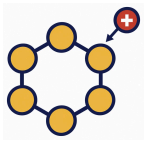
Substitution and Directing Map

OCR A Level Chemistry A · 6.1.1 Substitution, phenol and directing effects

1 The mechanism

6.1.1(e), (g)

- π-electrons attack E^+
- Horseshoe intermediate, + inside
- C–H breaks: **H^+ lost**
- Unfamiliar E^+: **same stages**



2 Nitration

6.1.1(d), (e)

- Conc HNO_3 + conc H_2SO_4
- **Below 55 °C**
- Electrophile **NO_2^+**
- H_2SO_4 is regenerated

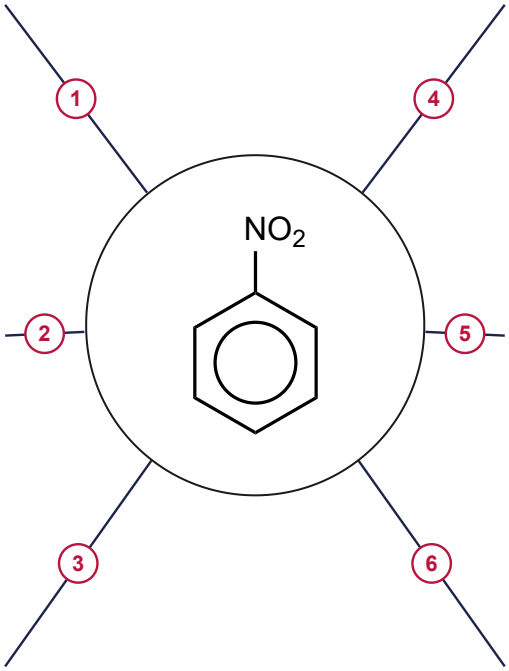


3 Halogenation

6.1.1(d), (e)

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





4 Friedel-Crafts

6.1.1(d)

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



5 Phenol

6.1.1(h)–(j)

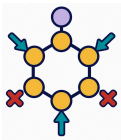
- Weak acid: **NaOH yes, carbonates no**
- O lone pair joins the π-system
- Br_2: 2,4,6-tribromophenol
- Dilute HNO_3: **2- and 4-nitrophenol**



6 Directing effects

6.1.1(k), (l)

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



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%**

Unfamiliar

- ICl: Cl more electronegative
- I is δ+, so I is E^+
- **C_6H_5I + HCl**

Planning

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

Nitrobenzene is reduced to phenylamine in 6.2.1 Amines.

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