

REACTIONS OF AROMATICS

ELECTROPHILIC SUBSTITUTION

Aromatic compounds are attacked by electrophiles (lone pair acceptors). This is because the aromatic ring is very electron rich due to the cloud of electrons above and below the ring.

They undergo substitution reactions where H atoms on the ring are replaced. They do not readily undergo addition reactions as they would lose their delocalisation and so extra stability in the process.

ELECTROPHIL	ELECTROPHILIC SUBSTITUTION 1 – nitration			
Reagent	conc HNO ₃ & conc H ₂ SO ₄			
Conditions	50°C			
What happens	H atom on ring is replaced by NO ₂ (nitro) group			
Products	Aromatic nitro compounds which are used • to make aromatic amines (e.g. used further to make azo dyes) • to make explosives (e.g. TNT which is 2,4,6-trinitromethybenzene)			
Overall equation	+ HNO ₃ + H ₂ O			
Mechanism	electrophilic substitution			
	Generation of electrophile = NO_2^+ (nitronium ion) HNO ₃ + $2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$			
	Reaction of electrophile with benzene			
Example 1	e.g. methylbenzene + conc HNO ₃ & conc H ₂ SO ₄ at 50°C to make 2-nitromethylbenzene			
	CH ₃ + HNO ₃ + H ₂ O			
	$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$			
	electrophilic substitution CH ₃ NO ₂ NO ₂ NO ₂			

Example 2

e.g. methylbenzene + conc HNO_3 & conc H_2SO_4 at $50^{\circ}C$ to make 4-nitromethylbenzene

 $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

electrophilic substitution

$$CH_3$$
 $+$
 NO_2
 $-H^+$
 NO_2

Example 2

e.g. 1,3-dimethylbenzene + conc HNO₃ & conc H₂SO₄ at 50°C to make 2-nitro-1,3-dimethylbenzene

$$CH_3$$
 $+$
 HNO_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

 $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

electrophilic substitution

$$CH_3$$
 NO_2
 CH_3
 NO_2
 CH_3
 NO_2
 CH_3
 CH_3
 CH_3
 CH_3

ELECTROPHILIC SUBSTITUTION 2 — Friedel-Crafts acylation				
Reagent	Acyl chloride or acid anhydride & AlCl ₃			
Conditions	Anhydrous (to prevent reaction of AlCl ₃			
What happens	H atom on ring is replaced by RCO (acyl) group			
Products	Aromatic ketones – this reaction is extremely useful for adding C atoms to aromatic rings and any reaction that adds C atoms onto the aromatic ring is very valuable in organic synthesis.			
Overall equation	with an acyl chloride + R—C—CI + HCI			
	with an acid anhydride + R-C-O-C-R + R-C-OH			
Mechanism	electrophilic substitution			
(acyl chloride)	electrophile = RCO ⁺ (acylium ion) Generation of electrophile O R—C—C + A C ₃ R—C ₊ + A C ₄ -			
	Reaction of electrophile with benzene			
	Regeneration of catalyst $AICI_4^- + H^+ \rightarrow AICI_3 + HCI$			
Mechanism	electrophilic substitution			
(acid anhydride)	electrophile = RCO ⁺ (acylium ion) Generation of electrophile $ \begin{array}{cccccccccccccccccccccccccccccccccc$			
	Reaction of electrophile with benzene Reaction of electrophile with benzene			
	Regeneration of catalyst $\begin{bmatrix} O \\ II \\ CI_3AI - O - C - R \end{bmatrix}^- + H^+ \longrightarrow AICI_3 + HO - C - R$			

Example 4	e a methylhon	zene with ethanoic anhydride and AICle to make 2-methylphenylethanone	
LAMINPIE 4	e.g. methylbenzene with ethanoic anhydride and AlCl ₃ to make 2-methylphenylethanone CH ₃ CH ₂ O		
		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
	electrophilic substitution	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	
		$\begin{bmatrix} O & & & & & & & & & & & & & & & & & & $	
Example 5	e.g. methylben.	zene with propanoyl chloride and AlCl ₃ to make H ₃ C CH ₂ -CH ₃	
	H₃C'	+ CH_3-CH_2-C CI CH_2-CH_3 + HCI	
		$CH_3-CH_2-C-CI + AICI_3$	
	electrophilic substitution	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	
		$AICI_4^- + H^+ \rightarrow AICI_3 + HCI$	

Example 6 e.g. nitrobenzene with ethanoyl chloride and AICl₃ to make electrophilic substitution $AICI_4^- + H^+ \rightarrow AICI_3 + HCI$ Example 7 e.g. 1,3-dimethylbenzene with ethanoic anhydride and AICl₃ to make $-CH_3 + AICI_3 \longrightarrow H_3C - C_+$ electrophilic substitution