Directing groups

Links to prior learning
6.1
Sigma and pi bonds
Reactions of alkenes
Bond enthalpies
Electron donating groups
6.2
Reactivity of benzene
Reactions of phenol

Learning Purpose

MUST (C)

Recall the directing and withdrawing groups

SHOULD (B/A)

Predict the products of a reaction, taking into account the directing groups

COULD

Predict a multistep synthesis to make a desired product relating to directing and withdrawing groups

Links to future learning
Organic synthesis

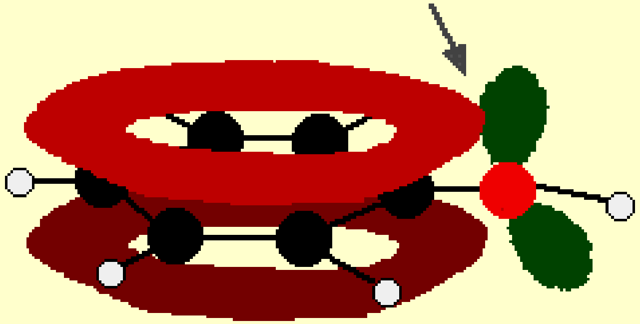
KEY WORDS
Arene
Benzene
Delocalised
Electron density
Electrophile
Electrophilic addition
Phenol
Directing group
Electron donating
Electron withdrawing
Lone pair

Explaining why phenol is more reactive then benzene

Bromine reacts much more readily with phenol than benzene. The increased reactivity occurs because:

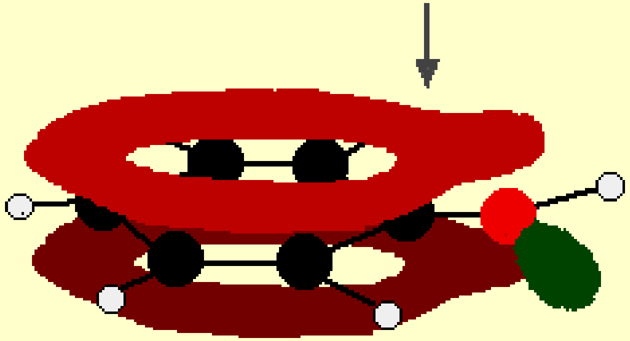
- A lone pair of electrons (occupying a p orbital) on the oxygen is delocalised into the ring
- This increases the electron density
- Phenol can polarises bromine molecules and generate the electrophile on its own without the need of a catalyst

One of the lone pairs on the oxygen atom in the -OH group overlaps with the delocalised ring electron system . . .



overlap between lone pair
and the ring electrons

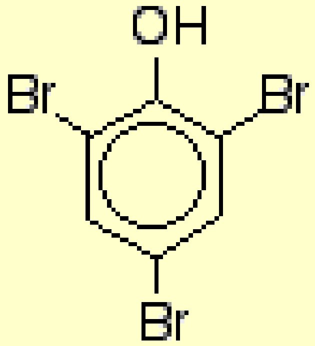
. . . giving a structure rather like this:



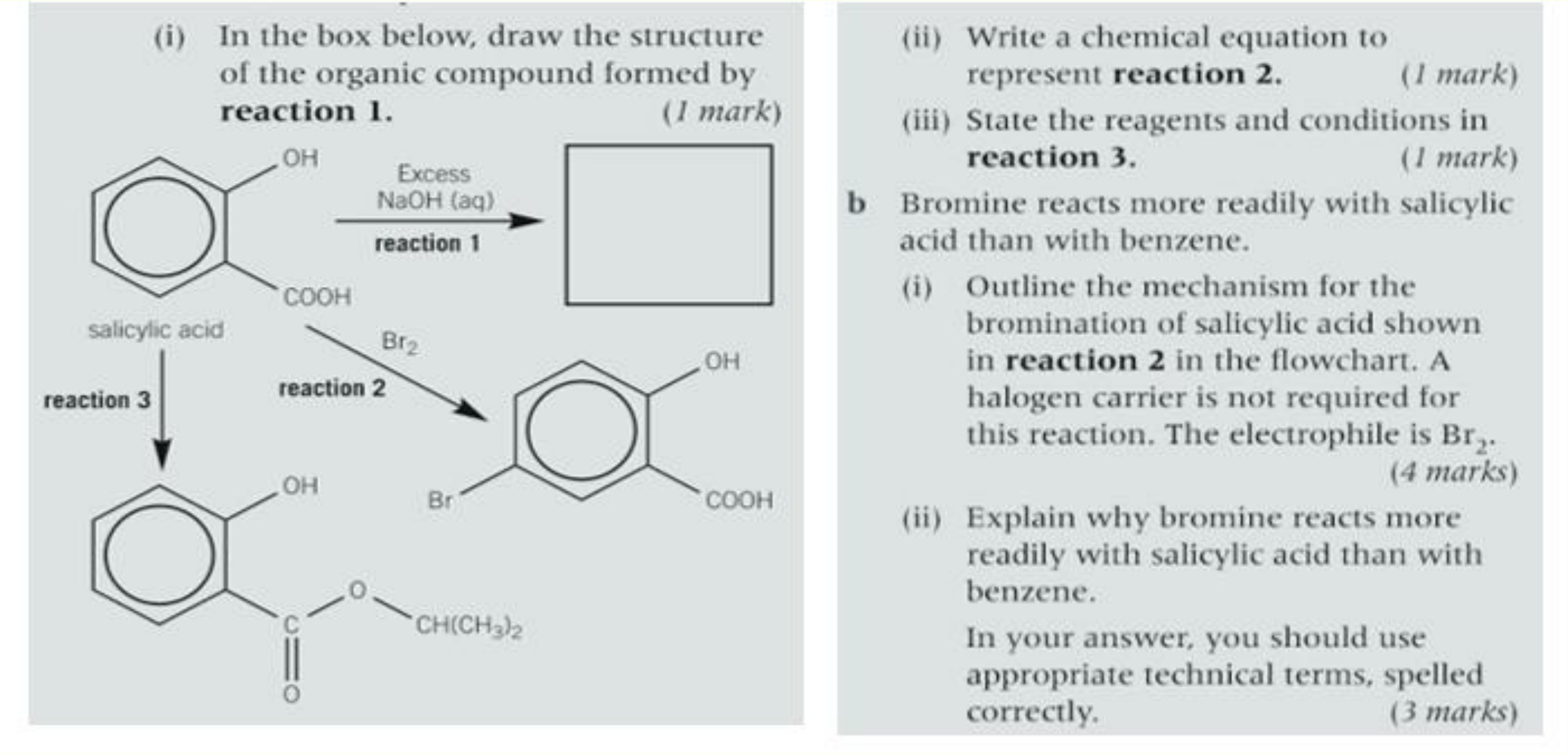
lone pair now delocalised
with the ring electrons

The donation of the oxygen's lone pair into the ring system increases the electron density around the ring.

- The -OH group has more activating effect on some positions around the ring than others .
- That means that incoming groups will go into some positions much faster than they will into others.
- The net effect of this is that the -OH group has a ***2,4-directing effect***. That means that incoming groups will tend to go into the 2- position (next door to the -OH group) or the 4- position (opposite the -OH group). You will get hardly any of the 3- isomer formed - it is produced too slowly



Mini plenary



(i) In the box below, draw the structure of the organic compound formed by **reaction 1.** *(1 mark)*

