds.

(a) Benzoic acid can be nitrated by concentrated nitric acid in the presence of concentrated sulfuric acid as a catalyst, as shown in **Equation 17.1**.

The organic product of this reaction is 3-nitrobenzoic acid.



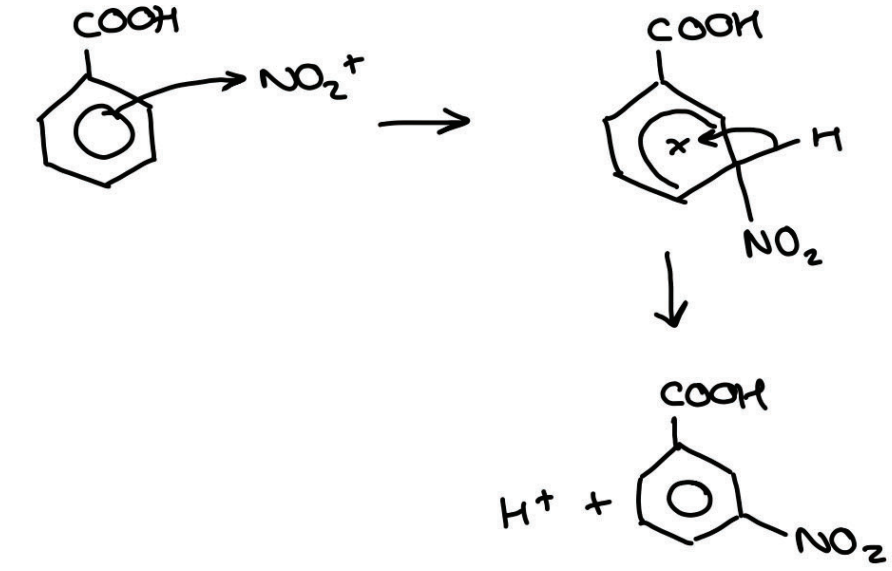
Equation 17.1

benzoic acid **3-nitrobenzoic acid**

(i) Outline the mechanism for this nitration of benzoic acid.

Show how H_2SO_4 behaves as a catalyst.

$H_2SO_4 + HNO_3 \longrightarrow H_2O + NO_2^+ + HSO_4^-$



$H^+ + HSO_4^- \longrightarrow H_2SO_4$

reformation of the catalyst.

[5]

(ii)* A chemist carries out the reaction in **Equation 17.1** using 4.97 g of benzoic acid.

The chemist obtains 3-nitrobenzoic acid as an impure solid.

The chemist purifies the solid to obtain 4.85 g of 3-nitrobenzoic acid.

Describe a method to obtain a pure sample of 3-nitrobenzoic acid from the impure solid, determine the percentage yield and check its purity.

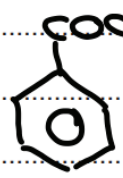
purification:

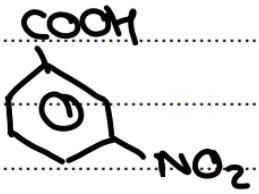
1. recrystalisation

2. dissolve solid in minimal amount of hot solvent

3. cool solution and filter solid

4. wash with cold solvent and dry.

$\frac{4.97}{122} = 0.0407$ mol of 

$\frac{4.85}{167} = 0.0290$ mol of 

$\frac{0.0290}{0.0407} \times 100 = 71.3\%$.

[6]

to check purity conduct a melting point test and compare to known values.

(b) A student investigates the relative ease of nitration of phenol, benzene, and benzoic acid.

phenol **benzene** **benzoic acid**

The student finds that the conditions required for the nitration of each compound are different, as shown in **Table 17.1**.

Compound	phenol	benzene	benzoic acid
Conditions required for nitration	Dilute HNO_3 20 °C No catalyst	Concentrated HNO_3 55 °C H_2SO_4 catalyst	Concentrated HNO_3 100 °C H_2SO_4 catalyst

Table 17.1

(i) State the trend in the relative ease of nitration of phenol, benzene, and benzoic acid.

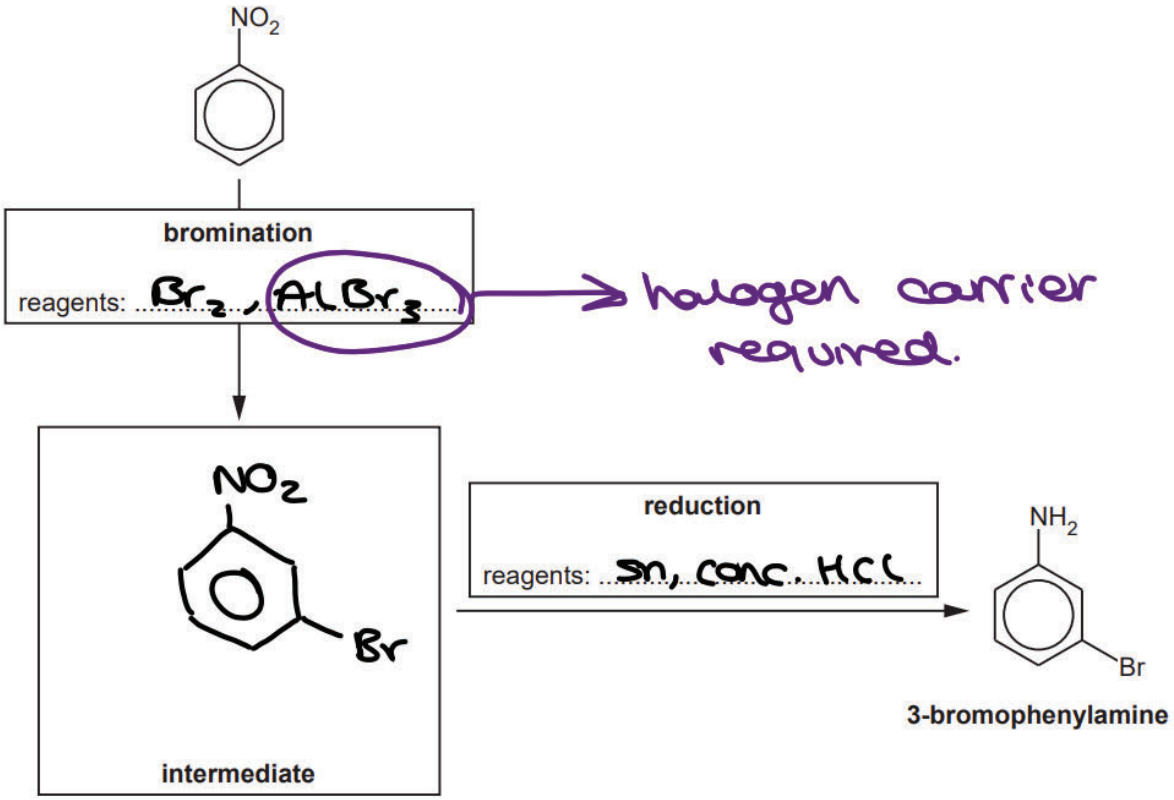
phenol is the easiest to nitrate and benzoic acid is the hardest / least reactive. **[1]**

