Chem Factsheet

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Activating And Deactivating Groups

This **Chemistry Factsheet:**

- Explains the structure of benzene as an example of an arene.
- Discusses the effect of activating and deactivating groups on arenes.
- Shows the differences between 2-, 4- and 6- directing and 3- and 5-directing groups.
- Defines Wheland intermediates.
- Gives examples of examination questions based on activating and deactivating groups.

The Structure of Benzene

Primary analysis revealed that the compound benzene has:

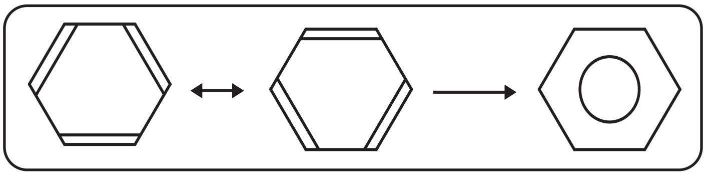
- an empirical formula of CH.
- a molecular mass of 78.
- a molecular formula of C_6H_6.

In 1865, the German chemist August Kekulé suggested that benzene was planar, cyclic and had alternating double and single bonds. However there was evidence that did not fit Kekule's theory:

- Benzene does not readily undergo electrophilic addition so does not contain true C=C bonds.
- All the six C-C bonds are the same length.
- The ring is more thermodynamically stable than the Kekulé structure suggests.

To explain these points, it was suggested that the structure of benzene oscillated between two Kekulé structures, but was not truly represented by either. The structure could be either cyclohexa-1,3,5-triene or cyclohexa-2,4,6-triene. The actual structure is a hybrid of these two theoretical resonance structures. This is called a **resonance hybrid structure**, see **Figure 1**. Six p-orbital electrons overlap above and below the plane of the benzene ring forming two delocalised rings of electrons. This is called a **π-ring system**.

Figure 1 Resonance structures for benzene



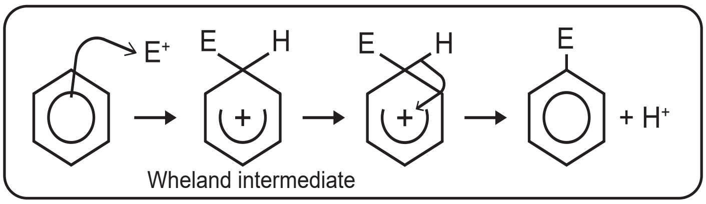
Electrophilic Substitution in Benzene Using The Wheland Model

The main type of reaction aromatic compounds undergo are electrophilic substitution reactions. The hydrogen on a carbon is substituted with an electrophile. The reaction occurs in two steps:

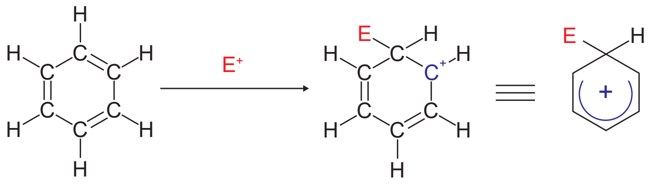
- The reaction between the delocalised π-ring of electrons and the electrophile (represented below as E^+) and an intermediate carbonium ion (also called a carbocation or carbenium ion).
- Loss of the leaving group (H^+).

The intermediate carbonium ion formed is called a **Wheland intermediate**, see **Figure 2**. It has a carbon atom with four bonds and has a positive charge which is shown as being delocalised over three carbons. The π-ring system, which was originally delocalised around the ring, has been disrupted. The ring has lost its **aromaticity** because the π-ring system now only contains 5 electrons.

Figure 2 Mechanism for electrophilic substitution in benzene



Exam Hint: *Mark schemes expect students to show the positive charge delocalised over 3 carbon atoms across the π-system, that is, within the depicted horse-shoe-shape:*



Typical electrophiles are NO_2^+, Hal^+, SO_3 and alkyl groups (R^+) via Friedel Craft's.

In an unsubstituted benzene ring, all carbons are the same. Once a substitution has occurred, the carbons are no longer all the same. This means that further substitutions go onto different carbons in the ring depending on whether the primary group is electron withdrawing or electron donating. These both affect the density of the delocalised ring system.

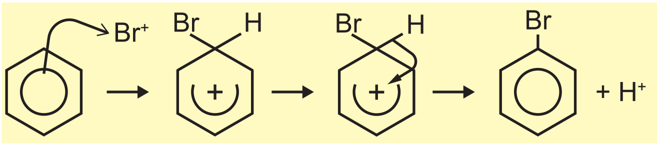
Exercise 1

Outline the mechanism for the formation of bromobenzene in the presence of the catalyst, $FeBr_3$. Show how $FeBr_3$ acts as a catalyst.

