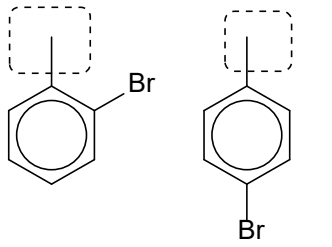
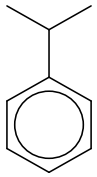
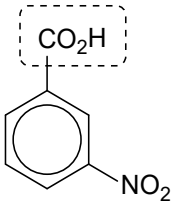
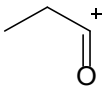
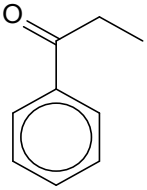
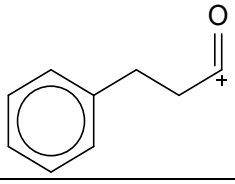
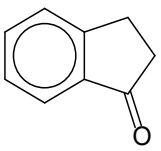
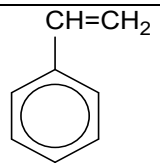
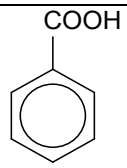
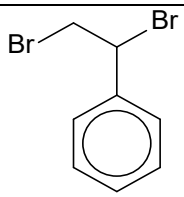
RAFFLES INSTITUTION
YEAR 5 H2 CHEMISTRY 2025
Tutorial 13 – Arenes

Suggested Solutions to Practice Questions

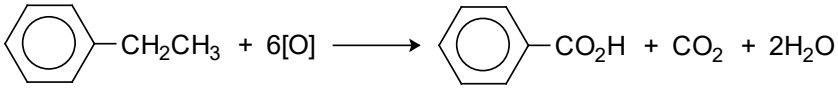
1

	Electrophile	Major Organic Product(s)
(i)	Br^+	$-CH_3$ group is 2,4-directing 
(ii)		
(iii)	NO_2^+	-COOH group is 3-directing 
(iv)		
(v)		

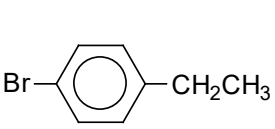
2(a)

Reaction	Reagents and conditions	Type of reaction	Unknown Reactant / Product
I	CH_3CH_2Cl, AlCl_3	electrophilic substitution	--
II	H_2, Ni catalyst	reduction	**A:** 
III	$KMnO_4$(aq), dilute H_2SO_4, heat / heat under reflux	oxidation	**C :** 
IV	limiting Br_2, uv light, room temperature	free radical substitution	--
V	Br_2, AlBr_3	electrophilic substitution	--
VI	conc. HNO_3, conc. H_2SO_4, 30 °C	electrophilic substitution	--
VII	Br_2 in CCl_4, dark	electrophilic addition	**B :** 

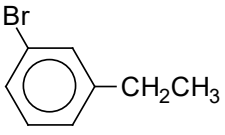
2(b)



2(c) Positional isomers of **D**:



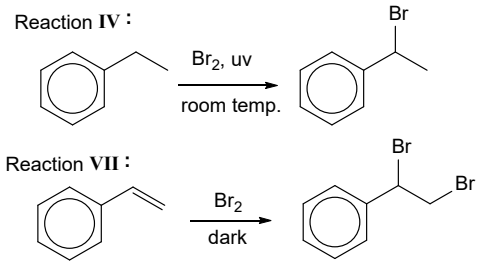
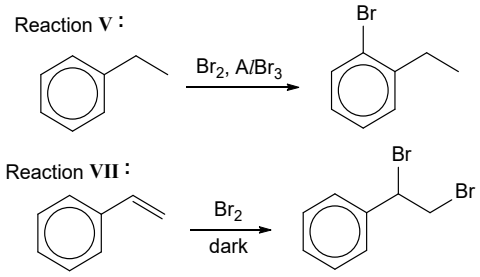
isomer **D1**



isomer **D2**

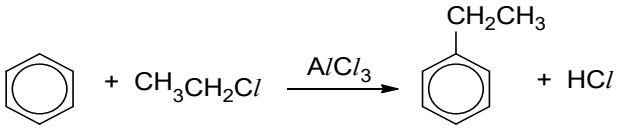
D1 is more likely to be formed along with **D**. This is because the $-CH_2CH_3$ group is 2,4-directing (and not 3-directing).