(ii) Apply your knowledge of the bonding in arenes to explain the trend in part **(b)(i)**.

phenol: the lone pair of electrons on O is partially delocalised into the π ring system.
benzoic acid: COOH is an electron withdrawing group overall in phenol the electron density is greater so is more susceptible to attack. **[3]**

(c) A student synthesises 3-bromophenylamine, shown below, starting from nitrobenzene.

(i) Complete the flowchart showing the structure of the intermediate and the **formulae** of the reagents for each stage.



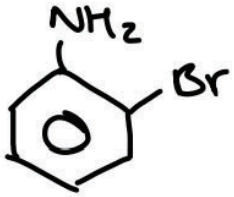
[3]

(ii) Another student attempts the same synthesis but carries out reduction **before** bromination. The student was surprised to find that two structural isomers of 3-bromophenylamine had been formed instead of the desired organic product.

Explain this result and suggest the structures of the two isomers that formed.

Explanation NH_2 is a 2,4 directing group so Br groups would be arranged differently on the benzene ring.

Structures

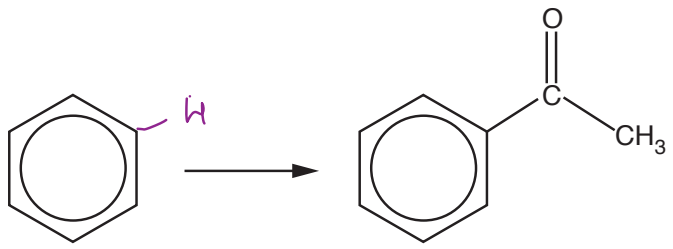


and

[3]

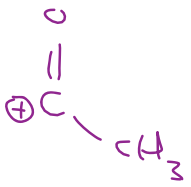
7. Benzene reacts with an organic reagent in the presence of a halogen carrier to form phenylethanone.

Electrophilic substitution



$AlCl_3$

phenylethanone



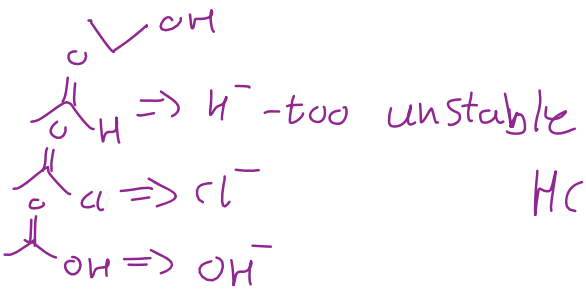
Which organic reagent is required?

~~A~~ CH_3CH_2OH

~~B~~ CH_3CHO

(C) CH_3COCl

~~D~~ CH_3COOH



$HCl \rightarrow H^+ + Cl^-$

$H_2O \rightleftharpoons H^+ + OH^-$

Your answer C

[1]

Cl^- more stable than OH^- as HCl is a stronger acid than H_2O. ∴ Cl^- is a better leaving group than OH^-.

8. Which statement(s) support(s) the delocalised model for the structure of benzene?

1 All carbon–carbon bonds have the same length. ✓ – delocalised system causes all C–C bonds to have same intermediate bond length

2 The enthalpy change of hydrogenation of benzene is less exothermic than expected. ✓

3 Bromine reacts with benzene less readily than with cyclohexene. ✓ ↳ bond breaking requires more energy due to stability of delocalised ring.

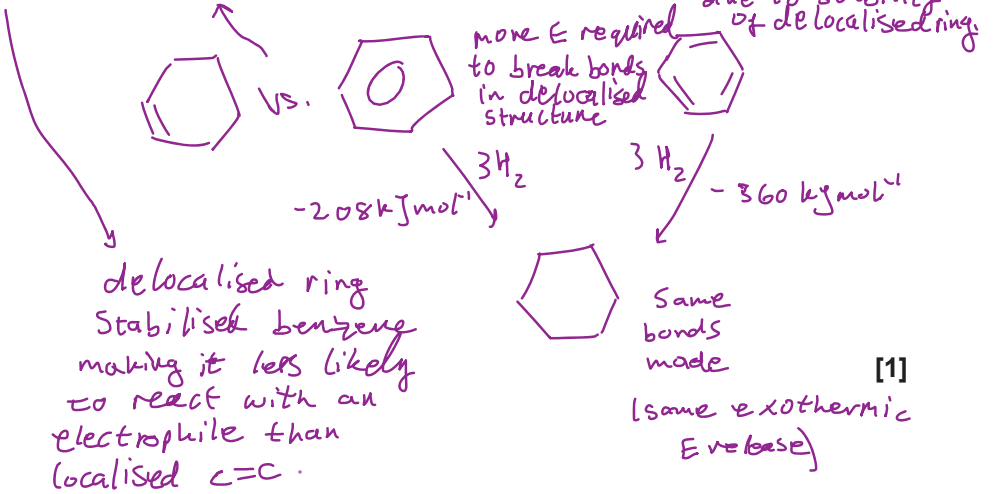
A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer A



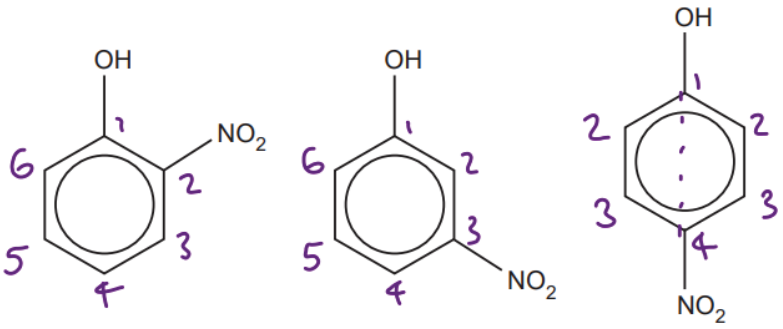
[1]

9. This question is about aromatic compounds.

(a) Phenol undergoes nitration more readily than benzene.