Electrophilic substitution.

Formation of Br^+: $FeBr_3 + Br_2 \rightarrow FeBr_4^- + Br^+$

Mechanism:



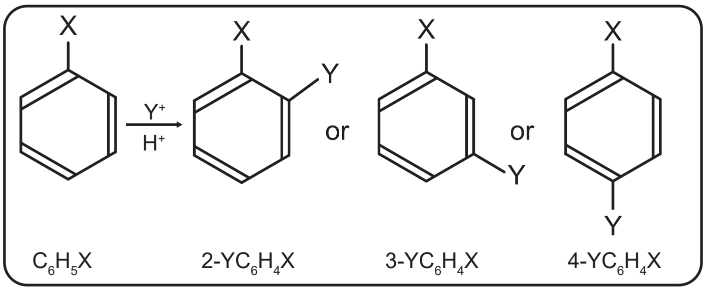
Regenerating $FeBr_3$ *catalyst:*

$FeBr_4^- + H+ \rightarrow FeBr_3 + HBr$

The Directing Positions

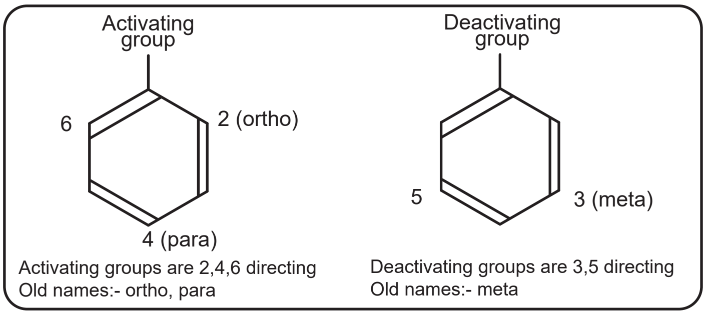
All the carbons atoms are equal in benzene so when one electrophile, X^+, substitutes for the H^+ on the ring, only one product is produced. However, a second substitution (Y^+) could occur at one of three different positions, see **Figure 3a**.

Figure 3a Directing positions (structures)



Once a group has been added to the benzene ring, a second substitution will be directed to a particular position depending on if the first group is electron withdrawing or electron donating, see **Figure 3b**.

Figure 3b Directing positions (notation)



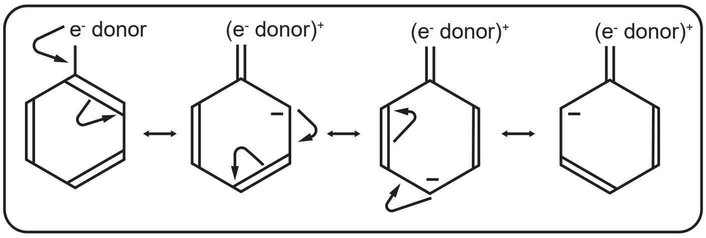
Activating and Deactivating Groups

Strongly **activating groups** are groups with an available lone pair of electrons on the atom (such as an oxygen or nitrogen) attached to the ring. This means they can **donate electrons** into the delocalised π-ring system of the benzene, see **Figure 4**.

The resulting resonant structures have electron-rich areas at the 2-, 4-, 6- positions (ortho- & para-) which attract electrophiles more strongly than at the 3- (or 5-) position (meta-). This means that incoming groups are directed to the 2-, 4- or 6- position. Mixtures of isomers occur and the ratio of 2- to 4- isomers varies with the groups involved.

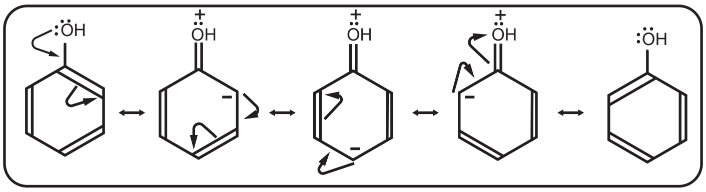
Further substitutions also occur at these positions.

Figure 4 Electron donating/releasing



For example, in phenol where the lone-pair on the hydroxy group overlaps the delocalised π-ring system, increasing the electron charge density, see **Figure 5**.

Figure 5 Substitution on phenol



Alkyl and phenyl groups are weakly activating due to the release of electrons towards the π-ring system. **Table 1** provides a list of common activating groups. These groups also make further substitution easier. For instance, to add a nitro ($-NO_2$) onto a benzene ring it is necessary to use sulfuric acid as a catalyst, but when adding the same group onto methylbenzene, the catalyst is not needed.

