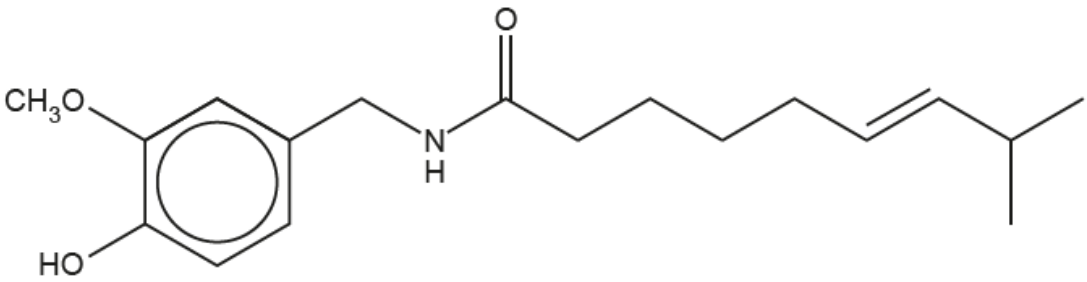
Hydrocarbons – 2023 A2 Chemistry 9701

1. Nov/2023/Paper_9701/41/No.8(c)

Capsaicin is found in chilli peppers.

capsaicin



You should assume the CH_3O group is unreactive in the reactions involved in this question.

(c) Capsaicin is heated with an excess of hydrogen gas in the presence of platinum metal.

The six-membered ring reacts in the same way as benzene under these conditions.

Draw the structure of the organic product formed.

[2]

2. June/2023/Paper_9701/41/No.4(a)

(a) State the hybridisation of the carbon atoms and the C–C–H bond angle in benzene, C_6H_6.
Explain how orbital overlap leads to the formation of σ and π bonds in benzene.

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..... [3]

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3. June/2023/Paper_9701/42/No.5(a _ c)

(a) Methylbenzene can undergo different reactions, as shown in Fig. 5.1.