(ii) Write a chemical equation to represent **reaction 2.** *(1 mark)*

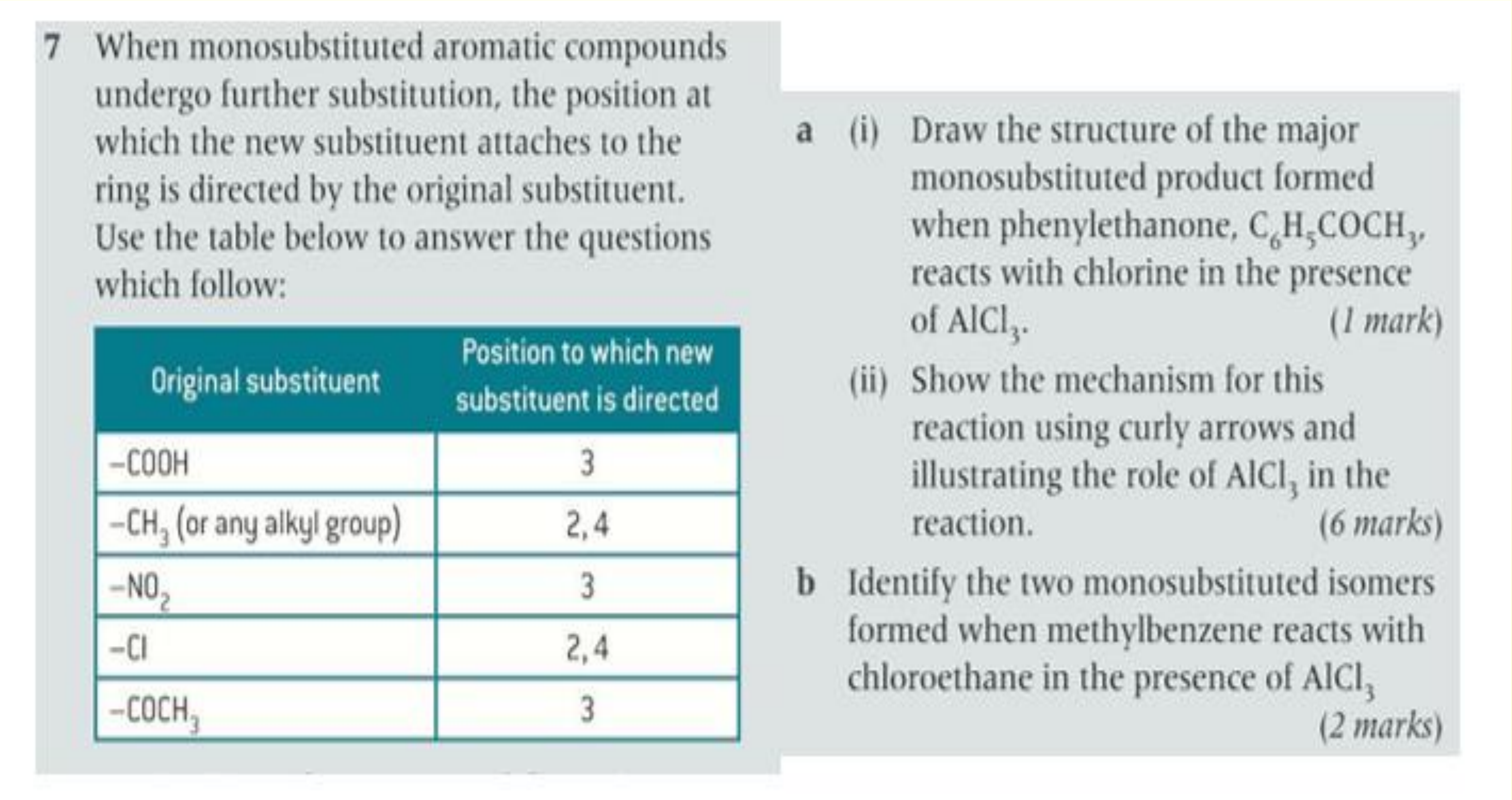
(iii) State the reagents and conditions in **reaction 3.** *(1 mark)*

b Bromine reacts more readily with salicylic acid than with benzene.

(i) Outline the mechanism for the bromination of salicylic acid shown in **reaction 2** in the flowchart. A halogen carrier is not required for this reaction. The electrophile is Br_2. *(4 marks)*

(ii) Explain why bromine reacts more readily with salicylic acid than with benzene.

In your answer, you should use appropriate technical terms, spelled correctly. *(3 marks)*



7 When monosubstituted aromatic compounds undergo further substitution, the position at which the new substituent attaches to the ring is directed by the original substituent. Use the table below to answer the questions which follow:

Original substituent	Position to which new substituent is directed
$-COOH$	3
$-CH_3$ (or any alkyl group)	2, 4
$-NO_2$	3
$-Cl$	2, 4
$-COCH_3$	3

a (i) Draw the structure of the major monosubstituted product formed when phenylethanone, $C_6H_5COCH_3$, reacts with chlorine in the presence of $AlCl_3$. *(1 mark)*

(ii) Show the mechanism for this reaction using curly arrows and illustrating the role of $AlCl_3$ in the reaction. *(6 marks)*

b Identify the two monosubstituted isomers formed when methylbenzene reacts with chloroethane in the presence of $AlCl_3$ *(2 marks)*

8 Phenol is much more susceptible to electrophilic attack than benzene.

a Explain why phenol reacts more readily with benzene with electrophiles. *(3 marks)*

b Phenol reacts with dilute nitric acid to form a mixture of two monosubstituted isomers.

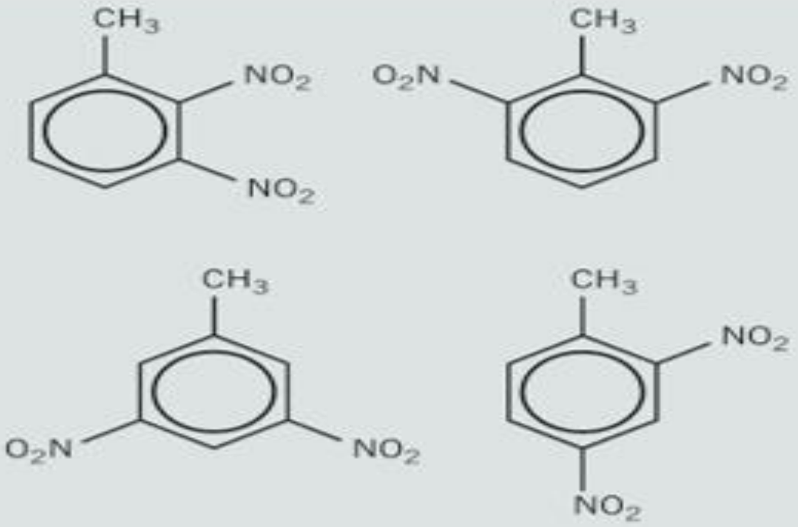
Draw the structures of these two isomers and write an equation for the formation of one of these isomers. *(3 marks)*

9 Methylbenzene, $C_6H_5CH_3$, is an aromatic hydrocarbon, used widely as a solvent. It is readily nitrated and can form mono-, di-, or tri-nitromethylbenzenes.

a 4-Nitromethylbenzene can be formed by the nitration of methylbenzene.

Outline the mechanism for the formation of 4-nitromethylbenzene from methylbenzene using NO_2^+ as the electrophile. *(4 marks)*

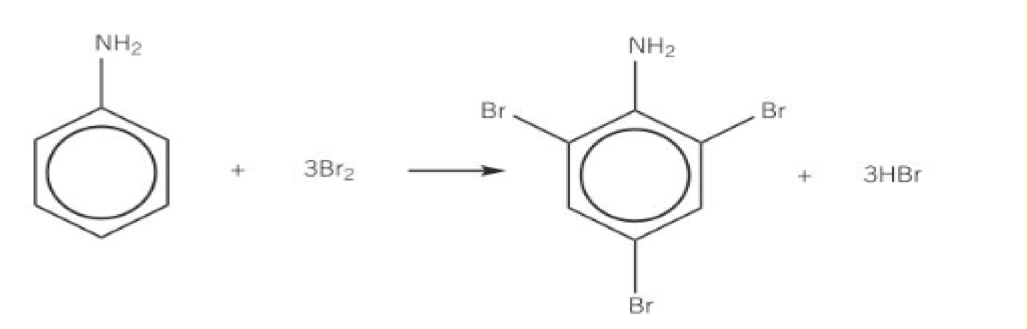
b There are six possible structural isomers of $CH_3C_6H_3(NO_2)_2$ that are dinitromethylbenzenes. Four of the isomers are shown below.



