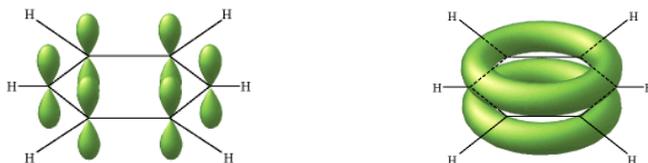


[A Second Year blog on Benzene, C₆H₆, Part 1: 15th December 2018](#)

(This is a revision blog. It is merely a summary of the things that you need to know about Benzene.)

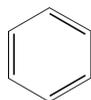
Benzene, C₆H₆, is a ring molecule surrounded by an area of high electron density above and below it.



The area of high electron density is a result of the overlap of unhybridised ‘p’ orbitals (shown in the diagram on the left above) on each of the C atoms in Benzene. This overlap causes the electron in each of the ‘p’ orbitals to become delocalised and they thus wander around freely all over the ring (both above and below the molecule).

The area of high electron density above and below the plane that contains the six C atoms repels any species that is negatively charged (“-”) or has a partial “ δ^- ” separation of charge or which possess a lone pair/an unbonded pair of electrons. In other words Benzene molecules repel nucleophiles and attract electrophilic species i.e. any species that has a positive charge (“+”) or has a partial “ δ^+ ” separation of charge or a completely empty orbital in which a lone pair of electrons can be deposited.

Even though it is not correct, the Benzene molecule is often drawn as in the depiction on the left below. The depiction on the right correctly highlights the fact that in reality there are no double or single bonds as in the (resonance) ring structure depiction of the molecule, but that C₆H₆ has a delocalised ring structure.



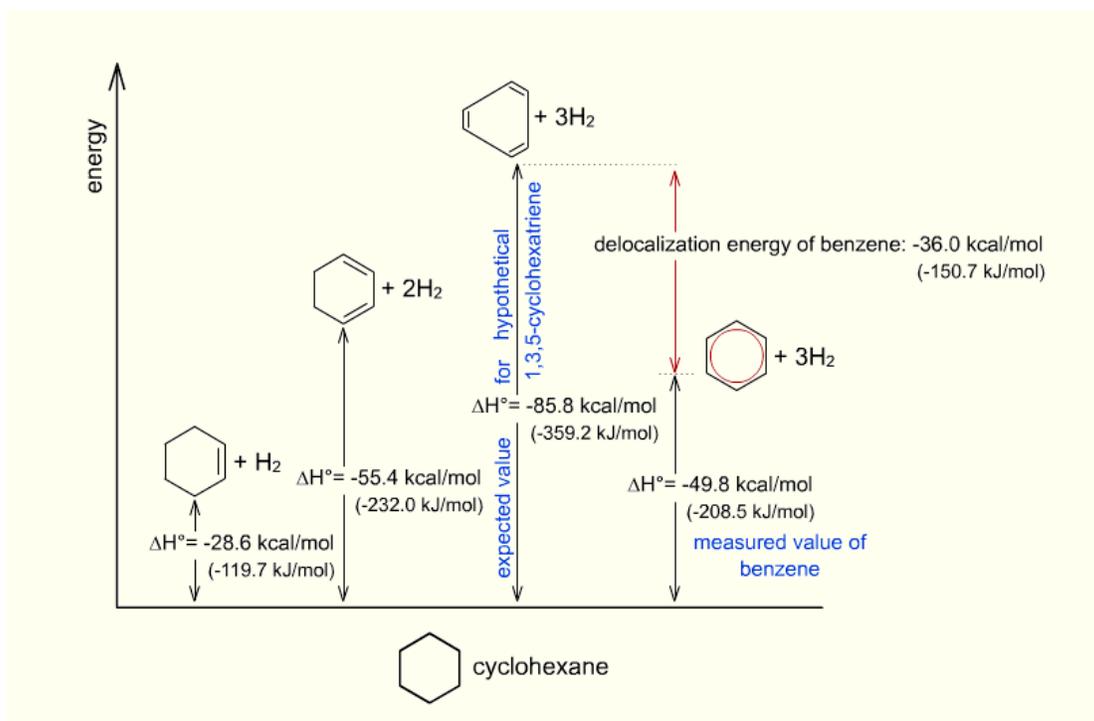
A ‘resonance’ depiction, but a convenient one for conveying the conjugated nature of the molecule (i.e. the alternating double and single bond structure that characterises a conjugated species).



