Beckfoot

Subject: Chemistry	Topic: Aromatic Chemistry 3.3.10	Year Group: 13

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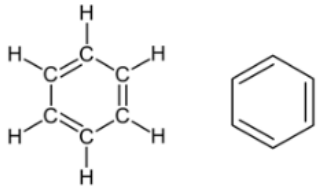
Nomenclature / Naming

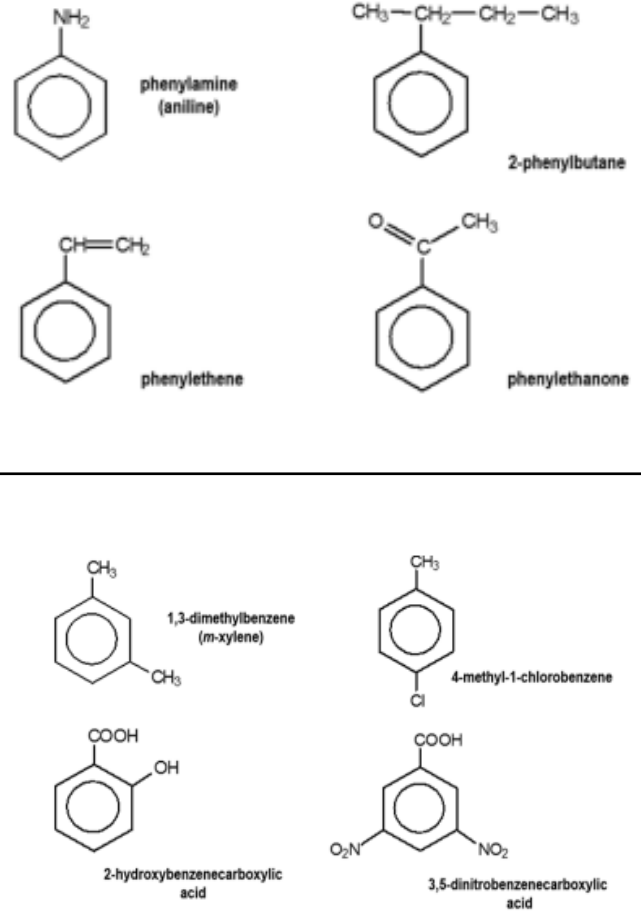
1	We name singly substituted benzene as *prefix* benzene
2	We name doubly substituted benzene using rules, ***i) prefixes listed in alphabetical order, ii) we use smallest numbers possible***
3	Name multiple substituted benzene using same rules and use *di-, tri- prefixes*
4	When naming molecules where benzene is not the focus e.g. higher priority groups / alkyl chain > 6 C long we use *phenyl-* before the main functional group
5	Functional groups, then alkanes are given priority & must have lowest numbers
6	Halogens & nitro groups are not considered functional groups in aromatics

Kekulé's early benzene model

This is a hypothetical compound structure Kekulé came up with, called Cyclohex-1,3,5-triene. However, several pieces of evidence did not match this model. See separate box.



Examples of aromatic compounds & their names



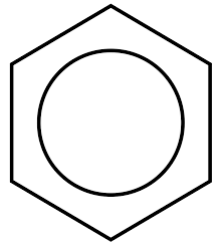
Key Vocabulary

1	Aromatic Compound	A compound which contains a benzene ring
2	Arene	A species containing at least one benzene ring
3	Aryl group	An aromatic group such as C_6H_5-
4	Delocalised	Electrons are free to move from atom to atom e.g. in benzene ring
5	Electrophile	**An electron-deficient species that can accept a lone pair of electrons**
6	Hydrogenation	A reaction in which hydrogen is added to a compound
7	Nitration	A nitro group (NO_2) replaces one of the hydrogen atoms

Accepted current model of benzene

Benzene is often drawn as a hexagon with a ring inside it to denote the ring of delocalised electrons. Benzene is still depicted as Kekulé's structure too but note that there are **no C=C bonds in benzene.**

Benzene is a planar, six carbon cyclical ring with the formula $\mathbf{C_6H_6}$. All six carbon atoms lie in the same plane and it is non-polar due to being a hydrocarbon. Additionally, all carbon to carbon bonds are the same length, intermediate between the length of a single & double bond.