(i) A student carries out the nitration of phenol with dilute nitric acid to produce 2-nitrophenol and 4-nitrophenol.

A small amount of 3-nitrophenol is also produced.



2-nitrophenol **3-nitrophenol** **4-nitrophenol**

The student thought that ^{13}C NMR spectroscopy could be used to distinguish between these three nitrophenols.

Explain whether the student is correct.

2 - nitrophenol and 3 - nitrophenol : 6 ^{13}C NMR peaks so aren't distinguishable.

4 - nitrophenol : 4 ^{13}C NMR peaks so is distinguishable.

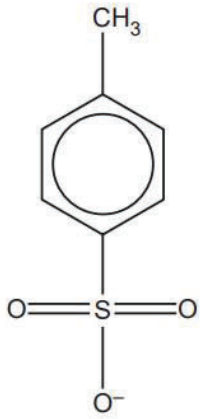
[3]

(ii) Explain why phenol is nitrated more readily than benzene.

phenol: lone pair of electrons on O is partially delocalised into the π ring system so electron density is higher than benzene and phenol is more susceptible to electrophilic attack.

[3]

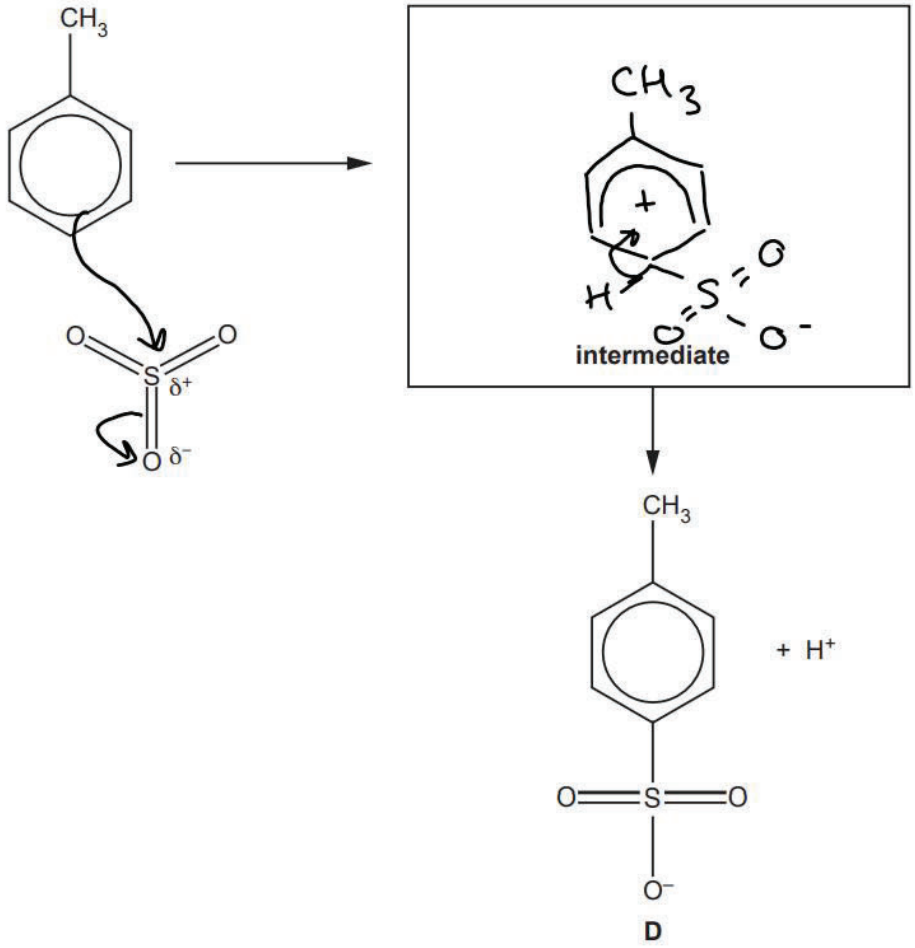
(b) Methylbenzene reacts with sulfur trioxide, SO_3, to form **D**, shown below.



D

The electrophile in this reaction is SO_3.

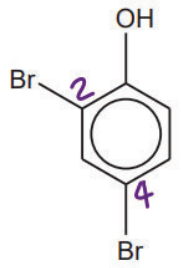
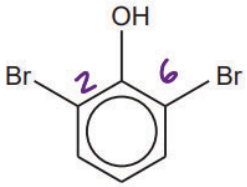
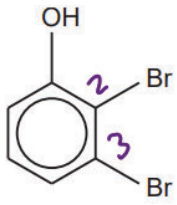
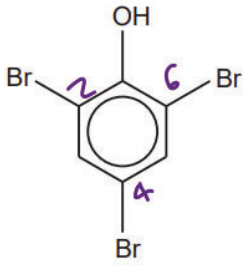
Complete the mechanism for the formation of **D**.
Show curly arrows and the structure of the intermediate.



[3]

10. Phenol reacts with bromine. 2,4,6 directing effect

Which is the **least** likely organic product?