The technically more ‘correct’ depiction.

Delocalisation confers an amount of stability on a molecule that it would not normally have, and thus Benzene is more thermodynamically stable than it would be if it had an alternating double and single bond structure (i.e. the structure on the left above), and this would require more energy to break the structure of the molecule than if it had three double bonds and three single bonds in it. We can confirm this by noting that where an alkene will decolourise bromine water instantaneously, even in the dark, and even in temperatures below 0°C (and this means that the mechanism cannot be that of *free radical substitution* as in an alkane), in contrast, Benzene will **not** decolourise bromine water at RTP. The examiners have tested examinees on this point in the past, so please be aware of it and please be ready to offer the explanation “the delocalisation of the π ring in Benzene confers thermodynamic stability on it”.

The amount of stability conferred is of the order of **151 kJ mol⁻¹** and this is shown in the next diagram.

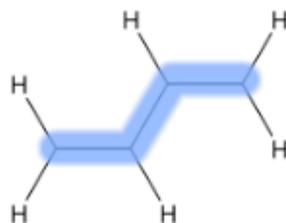


Source :

http://www.chemgapedia.de/vsengine/vlu/vsc/en/ch/12/oc/vlu_organik/aromaten/aromaten/benzol_stabilitaet.vlu/Page/vsc/en/ch/12/oc/aromaten/aromaten/stabilitaet/stabilitaet.vscml.html

Were Benzene to have three double bonds in it as in Kekulé's conjugated structure, then in transforming Benzene (C_6H_6) into Cyclohexane (C_6H_{12}) (3×119.7) kJ mol^{-1} of energy would be released i.e. $\Delta H = -359.2 \text{ kJ mol}^{-1}$, but by experimentation we have found that $\Delta H = -208.5 \text{ kJ mol}^{-1}$ in other words Benzene is $105.7 \text{ kJ mol}^{-1}$ more stable than it would be had it been a conjugated species.

A question on this matter has been asked at least once in previous 'A' Level exams. Make sure that you understand the point, which is actually a fairly simple point to understand; **delocalisation of the π ring confers thermodynamic stability on Benzene**. The same would be true for Butadiene, and one day the examiners might chose to test your understanding of delocalisation by asking you a question about Butadiene.