2(d)

(i)  Reaction of alkyl side chain vs alkene.	Reaction IV requires energy (in the form of uv light) to be provided while reaction VII does not. <u>Compare regions of high / low electron density</u> • Reaction IV involves the reaction of the alkyl group which does not possess any regions of high or low electron density. • Reaction VII involves reaction at the highly electron rich C=C which polarises the Br_2 electron cloud to generate the $Br^{\delta+}$ electrophilic site / attracts the Br_2 electrophile. <u>Comparing bonds broken</u> • The C–H bonds broken in Reaction IV are relatively strong. Hence, uv light is needed to generate the reactive bromine radicals which make the substitution reaction thermodynamically feasible. • The slow step of Reaction VII involves breaking of the relatively weak π bond of C=C.
(ii)  	Reaction V requires the use of a Lewis acid catalyst while reaction VII does not. In reaction V, the conversion of ethylbenzene to **D** involves disrupting the resonance stabilisation due to the delocalisation of the 6 π electrons of benzene. Hence an electrophile stronger than Br_2 is required for the electrophilic substitution. A Lewis acid such as A/Br_3 is required since it reacts with Br_2 to generate the stronger Br^+ electrophile. However, in reaction VII, the addition of Br_2 across the C=C bond does not disrupt any resonance stabilisation of the benzene ring. Also, the electron rich C=C bond of the alkene is able to polarise the Br_2 electron cloud to generate the $Br^{\delta+}$ electrophilic site. Hence, no lewis acid is required.

2(e)

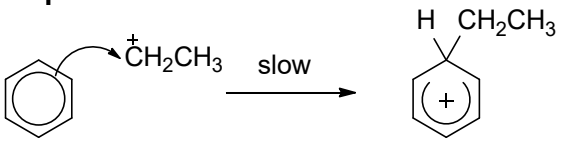
Reaction I



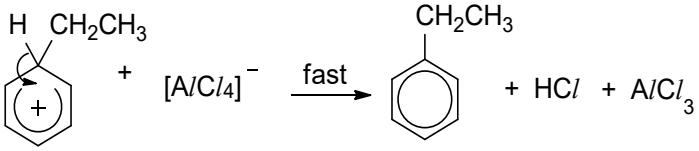
Electrophilic Substitution

$CH_3CH_2Cl + AlCl_3 \rightleftharpoons CH_3CH_2^+ + [AlCl_4]^-$

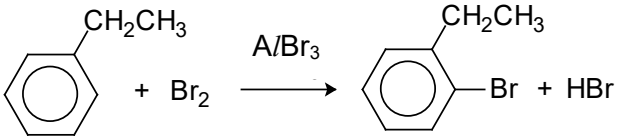
Step 1:



Step 2:



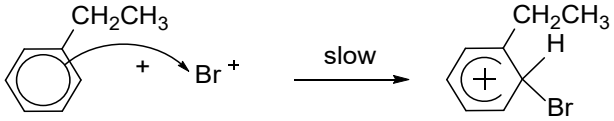
Reaction V



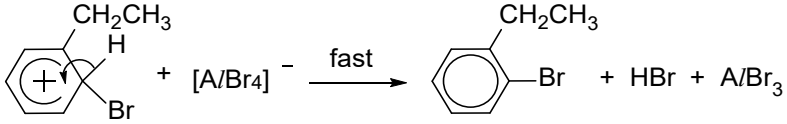
Electrophilic Substitution

$Br_2 + AlBr_3 \rightleftharpoons Br^+ + [AlBr_4]^-$

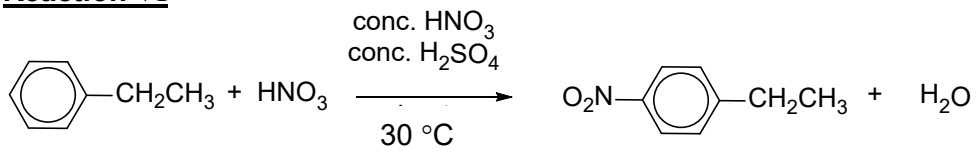
Step 1:



Step 2:



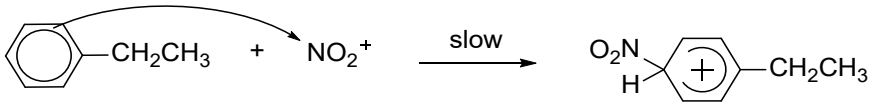
Reaction VI



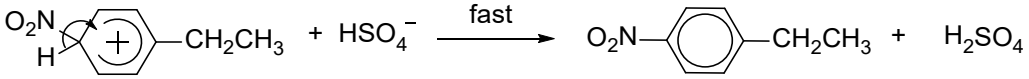
Electrophilic Substitution

$2H_2SO_4 + HNO_3 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$

Step 1:



Step 2:



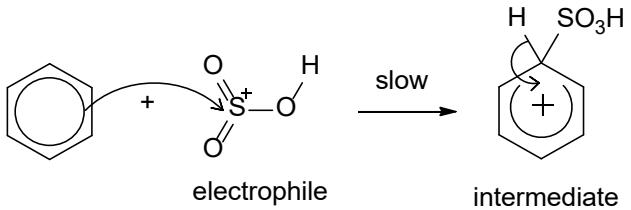
3 The product is bromobenzene. Since C*l* is more electronegative than Br, C*l* attracts the bonding electrons to itself when the Br–C*l* bond cleaves heterolytically to react with A*l*C*l*$_3$ to form Br^+ and A*l*C*l*$_4^-$. Br^+ acts as the electrophile which attacks benzene to form bromobenzene.

4(a)(i) The $-CH_3$ substituent is a 2,4-directing group and directs the substitution of $-SO_3H$ on the ring at the 2- and 4-positions with respect to it. **H**, however, has the $-SO_3H$ at the 3-position with respect to $-CH_3$. [1]

Comments
Students are required to provide an explanation, instead of just stating that $-CH_3$ is 2,4-directing (which is given in the *Data Booklet*).

4(a)(ii) The $-CH_3$ group poses steric hindrance to the approach of the electrophile at the 2-position [1] during the reaction. Hence, substitution by $-SO_3H$ at the 2-position with respect to $-CH_3$ occurs less than the 4-position, resulting in a lower concentration of **G** than **J**.

4(b)(i)



[3]

Comments
In the displayed structure of the electrophile, the positive charge is on the S atom (since C–S bond is formed in the product). Hence, the slow step involves the movement of 2 π electrons from the benzene ring to the S atom of the electrophile, forming a σ bond between S and one C atom of the benzene ring.

4(b)(ii) Benzene does not undergo addition reactions with fuming sulfuric acid as the addition product will not have the delocalisation of six π electrons [1], leading to the loss of aromaticity and resonance stabilisation [1].

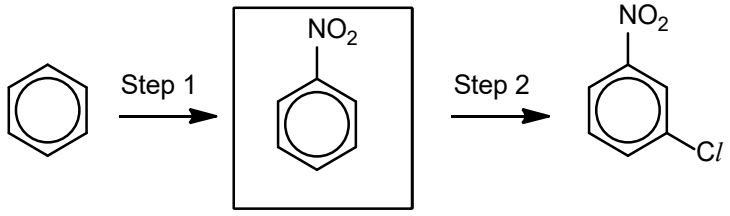
4(b)(iii) In decreasing order of reactivity with fuming sulfuric acid:

methylbenzene > benzene > **K**

methylbenzene : The $-CH_3$ group is an electron-donating group which increases the electron density of the benzene ring, making it more susceptible to electrophilic attack by SO_3H^+ than an unsubstituted benzene ring. [1]

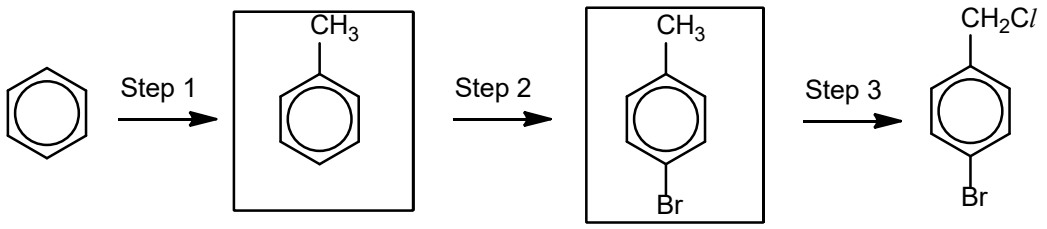
K: The $-COCH_3$ group is an electron-withdrawing group which decreases the electron density of the benzene ring, making it less susceptible to electrophilic attack by SO_3H^+ than an unsubstituted benzene ring. [1]

5(a)