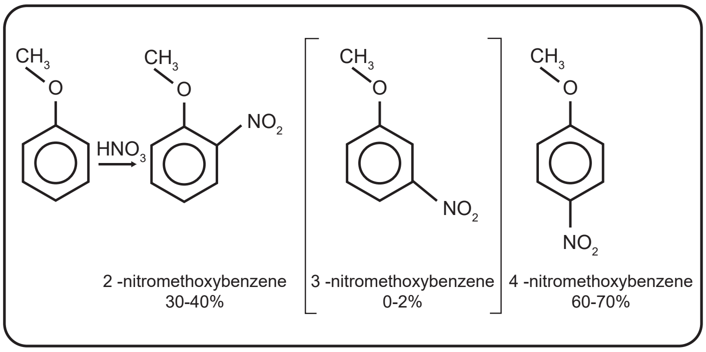
Table 1 Activating groups

Magnitude of activation	Name	Structure
Strong	Alkoxide	-O-
	Amines	$-NH_2$, -NHR
	Hydroxy	-OH
Moderate	Alkoxy	-OR
	Ester	-OCOR
	Amide	-NHCOR
Weak	Alky	$-CH_3$, $-CH_2CH_3$
	Phenyl	$-C_6H_5$
	Alkene	$-CH{=}CH_2$

When the substitution onto a benzene ring containing an activating group takes place, the **percentages of products** vary. For example, the addition of a nitro group onto methoxybenzene.

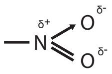
- The 3- position carbonium intermediate is much less stable than the 2- or 4- intermediates so far fewer substitutions occur at the 3- position.
- The 4- position is favoured (60-70%) and not the 2- position (30-40%) although there are twice as many opportunities for two substitutions. This is due to **steric hinderance**. Attack at the 4- position is more open than the 2- position.

Figure 6 Substitution of nitro group onto methoxybenzene



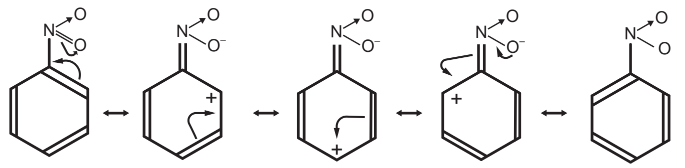
Deactivating groups withdraw electrons from the delocalised π-ring system and will **deactivate** the ring, making secondary substitutions more difficult. They will direct secondary substitutions to the 3- position (meta- directing). Groups that do this have an atom attached to the benzene ring which has a positive charge or partial positive charge. This can be due to the atom being attached to electronegative atoms. The nitro group -NO_2 is an example. The two electronegative oxygen atoms withdraw electrons leaving the nitrogen with a slight positive charge, see **Figure 7**. It is not possible for the lone pairs on the oxygens to overlap into the delocalised π-ring system.

Figure 7 Nitro- group



This would produce the following resonance structures below, see **Figure 8**. Notice that the result is positive charges at the 2-, 4- & 6- positions. This means that the 3- position would be electron-rich and hence more susceptible to attack by electrophiles.

Figure 8 Electron withdrawing



The degree of deactivation varies; **Table 2** lists common deactivating groups.

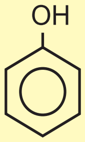
Table 2 Deactivating groups

Magnitude of deactivation	Name	Structure
Strong	Nitro	-NO_2
	Nitrile	-CN
	Trihalomethyl	-CX_3
Moderate	Carboxyl	-COOH
	Ester	-COOR
	Aldehyde	-CHO
	Ketone	-COR
Weak	Halogen	-Hal

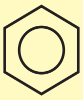
Note that when oxygen is attached directly to the ring (via a single bond, as in –OH), it acts as an activating group since it donates electrons to the delocalised π-ring system. However, when oxygen is indirectly attached to the delocalised π-ring system (e.g. via a carbon atom, as in –C=O or –COOH), overlap of the p-orbital is not possible and its greater electronegativity withdraws electrons from the π-ring system.

Exercise 2

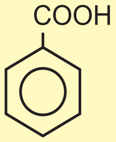
A student investigates the relative ease of nitration of phenol, benzene, and benzoic acid.



phenol



benzene



benzoic acid

They observe that the conditions required for the nitration of each compound are different:

Compound	*Phenol*	*Benzene*	*Benzoic Acid*
Nitric acid	*Dilute HNO_3*	*Concentrated HNO_3*	*Concentrated HNO_3*
Temperature (°C)	*20*	*55*	*100*
Catalyst	*No catalyst*	*H_2SO_4 catalyst*	*H_2SO_4 catalyst*

a) State the trend in the relative ease of nitration of phenol, benzene, and benzoic acid.
Phenol is the most easily nitrated and benzoic acid the hardest.

