18.1 Arenes – benzene compounds

Answers to Exam practice questions

Pages 230–232

1 a) Benzene has a planar molecule [1]; with six carbon atoms in a regular hexagon. [1] Each carbon atom forms a normal covalent (σ) bond with its two adjacent carbons atoms and a hydrogen atom. [1] These bonds involve three of the four outer shell electrons on each carbon atom. The fourth electron on each carbon atom occupies a p orbital [1]; at right angles to the benzene ring. Sideways overlap [1] of the p orbitals leads to the formation of π bonds [1]; involving rings of delocalised electrons [1] above and below the plane of the benzene molecule. (*maximum 6 marks*)

b) The delocalised π electron system in benzene is disrupted initially by formation of an intermediate cation [1], but is restored by elimination of H^+ and a reaction involving substitution. [1]

In ethene, the localised π bond is weaker than the delocalised π system in benzene. [1]

The breakage of the π bond in ethene and the formation of two single bonds by an addition reaction occurs easily. [1]

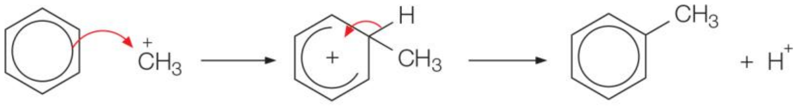
So addition is energetically more favourable than substitution [1] (*maximum 4 marks*)

2 a) An electrophilic substitution is a reaction in which an electron-deficient species, an electrophile [1], replaces an atom or group of atoms. [1]

b) Methylbenzene [1]

Iron(III) bromide or aluminium bromide or their chlorides. [1]

c) $CH_3—Br + FeBr_3 \longrightarrow \overset{+}{C}H_3 + FeBr_4^-$ [1]



[1] [1]

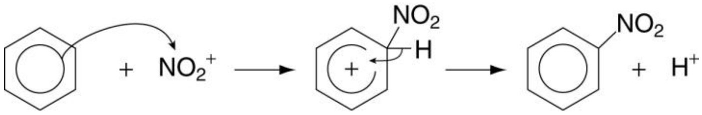
d) Friedel and Craft [1]

3 a) A is cyclohexane; B is hydrogen; C is aluminium chloride or iron(III) chloride; D is ethylbenzene; E and F are concentrated nitric acid and concentrated sulfuric acid. [6]

b) i) $CH_3C^+H_2$ [1]; NO_2^+ [1]

ii) Temperature 50–60 °C. [1]

$HNO_3 + H_2SO_4 \rightarrow H_2O + NO_2^+ + HSO_4^-$ [1]



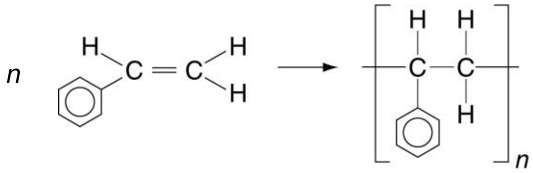
[2]

iii) Explosives/further reactions to produce dyes. [1]

c) i) Temperatures >150 °C, and high pressure. [1]

ii) As a solvent [1]

d) i)



[1]

ii) As an insulator or for packaging. [1]

4 a) i) Aluminium chloride or iron(III) chloride [1]

ii) Bubble chlorine into a boiling benzene and catalyst mixture [1]; under reflux [1]; in a fume cupboard. [1]

b) i) I is 1-chloro-4-methylbenzene. [1]

II is (chloromethyl)benzene. [1]

ii) Formation of I is by electrophilic substitution. [1]

Formation of II is by radical substitution. [1]

c) i) II reacts with sodium hydroxide. [1]

OH^- can attack the δ+ carbon of the CH_2Cl group in II. [1]

The electron cloud of the benzene ring will repel the OH^- so no reaction will take place with I. [1]

ii) $C_6H_5CH_2OH$ [1]; nucleophilic substitution. [1]

5 a) Any two from (*maximum 2 marks*):

- limiting the amount of concentrated HNO_3 used
- adding the nitrating mixture to the methyl benzoate in small amounts
- keeping the temperature below 15 °C.

b) Methyl 2-nitrobenzoate [1]; methyl 4-nitrobenzoate. [1]

c) To remove any nitric and sulfuric acid. [1]

d) The impurities dissolve in the hot ethanol but there is little present [1] so that none crystallises out when the ethanol is cooled down [1].

e) i) Some will remain dissolved in the ethanol even when it is cooled in ice. [1]

ii) Taking the minimum volume of ethanol needed to dissolve all the impure solid at the high temperature. [1]

Cooling the ethanol solution so that more crystallises. [1]

f) Larger crystals form if the solution cools slowly. [1]

g) Methyl benzoate is the limiting reactant.