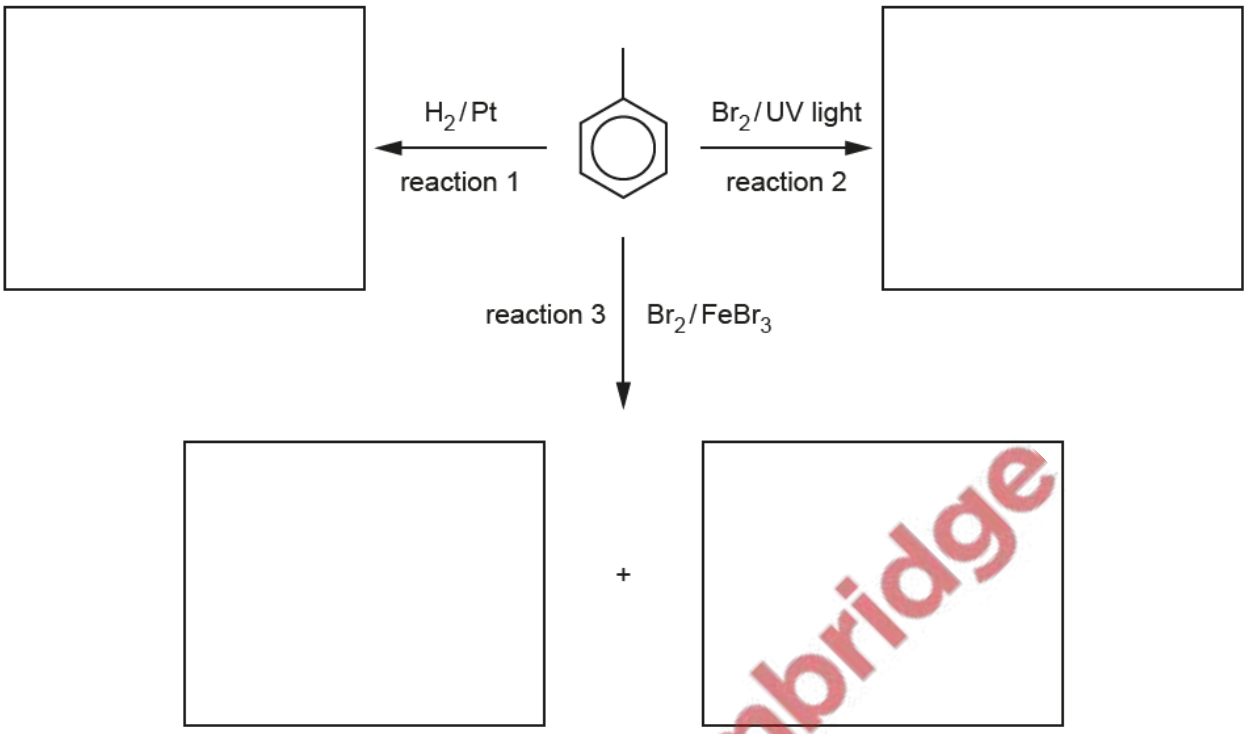

Fig. 5.1

(i) Draw structures in Fig. 5.1 for the possible organic products of the three reactions shown. [3]

(ii) Complete Table 5.1.

Table 5.1

	type of reaction	mechanism
reaction 1		
reaction 2		

[2]

(b) When methylbenzene reacts with an electrophile, a substitution reaction occurs. No addition reaction takes place under these conditions.

Explain why no addition reaction takes place.

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..... [1]

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(c) The reaction of methylbenzene with thionyl bromide, $SOBr_2$, in the presence of an iron(III) bromide catalyst, $FeBr_3$, is shown in Fig. 5.2.

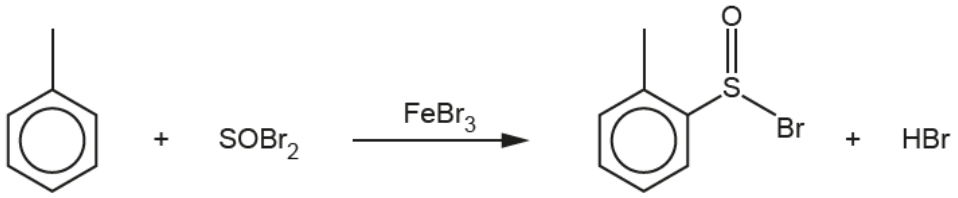

Fig. 5.2

The mechanism of this reaction is similar to that of the bromination of benzene.

The first step of the mechanism generates the $SOBr^+$ electrophile, as shown.

$$SOBr_2 + FeBr_3 \rightarrow SOBr^+ + FeBr_4^-$$

(i) The reaction of methylbenzene with $SOBr^+$ ions is shown in Fig. 5.3. Complete the mechanism in Fig. 5.3.

Include all relevant curly arrows and charges.

Draw the structure of the organic intermediate.