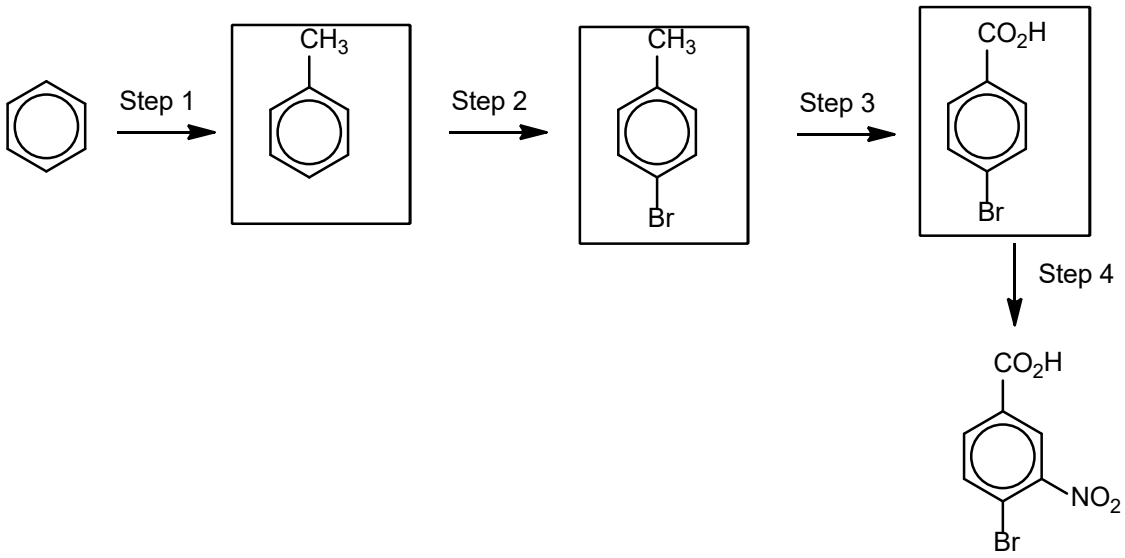
Reagents and conditions
Step 1: conc. HNO_3, conc. H_2SO_4, 50 °C
Step 2 : Cl_2, $AlCl_3$

5(b)



Reagents and conditions
Step 1: CH_3Cl, Al/Cl_3
Step 2 : Br_2, Al/Br_3
Step 3 : limited Cl_2, uv light, room temp.

5(c)



Reagents and conditions
Step 1: CH_3Cl, Al/Cl_3
Step 2 : Br_2, Al/Br_3
Step 3 : $KMnO_4(aq)$, $H_2SO_4(aq)$, heat / heat under reflux
Step 4: conc. HNO_3, conc. H_2SO_4, heat / heat under reflux

6(a)

Test
Add two drops of $KMnO_4$ acidified with dilute sulfuric acid to each compound in a test-tube, and heat each reaction mixture in a hot water bath. (Note: **DO NOT** heat under reflux)

Observation
- For methylbenzene, there is decolourisation of purple $KMnO_4(aq)$.
- For cyclohexane, there is no decolourisation of purple $KMnO_4(aq)$.

6(b)

Test
Add Br_2 to each compound in separate test-tubes and irradiate each mixture with uv light at room temperature.

Observation
- For cyclohexane, there is decolourisation of reddish-brown Br_2.
- For benzene, there is no decolourisation of reddish-brown Br_2.

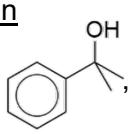
OR

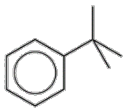
Test
Add concentrated HNO_3 and concentrated H_2SO_4 to each compound in a test tube, and heat each reaction in a water bath maintained at 50 °C (for about 10 min). Then pour each mixture into a small beaker containing some water.

Observation
- For benzene, pale yellow oily droplets of nitrobenzene will be observed at the base of the beaker.
- For cyclohexane, pale yellow oily droplets will not be observed.

6(c)

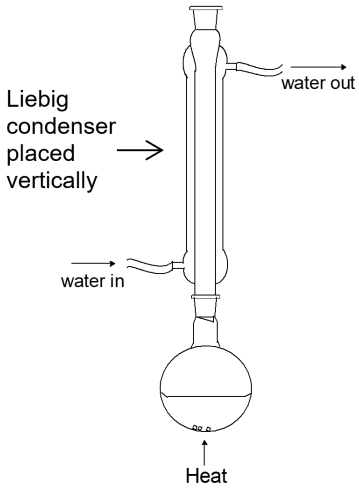
Test
Add two drops of $KMnO_4$ acidified with dilute sulfuric acid to each compound in a test-tube, and heat each reaction mixture in a hot water bath. (Note: **DO NOT** heat under reflux)

Observation
- For 

, there is decolourisation of purple $KMnO_4$(aq) and efferverscence of CO_2(g) which gives a white precipitate with limewater.
- For  , there is no decolourisation of purple $KMnO_4$(aq).

7(a)

A reflux set-up

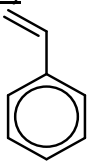
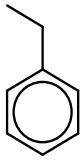
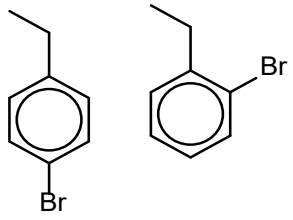


The apparatus for the reflux set-up essentially consists of a Liebig condenser attached vertically to the reaction flask.

