Week 45

A-Level Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

Contents 目录

A-Level Chemistry Name: _____ Score: _____

1. Benzene reacts mostly by electrophilic substitution because:
   - ☐ this keeps the stable delocalised ring, while addition would destroy it
   - ☐ the ring is unstable
   - ☐ it has no electrons
   - ☐ addition is impossible
2. A halogen reacts in the ring (not the side-chain) when there is:
   - ☐ a halogen-carrier catalyst ($AlCl_3$) and no UV light
   - ☐ UV light and no catalyst
   - ☐ only heat
   - ☐ water present
3. Nitration of benzene uses:
   - ☐ concentrated HNO_3 and concentrated H_2SO_4
   - ☐ bromine water
   - ☐ dilute NaOH
   - ☐ hydrogen and a catalyst
4. Under UV light with no catalyst, the halogen substitutes:
   - ☐ in the side-chain (free-radical substitution)
   - ☐ in the ring
   - ☐ nowhere
   - ☐ at the catalyst
5. A Friedel–Crafts reaction (with $AlCl_3$) is used to:
   - ☐ add an alkyl or acyl group to the ring
   - ☐ remove a hydrogen as a radical
   - ☐ oxidise the ring
   - ☐ hydrogenate the ring
6. Groups already on a benzene ring direct where the next group attaches.

   ☐ True ☐ False

7. Benzene reacts mainly by electrophilic substitution, not addition, because that keeps its stable delocalised ring intact.

   ☐ True ☐ False

8. An –OH group already on the ring directs the next substituent to:

   ☐ positions 2 and 4

   ☐ position 3 only

   ☐ no particular position

   ☐ the side-chain

9. In electrophilic substitution, after the ring bonds to the electrophile:

   ☐ an H^+ is lost, restoring the stable ring

   ☐ the ring opens up

   ☐ another electrophile adds

   ☐ a radical forms

10. Arenes such as benzene typically react by:

    ☐ electrophilic substitution

    ☐ electrophilic addition

    ☐ nucleophilic substitution

    ☐ free-radical addition

30. Hydrocarbons

Answers · 答案

A-Level Chemistry

1. **this keeps the stable delocalised ring, while addition would destroy it**

   Substitution preserves the aromatic stabilisation; addition would break up the delocalised system.

2. **a halogen-carrier catalyst ($AlCl_3$) and no UV light**

   The catalyst makes the electrophile for ring substitution; UV with no catalyst gives side-chain free-radical substitution.

3. **concentrated HNO_3 and concentrated H_2SO_4**

   The conc. acid mixture generates the NO_2^+ electrophile, giving nitrobenzene.

4. **in the side-chain (free-radical substitution)**

   UV light starts free-radical substitution in the alkyl side-chain.

5. **add an alkyl or acyl group to the ring**

   Friedel–Crafts alkylation/acylation adds a carbon-based group to benzene.

6. **True**

   This is the directing effect.

7. **True**

   Addition would break the delocalised ring and lose its stability, so substitution (swapping an H) is favoured.

8. **positions 2 and 4**

   $–NH_2$, –OH and –R are 2,4-directing; $–NO_2$, –COOH and –COR are 3-directing.

9. **an H^+ is lost, restoring the stable ring**

   Losing H^+ from that carbon restores the delocalised ring, completing the substitution.

10. **electrophilic substitution**

    Substitution keeps the stable ring intact.

A-LEVEL CHEMISTRY • EXERCISE SHEET

30.1 Arenes

Name: _____ Class: _____ Date: _____ **Total: 30 marks**

KEY WORDS electrophilic substitution 亲电取代 • arene 芳烃 • nitration 硝化 • friedel–crafts acylation 傅克酰基化 • friedel–crafts alkylation 傅克烷基化

Objective

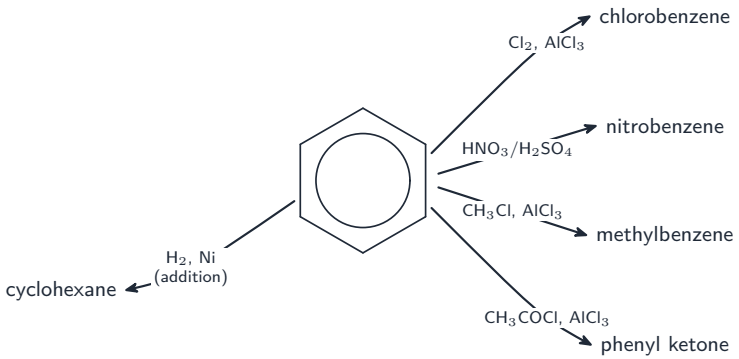
Build the skills to answer exam questions on **arenes** 芳烃 — the reactions of benzene and methylbenzene, the **electrophilic substitution** 亲电取代 mechanism, side-chain vs ring substitution, and **directing effects** 定位效应.

