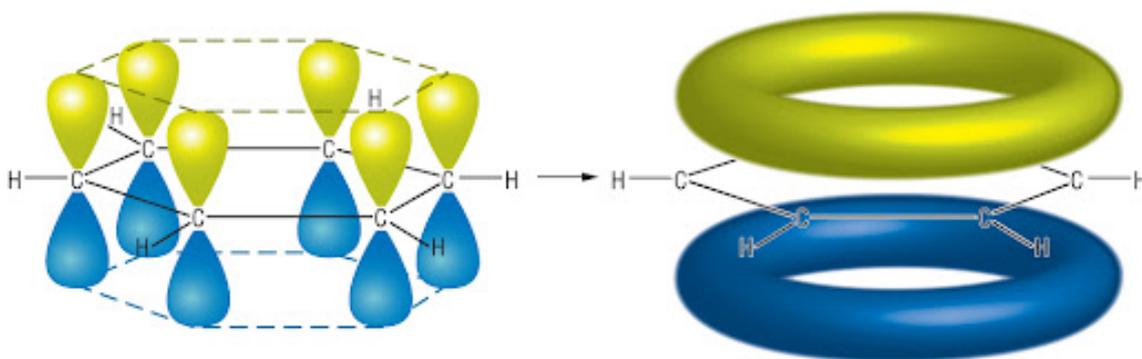


# AROMATIC CHEMISTRY



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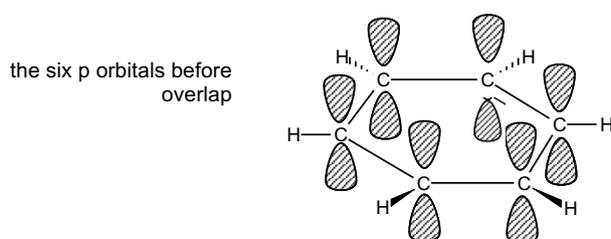


# 1 – The structure of benzene

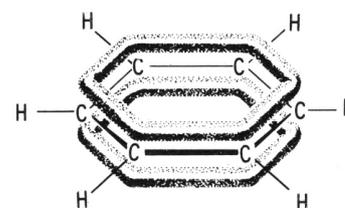
- Benzene has the formula  $C_6H_6$
- Its basic structure is six C atoms in a hexagonal ring, with one H atom bonded to each C atom.
- The molecule is planar.
- Kekulé made a significant breakthrough and was the first chemists to realise that benzene had a ring structure with six carbon atoms each joined to one hydrogen atom.
  - However, he thought incorrectly that the ring contains three C=C double bonds and three C-C single bonds.
  - This molecule would be a "triene" ("cyclohexa-1,3,5-triene") with three C=C double bonds rather than a delocalised ring system.



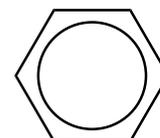
- The six C-C bonds are actually the same length – intermediate between single and double.
- Each C atom is bonded to two other C atoms and one H atom by single covalent  $\sigma$ -bonds.
- This leaves one unused electron on each C atom in a p orbital, perpendicular to the plane of the ring.
- Each p orbital overlaps with the neighbouring p orbitals to form a  $\pi$ -bond.
- The overall result is a ring of negative charge ("electron cloud") above and below the plane of the ring.



the  $\pi$  system formed



- The electrons in the  $\pi$  system do not belong to any particular C atom (or to a bond between two C atoms) – they are free to move throughout the whole  $\pi$  system – i.e. they are **delocalised**.
- As the electrons are delocalised and more spread out, there will be less electron-electron repulsion which makes the molecule more stable.
- Due to this delocalisation, the structure of benzene is represented with a circle in the middle of the structure.
- There are some key pieces of evidence to support the delocalised structure rather than the Kekulé structure.