A	
B	
C	
D	

Your answer C

[1]

11. Which chemical(s) can react with phenol?

1 Potassium hydroxide

2 Ethanoyl chloride

3 Nitric acid

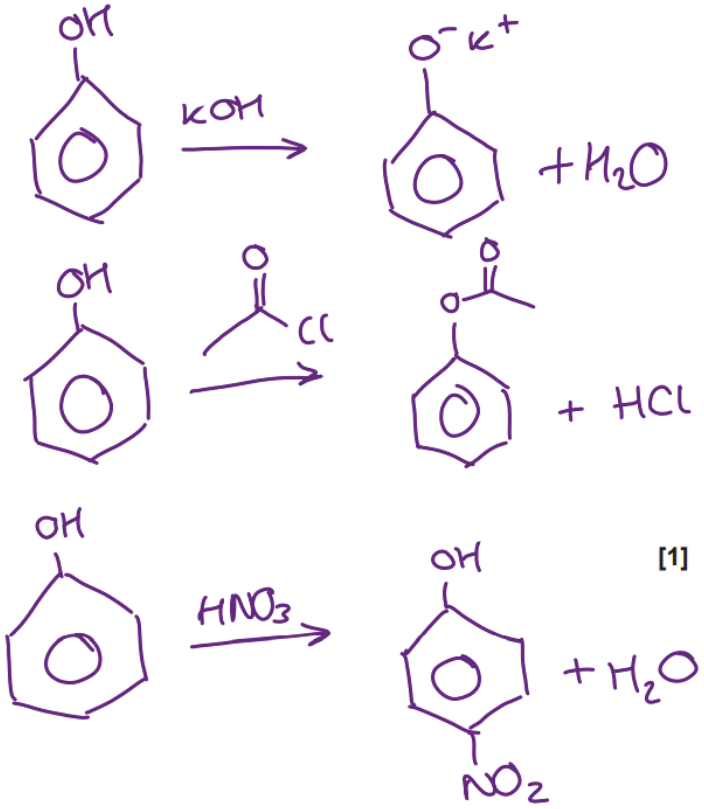
A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer A



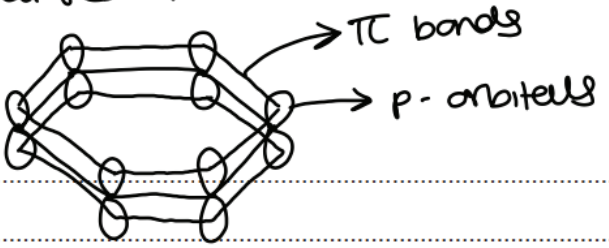
[1]

12. This question is about benzene.

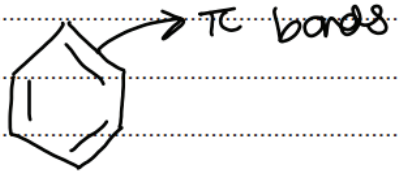
(a) Over time, the Kekulé and delocalised models have been used to describe the bonding and structure of a benzene molecule.

(i) Describe, in terms of orbital overlap, the similarities and differences between the bonding in the Kekulé model and the delocalised model of benzene.

delocalised model:



Kekulé:



differences:

Kekulé has 3 π bonds and the delocalised model has a π ring system [3]

(ii) Experimental evidence led to the general acceptance of the delocalised model over the Kekulé model.

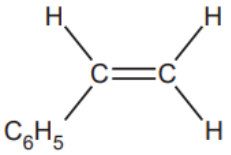
Describe **two** pieces of evidence to support the delocalised model of benzene.

- benzene is less reactive than alkenes
- all C–C bond lengths are the same

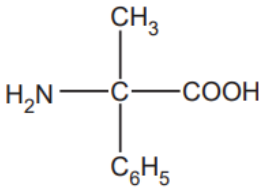
[2]

(b) Benzene can be used as the starting material for the synthesis of compounds **D** and **E**, shown below.

In the diagrams C_6H_5 is a phenyl group.



compound D



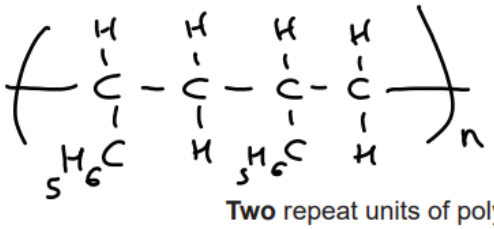
compound E

addition C=C → C-C

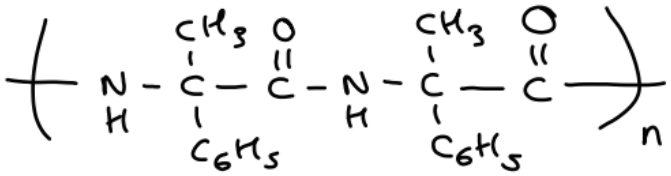
condensation forms $R_2N-\overset{H}{\underset{}{}}-\overset{O}{\overset{\|}{C}}-R_1$

Compounds **D** and **E** can be converted into polymers. amide

(i) Draw **two** repeat units of these polymers.



Two repeat units of polymer formed from **D**



Two repeat units of polymer formed from **E**

[3]

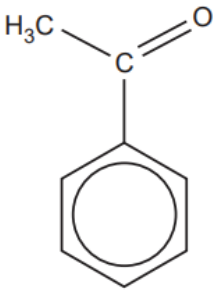
(ii) State the **type** of polymer formed from compounds **D** and **E**.

From compound **D** addition

From compound **E** condensation

[1]

(iii) In the synthesis of compounds **D** and **E**, benzene is first reacted with ethanoyl chloride, CH_3COCl, to form phenylethanone, shown below.



electrophilic substitution

phenylethanone

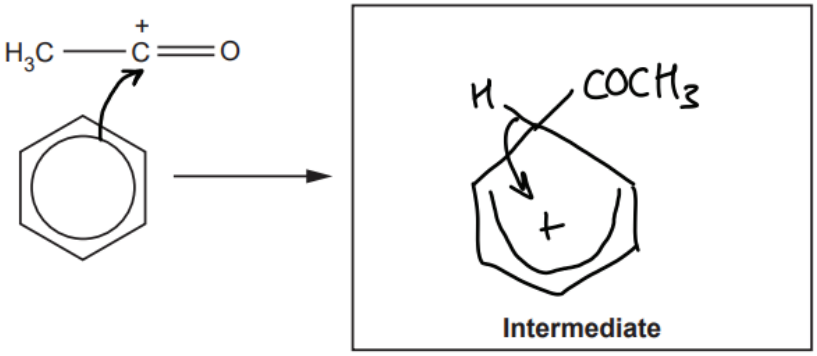
The reaction takes place in the presence of aluminium chloride, $AlCl_3$, which acts as a catalyst.

