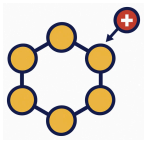
# Reactions of Arenes Map

Cambridge International A Level Chemistry · Topic 30 Reactions of arenes

### 1 The mechanism 30.1.2

- π-electrons attack $E^+$
- Horseshoe intermediate, + inside
- C–H breaks: **$H^+$ lost**
- Aromatic stabilisation **restored**



### 2 Nitration 30.1.1(b)

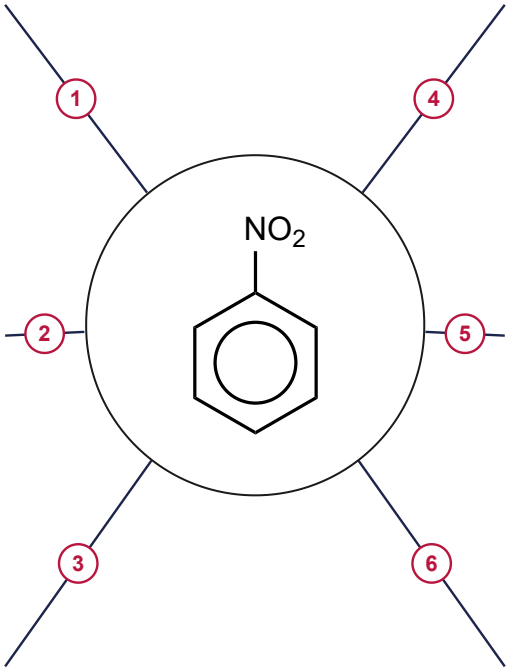
- Conc $HNO_3$ + conc $H_2SO_4$
- **25 °C to 60 °C**
- Electrophile **$NO_2^+$**
- Methylbenzene: 2- and 4-



### 3 Halogenation 30.1.1(a)

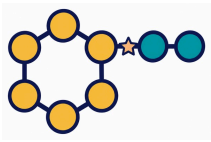
- Catalyst $AlCl_3$ or $AlBr_3$
- $Br_2 + AlBr_3 \rightarrow Br^+ + AlBr_4^-$
- Product bromobenzene + HBr
- Catalyst is **regenerated**





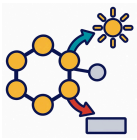

### 4 Friedel-Crafts 30.1.1(c), (d)

- **$AlCl_3$** and heat
- $CH_3Cl$ gives $CH_3^+$: alkylation
- $CH_3COCl$ gives $CH_3CO^+$: acylation
- New **C–C bond** to the ring



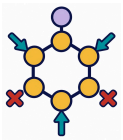
### 5 Ring or side chain 30.1.3

- $Cl_2$ + $AlCl_3$, dark: **the ring**
- $Cl_2$ + UV light: **the side chain**
- Electrophilic or free radical
- Conditions decide



### 6 Directing effects 30.1.4

- OH, $NH_2$, R: **2- and 4-directing**
- $NO_2$, COOH, COR: **3-directing**
- Donating or withdrawing
- Put the directing group on **first**



## Reactions of arenes reagents, conditions and product

| Reaction | Reagents and conditions | Product from benzene or methylbenzene |
|---|---|---|
| Nitration | Conc $HNO_3$, conc $H_2SO_4$, 25–60 °C | Nitrobenzene |
| Bromination | $Br_2$, $AlBr_3$ | Bromobenzene |
| Alkylation | $CH_3Cl$, $AlCl_3$, heat | Methylbenzene |
| Acylation | $CH_3COCl$, $AlCl_3$, heat | Phenylethanone |
| Oxidation | Hot alkaline $KMnO_4$, then dilute acid | Benzoic acid |
| Hydrogenation | $H_2$, Pt or Ni, heat | Cyclohexane |

## Worked examples

### Yield

- 7.8 g $C_6H_6$: 0.100 mol
- 8.61 g product: 0.0700 mol
- **70%**

### Hydrogenation

- 7.8 g benzene: 0.100 mol
- × 3 $H_2$
- **7.2 dm³ at r.t.p.**

### Planning

- Target 1-bromo-3-nitrobenzene
- $NO_2$ directs to 3
- **Nitrate, then brominate**

Phenol follows in Topic 32.

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