Volume of methyl benzoate used = 5 cm^3

Mass of methyl benzoate used = 5.5 g [1]

Moles of methyl benzoate used = $\frac{5.5\text{ g}}{136.0\text{ g mol}^{-1}}$ = 0.0404 mol [1]

From the equation: 1 mol methyl benzoate → 1 mol methyl 3-nitrobenzoate

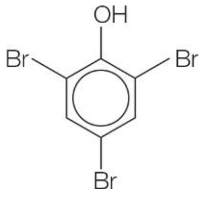
0.0404 mol methyl benzoate → 0.0404 mol methyl 3-nitrobenzoate

∴ Theoretical yield of methyl 3-nitrobenzoate = 0.0404 mol × 181.0 g mol^{-1} [1] = 7.3 g [1]

h) Percentage yield = $\frac{3.5}{7.3} \times 100\%$ = 48% (2 s.f.) [1]

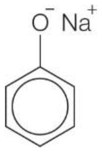
6 a) A is dilute nitric acid. [1]

b) B



[1]

C



[1]

c) i) EITHER – warming [1] with dilute nitric acid [1]

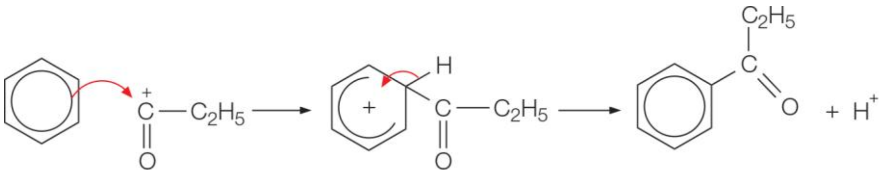
OR – conc. nitric acid [1] at room temperature. [1]

ii) 2,4-dinitrophenol, 2,5-dinitrophenol, 2,6-dinitrophenol, 3,4-dinitrophenol, 3,5-dinitrophenol.

All 5 correct [3]; 3 or 4 correct [2]; 1 or 2 correct [1]. (Subtract [1] for any incorrect isomers to a minimum of 0.)

7 a) i) CH_3CH_2COCl [1]; catalyst $AlCl_3$ [1]

ii) $CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2C^+O + AlCl_4^-$ [1]



[1] [1]

b) $LiAlH_4$ [1]; nucleophilic addition. [1]

c) Conc. phosphoric or conc. sulfuric acid [1]; dehydration or elimination. [1]

d) *Step 2*: Optical isomerism occurs as product has four groups attached to central C. [1]

Racemic mixture of optical isomers formed. [1]

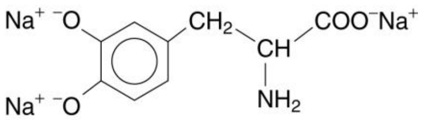
H^- can attack from either side of planar C=O. [1]

Step 3: *E*/*Z* isomerism. [1]

No rotation about C=C. [1]

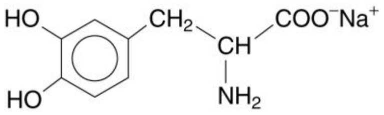
Two different groups on each end of the C=C. [1]

8 **a)** **i)**



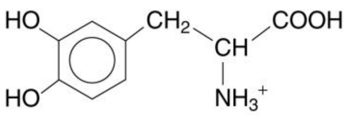
[1]

ii)



[1]

b)

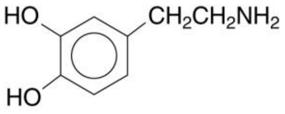


[1]

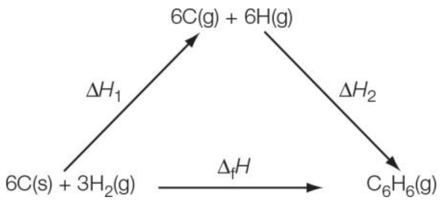
c) A lone pair of electrons on each of the –OH groups in L-dopa interacts with the delocalised electrons in the benzene ring [1], releasing electrons into the ring and making it more susceptible to electrophilic attack. [1]

d) **i)** Primary amines are organic compounds containing the $–NH_2$ group.

ii)



9 **a)**



ΔH_1 = 6 $\Delta_{at}H$(carbon) + 6 $\Delta_{at}H$(hydrogen) [1]

ΔH_1 = 6(+715) + 6(+218) [1]

ΔH_1 = +5598 kJ mol^{-1} [1]

For Kekulé benzene:

ΔH_2 involves formation of 3 C–C bonds + 3 C=C bonds + 6 C–H bonds. [1]

ΔH_2 = 3(–347) + 3(–612) + 6(–413) kJ mol^{-1} [1]

ΔH_2 = –5355 kJ mol^{-1} [1]

$\Delta_f H = \Delta H_1 + \Delta H_2$ = +5598 – 5355 kJ mol^{-1}

= +243 kJ mol^{-1} [1]

b) Experimental value is +82 kJ mol^{-1}.

Difference is 161 kJ mol^{-1}. [1]

So actual benzene is 161 kJ mol^{-1} lower in energy than the Kekulé structure. [1]

Delocalisation of electron density gives extra stability to benzene. [1]

10 a) This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully sustained line of reasoning. Assess the quality of the answer taking into account both the key points made (*up to 4 marks*) and the logic and coherence of the discussion (*up to 2 marks*).

Points to make in the answer:

- Ethanol is much weaker acid than phenol.
- Dissociation of alcohols is according to $ROH(aq) \rightleftharpoons RO^-(aq) + H^+(aq)$.
- For phenol, the negative charge is delocalised into benzene ring.
- Therefore the anion is stabilised and proton loss is easier.
- For ethanol, the inductive effect of the ethyl group pushes electrons towards the oxygen so its electron density is increased.
- Therefore the anion is more likely to bond to H^+ to reform the OH bond.

b) Ethanol forms $CH_3COOCH_2CH_3$; ethyl ethanoate [1]

Phenol forms $CH_3COOC_6H_5$; phenyl ethanoate [1]