

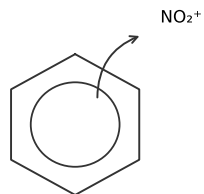
## Solutions

Original marking guidance: M1 method, A1 accuracy, B1 explanation.

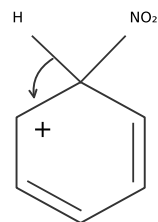
### 2.1

Nitration mechanism after  $\text{NO}_2^+$  generation; curly arrows show electron pairs

1 Ring electron pair attacks

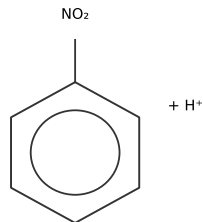


2 Positive intermediate



C-H bond pair restores ring

3 Nitrobenzene +  $\text{H}^+$



B1 ring attack arrow; B1 intermediate with H and  $\text{NO}_2$  on the same carbon and positive charge; B1 C-H pair returning to ring; B1 nitrobenzene and  $\text{H}^+$ .

**2.2** Concentrated sulfuric acid;  $\text{HSO}_4^-$  accepts  $\text{H}^+$  to regenerate  $\text{H}_2\text{SO}_4$ .

**2.3**  $\text{C}_2\text{H}_5\text{Cl} + \text{AlCl}_3 \rightarrow \text{C}_2\text{H}_5^+ + \text{AlCl}_4^-$ ;  $\text{AlCl}_4^- + \text{H}^+ \rightarrow \text{AlCl}_3 + \text{HCl}$ .

**3.1**  $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CO}^+ + \text{AlCl}_4^-$ .  $\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{COCH}_3 + \text{HCl}$ , phenylethanone.

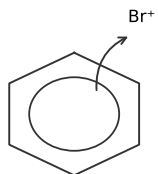
**3.2** Oxygen lone-pair interaction increases ring electron density, easing electrophile attack.  $\text{C}_6\text{H}_5\text{OH} + 3\text{Br}_2 \rightarrow \text{C}_6\text{H}_2\text{Br}_3\text{OH} + 3\text{HBr}$ .

**3.3** The first arrow must start at the ring electron pair and end at the electrophile. The second must start at the C-H bond pair and end at the ring bond as  $\text{H}^+$  leaves.

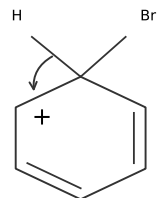
### 3.4

Bromination: simple electrophile model

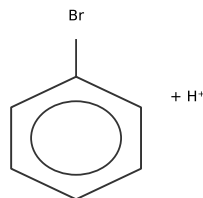
1 Ring pair attacks  $\text{E}^+$



2 C-H pair restores ring



3 Bromobenzene



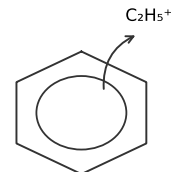
$\text{Br}_2 + \text{FeBr}_3 \rightarrow \text{Br}^+ + \text{FeBr}_4^-$ ;  $\text{FeBr}_4^- + \text{H}^+ \rightarrow \text{FeBr}_3 + \text{HBr}$

B1 electrophile generation; B1 ring electron-pair attack; B1 positive intermediate with H and incoming group on one carbon; B1 C-H bond arrow restoring ring; B1 correct aromatic product; B1 catalyst regeneration.

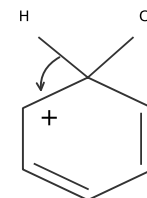
### 3.5

Alkylation: simple electrophile model

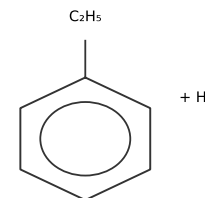
1 Ring pair attacks  $\text{E}^+$



2 C-H pair restores ring



3 Ethylbenzene



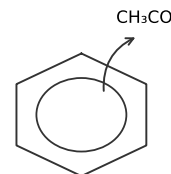
$\text{C}_2\text{H}_5\text{Cl} + \text{AlCl}_3 \rightarrow \text{C}_2\text{H}_5^+ + \text{AlCl}_4^-$ ;  $\text{AlCl}_4^- + \text{H}^+ \rightarrow \text{AlCl}_3 + \text{HCl}$

B1 electrophile generation; B1 ring electron-pair attack; B1 positive intermediate with H and incoming group on one carbon; B1 C-H bond arrow restoring ring; B1 correct aromatic product; B1 catalyst regeneration.

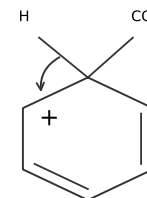
### 3.6

Acylation: simple electrophile model

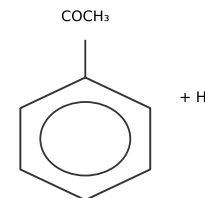
1 Ring pair attacks  $\text{E}^+$



2 C-H pair restores ring



3 Phenylethanone



$\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CO}^+ + \text{AlCl}_4^-$ ;  $\text{AlCl}_4^- + \text{H}^+ \rightarrow \text{AlCl}_3 + \text{HCl}$

B1 electrophile generation; B1 ring electron-pair attack; B1 positive intermediate with H and incoming group on one carbon; B1 C-H bond arrow restoring ring; B1 correct aromatic product; B1 catalyst regeneration.