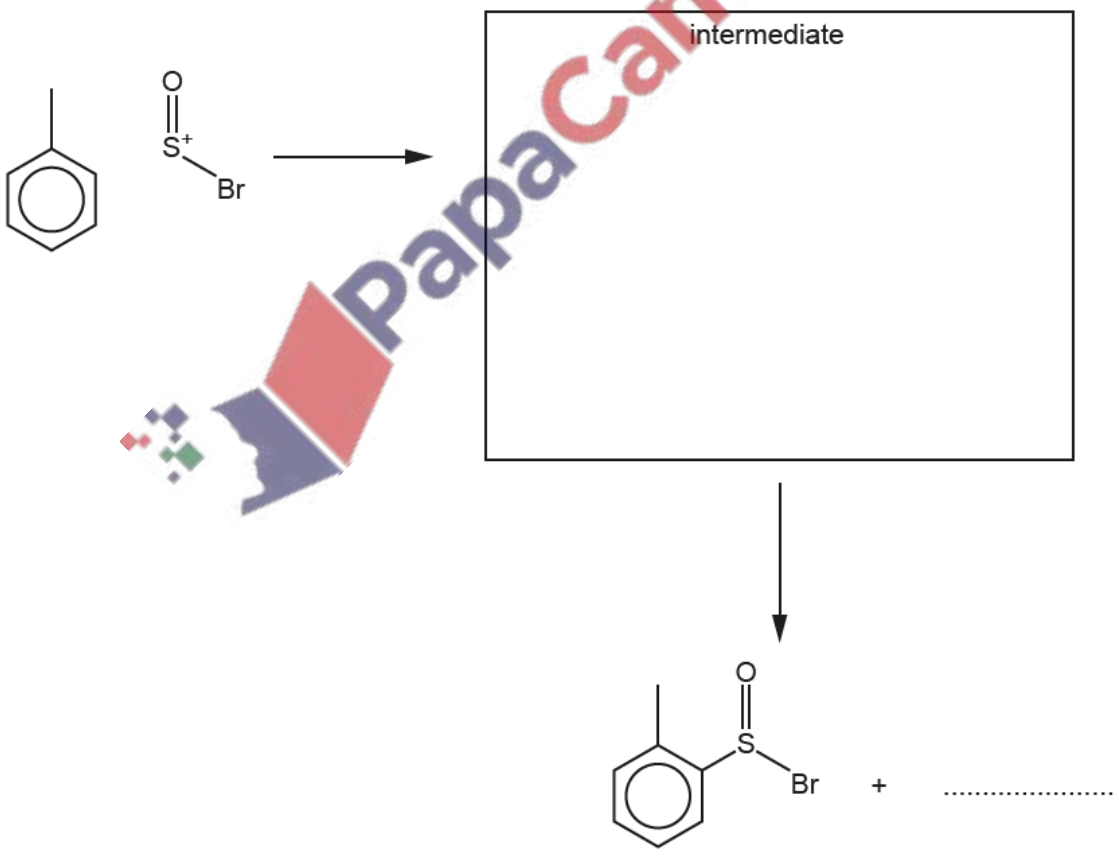

Fig. 5.3

[3]

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(ii) The reaction shown in Fig. 5.2 produces a small amount of a by-product, **P**, with the molecular formula $C_{14}H_{14}OS$.

Suggest a structure for by-product **P**.

[1]

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4. June/2023/Paper_9701/42/No.7(a _ c)

(a) Explain why phenol is brominated much more easily than benzene is brominated.

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..... [3]

(b) Iodine monobromide, I–Br, reacts with benzene in the presence of an $AlBr_3$ catalyst.

Predict whether the organic product will be bromobenzene or iodobenzene.
Explain your answer.

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..... [1]

(c) Fig. 7.1 shows some reactions of phenol.

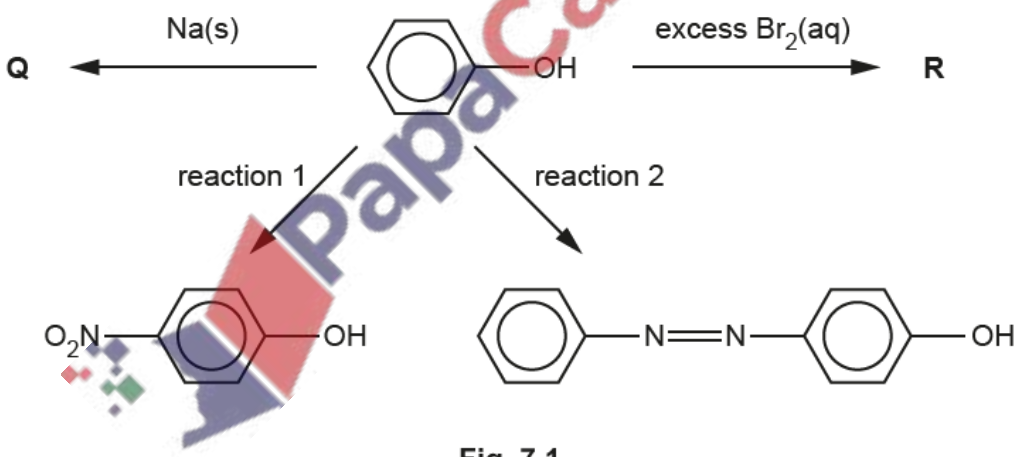

Fig. 7.1

(i) Give an equation for the reaction of phenol with Na(s).