Draw the structures of the other two isomers. *(2 marks)*

Directing groups and further substitution

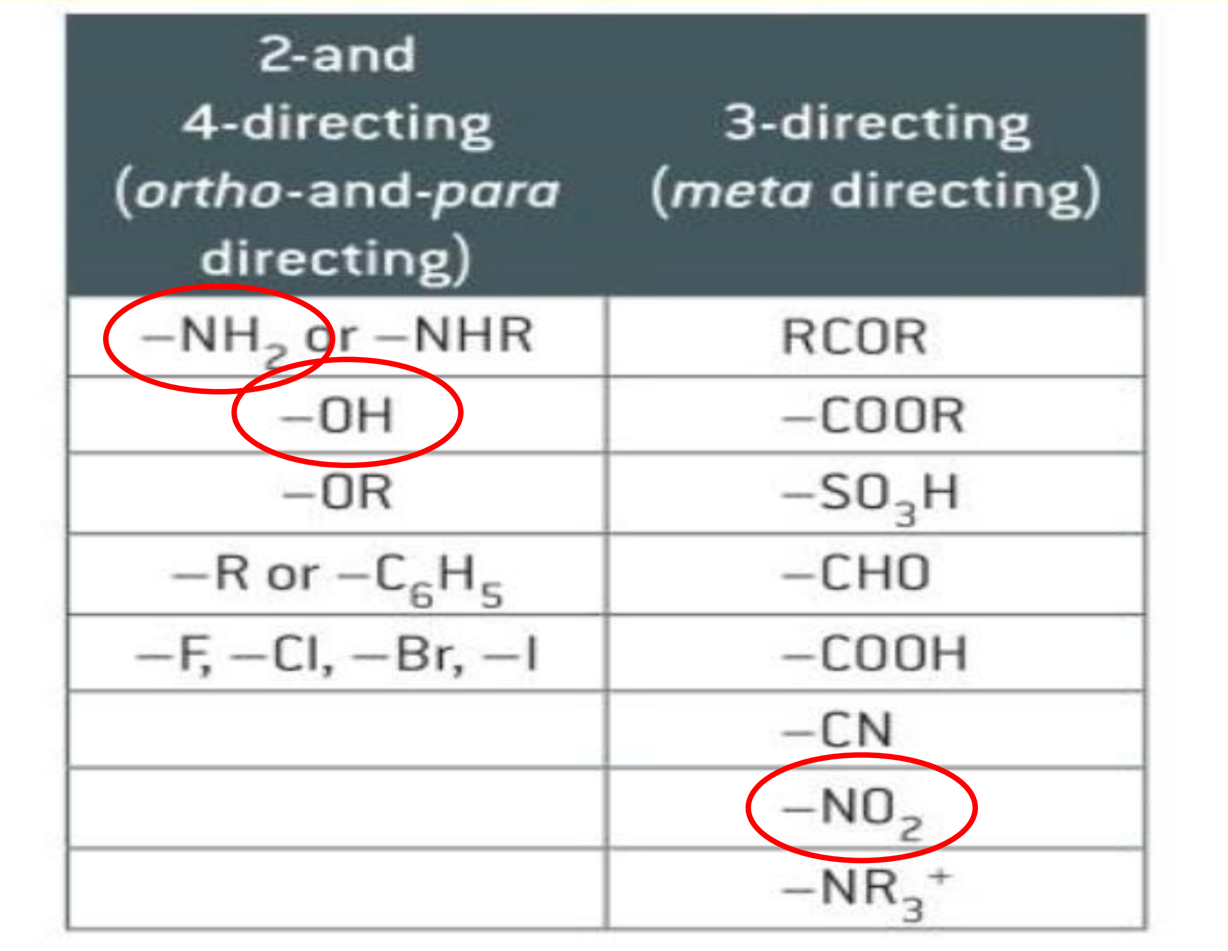
- The reactivity of benzene is affected by substituted groups
- We say that the substituted groups have **directing** and **withdrawing** effects
- For example bromine will react rapidly with phenyl amine without the need for a halogen carrier catalyst. The substituted amine group has activated the benzene ring



- Substituted groups can increase and decrease the reactivity of benzene and also effect the positions substitutions will take place

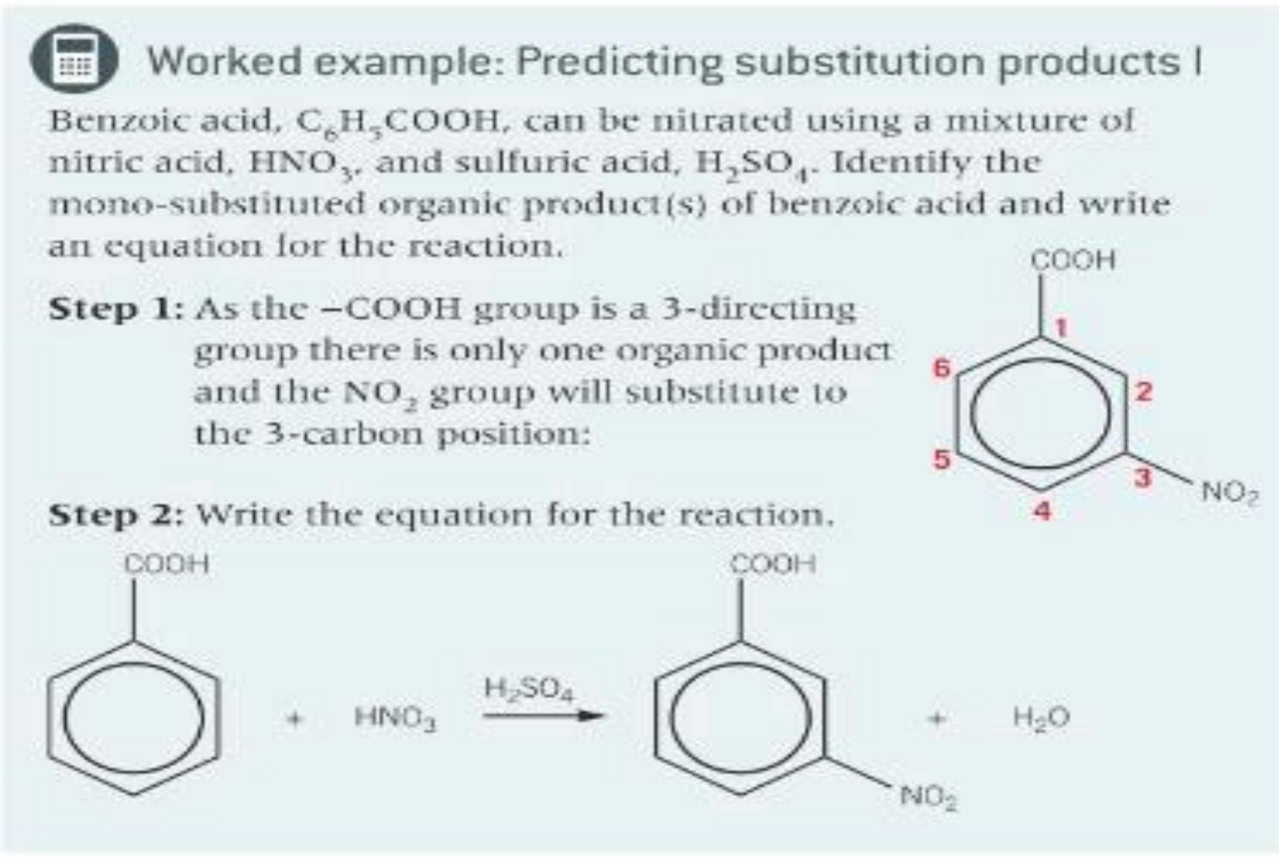
Directing effects

You need to remember the 2,4 directing effects of electron donating groups OH and NH_2 and the 3 directing effect of electron withdrawing groups NO_2.
Any other examples will be provided in the exam question



2-and 4-directing (*ortho*-and-*para* directing)	3-directing (*meta* directing)
$-NH_2$ or $-NHR$	RCOR
$-OH$	$-COOR$
$-OR$	$-SO_3H$
$-R$ or $-C_6H_5$	$-CHO$
$-F$, $-Cl$, $-Br$, $-I$	$-COOH$
	$-CN$
	$-NO_2$
	$-NR_3^+$

Worked example



Worked example: Predicting substitution products I

Benzoic acid, C_6H_5COOH, can be nitrated using a mixture of nitric acid, HNO_3, and sulfuric acid, H_2SO_4. Identify the mono-substituted organic product(s) of benzoic acid and write an equation for the reaction.