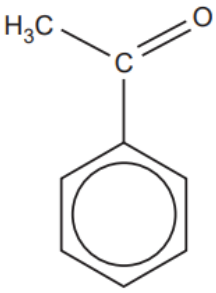
In the mechanism for this reaction,
- ethanoyl chloride first reacts with aluminium chloride to form the $CH_3–C^+=O$ cation
- the $CH_3–C^+=O$ cation then behaves as an electrophile.

Complete the mechanism for the reaction.

Include equations to show the role of the $AlCl_3$ catalyst, relevant curly arrows and the structure of the intermediate.

Formation of electrophile $CH_3COCl + AlCl_3 \rightarrow CH_3-C^+=O + AlCl_4^-$



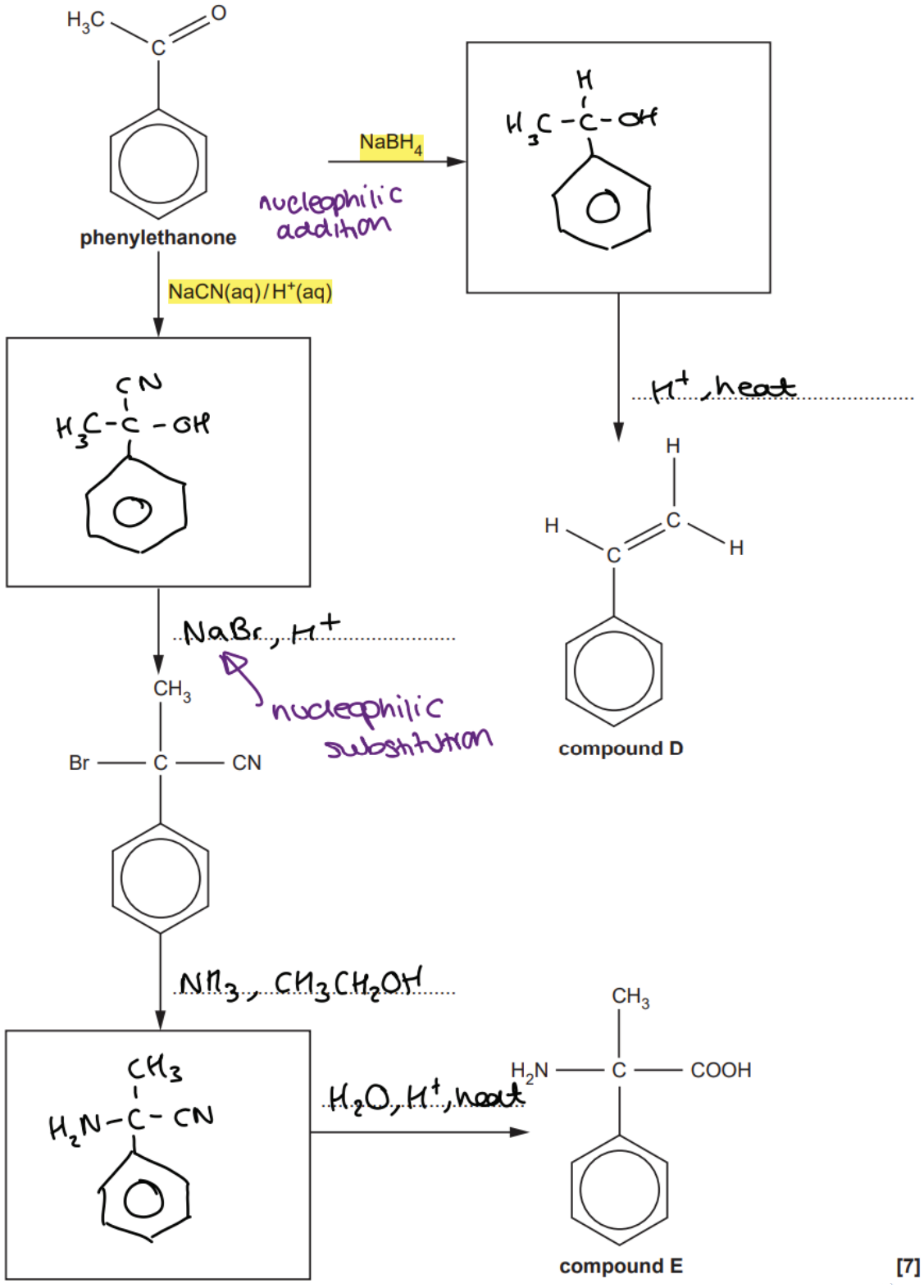


+ H^+

Regeneration of catalyst $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

[5]

(iv) Complete the flowchart for the synthesis of compounds **D** and **E** from phenylethanone.



[7]

13. Benzoic acid, C_6H_5COOH, is added to some foods as a preservative.

A student prepares benzoic acid as outlined below.

Step 1 The student mixes 4.00 cm^3 of phenylmethanol, $C_6H_5CH_2OH$, (density = 1.04 $g\,cm^{-3}$) with sodium carbonate and aqueous potassium manganate(VII), as an oxidising agent. The mixture is heated under reflux.

Step 2 The resulting mixture is cooled and then acidified with concentrated HC*l*. Impure crystals of benzoic acid appear.

Step 3 The student recrystallises the impure crystals to obtain 1.59 g of pure benzoic acid.

(a) In **Step 1**, sodium carbonate, Na_2CO_3, makes the reaction mixture alkaline.

Write an ionic equation to show how carbonate ions form an alkaline solution in water.

$CO_3^{2-} + H_2O \rightarrow OH^- + HCO_3^-$ **[1]**

(b) In **Step 2**, explain why the mixture must be acidified so that crystals of benzoic acid appear.