..... [1]

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(ii) Draw the structure of the organic product, **R**, formed when phenol reacts with an excess of $Br_2(aq)$.

[1]

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

reaction 1 .....

reaction 2 .....

[2]

[Total: 8]

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5. March/2023/Paper_9701/42/No.5(a_ e)

Tulobuterol is used in some medicines.

tulobuterol

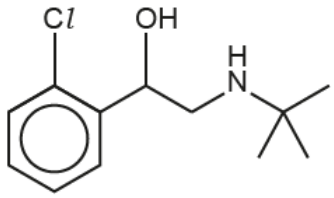

Fig. 5.1

(a) Tulobuterol contains a benzene ring in its structure.

Describe and explain the shape of benzene.

In your answer, include:

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

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..... [3]

(b) In a synthesis of tulobuterol, the first step involves the formation of chlorobenzene. Benzene reacts with Cl_2 in the presence of an $AlCl_3$ catalyst.

Fig. 5.2

(i) Write an equation to show how Cl_2 reacts with $AlCl_3$ to generate an electrophile.

..... [1]

(ii) Complete the mechanism in Fig. 5.3 for the reaction of benzene with the electrophile generated in **(b)(i)**.

Include all relevant curly arrows and charges.

Draw the structure of the intermediate.

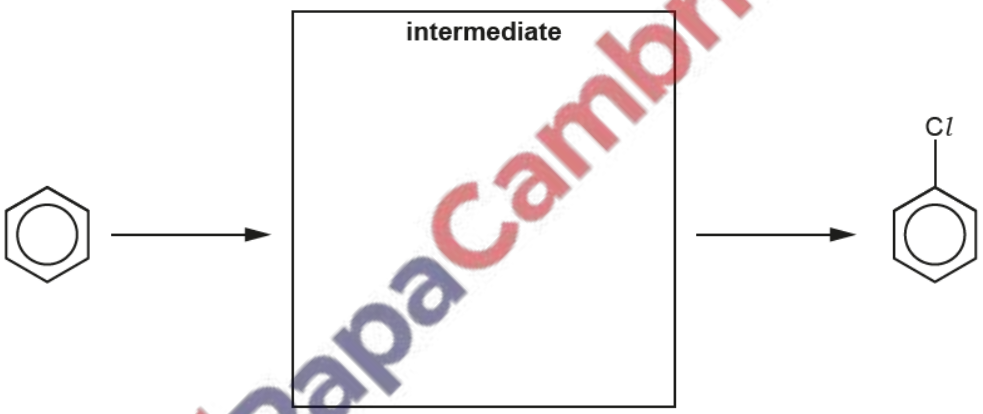

Fig. 5.3

[3]

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(c) The second step of the synthesis involves the reaction of chlorobenzene with $ClCOCH_2Cl$, also in the presence of an $AlCl_3$ catalyst, forming compound **Q**.

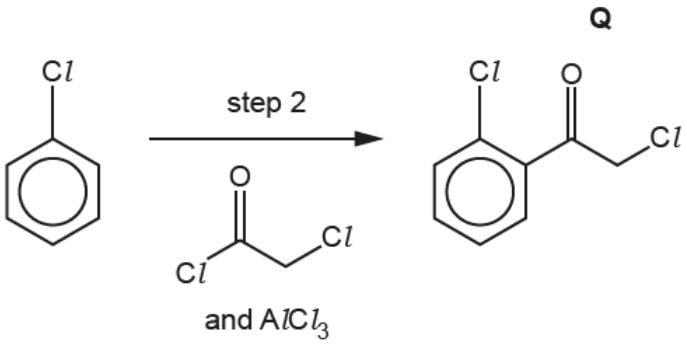

Fig. 5.4

(i) Name the mechanism of the reaction in step 2.

