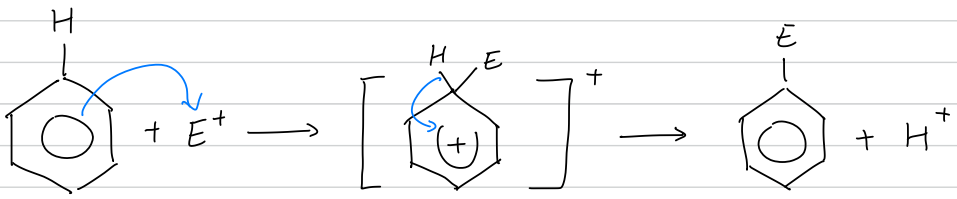
Benzene reactions

electrophilic substitution



Halogens

$$C_6H_{6\,(l)} + X_2 \xrightarrow{\text{Catalyst}} C_6H_5X_{(l)} + HX_{(g)}$$

Reagent: $Cl_{2\,(g)}$ $Br_{2\,(l)}$
Cond: r.t.p. (temp & press) Catalyst: Anhydrous $AlCl_{3\,(s)}$ or $FeBr_{3\,(s)}$

$$AlCl_3 + Cl_2 \longrightarrow [AlCl_4]^- + Cl^+$$
$$[AlCl_4]^- + H^+ \longrightarrow AlCl_3 + HCl$$

Nitration

$$C_6H_{6\,(l)} + HNO_3/H_2SO_4 \longrightarrow C_6H_5NO_2 + H_2O + H_2SO_{4\,(g)}$$

Reagent: nitrating mixture (conc HNO_3 conc H_2SO_4)
Condition: 45 – 55 °C , reflux

$$2H_2SO_4 + HNO_3 \longrightarrow 2HSO_4^- + NO_2^+ + H_3O^+$$
$$2HSO_4^- + H^+ + H_3O^+ \longrightarrow 2H_2SO_4 + H_2O$$

Alkylation

$$C_6H_{6\,(l)} + RCl \xrightarrow{AlCl_3} C_6H_5R_{(l)} + HCl_{(g)}$$
$$C_6H_{6\,(l)} + RCOCl \xrightarrow{AlCl_3} C_6H_5RCO + HCl_{(g)}$$

Reagent: RCl or RCOCl
Cond: heat under reflux Catalyst: Anhydrous $AlCl_{3\,(s)}$

$$AlCl_3 + RCOCl \longrightarrow [AlCl_4]^- + RCO^+$$
$$[AlCl_4]^- + H^+ \longrightarrow AlCl_3 + HCl$$

Electrophilic Addition

Turns to cyclohexane.

$$C_6H_6 + 3H_{2(g)} \xrightarrow{\text{Nickel}} C_6H_{12}$$

Temp: 150°C Catalyst: Nickel

Side Chain Reactions

Chloro (free rad)

$$C_6H_5CH_{3(l)} + Cl_{2(g)} \longrightarrow C_6H_5CH_2Cl + HCl$$

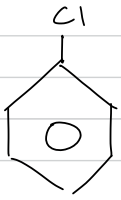
Reagent: Cl_2
Cond: u.v. light, heat

Oxidation

$$C_6H_5CH_3 + 3[O] \longrightarrow C_6H_5COOH + H_2O$$

Reagent: $K_2Cr_2O_7$ or $KMnO_4$
Cond: Heat, reflux for 2-3 hrs

Halo arenes

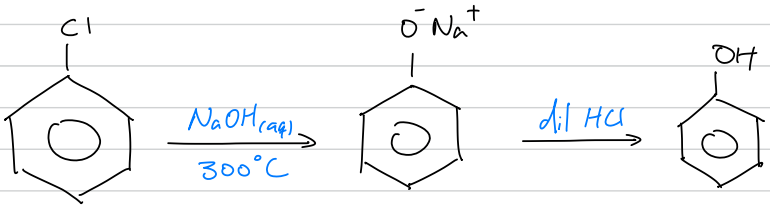


less reactive than RCl

Cl withdraws e^-, so C-Cl is almost like a double bond.
e^- in benzene also repels Nu^-.

Nucleophilic substitution

hydrolysis



$$C_6H_5Cl + NaOH_{(aq)} \xrightarrow{HCl} C_6H_5OH + NaCl_{(aq)}$$

Condition: 300 - 330°C, 150-300 atm
Reagents: NaOH, dil. HCl

C_6H_5I is fast to hydrolyse but C_6H_5Cl is slow.