## 1) C-C bond length

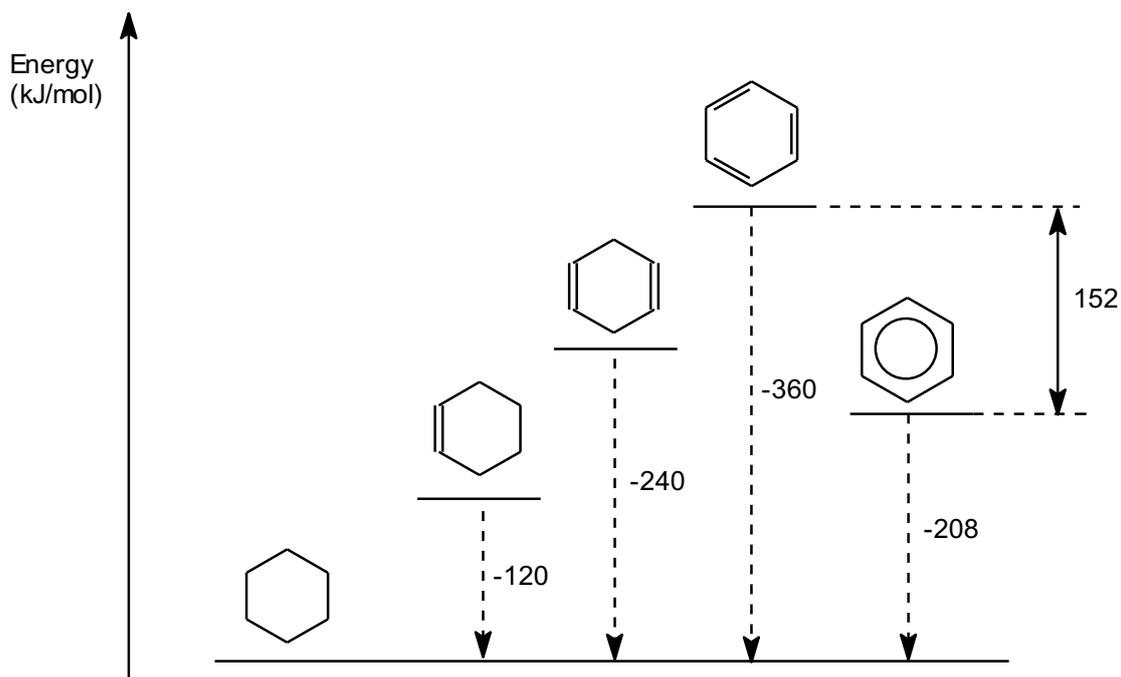
- All the C-C bonds are the same length; and this length is in-between the length of C-C single and C=C double bonds.
- If benzene was a triene we would expect three longer C-C single bonds and three shorter C=C double bonds.

## 2) Addition reactions

- Benzene does not readily undergo addition reactions (e.g. benzene does not decolourise bromine water)
- If benzene was a triene, we would expect it to readily undergo addition reactions such as this – but it doesn't.

### 3) Enthalpy of hydrogenation

- When cyclohexene reacts with  $\text{H}_2$  to make cyclohexane, the enthalpy change is  $-120 \text{ kJ mol}^{-1}$
- When cyclohex-1,3-diene reacts with  $2 \text{ H}_2$  to make cyclohexane, the enthalpy change is  $-240 \text{ kJ mol}^{-1}$
- We might expect a triene to react with  $3 \text{ H}_2$  to make cyclohexane with an enthalpy change of  $-360 \text{ kJ mol}^{-1}$  (i.e.  $3 \times -120 \text{ kJ mol}^{-1}$ )
- However, the enthalpy change is  $-208 \text{ kJ mol}^{-1}$  which is  $152 \text{ kJ mol}^{-1}$  less exothermic than we might expect.
- This means that benzene is  $152 \text{ kJ mol}^{-1}$  more stable than the hypothetical triene molecule.
- This extra stability is due to the delocalisation of electrons and is known as the **delocalisation stability**.