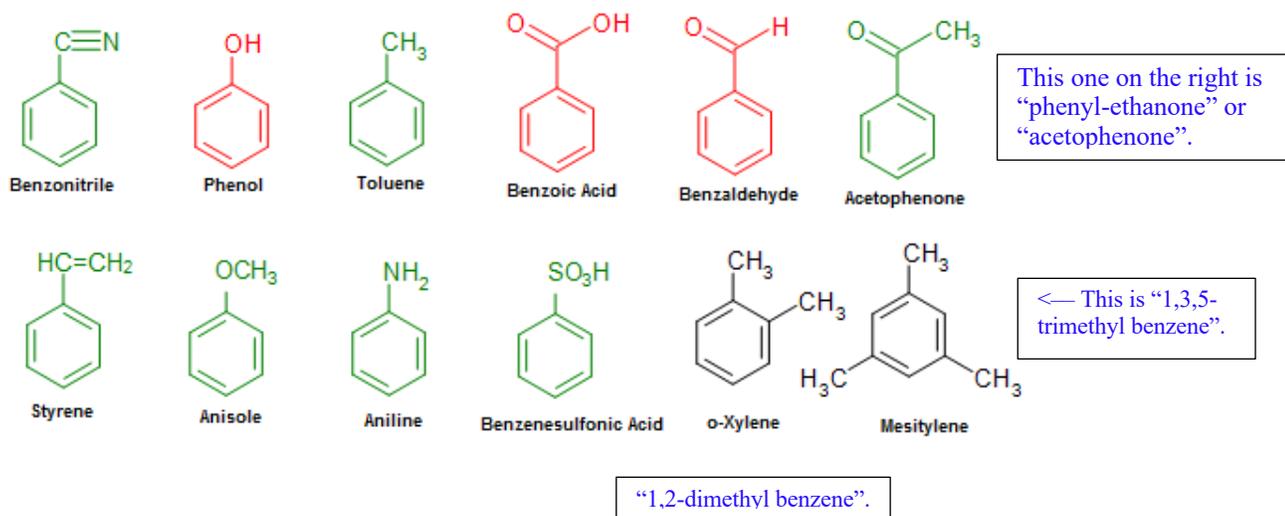


NB An Alkene will, but Benzene will NOT decolourise bromine water in the cold and in the dark.

Benzene requires something called a Friedel-Crafts' (F-C) catalyst for it to do so.

The website “LibreTexts” is an outstanding Chemistry website, and I cannot recommend it to you highly enough. The diagram below is taken from it and shows some of the derivatives of Benzene.

[https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry_Textbook_Maps/Map%3A_Organic_Chemistry_\(Smith\)/Chapter_17%3A_Benzene_and_Aromatic_Compounds/17.03_Nomenclature_of_Benzene_Derivatives](https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry_Textbook_Maps/Map%3A_Organic_Chemistry_(Smith)/Chapter_17%3A_Benzene_and_Aromatic_Compounds/17.03_Nomenclature_of_Benzene_Derivatives)

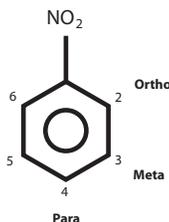


The derivatives of Benzene that you need to know for UK ‘A’ Level Chemistry are

- | | |
|---|----------------|
| - Benzaldehyde | $C_6H_5.CHO$ |
| - Benzoic acid (Benzenecarboxylic acid) | $C_6H_5.COOH$ |
| - Benzenesulphonic acid (also called benzene mono-sulphonic acid) | $C_6H_5.HSO_3$ |
| - Benzonitrile (sometimes referred to as cyanobenzene) | $C_6H_5.CN$ |
| - Chlorobenzene | $C_6H_5.Cl$ |
| - Methylbenzene (also known as Toluene) | $C_6H_5.CH_3$ |
| - Nitrobenzene | $C_6H_5.NO_2$ |
| - Phenol | $C_6H_5.OH$ |
| - Phenylamine/Aniline/Aminobenzene | $C_6H_5.NH_2$ |

The use of Ortho (2)/Meta (3)/Para (4) in the naming of Benzene-derived substances.

In the diagram below I have chosen Nitrobenzene as my compound to illustrate OMP.