Step 1: As the $-COOH$ group is a 3-directing group there is only one organic product and the NO_2 group will substitute to the 3-carbon position:

Step 2: Write the equation for the reaction.

2-and 4-directing (*ortho*-and-*para* directing)	3-directing (*meta* directing)
$-NH_2$ or $-NHR$	RCOR
$-OH$	$-COOR$
$-OR$	$-SO_3H$
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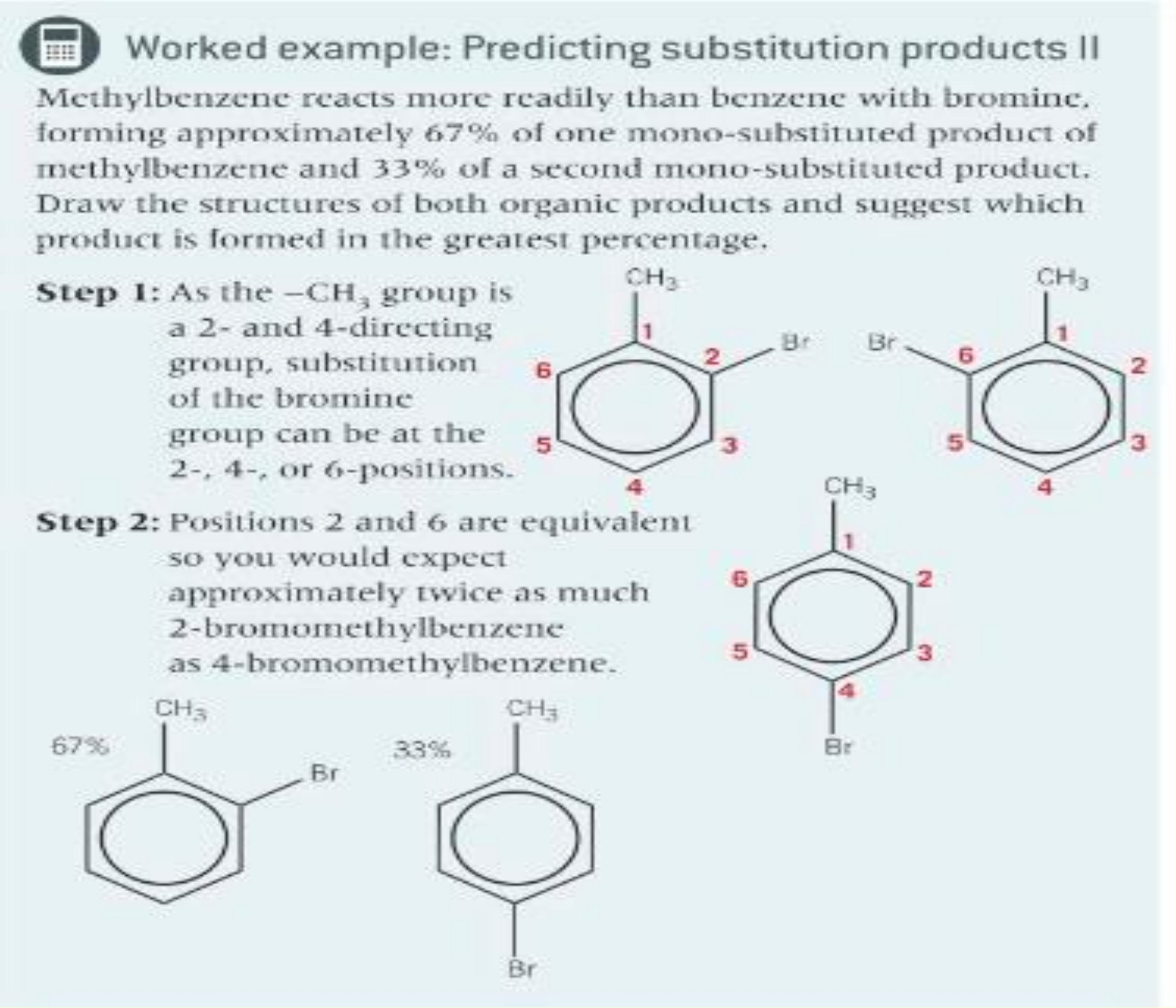
$-F$, $-Cl$, $-Br$, $-I$	$-COOH$
	$-CN$
	$-NO_2$
	$-NR_3^+$

Worked example

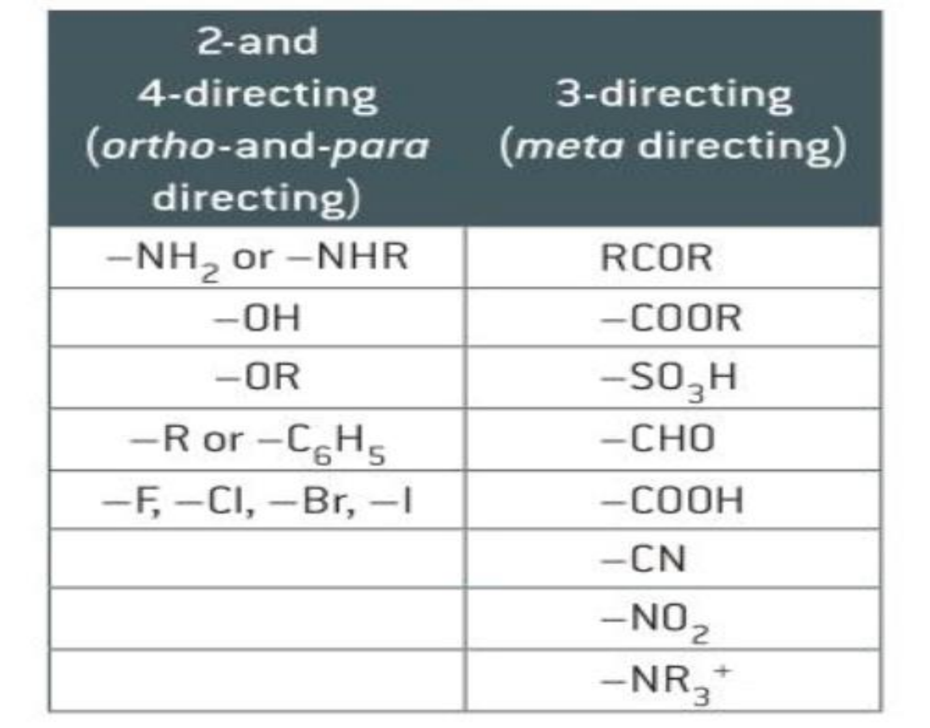


Worked example: Predicting substitution products II

Methylbenzene reacts more readily than benzene with bromine, forming approximately 67% of one mono-substituted product of methylbenzene and 33% of a second mono-substituted product. Draw the structures of both organic products and suggest which product is formed in the greatest percentage.

Step 1: As the $-CH_3$ group is a 2- and 4-directing group, substitution of the bromine group can be at the 2-, 4-, or 6-positions.

Step 2: Positions 2 and 6 are equivalent so you would expect approximately twice as much 2-bromomethylbenzene as 4-bromomethylbenzene.