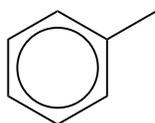


## 2 – Naming aromatic compounds

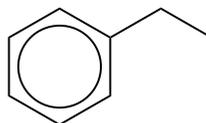
### Mono-substituted derivatives of benzene

Aromatic compounds are named in one of three ways:

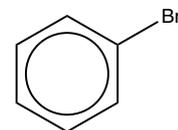
as benzene with substituents on the ring



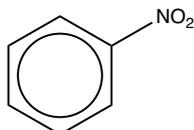
methylbenzene  
(toluene)



ethylbenzene

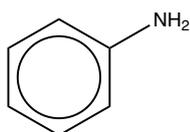


bromobenzene

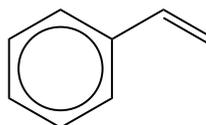


nitrobenzene

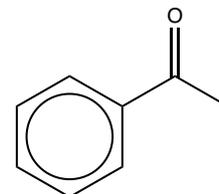
compounds containing a phenyl group (where C<sub>6</sub>H<sub>5</sub> is a phenyl group)



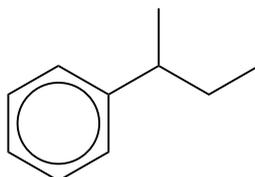
phenylamine



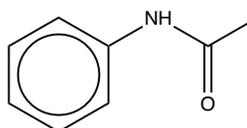
phenylethene



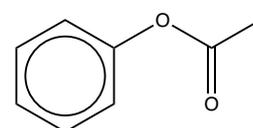
phenylethanone



2-phenylbutane

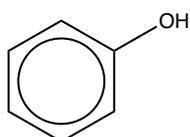


N-phenylethanamide

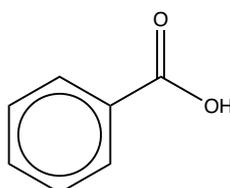


phenyl ethanoate

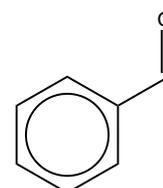
or some have a special name



phenol



benzenecarboxylic acid  
(benzoic acid)

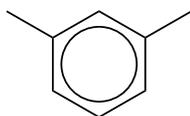


benzenecarbaldehyde  
(benzaldehyde)

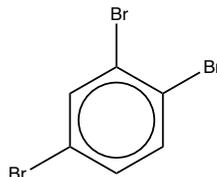
## Derivatives of benzene with more than one substituent

When a benzene ring has more than one group substituted onto it:

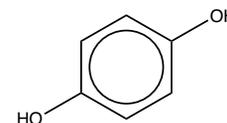
If the groups are all the same, then the position of one of them is taken as C-1 and the ring is counted in the direction to give the substituents the lowest numbers



1,3-dimethylbenzene

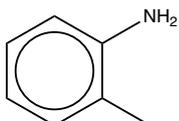


1,2,4-tribromobenzene

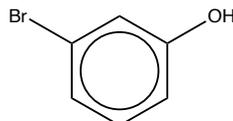


benzene-1,4-diol

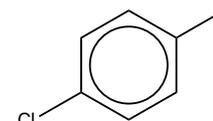
If the groups are different, choose the parent compound (giving the position of this substituent C-1) and then add the substituent(s) to that name counting in the direction to give the substituents the lowest numbers.



2-methylphenylamine

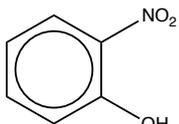


3-bromophenol

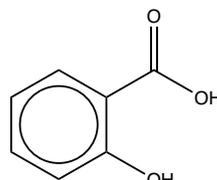


1-chloro-4-methylbenzene

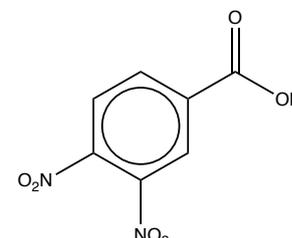
When choosing which group to determine that parent compound, choose the most significant group (there is an order of priorities but you are not expected to know this).



2-nitrophenol

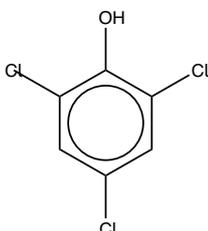


2-hydroxybenzenecarboxylic acid

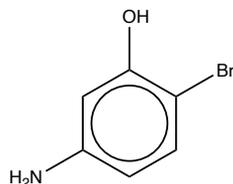


3,4-dinitrobenzenecarboxylic acid

Substituents are listed in alphabetical order.

