11.4 Arenes

Set B **Answer key**

A Multiple choice

4 MARKS

1 **C** concentrated HNO_3 and concentrated H_2SO_4, 10 °C [1]

Nitration of benzene requires the strong electrophile, NO_2^+, formed when nitric acid is protonated by the stronger sulfuric acid, followed by loss of water: $HNO_3 + 2H_2SO_4 \rightarrow H_2O + NO_2^+ + 2HSO_4^-$

The nitration reaction is highly exothermic. Mononitration occurs below 55 °C, further nitration to dinitrobenzene can occur above 55 °C and trinitration occurs above 100 °C. Hence the reaction mixture must be cooled and maintained below 55 °C for mononitration.

2 **C** It donates protons to the nitric acid, thus forming NO_2^+ ions. [1]

The function of sulfuric acid is to aid in the generation of the strong electrophile, NO_2^+, by first, protonation of nitric acid (sulfuric acid is a stronger Brønsted–Lowry acid).

3 **C** $CH_3Cl, AlCl_3 \rightarrow KMnO_4, H_2SO_4 \rightarrow Cl_2, AlCl_3$ [1]

A Wrong relative positions.

B $KMnO_4, H_2SO_4$: no reaction, unable to access $–CO_2H$.

C $C_6H_5CH_3 \rightarrow C_6H_5CO_2H \rightarrow$ 3-chlorobenzoic acid

D Wrong relative positions.

4 **C** alkylation, nitration, free radical substitution [1]

Alkylation gives $C_6H_5CH_3$. Nitration ($–CH_3$ is 2,4-directing) gives 4-nitromethylbenzene. Free radical substitution then gives $ClCH_2C_6H_4NO_2$.

In B, $–NO_2$ is 3-directing.

B Structured questions

16 MARKS

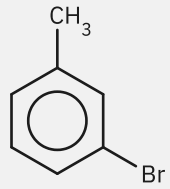
5 **(a)**

I reagent: $KMnO_4$ with dilute H_2SO_4. Condition: heat under reflux. Type of reaction: side-chain oxidation [1]

II reagent: Br_2, excess methylbenzene. Condition: uv light. Type of reaction: free radical (side-chain) substitution [1]

III reagent: Br_2, anhydrous $FeBr_3$ catalyst. Condition: room temperature. Type of reaction: electrophilic (aromatic) substitution [1]

(b)

The positional isomers are  and  [1]

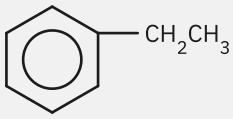
4-bromomethylbenzene is more likely to be formed along with A. [1]

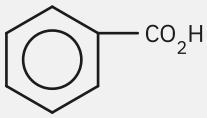
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B reacts with Cl_2 in the absence of uv light to give dense white fumes (of HCl) with a suitable catalyst ⇒ electrophilic substitution ⇒ presence of benzene ring (since it requires a catalyst to react with Cl_2).

B can be oxidised by $KMnO_4$ to form C ⇒ presence of alkyl side-chain on benzene.

C is exactly neutralised by one mole of NaOH ⇒ C only has 1 $-CO_2H$ group after side-chain oxidation ⇒ B only has 1 alkyl substituent.

B:  [1]

C:  [1]

$C_6H_5CH_2CH_3 + 6[O] \rightarrow C_6H_5CO_2H + 2H_2O + CO_2$ [1]

7 **(a)**

$CH_3COCl + FeCl_3 \rightarrow CH_3CO^+ + FeCl_4^-$ [1]

(b)

The $-NO_2$ group is a highly deactivating substituent. It reduces the electron density of the benzene ring such that it becomes less susceptible to an electrophilic attack by a rather unreactive electrophile like CH_3CO^+. [1]

The presence of a second, strongly activating group like $-OCH_3$ increases the electron density of the benzene ring sufficiently for it to be susceptible to electrophilic attack by CH_3CO^+. [1]

8 **(a)(i)**

Enthalpy change = 5 × (−118) = −590 kJ mol^{-1} [1]

(ii)

Having a less exothermic enthalpy of hydrogenation, naphthalene is (590 − 335 =) 255 kJ mol^{-1} more stable than the hypothetical molecule with 5 C=C bonds. [1]

(iii)

Each of the 10 carbon atoms in naphthalene is sp^2 hybridised, with one singly filled 2p orbital perpendicular to the plane of the molecule. A C–C σ bond is formed with neighbouring C atoms via sp^2–sp^2 overlap. [1]

All 10 p orbitals with one electron each overlap sideways, leading to a delocalised electron cloud of 10 π electrons covering all 10 C atoms. The bonds between the carbon atoms are in between a single C–C and a double C=C bond. [1]

(b) For complete hydrogenation of naphthalene, excess hydrogen gas should be used with nickel catalyst under high temperature and high pressure. **[1]**