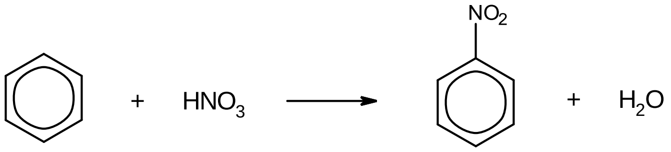
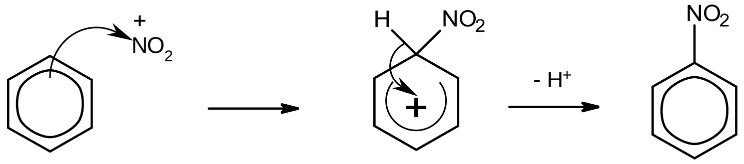
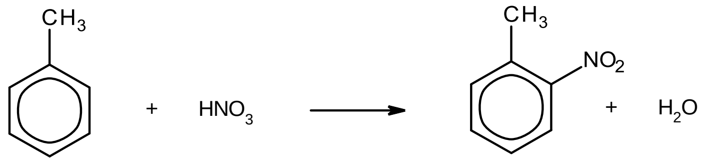
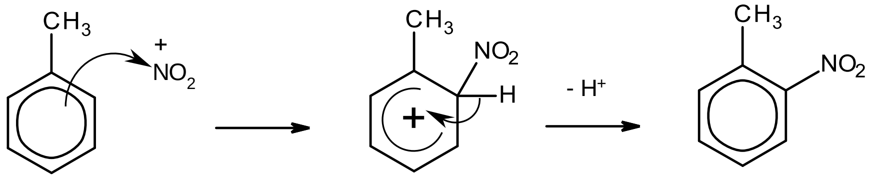
REACTIONS OF AROMATICS

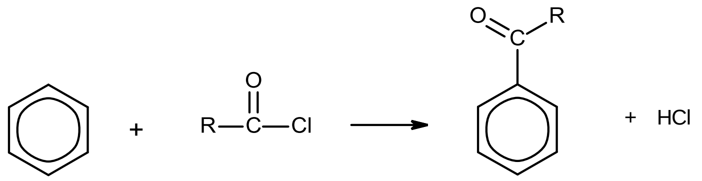
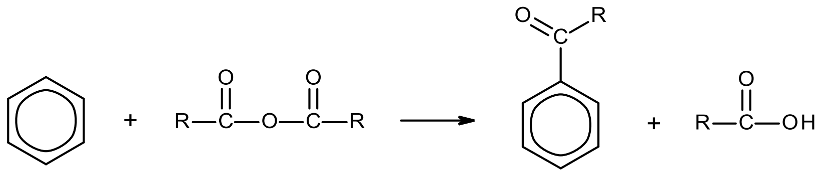
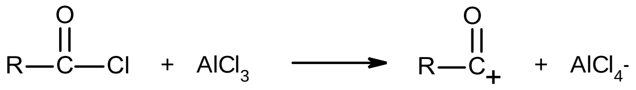
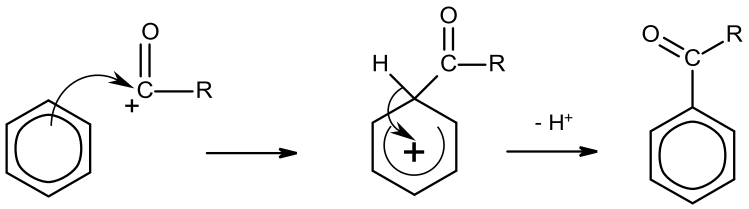
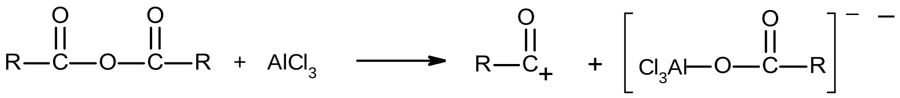
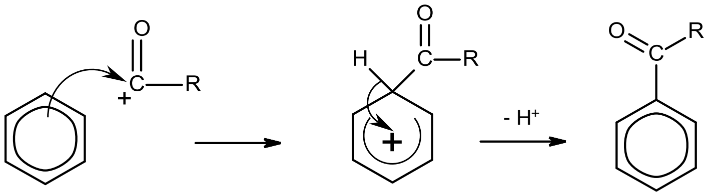
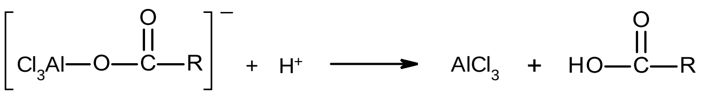
ELECTROPHILIC SUBSTITUTION	Aromatic compounds are attacked by electrophiles (lone pair acceptors). This is because the aromatic ring is very electron rich due to the cloud of electrons above and below the ring. They undergo substitution reactions where H atoms on the ring are replaced. They do not readily undergo addition reactions as they would lose their delocalisation and so extra stability in the process.