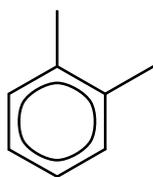


2,4,6-trichlorophenol  
(TCP)

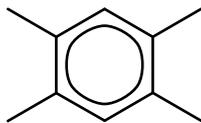


2-bromo-5-aminophenol or  
4-bromo-3-hydroxyphenylamine

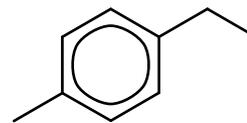
## TASK – Naming aromatic compounds



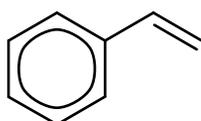
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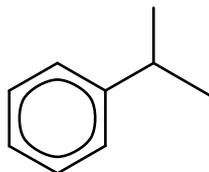
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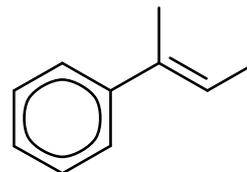
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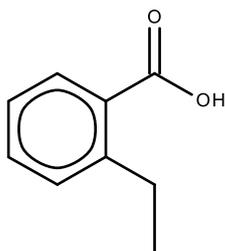
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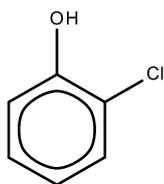
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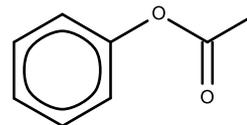
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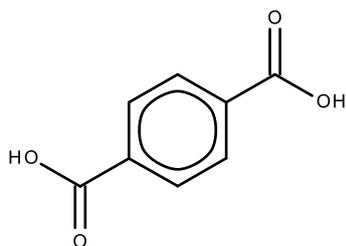
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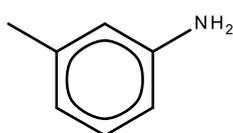
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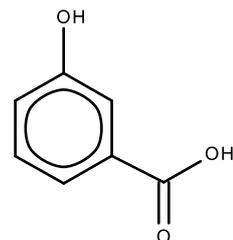
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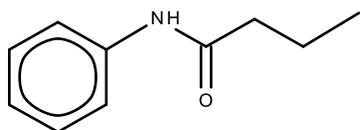
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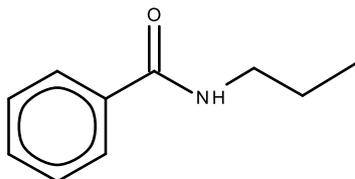
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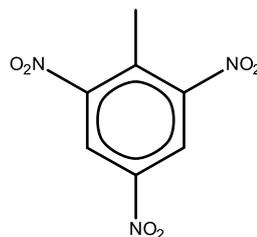
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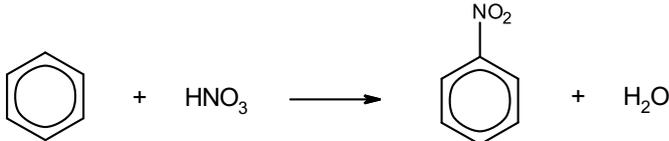
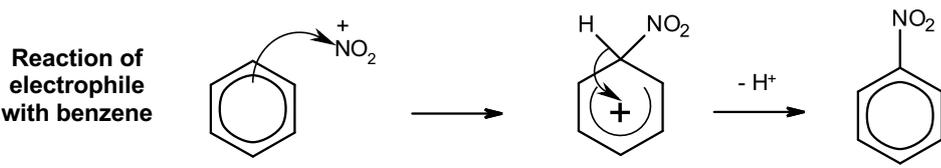
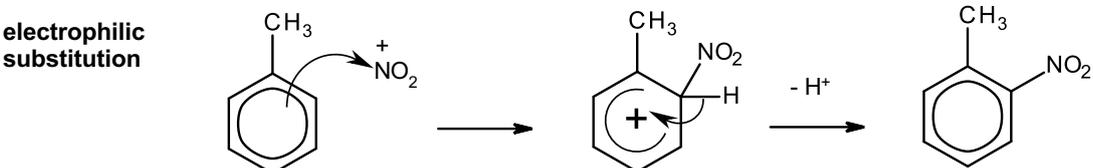
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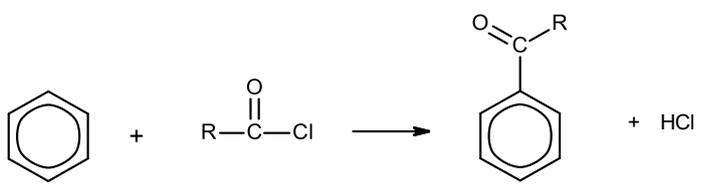
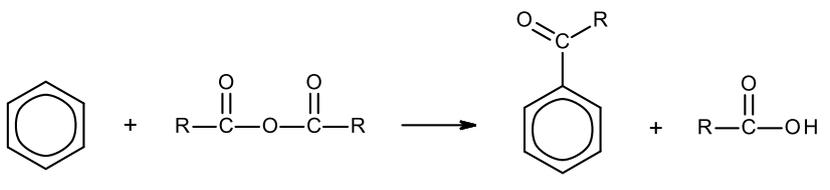
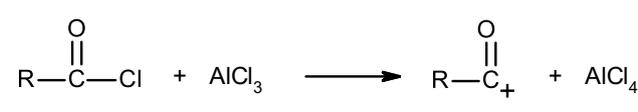
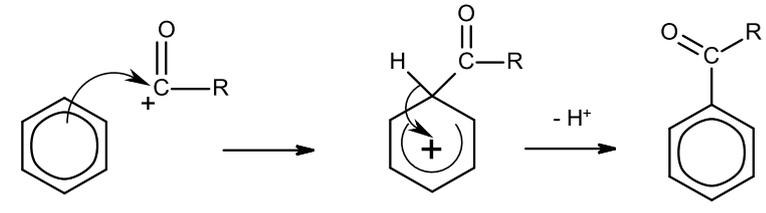
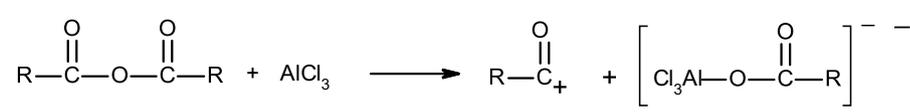
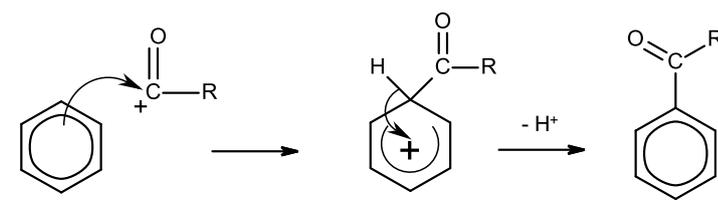
## 3 – Reactions of aromatic compounds