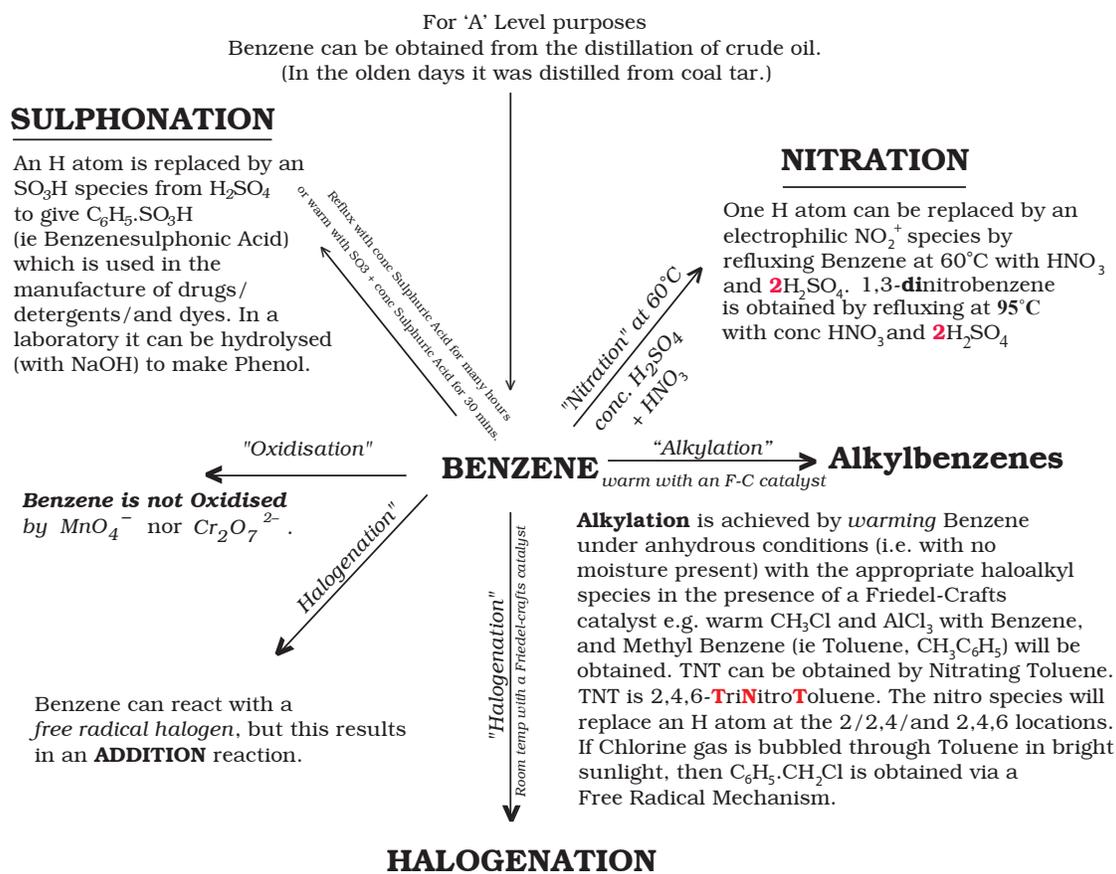


When looking from behind the molecule “1,2,3,4,5,6” becomes “1,6,5,4,3,2”, but there is no such thing as “front” and “behind” in space because there is no reference point from which to start measuring. Today the OMP system of naming is used more by American chemists than European chemists, and in the naming of medicinal drugs than it is in Chemistry itself.

Before talking about the reactions of Benzene, let me give you an information tree for the main reactions of Benzene. I would urge you most strongly to commit it to memory. Having this information in your head will serve you *immensely* well in the exams.

Both Alkylation and Acylation must be carried out under anhydrous conditions.