You must be able to:

- give the reagents, conditions and products for benzene's reactions (halogenation, nitration, Friedel–Crafts, oxidation, hydrogenation)
- describe the electrophilic substitution mechanism (e.g. nitration)
- explain why benzene substitutes rather than adds
- predict where a second group goes from directing effects

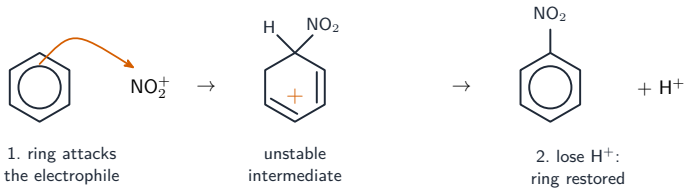
1 Worked examples

Reactions and mechanism



Benzene keeps its stable ring, reacting mostly by electrophilic substitution (addition only with H_2)

- **nitration:** conc. HNO_3 + conc. H_2SO_4, 25–60 °C → nitrobenzene.
- **Friedel–Crafts:** RCl (or RCOCl) + $AlCl_3$, heat → alkyl/acyl benzene.
- **side-chain oxidation:** hot alkaline $KMnO_4$ then acid → benzoic acid.



Electrophilic substitution: the ring attacks the electrophile, then loses H^+ to restore the stable ring

Why substitution, not addition? Substitution keeps the stable delocalised ring; addition would destroy it.

Benzene: the reagents table, and why it substitutes

Benzene's delocalised π system is **stable**, so it does not undergo addition like an alkene, which would destroy the delocalisation. Instead it undergoes **electrophilic substitution** 亲电取代: an electrophile attacks the ring, and a hydrogen is lost, so the delocalised system survives.

Reaction	Reagents	Conditions	Product
nitration	conc. HNO_3 + conc. H_2SO_4	55 °C	nitrobenzene
halogenation	Cl_2 or Br_2 + $AlCl_3$ / $FeBr_3$	room temperature, anhydrous	chloro- or bromobenzene
Friedel–Crafts alkylation	RCl + $AlCl_3$	reflux, anhydrous	alkylbenzene
Friedel–Crafts acylation	RCOCl + $AlCl_3$	reflux, anhydrous	phenyl ketone
hydrogenation	H_2, Ni catalyst	150 °C, high pressure	cyclohexane

The mechanism, written the way it earns marks (nitration):

1. **Generate the electrophile:** $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$. The nitronium ion NO_2^+ is the electrophile.
2. **Attack:** a curly arrow from **inside the ring** to the nitrogen of NO_2^+, forming the unstable intermediate drawn with a **horseshoe** (a broken delocalised ring) and a + inside it.
3. **Lose H^+:** a curly arrow from the C–H bond back into the ring, restoring the delocalisation, and H^+ is released.
4. **Regenerate the catalyst:** $H^+ + HSO_4^- \rightarrow H_2SO_4$.

The horseshoe intermediate and the arrow **from the ring, not from a double bond**, are the two marks candidates most often lose.

Methylbenzene differs in two ways. The methyl group is **electron-releasing**, so it activates the ring and directs substitution to the **2- and 4- (ortho/para)** positions, and the reaction is faster than benzene's. The side chain can also be **oxidised** by hot alkaline $KMnO_4$ followed by acid, giving benzoic acid — a reaction the ring itself never undergoes.

2 Practice

2.1 Give the reagents and conditions for the **nitration** of benzene. [2]

2.2 Name the electrophile formed in the nitration of benzene. [1]

2.3 Give the reagents and conditions for the nitration of benzene. [2]

2.4 State why benzene undergoes substitution rather than addition. [2]

2.5 Name the product when methylbenzene is refluxed with alkaline $KMnO_4$ and then acidified. [1]

3 Exam-style questions

3.1 Benzene reacts with CH_3COCl and $AlCl_3$. This is an example of: [1]

- **A** Friedel–Crafts acylation
- **B** nitration
- **C** side-chain oxidation
- **D** hydrogenation