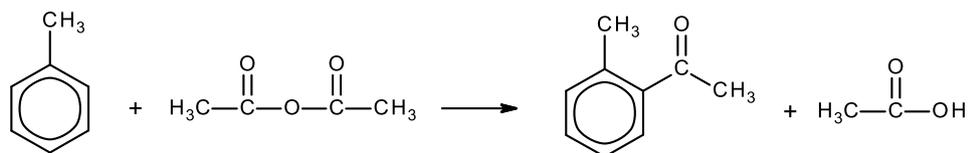
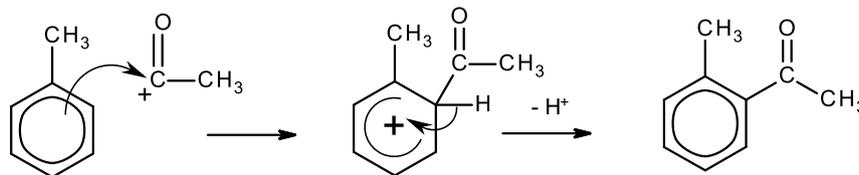
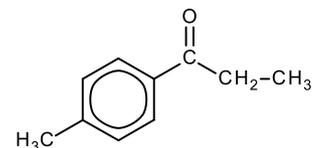
- The benzene ring in aromatic compounds is very electron rich due to the cloud of electrons above and below the ring.
- This means that the benzene ring is attacked by electrophiles (lone pair acceptors).
- Aromatic compounds undergo substitution reactions where H atoms on the ring are replaced.
- Therefore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