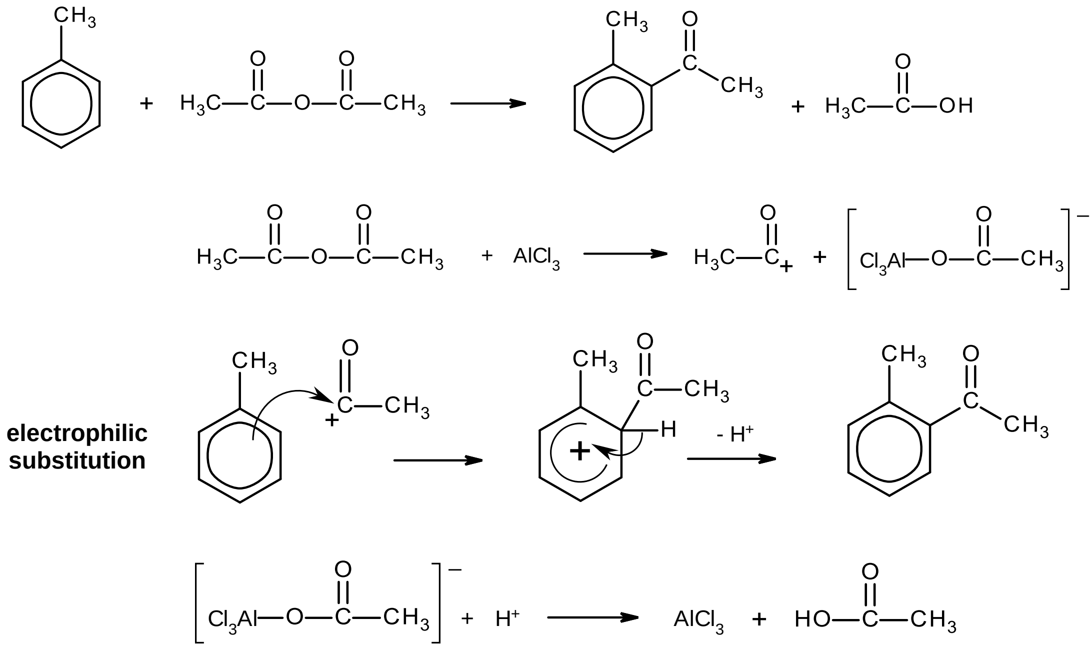
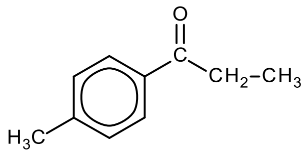
ELECTROPHILIC SUBSTITUTION 1 – nitration

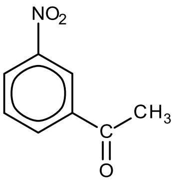
Reagent	conc HNO_3 & conc H_2SO_4
Conditions	50°C
What happens	H atom on ring is replaced by NO_2 (nitro) group
Products	Aromatic nitro compounds which are used • to make aromatic amines (e.g. used further to make azo dyes) • to make explosives (e.g. TNT which is 2,4,6-trinitromethybenzene)
Overall equation	
Mechanism	**electrophilic substitution**
	Generation of electrophile 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_2SO_4 at 50°C to make 2-nitromethylbenzene  $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$ **electrophilic substitution** 

Example 2	e.g. methylbenzene + conc HNO_3 & conc H_2SO_4 at 50°C to make 4-nitromethylbenzene
Example 3	e.g. 1,3-dimethylbenzene + conc HNO_3 & conc H_2SO_4 at 50°C to make 2-nitro-1,3-dimethylbenzene

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  with an acid anhydride 
Mechanism **(acyl chloride)**	**electrophilic substitution**
	electrophile = RCO^+ (acylium ion)
	Generation of electrophile  $R-\overset{O}{\overset{\Vert}{C}}-Cl + AlCl_3 \longrightarrow R-\overset{O}{\overset{\Vert}{C}}_{+} + AlCl_4^{-}$
	Reaction of electrophile with benzene 
	Regeneration of catalyst $AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$
Mechanism **(acid anhydride)**	**electrophilic substitution**
	electrophile = RCO^+ (acylium ion)
	Generation of electrophile  $R-\overset{O}{\overset{\Vert}{C}}-O-\overset{O}{\overset{\Vert}{C}}-R + AlCl_3 \longrightarrow R-\overset{O}{\overset{\Vert}{C}}_{+} + \left[Cl_3Al-O-\overset{O}{\overset{\Vert}{C}}-R\right]^{-}\ -$
	Reaction of electrophile with benzene 
	Regeneration of catalyst  $\left[Cl_3Al-O-\overset{O}{\overset{\Vert}{C}}-R\right]^{-} + H^+ \longrightarrow AlCl_3 + HO-\overset{O}{\overset{\Vert}{C}}-R$

Example 4	e.g. methylbenzene with ethanoic anhydride and $AlCl_3$ to make 2-methylphenylethanone 
Example 5	e.g. methylbenzene with propanoyl chloride and $AlCl_3$ to make 

Example 6	e.g. nitrobenzene with ethanoyl chloride and $AlCl_3$ to make 
Example 7	e.g. 1,3-dimethylbenzene with ethanoic anhydride and $AlCl_3$ to make