3.2 Methylbenzene is treated with Cl_2 in **UV light with no catalyst**. Substitution occurs at the: [1]

- **A** ring, at positions 2 and 4
- **B** ring, at position 3
- **C** side-chain ($–CH_3$)
- **D** both ring and side-chain equally

3.3 Describe the mechanism of the nitration of benzene. Include the formation of the electrophile and use curly arrows in words. [4]

3.4 Nitrobenzene already carries a $–NO_2$ group. Predict and explain the position a second nitro group will take. [2]

3.5 Benzene is converted to nitrobenzene and then, in a separate route, to a phenyl ketone.

(a) Give the equation showing how the electrophile for nitration is generated. [2]

(b) Draw the mechanism for the nitration of benzene, showing the curly arrows, the intermediate and the loss of H^+. [4]

(c) Explain why the intermediate is drawn with a horseshoe rather than with three double bonds. [2]

(d) Suggest the reagents and conditions needed to convert benzene into phenylethanone, $C_6H_5COCH_3$, and name the type of reaction. [3]

(e) Methylbenzene reacts faster than benzene and gives mainly the 2- and 4- products. Explain both observations. [3]

Solutions

2.1 concentrated nitric acid and concentrated sulfuric acid; 25–60 °C / warm.

2.2 NO_2^+ (the nitryl/nitronium cation).

2.3 Concentrated nitric acid and concentrated sulfuric acid; a temperature of about 55 °C.

2.4 The ring's delocalised π electrons make it unusually stable; addition would destroy that delocalisation, so substitution, which restores it, is preferred.

2.5 Benzoic acid.

3.1 **A**. $RCOCl + AlCl_3$ adds an acyl group — Friedel–Crafts acylation.

3.2 **C**. UV light with no catalyst gives free-radical substitution in the side-chain.

3.3 the acid mixture makes the electrophile NO_2^+; the delocalised ring electrons form a bond to NO_2^+, giving a positively charged intermediate; the C–H bond breaks and H^+ is lost; this restores the delocalised ring, giving nitrobenzene.

3.4 $-NO_2$ directs the next group to **position 3**; because $-NO_2$ is an electron-withdrawing (deactivating) group that directs to the 3-position.

3.5 (a) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$.
(b) Curly arrow from **inside the ring** to the nitrogen of NO_2^+; intermediate drawn with a horseshoe and a + inside it, with the NO_2 and H on the same carbon; curly arrow from the C–H bond into the ring; H^+ released and the delocalised ring restored.
(c) The delocalised system is broken but not destroyed — four π electrons remain delocalised over five carbons; a horseshoe shows that partial delocalisation, which three localised double bonds would not.
(d) Ethanoyl chloride, CH_3COCl, with an $AlCl_3$ catalyst; reflux under anhydrous conditions; Friedel–Crafts acylation.
(e) The methyl group is electron-releasing, so it increases the electron density of the ring and makes it more attractive to an electrophile, hence the faster reaction; the electron density is increased most at the 2- and 4- positions, so substitution occurs mainly there.

8 **(a)** In the electrophilic substitution of arenes, different substituents can direct to different ring positions.

(i) Describe the directing effect of the $-NO_2$ group. Explain your answer.

.....

..... [1]

(ii) The nitration of arenes uses a mixture of concentrated HNO_3 and concentrated H_2SO_4 to generate the NO_2^+ electrophile.

Write an equation for the formation of the NO_2^+ electrophile.

..... [1]

(b) Carbon-carbon bond formation is an important reaction in organic synthesis.

Fig. 8.1 shows the synthesis of compound **Q** from benzene in two reaction steps.

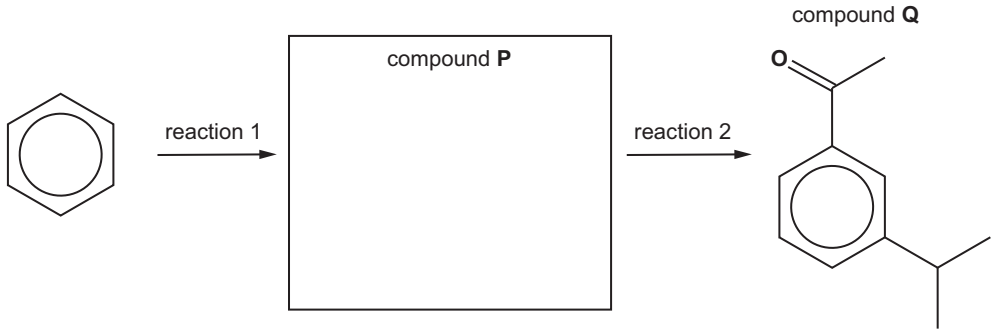


Fig. 8.1

(i) Draw the structure of compound **P** in the box in Fig. 8.1. [1]

(ii) Suggest reagents and conditions for reactions 1 and 2 in Fig. 8.1.

reaction 1 .....

reaction 2 .....