2-and 4-directing (*ortho*-and-*para* directing)	3-directing (*meta* directing)
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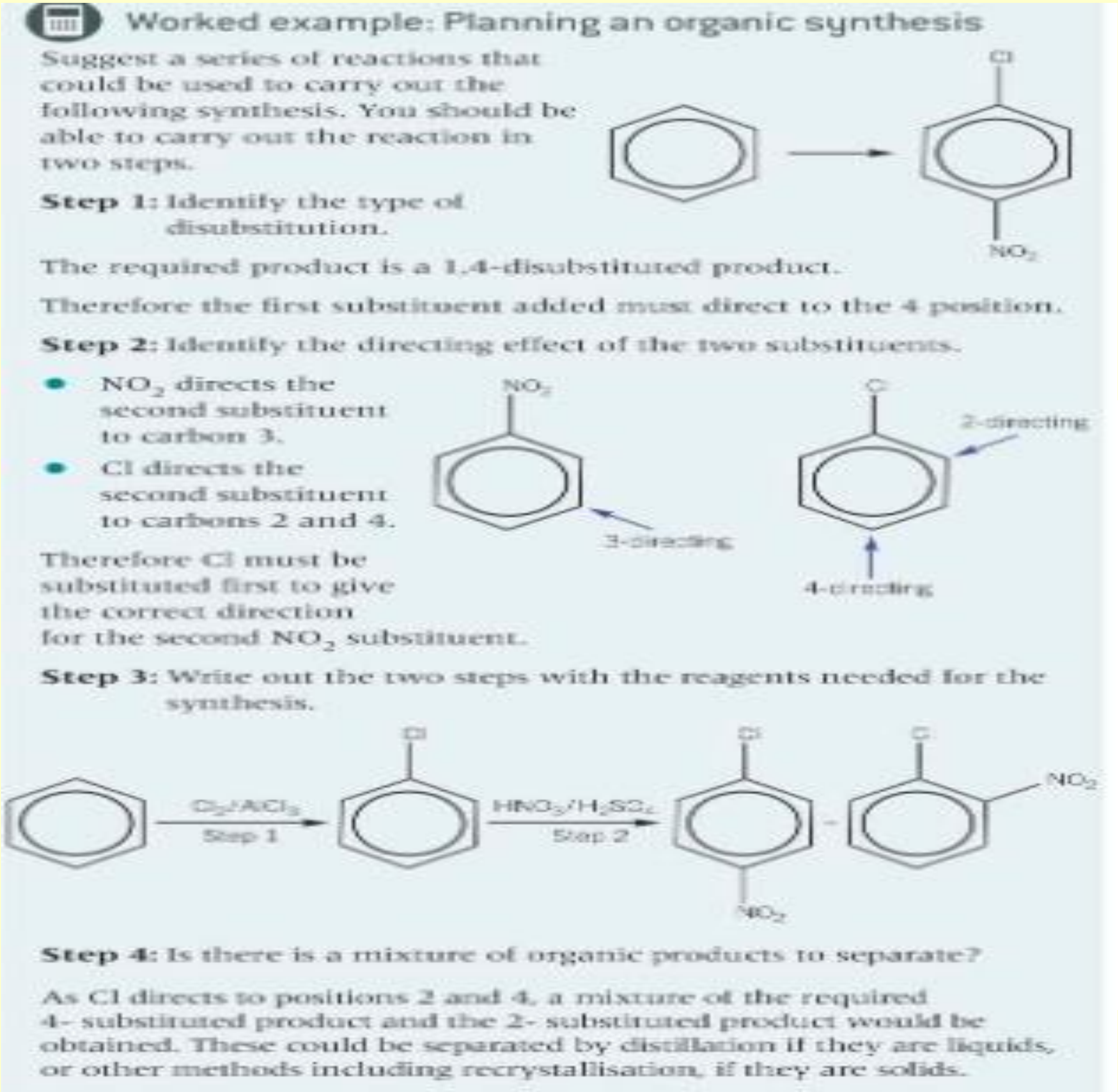
$-R$ or $-C_6H_5$	$-CHO$
$-F$, $-Cl$, $-Br$, $-I$	$-COOH$
	$-CN$
	$-NO_2$
	$-NR_3^+$

Worked example



Worked example: Planning an organic synthesis

Suggest a series of reactions that could be used to carry out the following synthesis. You should be able to carry out the reaction in two steps.

Step 1: Identify the type of disubstitution.

The required product is a 1,4-disubstituted product.

Therefore the first substituent added must direct to the 4 position.

Step 2: Identify the directing effect of the two substituents.

- NO_2 directs the second substituent to carbon 3.
- Cl directs the second substituent to carbons 2 and 4.

Therefore Cl must be substituted first to give the correct direction for the second NO_2 substituent.

Step 3: Write out the two steps with the reagents needed for the synthesis.

Step 4: Is there is a mixture of organic products to separate?

As Cl directs to positions 2 and 4, a mixture of the required 4- substituted product and the 2- substituted product would be obtained. These could be separated by distillation if they are liquids, or other methods including recrystallisation, if they are solids.

2-and 4-directing (*ortho*-and-*para* directing)	3-directing (*meta* directing)
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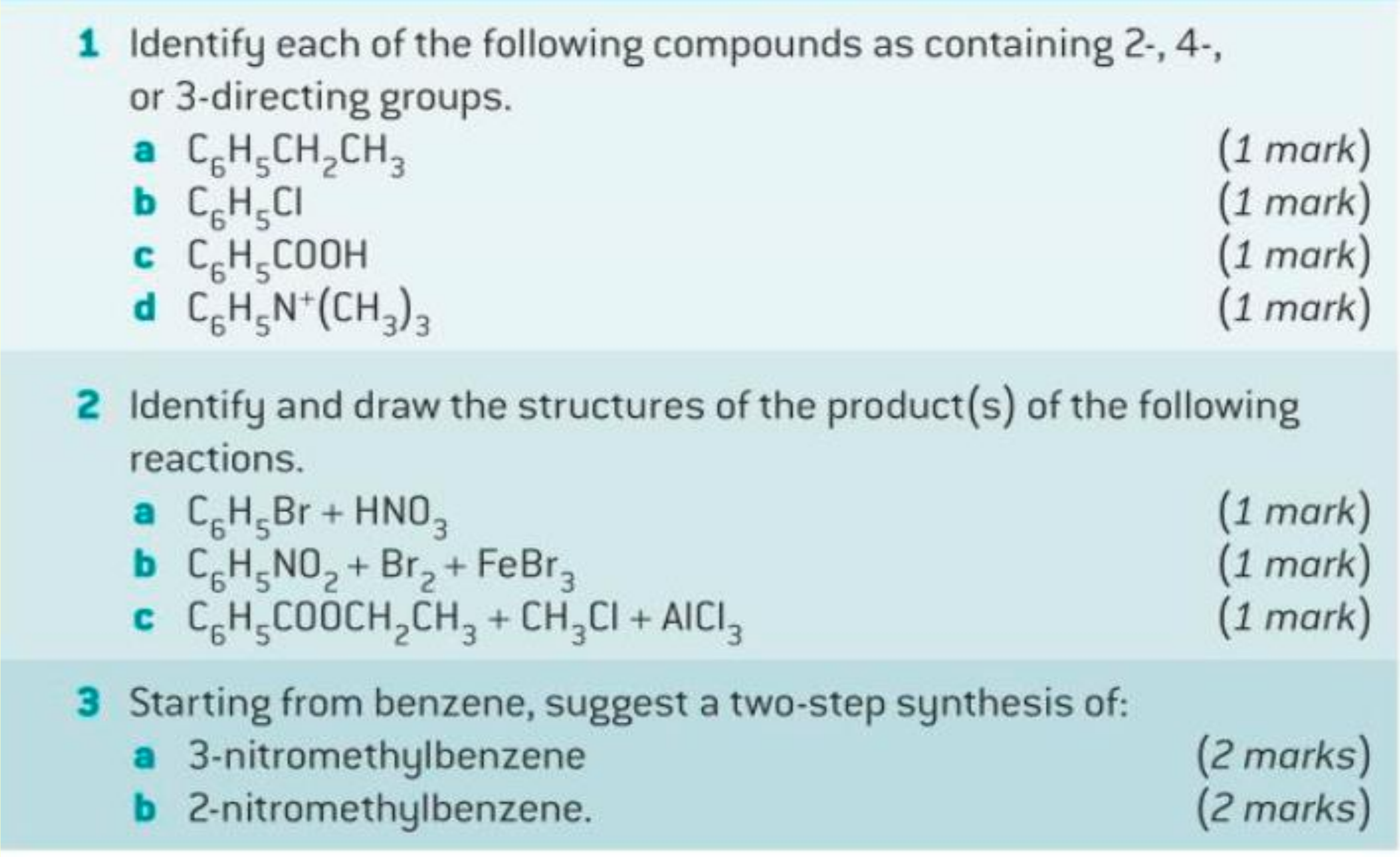
$-OR$	$-SO_3H$
$-R$ or $-C_6H_5$	$-CHO$
$-F$, $-Cl$, $-Br$, $-I$	$-COOH$
	$-CN$
	$-NO_2$
	$-NR_3^+$