H^+ reacts with $C_6H_5COO^-$:

$H^+ + C_6H_5COO^- \rightarrow C_6H_5COOH$

[1]

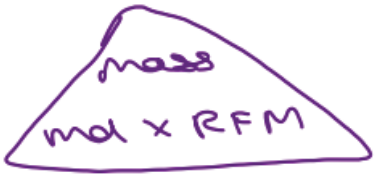
(c) Write the overall equation for the preparation of benzoic acid from phenylmethanol.

Use [O] for the oxidising agent.

$C_6H_5CH_2OH + 2[O] \rightarrow C_6H_5COOH + H_2O$ **[1]**

(d) Calculate the percentage yield of benzoic acid.

Give your answer to **3** significant figures.



$\frac{4 \times 1.04}{((12\times6)+5+12+2+16+1)} = 0.0385$ mol of $C_6H_5CH_2OH$

$\frac{1.59}{((12\times6)+5+12+((16\times2)+1)} = 0.013$ mol of C_6H_5COOH

$\frac{0.013}{0.0385} \times 100 = 33.8\%$ (3sf)

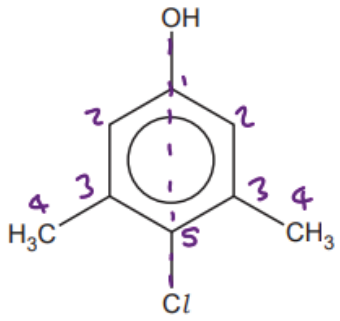
percentage yield = 33.8 % **[3]**

(e) In **Step 3**, describe how the student can recrystallise the impure crystals to obtain pure benzoic acid.

dissolve in a minimal amount of hot solvent. Cool, filter, and leave to dry.

[2]

14. Dettol® is a disinfectant containing the antiseptic chloroxylenol, shown below.



chloroxylenol

(a) Chloroxylenol is a weak Brønsted–Lowry acid.

(i) What is the systematic name of chloroxylenol?

4 - chloro - 3,5 - dimethyl phenol ..... **[1]**

(ii) Predict the number of peaks in a ^{13}C NMR spectrum of chloroxylenol.

5 ..... **[1]**

(iii) Name the functional group responsible for the acidity of chloroxylenol and describe a simple test which would confirm the presence of this group.

Functional group phenol .....

Test indicator turns red / orange (pH < 7) and no reaction with Na_2CO_3 .....

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

(iv) A student measures the pH of the contents in a bottle of Dettol® as 5.14.

The label on the bottle shows the percentage of chloroxylenol in Dettol® as 4.80% i.e. 100 cm^3 of Dettol® contains 4.80 g of chloroxylenol.

Assume the following:
- Chloroxylenol is the only acidic component in Dettol®.
- Chloroxylenol is a weak monobasic acid.
- The density of Dettol® is 1.00 g cm^{-3}.

Write the equation, using molecular formulae, for the acid dissociation of chloroxylenol.

Calculate the acid dissociation constant, K_a, for chloroxylenol.

$C_8H_9ClO \rightleftharpoons H^+ + C_8H_8ClO^-$

$RFM = (12\times8) + 9 + 35.5 + 16 = 156.5\ g\,mol^{-1}$

$K_a = \frac{[H^+]^2}{[HA]}$

$[H^+] = 10^{-pH}$

$\frac{4.8}{156.5} = 0.03067\ mol$

$\frac{0.03067}{100\times10^{-3}} = 0.3067\ mol\,dm^{-3} = [HA]$

$[H^+] = 10^{-5.14} = 7.244\times10^{-6}\ mol\,dm^{-3}$

$K_a = \frac{[7.244\times10^{-6}]^2}{[0.3067]}$

$K_a = 1.71\times10^{-10}\ mol\,dm^{-3}$

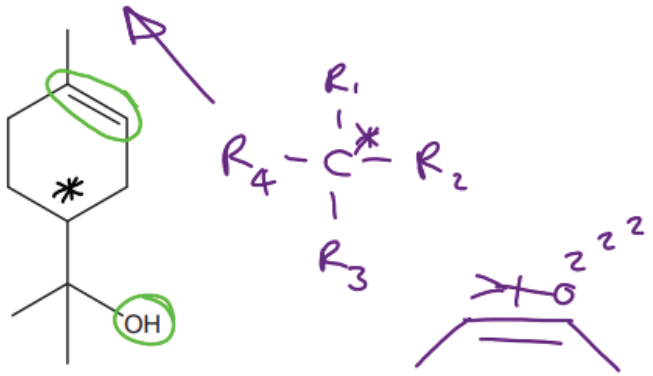
$ka = 1.71\times10^{-10}\ mol\,dm^{-3}$

K_a = 1.71 x 10^{-10} mol dm^{-3} **[5]**

(b) Dettol® contains other chemicals including α-terpineol, shown below.

(i) α-Terpineol is a chiral compound.

Show with an asterisk, (*), the chiral centre(s) in the structure of α-terpineol.



α-terpineol

[1]

(ii) α-Terpineol meets the requirements for *E*/*Z* isomerism.
However, only one *E*/*Z* isomer of α-terpineol exists.

Explain
- why α-terpineol meets the requirements for *E*/*Z* isomerism
- whether α-terpineol is an *E*- or *Z*- isomer
- why only one *E*/*Z* isomer of α-terpineol exists.

• C=C double bond, each C attached to 2 different groups
• E/Z isomerism linked to high priority groups. Z- isomer groups are on the same side
• ring would be strained

[4]

(iii) α-Terpineol contains two functional groups.

For each functional group, choose a reagent that reacts with that group **only**.
Draw the structures for the organic products of the reactions.

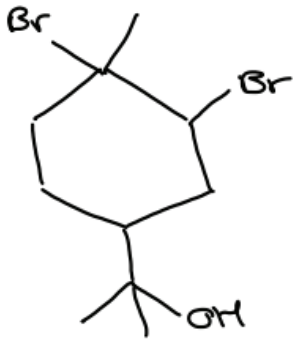
Show structures for organic compounds.