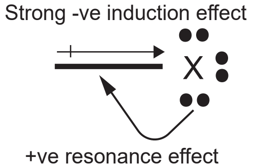
b) Apply your knowledge of the bonding in arenes to explain the trend.
A lone pair of electrons on the ‘O’ of the –OH in phenol are delocalised/donated into the π-ring system. The electron density is higher and therefore the ring is more easily attacked.

In benzoic acid, the –COOH group is electron withdrawing. This lowers the electron density in the π-system making it less susceptible to attack.

The halogens can donate lone-pairs to the π-ring system, which suggests they will activate the ring facilitating electrophilic attack. However due to the halogens electronegativity, they are electron withdrawing, thus **deactivating the ring**.

During substitution reactions, the intermediate carbocation has a resonance form adjacent to the ortho- and para- positions, but not the meta- position. This promotes **substitution at the ortho- and para- positions**.

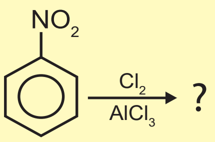
Figure 9 Directing groups – The halogens

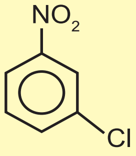


Chem Factsheets, 2021/22 Series, Issue 3 of 3, April 2022. **ISSN: 1351-5136**

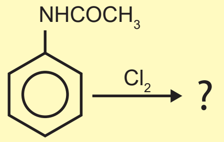
Exercise 3

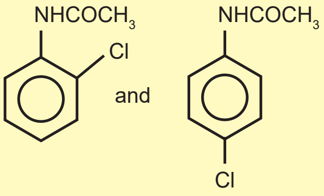
Draw all of the organic products from mono-substitution reactions of the substituted benzene compounds shown below.





The nitro group is deactivating so will direct the incoming Cl to the 3- position.



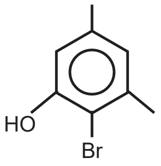


The amide group is activating and hence 2-, 4-, 6- directing.
There will be two mono-substituted products.
Note that the $AlCl_3$ catalyst is not needed in this reaction.

Questions

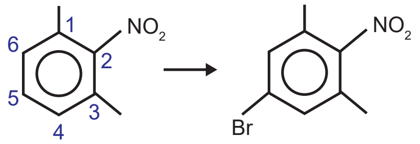
1) How many electrons make up the broken ring structure in the Wheland intermediate?

2) a) A student attempted to perform a reaction to form compound A from 3,5-dimethylphenol using Br_2 with $FeBr_3$ as a catalyst. Explain why this is likely to be a minor product and suggest the identity of the major product.



Compound A

b) The student then carried out the following reaction; again using Br_2 with $FeBr_3$ as a catalyst. Explain why this reaction will yield a different major product to that show below.



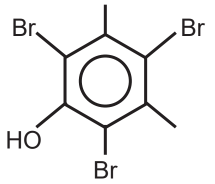
Note: IUPAC recommendations for naming substituted aromatic compounds list substituted groups in alphabetical order and the '1' position is assigned to the first group.

3) How can you make 2-nitrotoluene (2-nitromethylbenzene) from benzene?

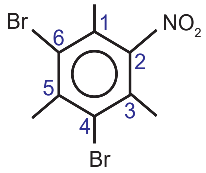
Answers

1) 5 electrons.

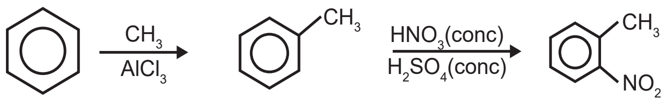
2) a) Lone pair from the oxygen is delocalised/donated into the ring, increasing electron density in the ring system and increasing susceptibility of electrophilic attack. Major product is 2,4,6-tribromo-3,5-dimethylphenol.



b) Alkyl groups are ortho- and para- directing; the nitro- group meta- directing, increasing the likelihood of substitution at the 4- and 6- positions.



3) The first step requires substituting the methyl group, as this is ortho- and para- directing. Thus ensuring the subsequent substitution of the nitro- group is on the 2- position.



Note that switching the synthesis steps will result in the substituted nitro- group directing the substitution of the methyl group on the 3- position, i.e. the major product would be 3-nitromethylbenzene.

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