Mini plenary



1 Identify each of the following compounds as containing 2-, 4-, or 3-directing groups.

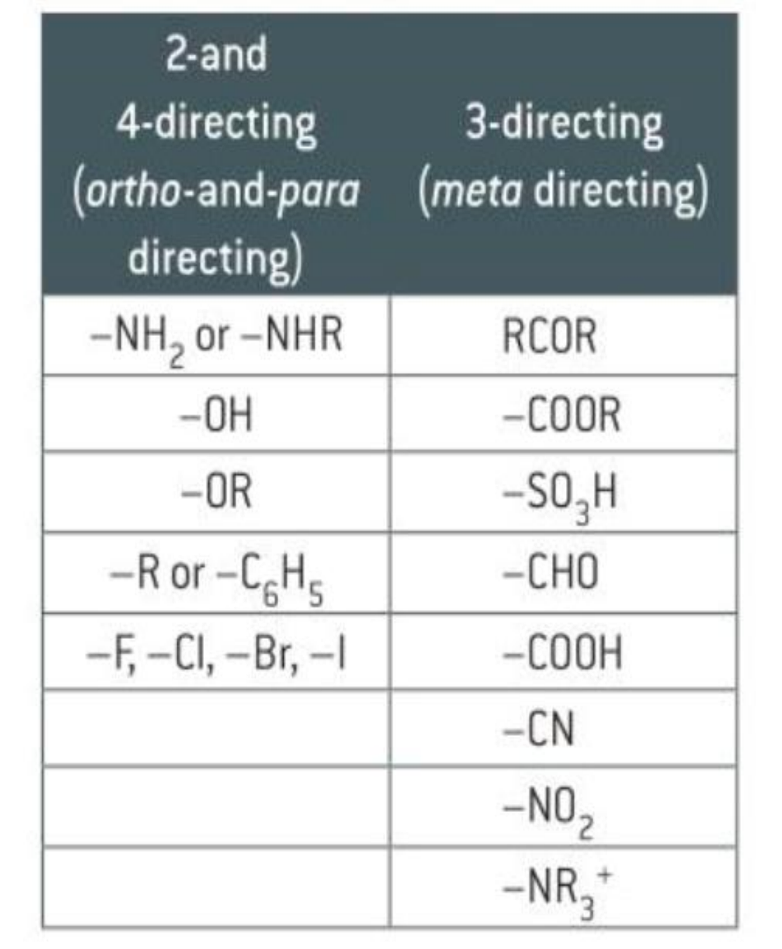
- **a** $C_6H_5CH_2CH_3$ (*1 mark*)
- **b** C_6H_5Cl (*1 mark*)
- **c** C_6H_5COOH (*1 mark*)
- **d** $C_6H_5N^+(CH_3)_3$ (*1 mark*)

2 Identify and draw the structures of the product(s) of the following reactions.

- **a** $C_6H_5Br + HNO_3$ (*1 mark*)
- **b** $C_6H_5NO_2 + Br_2 + FeBr_3$ (*1 mark*)
- **c** $C_6H_5COOCH_2CH_3 + CH_3Cl + AlCl_3$ (*1 mark*)

3 Starting from benzene, suggest a two-step synthesis of:

- **a** 3-nitromethylbenzene (*2 marks*)
- **b** 2-nitromethylbenzene. (*2 marks*)



2-and 4-directing (*ortho*-and-*para* directing)	3-directing (*meta* directing)
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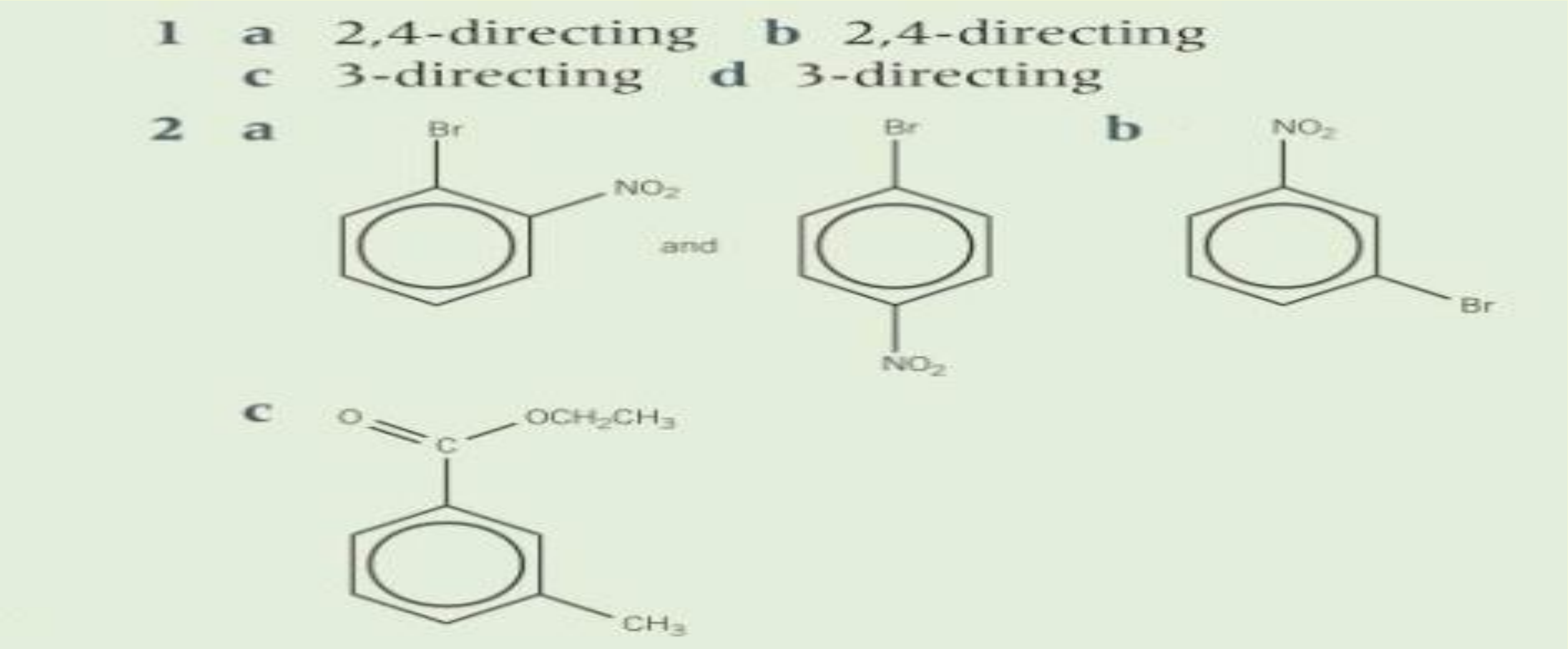
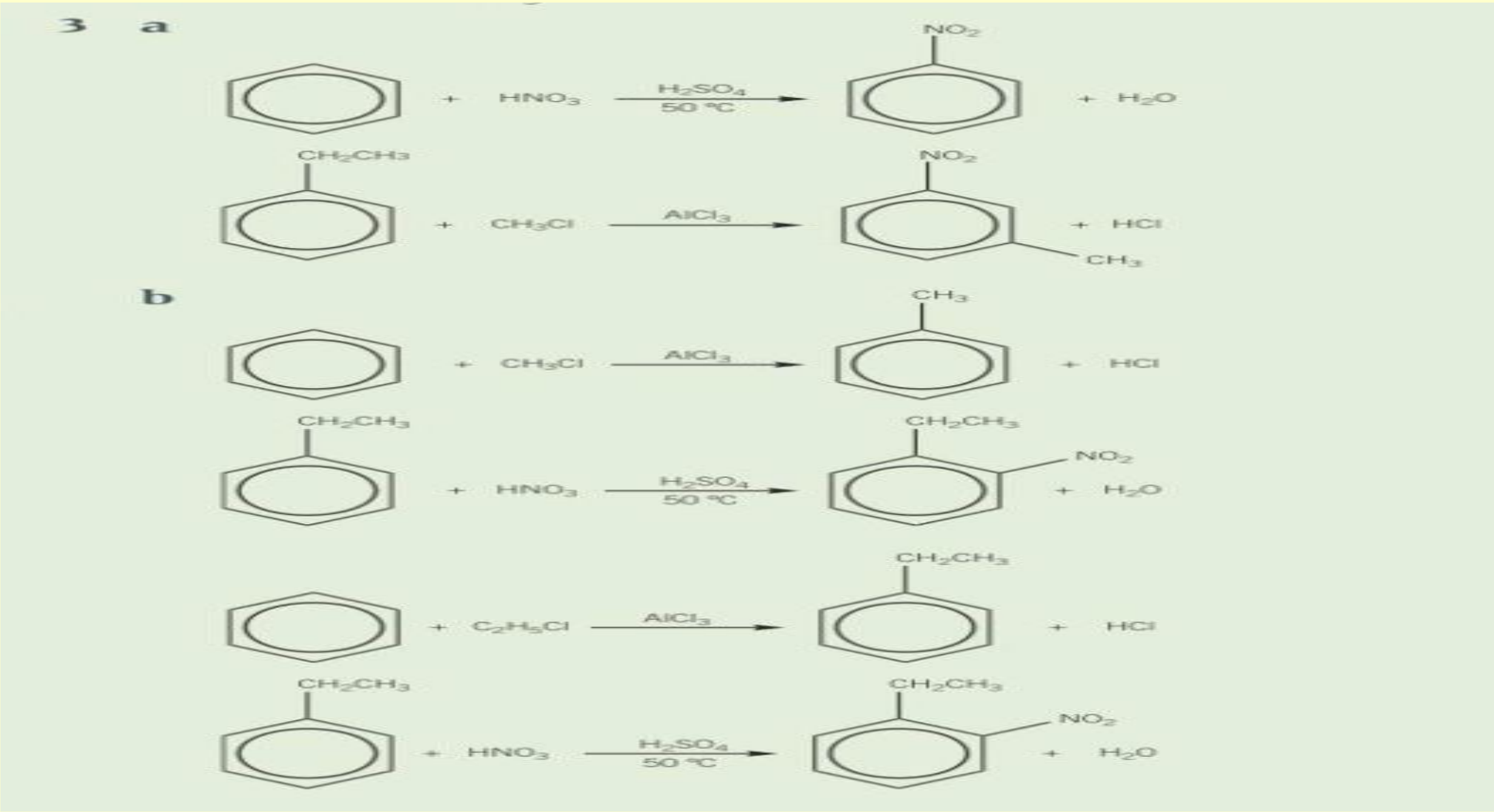
$-R$ or $-C_6H_5$	$-CHO$
$-F$, $-Cl$, $-Br$, $-I$	$-COOH$
	$-CN$
	$-NO_2$
	$-NR_3^+$



