Solutions

Each answer shows the steps, then the **result**.

2.1

- concentrated nitric acid and concentrated sulfuric acid; 25–60 °C / warm

2.2

- NO_2^+ (the nitryl/nitronium cation)

2.3

- Concentrated nitric acid and concentrated sulfuric acid; a temperature of about 55 °C

2.4

- The ring's delocalised π electrons make it unusually stable; addition would destroy that delocalisation, so substitution, which restores it, is preferred

2.5

- Benzoic acid

3.1 A

- $RCOCl + AlCl_3$ adds an acyl group — Friedel–Crafts acylation

3.2 C

- UV light with no catalyst gives free-radical substitution in the side-chain

3.3

- the acid mixture makes the electrophile NO_2^+; the delocalised ring electrons form a bond to NO_2^+, giving a positively charged intermediate; the C–H bond breaks and H^+ is lost; this restores the delocalised ring, giving nitrobenzene

3.4

- $–NO_2$ directs the next group to **position 3**; because $–NO_2$ is an electron-withdrawing (deactivating) group that directs to the 3-position

3.5

(a)

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

(b)

- Curly arrow from **inside the ring** to the nitrogen of NO_2^+; intermediate drawn with a horseshoe and a + inside it, with the NO_2 and H on the same carbon; curly arrow from the C–H bond into the ring; H^+ released and the delocalised ring restored

(c)

- The delocalised system is broken but not destroyed — four π electrons remain delocalised over five carbons; a horseshoe shows that partial delocalisation, which three localised double bonds would not

(d)

- Ethanoyl chloride, CH_3COCl, with an $AlCl_3$ catalyst; reflux under anhydrous conditions; Friedel–Crafts acylation

(e)

- The methyl group is electron-releasing, so it increases the electron density of the ring and makes it more attractive to an electrophile, hence the faster reaction; the electron density is increased most at the 2- and 4- positions, so substitution occurs mainly there