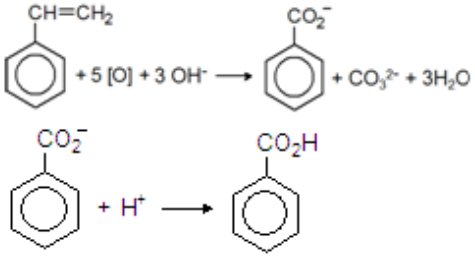
When the reaction mixture is heated to the desired temperature, its vapour formed rises and condenses at the cold inner surface of the condenser, and the liquid drips back into the flask.

Thus heating under reflux allows the reactants to be heated to the desired temperature for reaction, with minimal loss of the reactants/products/solvent to the atmosphere due to vapourisation.

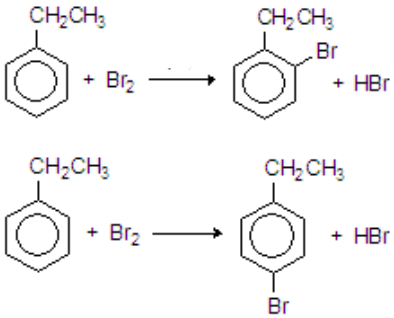
7(b)

Evidence	Deductions
P has molecular formula of C_8H_8.	Since C:H = 1:1, **P** may contain a benzene ring.
P instantly decolourises Br_2 in CCl_4.	**Electrophilic addition** occurs. **P** is an alkene.
P $\xrightarrow[\text{then } H^+]{\text{alkaline } KMnO_4, \text{ heat under reflux}}$ **Q** $C_7H_6O_2$	**Side-chain oxidation** occurs. **Q** is benzoic acid. **P** contains only 1 alkyl side chain (or alkenyl side chain). **P** is 
P + H_2 $\xrightarrow{Ni}$ **R** (1:1 ratio)	**Reduction** of C=C bond occurs. **P** contains only 1 –C=C– group. **R** is 
R $\xrightarrow{Br_2}$ No reaction **R** $\xrightarrow{A/Br_3}$ **dense white fumes, S + T** and **U**	**Electrophilic addition** does **not** occur for **R**. **R** is not an alkene. When A/Br_3 is added, **electrophilic substitution** occurs to give dense white fumes of HBr, **S** is HBr. Since $-CH_2CH_3$ group in **R** is 2,4-directing, **T** and **U** are 

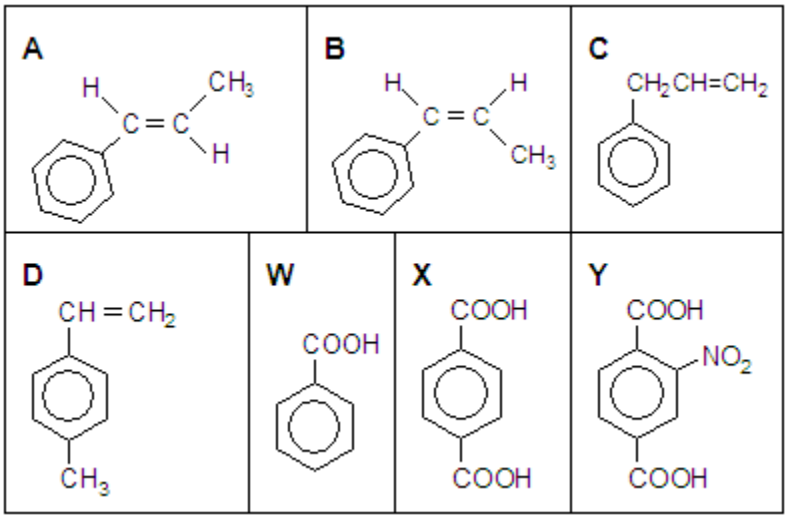
7(c)(i)



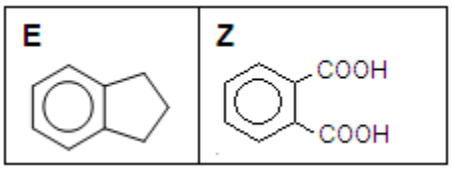
7(c)(ii)



8(a)


A
H
CH3
C = C
H
B
H
H
C = C
CH3
C
CH2CH=CH2
D
CH = CH2
CH3
W
COOH
X
COOH
COOH
Y
COOH
NO2
COOH

8(b)


E
Z
COOH
COOH