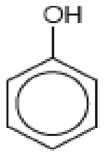
1 **a** 2,4-directing **b** 2,4-directing
c 3-directing **d** 3-directing

2 **a** and **b**

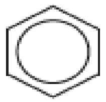
c


3
a
NO2
+
HNO3
H2SO4
50 °C
+
H2O
CH2CH3
NO2
+
CH3Cl
AlCl3
+
HCl
CH3
b
CH3
+
CH3Cl
AlCl3
+
HCl
CH2CH3
CH2CH3
NO2
+
HNO3
H2SO4
50 °C
+
H2O
CH2CH3
+
C2H5Cl
AlCl3
+
HCl
CH2CH3
CH2CH3
NO2
+
HNO3
H2SO4
50 °C
+
H2O

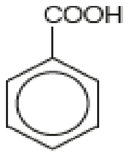
(b) A student investigates the relative ease of nitration of phenol, benzene, and benzoic acid.



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.

....

....

.... **[1]**

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

....

....

....

....

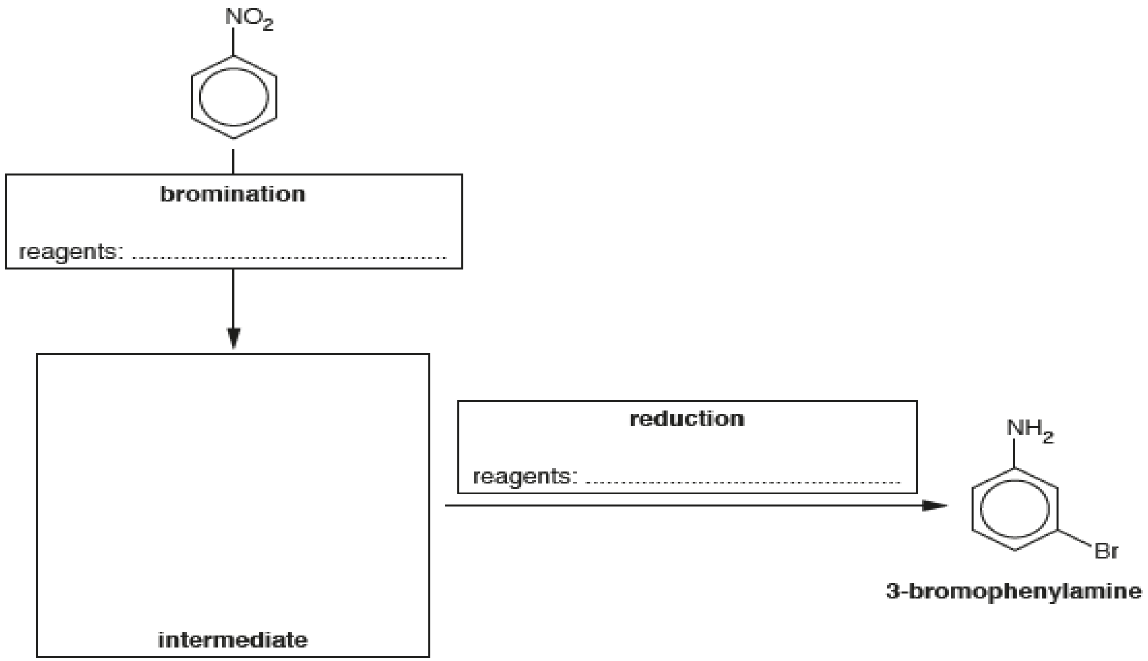
....

....

.... **[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 ....

....

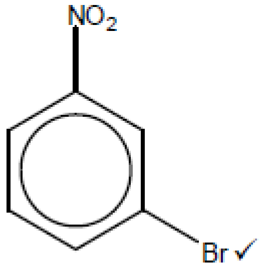
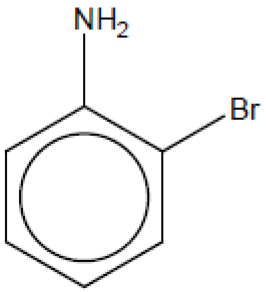
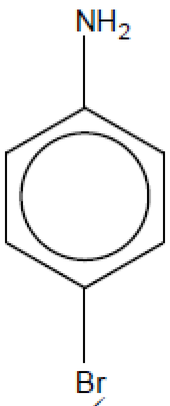
....