Phenols

OH group activates ⇒ phenol more reactive than Benzene.
slightly acidic, as the H^+ breaks off, and the conjugate base is more stable. (stabalised by the benzene rings)

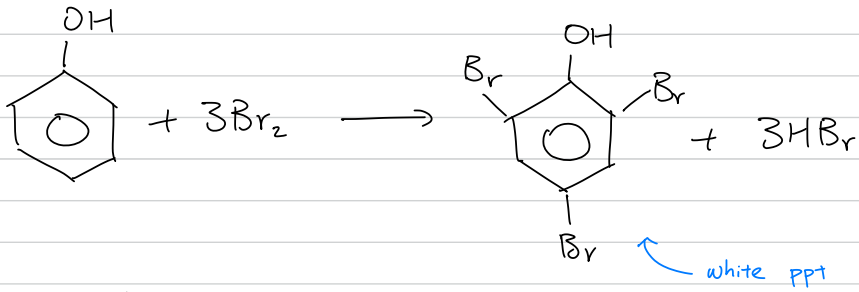
Acid Base

$$C_6H_5OH + NaOH \longrightarrow C_6H_5O^-Na^+ + H_2O$$
Cond: r.t.p.

$$C_6H_5OH + Na_{(s)} \longrightarrow C_6H_5O^-Na^+ + \tfrac{1}{2}H_{2\,(g)}$$
Cond: r.t.p.

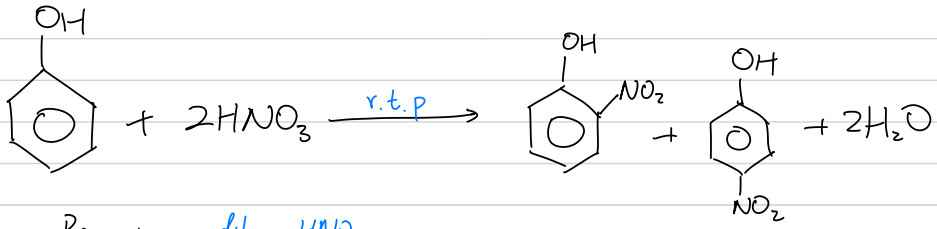
Phenol doesn't react with CO_3^{2-}. It's a weak acid

Bromination



Cond: r.t.p (no catalyst).

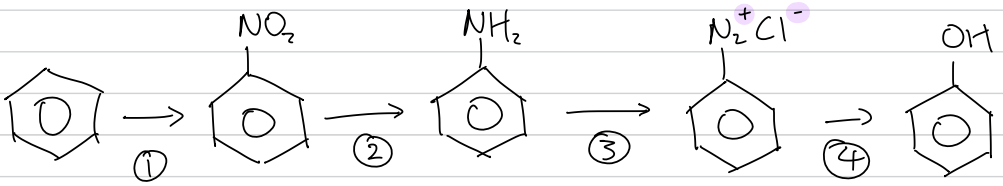
Nitration



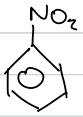
Reagent: dil HNO_3
Cond: r.t.p

Tests for phenol: $Br_{2\,(aq)}$ → white ppt
$FeCl_{3\,(aq)}$ → violet colour

Making phenol from benzene.



①: nitration of Benzene.

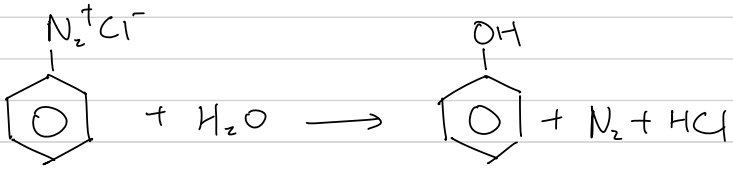
②: reduction of  Conc. HCl and Sn catalyst heat reflux.

③: HNO_2 and excess HCl (HNO_2 unstable so keep below 10°C. it's $NaNO_2$ and HCl)

$$C_6H_5NH_2 + HNO_2 + HCl \longrightarrow C_6H_5N_2^+Cl^- + 2H_2O$$

diazotisation

④: reagent: H_2O cond: above 10°C Substitution/Hydrolysis



Acyl Chlorides

preparation

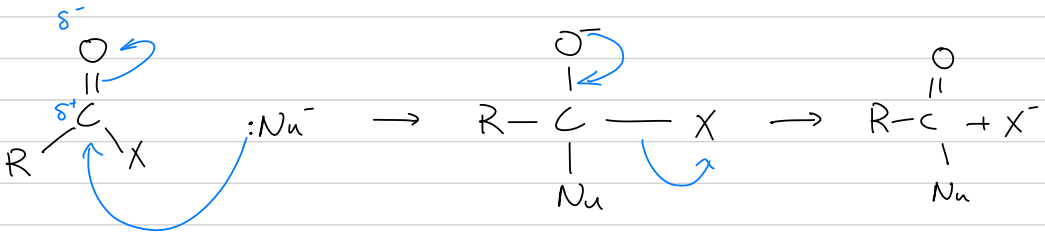
$R-COOH$ (carbox. acid.) + PCl_5 → $R-CO-Cl + POCl_3 + HCl_{(g)}$

$R-COOH$ + PCl_3 → $R-CO-Cl + H_3PO_3$

$R-COOH$ + $SOCl_2$ → $R-CO-Cl + SO_2 + HCl_{(g)}$

acyl chlorides are reactive as O and Cl are partially negative. (Big +ve carbocation)

Nucleophilic condensation



Hydrolysis

cond: r.t.p

$R-CO-Cl$ + H_2O → $R-COOH + HCl_{(g)}$ (acid)

