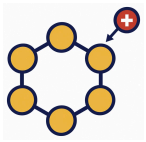
Substitution and Phenol Map

Edexcel International A Level Chemistry · Unit 5 · Topic 18B Electrophilic Substitution and Phenol

1 The mechanism

18.5

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



2 Nitration

18.4, 18.5

- Conc HNO_3 + conc H_2SO_4
- **Below 55 °C**
- Electrophile **NO_2^+**
- Hotter: 1,3-dinitrobenzene

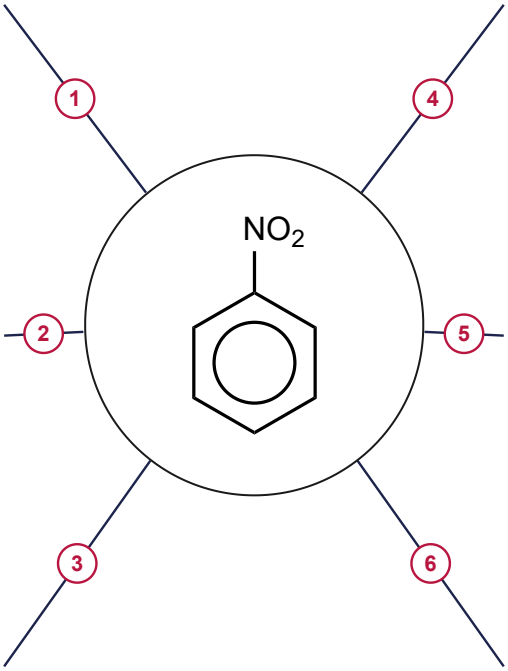


3 Halogenation

18.4, 18.5

- Halogen carrier: $FeBr_3$, Fe, $AlBr_3$
- $Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$
- Product bromobenzene + HBr
- Carrier is **regenerated**

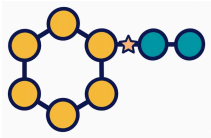




4 Friedel-Crafts

18.4, 18.5

- Anhydrous **$AlCl_3$**, reflux
- RCl gives R^+: alkylation
- RCOCl gives RCO^+: acylation
- New **C–C bond** to the ring



5 Burning and sulfonation

18.4

- High C:H: **smoky flame**
- Soot is unburnt carbon
- Fuming sulfuric acid, **40 °C**
- Benzenesulfonic acid



6 Phenol

18.6

- O lone pair joins the π-system
- Higher density **polarises Br_2**
- No carrier: white precipitate
- 2,4,6-tribromophenol



Electrophiles

how each one forms, and the catalyst that returns

Reaction	Electrophile	Forming it	Catalyst back
Nitration	NO_2^+	$HNO_3 + H_2SO_4$	$H^+ + HSO_4^- \rightarrow H_2SO_4$
Bromination	Br^+	$Br_2 + FeBr_3$	$H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr$
Chlorination	Cl^+	$Cl_2 + AlCl_3$	$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$
Alkylation	$CH_3CH_2^+$	$CH_3CH_2Cl + AlCl_3$	$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$
Acylation	CH_3CO^+	$CH_3COCl + AlCl_3$	$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

Worked examples

Yield

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

Phenol

- 0.940 g: 0.0100 mol
- Mr of product 331
- **3.31 g**

Combustion

- 0.200 mol benzene
- × 7½
- **1.50 mol O_2**

Nitrobenzene is reduced to phenylamine in Topic 19.

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