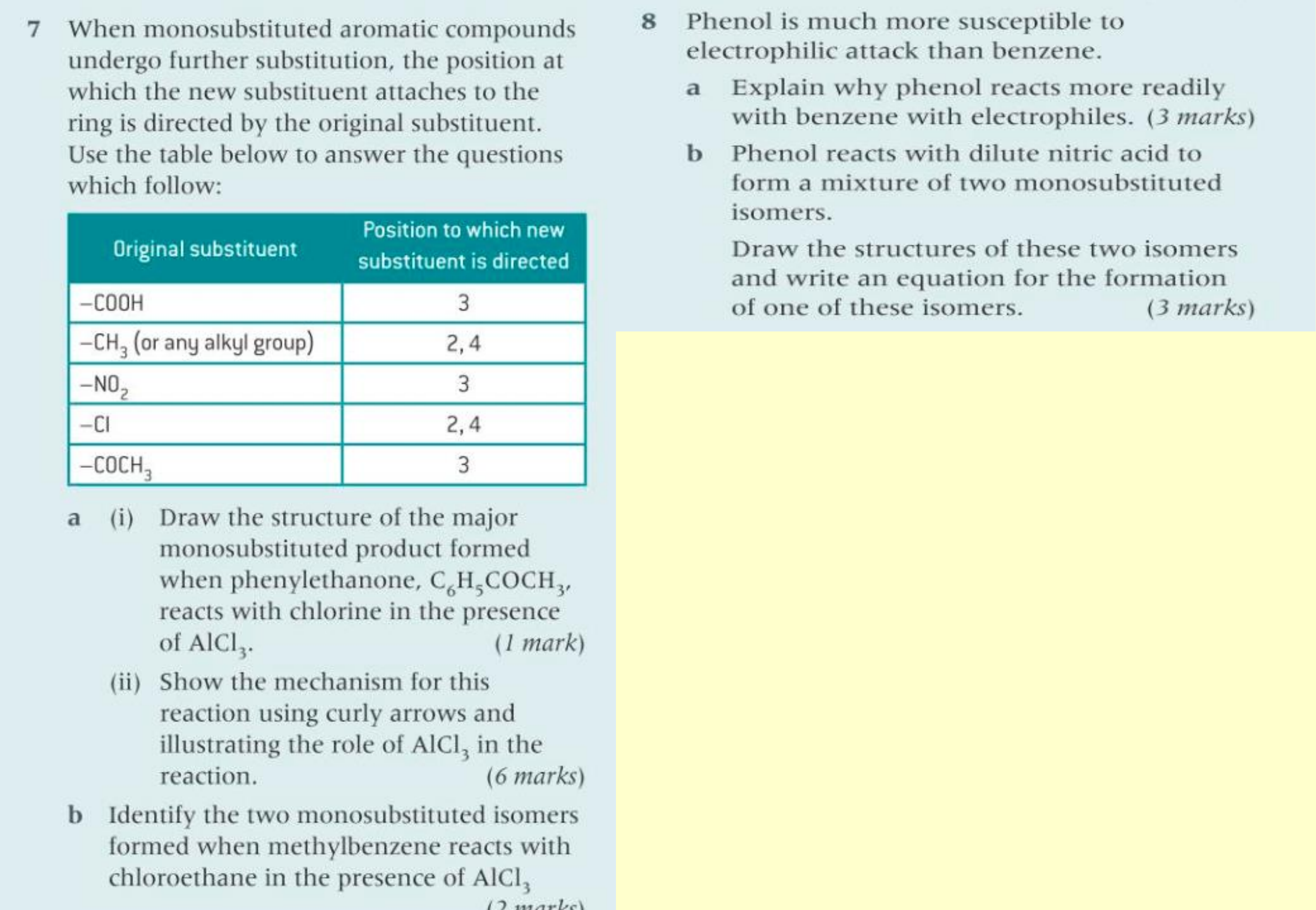
Structures

[3]

	(b)	**(i)**	Phenol is the most easily nitrated/ most reactive **AND** Benzoic acid is the least easily nitrated /least reactive ✓	**1**	Response **must** give rank order of reactivity e.g. nitration becomes more difficult from phenol (to benzene) to benzoic acid **OR** nitration becomes easier from right to left in the table
		(ii)	**Reactivity of phenol** a (lone) pair of electrons on O is (partially) **delocalised/donated** into the π-system / ring ✓	**3**	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** the electron pair in the p orbitals of the O atom becomes part of the π-system / ring **ALLOW** diagram to show movement of lone pair into ring

Question			Answer	Marks	Guidance
			Reactivity of benzoic acid The –COOH group on benzoic acid is an electron withdrawing group ✓ **Links electron density in π-bond to reactivity** In phenol electron density is higher **AND** The ring is more susceptible to attack **OR** In benzoic acid electron density is lower **AND** The ring is less susceptible to attack ✓		**ALLOW** lone pair of electrons on O is (partially) drawn/attracted/pulled into π-system / ring **IGNORE** activating and deactivating. **ALLOW** the following alternatives for susceptibility to attack: • phenol attracts electrophiles / NO_2^+ **more** • phenol polarises electrophiles / NO_2^+ **more** • benzoic acid attracts electrophiles / NO_2^+ **less** • benzoic acid polarises electrophiles / NO_2^+ **less**
	(c)	(i)	**Bromination**: Br_2 **AND** $AlBr_3$/$FeBr_3$/Fe ✓ **Intermediate**	3	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** any suitable halogen carrier catalyst

Question			Answer	Marks	Guidance
			 **Reduction**: Sn **AND** (concentrated) HCl ✓		**ALLOW** Kekulé structure **IGNORE** names *(question asks for formulae)* **IGNORE** reaction conditions even if incorrect **IGNORE** 'dilute' for HCl **IGNORE** H_2 **IGNORE** NaOH if seen as a reagent to convert nitro group into amine e.g 'Sn/(concentrated) HCl then NaOH' scores the mark
		(ii)	NH_2 is 2,4 directing ✓ Products (1 mark for each):  ✓  ✓	**3**	**IGNORE** references to electron donating/withdrawing groups **ALLOW** –NH_2 activates the ring causing the new group to join at positions 2 and 4. **ALLOW** ortho and para directing for 2,4 directing **IGNORE** 6-directing **ALLOW** Kekulé structure **IGNORE** names
			Total	**21**	



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a (i) Draw the structure of the major monosubstituted product formed when phenylethanone, $C_6H_5COCH_3$, reacts with chlorine in the presence of $AlCl_3$. (*1 mark*)

(ii) Show the mechanism for this reaction using curly arrows and illustrating the role of $AlCl_3$ in the reaction. (*6 marks*)

b Identify the two monosubstituted isomers formed when methylbenzene reacts with chloroethane in the presence of $AlCl_3$ (*2 marks*)

8 Phenol is much more susceptible to electrophilic attack than benzene.

a Explain why phenol reacts more readily with benzene with electrophiles. (*3 marks*)

b Phenol reacts with dilute nitric acid to form a mixture of two monosubstituted isomers.

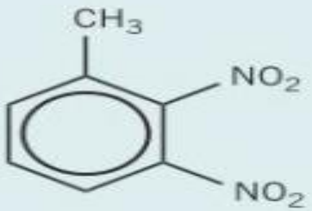
Draw the structures of these two isomers and write an equation for the formation of one of these isomers. (*3 marks*)

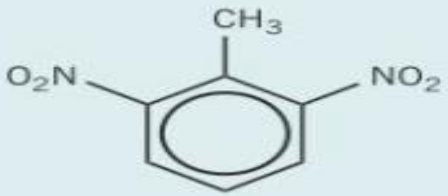
9 Methylbenzene, $C_6H_5CH_3$, is an aromatic hydrocarbon, used widely as a solvent. It is readily nitrated and can form mono-, di-, or tri-nitromethylbenzenes.

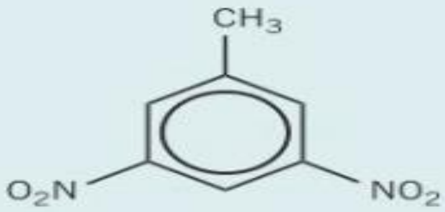
a 4-Nitromethylbenzene can be formed by the nitration of methylbenzene.

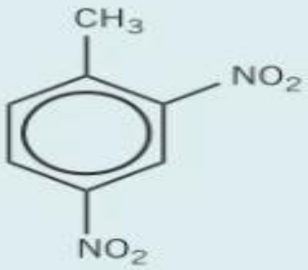
Outline the mechanism for the formation of 4-nitromethylbenzene from methylbenzene using NO_2^+ as the electrophile. *(4 marks)*

b There are six possible structural isomers of $CH_3C_6H_3(NO_2)_2$ that are dinitromethylbenzenes. Four of the isomers are shown below.









Draw the structures of the other two isomers. *(2 marks)*