$R-CO-Cl$ + $2NaOH$ → $R-COO^-Na^+ + H_2O + NaCl_{(aq)}$ (alkali)

Amides (Nucleophilic sub)

primary:

$R-CO-Cl + NH_3 \rightarrow R-CO-NH_2 + HCl$

Secondary:

$R-CO-Cl + R'-NH_2 \rightarrow R-CO-NHR' + HCl$

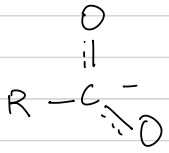
cond: r.t.p reagent: conc. NH_3

Esterification

$R-CO-Cl + HO-R \rightarrow R-CO-OR + HCl$

Reagent: $-OH$ (Normal) at r.t.p or warm alkali phenol

Carboxylic Acids

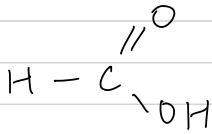


-ve charge reduced: more spread out.

If R donates e^- then less acidic.

Oxidation

Acid + warm oxidising agent $\longrightarrow$ $CO_2 + H_2O$

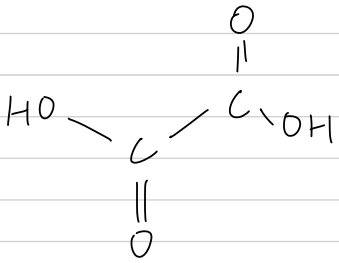


$+ [O] \longrightarrow CO_2 + H_2O$

Cond: Warm

Tollens: Ag^+ reduced to Ag

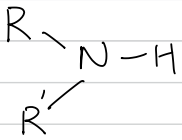
Fehlings: Cu^{2+} reduced to Cu^+ Cu_2O (red)

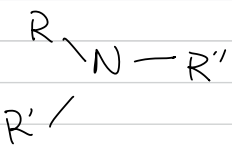


reacts with MnO_4^- / H^+ or $Cr_2O_7^{2-} / H^+$

Nitrogen Compounds

primary: $R-NH_2$

Secondary: 

Tertiary: 

Formation of Alkyl amine

Substitution (nucleophilic)

$$H-X + NH_3 \longrightarrow H-NH_2 + HX_{(g)}$$

Reagent: Hot, conc, alcoholic NH_3
Cond: Heat, reflux

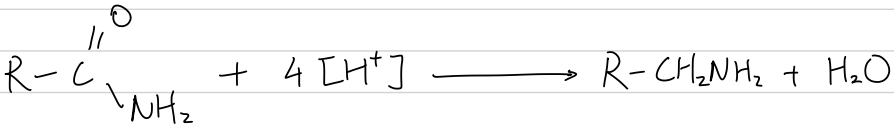
Reduction

Nitriles

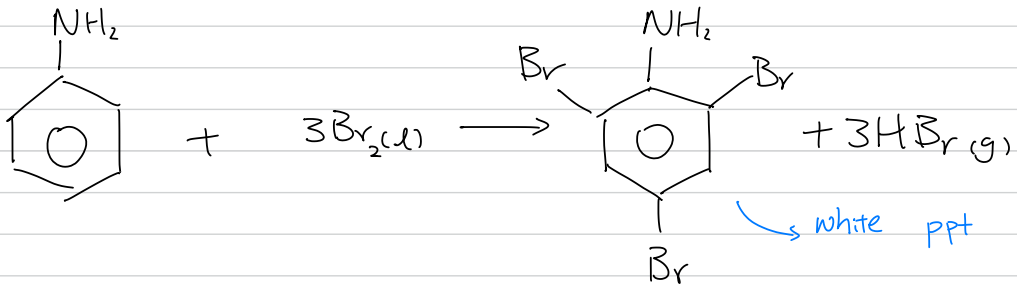
$$R-C\equiv N + 4[H^+] \longrightarrow R-CH_2NH_2$$

Reagent: H_2 (g)
Catalyst: Reduction agents ($LiAlH_4$ in dry ether, Nickel)
Cond: High temp, pressure.

Amide



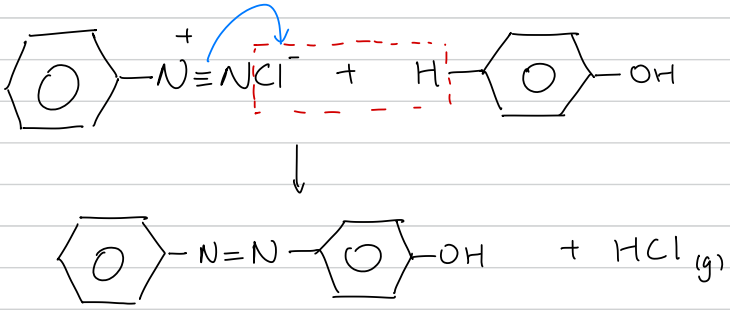
Reagent: H_2 (g)
Catalyst: $LiAlH_4$ in dry ether
cond: r.t.p.



reagent: liquid Br_2
cond: r.t.p

Coupling

electrophilic substitution



Reagent: Aromatic amines / phenols
cond: r.t.p.

Amide Hydrolysis