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Evidence **against** Kekulé's model of benzene & **for** the actual structure of benzene

1	His model depicts 3 C=C bonds which are **shorter** than single bonds	This means the benzene molecule would **not** be a symmetrical structure, as single bonds are longer than double bonds. However, ***actual benzene is a symmetrical structure***
2	The **test for alkenes**	*Benzene **does not** decolourise bromine water, if it has 3 C=C bonds, it should readily do so*
3	The **standard enthalpy of hydrogenation** of cyclohexa-1,3,5-triene should **be 3 times** that of cyclohexene	The enthalpy of hydrogenation of cyclohexene is -120 kJ mol^{-1} **so cyclohex-1,3,5-triene should have an enthalpy of 3 x -120 = -360 kJ mol^{-1}**. However, **benzene has an enthalpy of hydrogenation of -208 kJ mol^{-1}**, this is 152 kJ mol^{-1} **less exothermic** than expected and can be attributed to the ***extra stabilty conferred to the molecule due to ring of delocalied electrons.***
4	**Addition versus substitution** reactions	If Kekulé's model of benzene being identical to cyclohexa-1,3,5-triene was correct then it would **undergo electrophilic addition reactions**. However, it does not decolourise bromine water and therefore undergo addition reactions, in fact **actual benzene undergoes electrophilic substitution reactions**.

Why does benzene undergo electrophilic substitution & not addition reactions?

1	Each carbon atom in the benzene ring has one electron not localised in a bond, the p orbitals of each carbon atom overlap to form a ring of delocalised electrons above & below the plane of the molecule.
2	This ring of delocalized electrons makes benzene more stable and would be destroyed if addition reactions ensued. Substitution reactions allow new atoms to be substituted on to the ring with the removal of a H atom, hence the ring of delocalized electrons, & therefore the stability, is maintained.

Key Vocabulary

6	Acylation	The process of replacing a hydrogen atom in certain molecules by an acyl group (RCO-)
7	Enthalpy change, ΔH	The heat energy change in a reaction occurring at constant pressure
8	Catalyst	A substance that alters the rate of a chemical reaction , without itself being changed by the reaction

Reactions of benzene: Electrophilic Substitution

Nitration	Friedel-Crafts Acylation
Electrophile = Nitronium ion, **NO_2^+**	**Electrophile** = Acylium ion, **RCO^+**
Importance = Synthesis of TNT (explosives) & converted to aromatic amines which are used in the **synthesis of azo-dyes**	**Importance** = Organic synthesis as this reaction adds an extra carbon on to the benzene ring. **Used in production of plastics, detergents & petrol**
Reagents = **concentrated HNO_3** & **concentrated H_2SO_4**	**Reagents** = **Acyl chloride** or **acid anhydride**
Conditions = **50°C** to prevent further substitution of nitro group on benzene ring	**Conditions** = Catalyst **$AlCl_3$**

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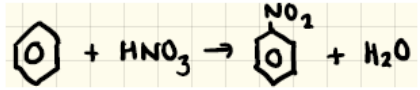
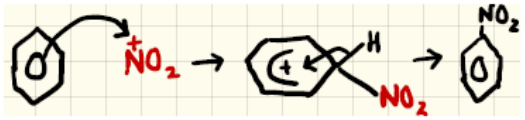
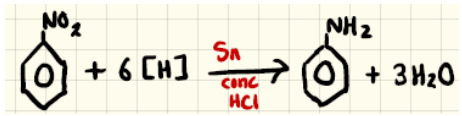
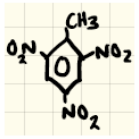
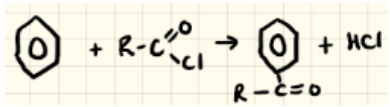
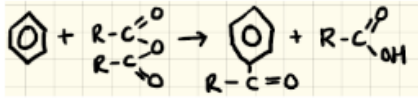
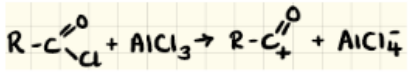
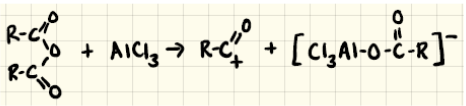
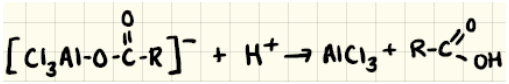
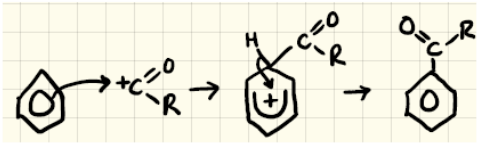
ELECTROPHILIC SUBSTITUTION: Nitration reaction

1	Overall reaction	
2	Equation for generation of electrophile	$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$ *Alternative:* $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$
3	Mechanism	
4	Equation for the reduction of aromatic nitro compounds	
5	Uses – making TNT (trinitrotoluene) or 2-methyl -1,3,5-trinitrobenzene	

ELECTROPHILIC SUBSTITUTION: Friedel-Crafts (FC) Acylation

1	Overall reaction with acyl chloride	 
2	Equation for generation of electrophile	 
3	Equation for regeneration of catalyst	$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$ 
4	Mechanism	
5	WARNING! Do not confuse FC Acylation & other types of acylation	You can recognise FC acylation because the **acyl group attaches directly to the benzene ring** whereas in other types of acylation (i.e. Nucelophilic addition-elimination), **the acyl group replaces a hydrogen atom in a molecule** such as water, alcohol, ammonia or a primary amine