The SUBSTITUTION reactions of Benzene

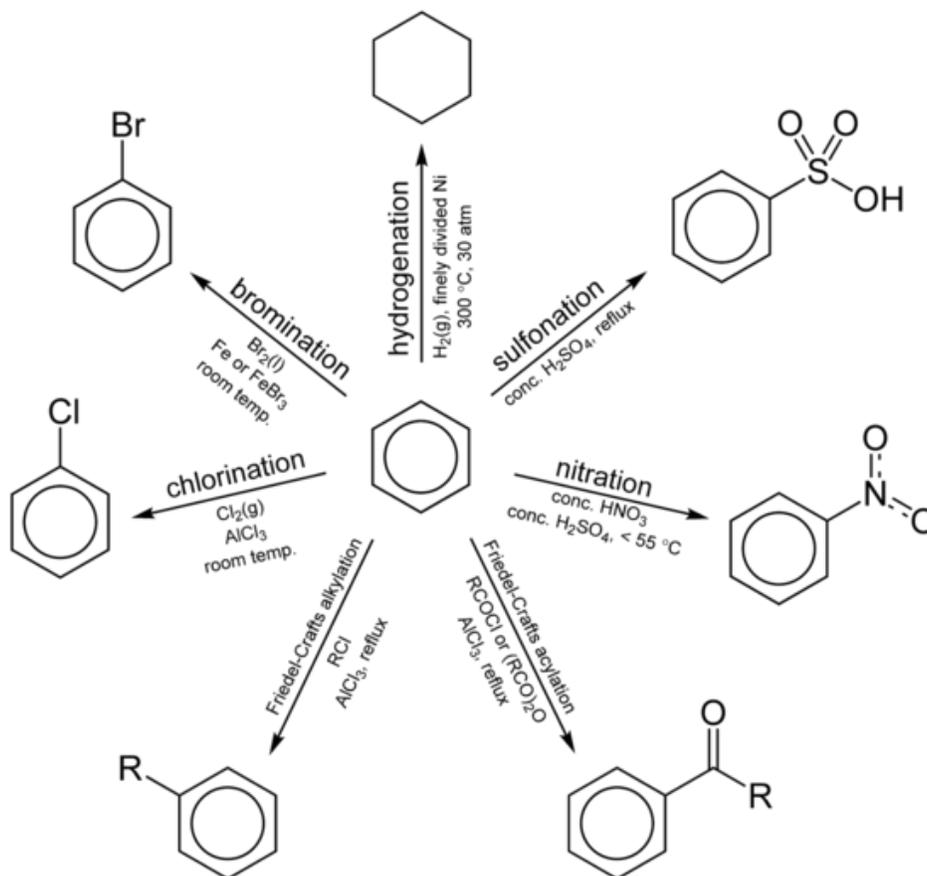


ADDITION REACTIONS

- Benzene will react with **Hydrogen** gas at 150°C in the presence of finely powdered Nickel to give C_6H_{12} .
- Benzene will react with a **Halogen** gas via a Free Radical Mechanism to give for example 1,2,3,4,5,6-hexachlorocyclohexane (with an H and a Halogen at each of the six apices).

NB Benzene is not oxidised by Potassium Permanganate nor by Potassium Dichromate, but the $-\text{CH}_3$ group in *Toluene* will be oxidised by an alkaline manganate ion to give Benzoic Acid ($\text{C}_6\text{H}_5\text{COOH}$).

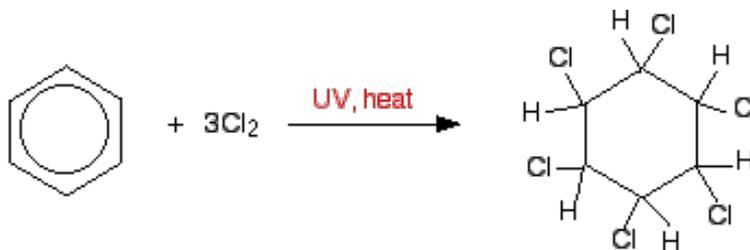
This is how Wikipedia portrays the same reactions.



Source : [http://en.wikibooks.org/wiki/A-level_Chemistry/OCR_\(Salters\)/Reactions_of_arenes](http://en.wikibooks.org/wiki/A-level_Chemistry/OCR_(Salters)/Reactions_of_arenes)

Both info trees talk about the halogenation of Benzene, and the little diagram below shows you how to create C₆H₆Cl₆. (Bubble Chlorine gas through boiling Benzene in bright sunlight, but **not** in a school lab!) The name for C₆H₆Cl₆ is **1,2,3,4,5,6-hexachlorocyclohexane**. The molecule does not have a delocalised π ring.