Reagent(s) Br_2

Name of functional group that reacts alkene

Structure of organic product

electrophilic addition mechanism

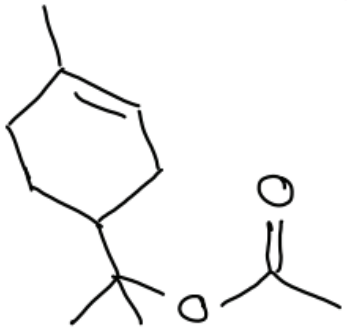


Reagent(s) CH_3COOH, H^+ catalyst

Name of functional group that reacts 3° alcohol

Structure of organic product

esterification



[4]

15. Which one of the following reacts with ethanoic acid **and** with phenol?

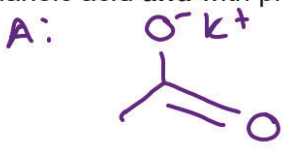
(A) Aqueous potassium hydroxide

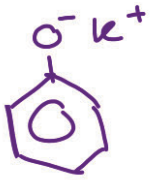
~~B~~ Bromine only reacts with phenol

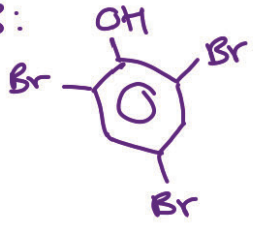
~~C~~ Calcium carbonate only reacts with CH_3COOH

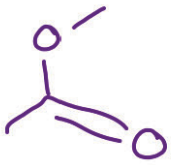
~~D~~ Methanol and an acid catalyst only reacts with ethanoic acid (CH_3COOH)

Your answer [A]

A: 



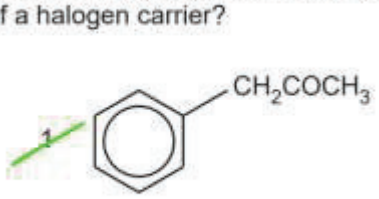
B: 

D: 

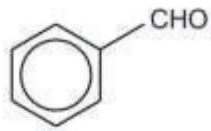
test for acid but phenol isn't a strong enough acid

[1]

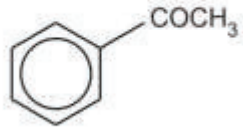
16. Which compound(s) could be prepared by reacting benzene with an acyl chloride in the presence of a halogen carrier?



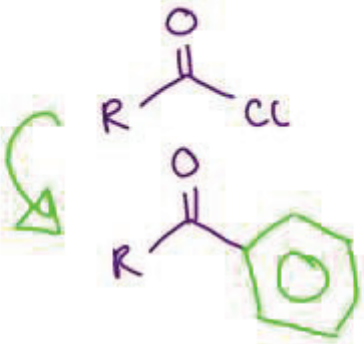
1



2 R = H



3 R = CH_3



A 1, 2 and 3

B Only 1 and 2

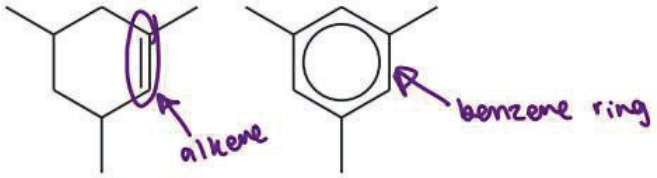
C Only 2 and 3

D Only 1

Your answer C

[1]

17. Compounds **B** and **C**, shown below, are unsaturated hydrocarbons containing nine carbon atoms.

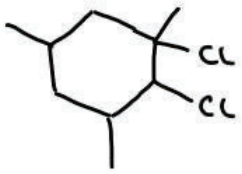
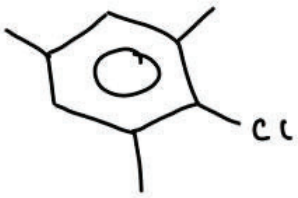


B **C**

(a) Compound **B** reacts with chlorine at room temperature, but compound **C** requires the presence of a halogen carrier.

In both reactions, the organic compound reacts with chlorine in a 1:1 molar ratio.

(i) Draw the structures of the organic product of each reaction.

electrophilic addition 	electrophilic substitution 
Organic product with **B**	Organic product with **C**

[2]

(ii) Explain the relative resistance to chlorination of compound **C** compared with compound **B**.

In B the electrons / π bond is localised

In C the electrons / π ring system is delocalised

In B the electron density is higher so is more susceptible to electrophilic attack / B attracts / accepts the electrophile (CCl_2) more / B polarises the electrophile (CCl_2) more.

[3]

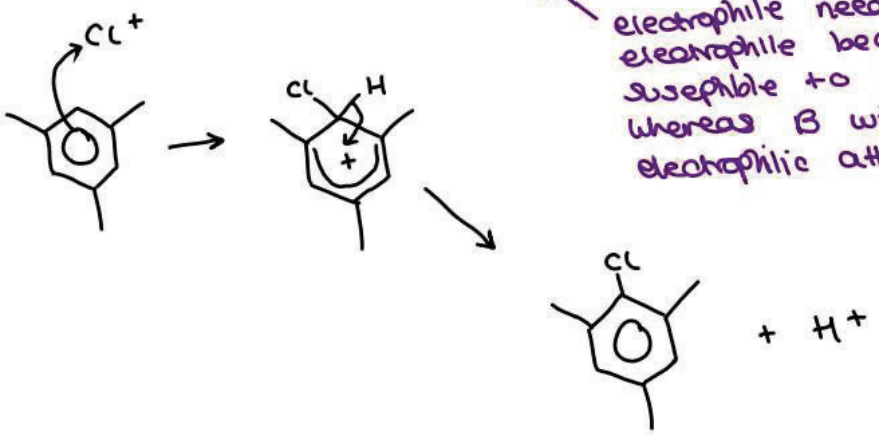
(iii) Outline the mechanism for the reaction of compound **C** with chlorine.

Show the role of the halogen carrier.

forming electrophile

$AlCl_3 + Cl_2 \longrightarrow Cl^+ + AlCl_4^-$

electrophile needs a stronger electrophile because C is less susceptible to electrophilic attack whereas B will undergo electrophilic attack with $Cl^{\delta+}$



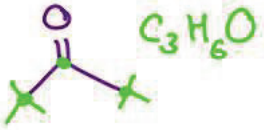
$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$

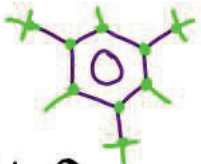
regenerating halogen carrier

[5]

(b) Compound **C** can be prepared by 'trimerisation' of propanone using concentrated sulfuric acid as a catalyst.