..... [1]

(ii) Draw the structure of an isomer of **Q** that forms as an organic by-product of the reaction in step 2.

[1]

(iii) The reactants used in step 2 contain acyl chloride, alkyl chloride and aryl chloride functional groups.

State and explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides.

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easiest to hydrolyse hardest to hydrolyse

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..... [3]

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(d) Tulobuterol is produced from **Q** as shown in Fig. 5.5.

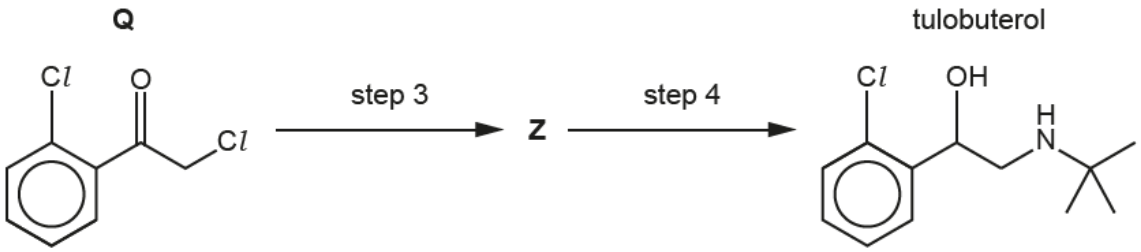

Fig. 5.5

Suggest reagents and conditions for steps 3 and 4.

Draw the structure of **Z** in the box.

step 3 .....

step 4 .....

Z

[3]

(e) The synthesis produces two enantiomers of tulobuterol.

(i) Define enantiomers.

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..... [1]

(ii) Suggest **one** disadvantage of producing two enantiomers in this synthesis.

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..... [1]

(iii) Suggest a method of adapting the synthesis to produce a single enantiomer.

..... [1]

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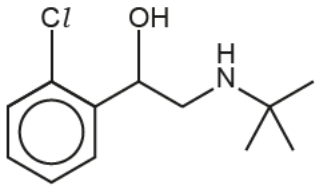
tulobuterol



(f) **(i)** Predict the number of peaks that would be seen in the carbon-13 NMR spectrum of tulobuterol.

..... [1]

(ii) The proton (^{1}H) NMR spectrum of tulobuterol dissolved in D_2O shows peaks in four different types of proton environment.

The peak for the —CH_2N— environment is a doublet in the chemical shift range δ = 2.0–3.0 ppm.

Give details for each of the other **three** peaks in the proton NMR spectrum of tulobuterol, to include:

- chemical shift
- environment of the proton
- splitting pattern
- number of ^{1}H atoms responsible.

Table 5.1 gives information about typical chemical shift values.

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..... [3]

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Table 5.1

environment of proton	example	chemical shift range δ / ppm
alkane	–C**H**$_3$, –C**H**$_2$–, >C**H**–	0.9–1.7
alkyl next to C=O	C**H**$_3$–C=O, –C**H**$_2$–C=O, >C**H**–C=O	2.2–3.0
alkyl next to aromatic ring	C**H**$_3$–Ar, –C**H**$_2$–Ar, >C**H**–Ar	2.3–3.0
alkyl next to electronegative atom	C**H**$_3$–O, –C**H**$_2$–O, –C**H**$_2$–C*l*	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0
alkyl amine	R–N**H**–	1.0–5.0
aryl amine	Ar–N**H**$_2$	3.0–6.0
amide	RCONHR	5.0–12.0

[Total: 22]

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