[2]

(c) Separate samples of C_6H_5Br and $C_6H_5CH_2Br$ are added to warm $AgNO_3(aq)$.

State the expected observations, if any. Explain your answer.

C_6H_5Br with $AgNO_3(aq)$ .....

$C_6H_5CH_2Br$ with $AgNO_3(aq)$ .....

explanation .....

.....

.....

.....

[3]

(d) Acyl bromides, RCOBr, react readily with H_2O.

The mechanism of this reaction is similar to that of the reaction of H_2O with acyl chlorides, RCOC*l*.

(i) Name the mechanism of this reaction.

..... [1]

(ii) Complete the mechanism in Fig. 8.2 for the reaction of RCOBr with H_2O.

Include all relevant lone pairs of electrons, curly arrows, charges and dipoles.

Draw the structure of the intermediate.

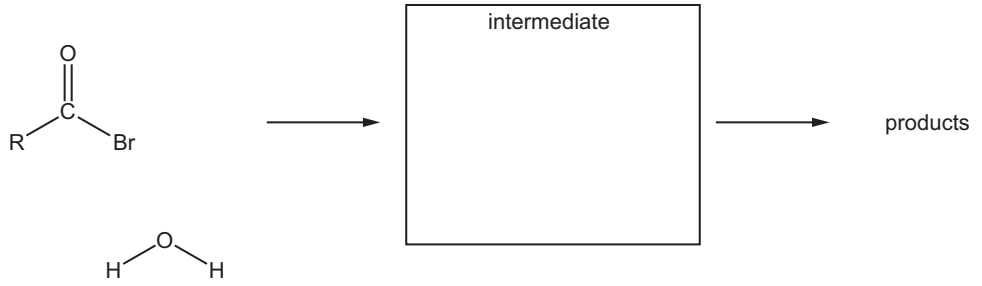


Fig. 8.2

[4]

[Total: 13]

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

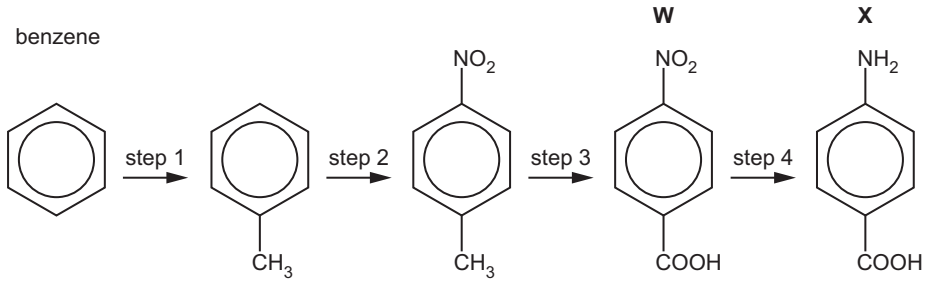


Fig. 9.1

(a) Describe the bonding in benzene, C_6H_6.

Your answer should include:

- the hybridisation of the six carbon atoms
- the types of bond between the carbon atoms
- the orbitals that overlap to produce the bonds between the carbon atoms
- the type of bond between the carbon atoms and the hydrogen atoms
- the orbitals that overlap to produce the bonds between the carbon atoms and the hydrogen atoms.

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..... [3]

(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 $^+CH_3$.

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.

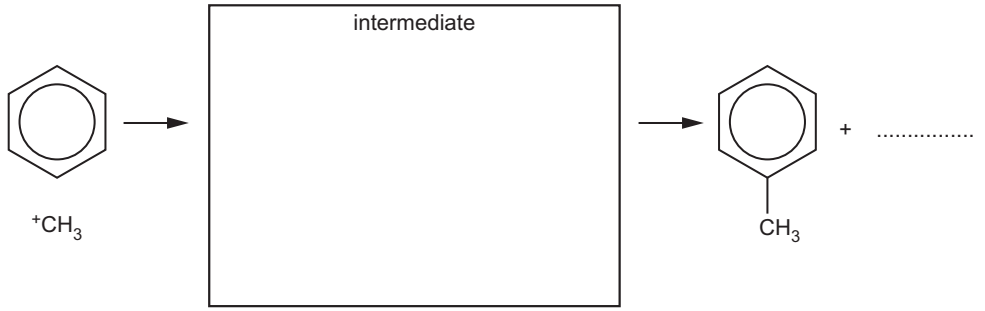


Fig. 9.2

[3]

(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]

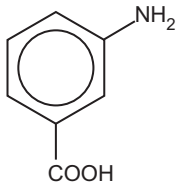
(g) The reagents commonly used for step 4 will **not** reduce the –COOH group.