Suggest an equation for this reaction, using **molecular** formulae.





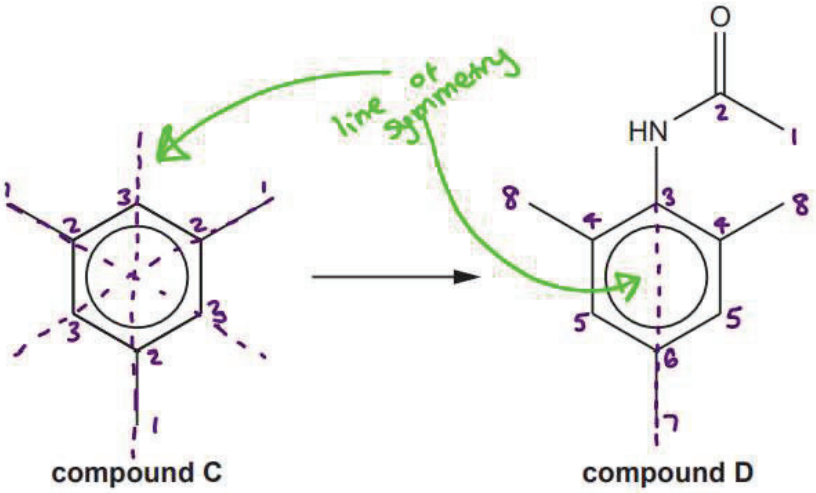
C_9H_{12}

Question confirms 9 carbons in compound C

$3C_3H_6O \longrightarrow C_9H_{12} + 3H_2O$ **[3]**

(c) An organic chemist is investigating compound **D** for possible use as a medicine.

The chemist proposes a synthesis of compound **D** from compound **C**.



compound C **compound D**

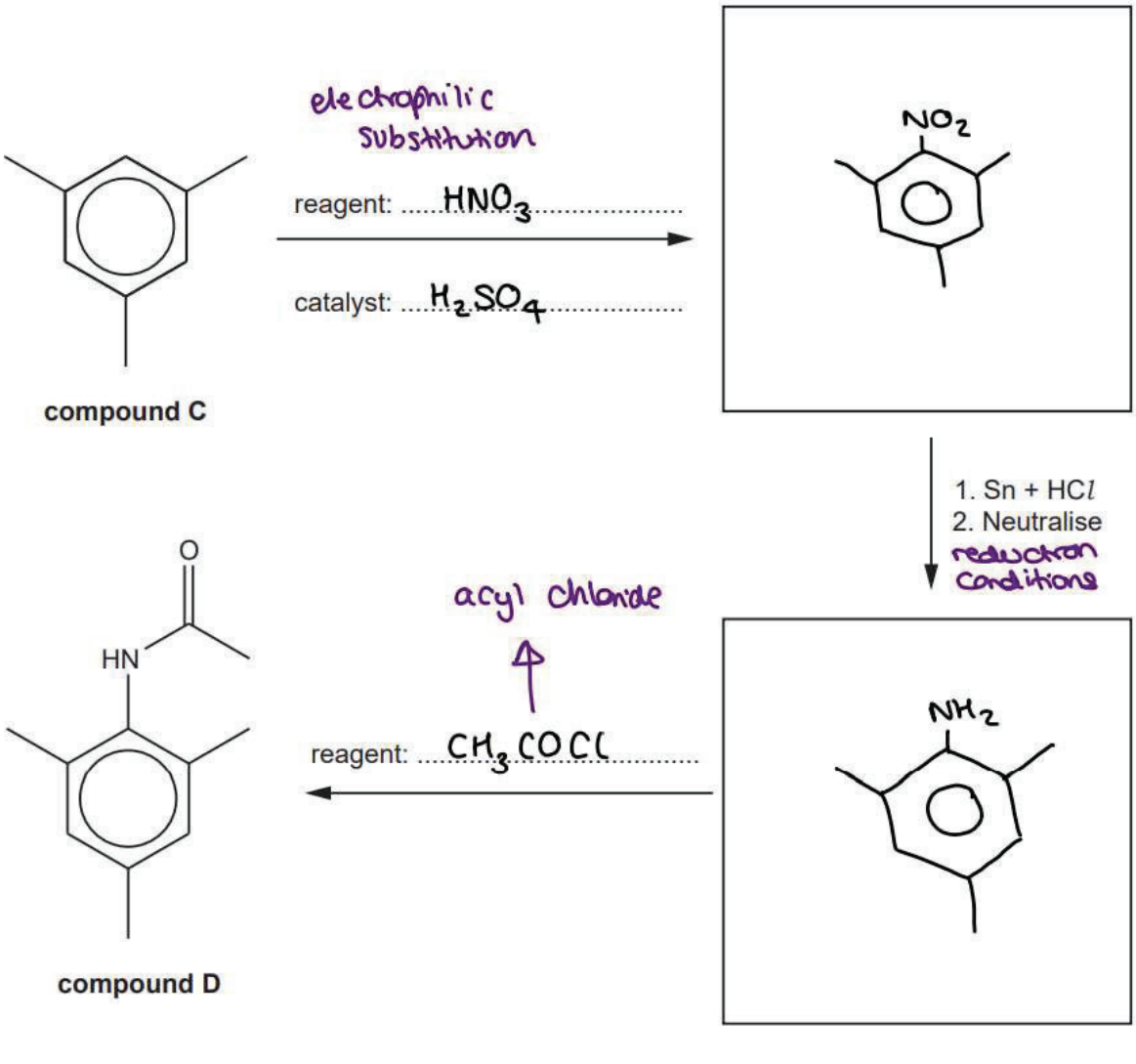
(i) Predict the number of peaks in the ^{13}C NMR spectra of compounds **C** and **D**.

	Compound **C**	Compound **D**
Number of peaks	3	8

[2]

(ii) The chemist develops a three-stage synthesis of compound **D** from compound **C**.

Complete the flowchart.
Show structures for organic compounds.



[5]