

## Solutions

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

### 2.1

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

### 2.2

- $\text{NO}_2^+$  (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  $\pi$  electrons make it unusually stable; addition would destroy that delocalisation, so substitution, which restores it, is preferred

### 2.5

- Benzoic acid

### 3.1 A

- $\text{RCOCl} + \text{AlCl}_3$  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

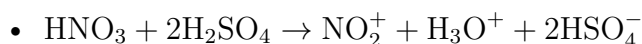
- the acid mixture makes the electrophile  $\text{NO}_2^+$ ; the delocalised ring electrons form a bond to  $\text{NO}_2^+$ , giving a positively charged intermediate; the C–H bond breaks and  $\text{H}^+$  is lost; this restores the delocalised ring, giving nitrobenzene

### 3.4

- $-\text{NO}_2$  directs the next group to **position 3**; because  $-\text{NO}_2$  is an electron-withdrawing (deactivating) group that directs to the 3-position

### 3.5

(a)



(b)

- Curly arrow from **inside the ring** to the nitrogen of  $\text{NO}_2^+$ ; intermediate drawn with a horseshoe and a + inside it, with the  $\text{NO}_2$  and H on the same carbon; curly arrow from the C–H bond into the ring;  $\text{H}^+$  released and the delocalised ring restored

(c)

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

(d)

- Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , with an  $\text{AlCl}_3$  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