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.

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.....

.....

..... [2]

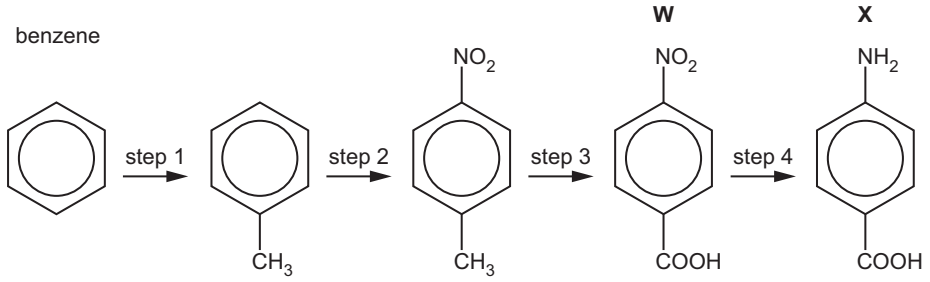

Fig. 9.1

[Total: 14]

Important values, constants and standards

molar gas constant	$R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^{4}\,\text{C mol}^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23}\,\text{mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,\text{C}$
molar volume of gas	$V_m = 22.4\,\text{dm}^3\,\text{mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,\text{dm}^3\,\text{mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,\text{kJ kg}^{-1}\,\text{K}^{-1}$ ($4.18\,\text{J g}^{-1}\,\text{K}^{-1}$)

The Periodic Table of Elements

Group 1	2												13	14	15	16	17	18
												1 H hydrogen 1.0						2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0												5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3												13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

Key

atomic number
atomic symbol
name
relative atomic mass

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

5 **(a)** Describe and explain the shape of benzene.

In your answer, include:

- the shape and bond angle in the ring
- the hybridisation of the carbon atoms
- how orbital overlap forms σ and π bonds between the carbon atoms in the ring.

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..... [4]

(b) Fig. 5.1 shows two reactions of benzoic acid.

Fig. 5.1

(i) Suggest reagents and conditions for reaction 5 and for reaction 6 in Fig. 5.1.

reaction 5 .....

reaction 6 .....

[2]

(ii) State the type of reaction for reaction 5 in Fig. 5.1.

..... [1]

(c) In the electrophilic substitution of arenes, different substituents can direct to different ring positions.

(i) Describe the directing effect of the $-CH_2CH_3$ group.

Explain your answer.

.....

..... [1]

(ii) The alkylation of arenes uses a mixture of CH_3CH_2Br and $FeBr_3$ to generate the $CH_3CH_2^+$ electrophile.

Write an equation for the formation of the $CH_3CH_2^+$ electrophile.

..... [1]

(iii) Complete the mechanism in Fig. 5.2.

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

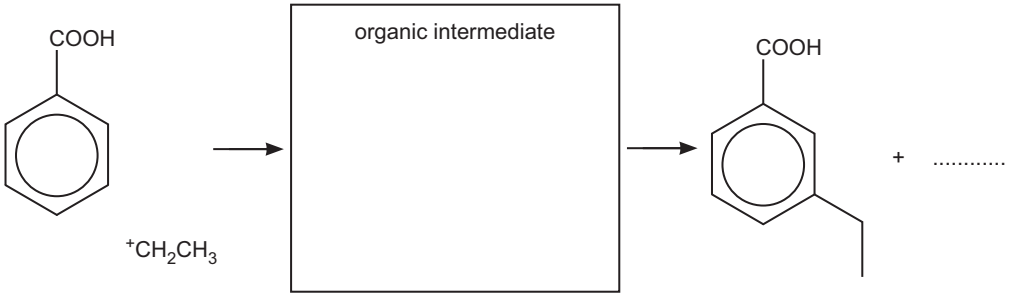

Fig. 5.2

[3]

(iv) Write an equation to show how $FeBr_3$ is regenerated after the reaction in Fig. 5.2.

..... [1]

[Total: 13]