ELECTROPHILIC SUBSTITUTION 1 – nitration	
<b>Reagent</b>	conc HNO <sub>3</sub> & conc H <sub>2</sub> SO <sub>4</sub>
<b>Conditions</b>	50°C
<b>What happens</b>	H atom on ring is replaced by NO <sub>2</sub> (nitro) group
<b>Products</b>	Aromatic nitro compounds which are used <ul style="list-style-type: none"> <li>• to make aromatic amines (e.g. used further to make azo dyes)</li> <li>• to make explosives (e.g. TNT which is 2,4,6-trinitromethylbenzene)</li> </ul>
<b>Overall equation</b>	
<b>Mechanism</b>	<p style="text-align: center;"><b>electrophilic substitution</b></p> <p><b>Generation of electrophile</b> electrophile = NO<sub>2</sub><sup>+</sup> (nitronium ion)  <math>\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+</math></p> <p><b>Reaction of electrophile with benzene</b></p> 
<b>Example 1</b>	<p>e.g. methylbenzene + conc HNO<sub>3</sub> &amp; conc H<sub>2</sub>SO<sub>4</sub> at 50°C to make 2-nitromethylbenzene</p>  <p><math>\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+</math></p> <p><b>electrophilic substitution</b></p> 

<b>Example 2</b>	e.g. methylbenzene + conc HNO <sub>3</sub> & conc H <sub>2</sub> SO <sub>4</sub> at 50°C to make 4-nitromethylbenzene
<b>Example 3</b>	e.g. 1,3-dimethylbenzene + conc HNO <sub>3</sub> & conc H <sub>2</sub> SO <sub>4</sub> at 50°C to make 2-nitro-1,3-dimethylbenzene

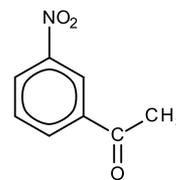
## ELECTROPHILIC SUBSTITUTION 2 – Friedel-Crafts acylation

<b>Reagent</b>	Acyl chloride or acid anhydride & $\text{AlCl}_3$
<b>Conditions</b>	Anhydrous (to prevent reaction of $\text{AlCl}_3$ )
<b>What happens</b>	H atom on ring is replaced by RCO (acyl) group
<b>Products</b>	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.
<b>Overall equation</b>	<p>with an acyl chloride</p>  <p>with an acid anhydride</p> 
<b>Mechanism (acyl chloride)</b>	<p style="text-align: center;"><b>electrophilic substitution</b></p> <p>electrophile = <math>\text{RCO}^+</math> (acylium ion)</p> <p><b>Generation of electrophile</b></p>  <p><b>Reaction of electrophile with benzene</b></p>  <p><b>Regeneration of catalyst</b></p> $\text{AlCl}_4^- + \text{H}^+ \rightarrow \text{AlCl}_3 + \text{HCl}$
<b>Mechanism (acid anhydride)</b>	<p style="text-align: center;"><b>electrophilic substitution</b></p> <p>electrophile = <math>\text{RCO}^+</math> (acylium ion)</p> <p><b>Generation of electrophile</b></p>  <p><b>Reaction of electrophile with benzene</b></p>  <p><b>Regeneration of catalyst</b></p> $\left[ \text{Cl}_3\text{Al}-\text{O}-\text{C}-\text{R} \right]^- + \text{H}^+ \rightarrow \text{AlCl}_3 + \text{HO}-\text{C}-\text{R}$

**Example 4**e.g. methylbenzene with ethanoic anhydride and  $\text{AlCl}_3$  to make 2-methylphenylethanone**electrophilic substitution****Example 5**e.g. methylbenzene with propanoyl chloride and  $\text{AlCl}_3$  to make

**Example 6**

e.g. nitrobenzene with ethanoyl chloride and  $\text{AlCl}_3$  to make

**Example 7**

e.g. 1,3-dimethylbenzene with ethanoic anhydride and  $\text{AlCl}_3$  to make