Please remember that delocalisation confers stability on the Benzene ring therefore where an Alkene would react readily with Bromine or Chlorine at RTP, you need to *boil* the Benzene to get it to react with the Halogen.



Benzene is surrounded by/protected by a huge area of electron density above and below the plane that contains the six C atoms. It therefore is most unlikely to undergo nucleophilic attack, but it will react with electrophilic species – and these reactions are called “**Electrophilic Aromatic Substitution, EAS,**” **reactions**. Let us look at a simplified mechanism of the EAS reaction of Benzene – and please draw the four steps in this mechanism for yourself again and again *until you can do it in your sleep*.

Halogenation, Alkylation and Acylation (all three of them require an F-C catalyst)

(I will discuss F-C catalysts very soon.)

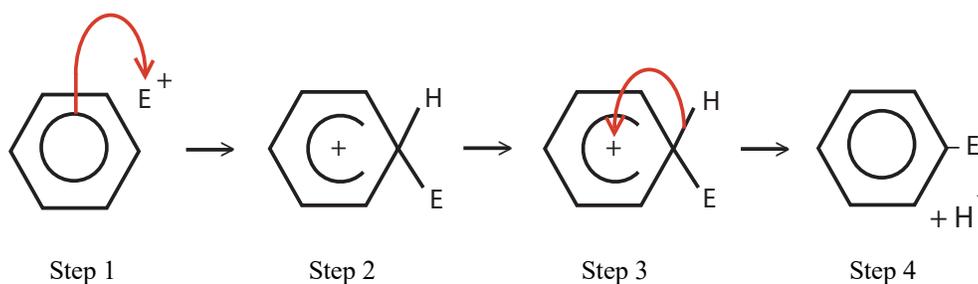
The three reactions above are extremely important in the synthesis of drug production where the manufacturers start with Benzene that has been obtained from the fractional distillation and then the Platforming/Reforming of crude oil extracted from under the ground or from under the sea (or from under the *ice* in Alaska and in Siberia).

The reaction mechanism for the Halogenation, Alkylation, and Acylation of Benzene is the same for all three reactions, except that the identity of the attacking electrophile changes – therefore I am going to show the reaction mechanism using E^+ as the electrophile, and E^+ could be

- Br^+ in the case of **Bromination** (this is a halogenation reaction)
- Cl^+ in the case of **Chlorination** (this is a halogenation reaction)
- $C_nH_{2n+1}^+$ in the case of **Alkylation**, and
- in the case of **Acylation** it will be the “ $R-(C^+=O)-$ ” depicted below (where the “ $-C=O$ ” is a Carbonyl group)¹



The common reaction mechanism for the **Halogenation** (replacing an H atom with an “Hal” species), **Alkylation** (replacing an H atom with a “ C_nH_{2n+1} ” species), **Acylation** (replacing an H atom with an “ $R-C^+=O$ ” species) and the **Nitration** (replacing an H atom with a “ NO_2^+ ” species) of Benzene is



where “ E^+ ” is the attacking electrophile. My way of drawing what happens may be different from how some textbooks draw it, therefore let me explain in words what is happening.

In the four steps involved

¹ Just in case you need reminding, a Carboxylic Acid has the form “ $R.COOH$ ”, and if we tear off the “ $R-$ ” and the “ $-OH$ ” bits, we will be left with a “Carbonyl” (“ $-C=O$ ”) group. However, if you tear off **just** the “ $-OH$ ” bit from a Carboxylic Acid, then you will be left with the “*Acy*l” group (“ RCO ”) that we are currently discussing.

Step 1

The electrophile E^+ attached to an F-C catalyst is attracted to the area of high electron density surrounding the Benzene ring, and Benzene then forms a dative bond with E^+ and Benzene thus “loses” one electron in doing so.

Step 2

E^+ is now no longer short of an electron – but the Benzene ring has lost an electron and the ring has been broken² and it must therefore be shown as *incomplete* and with a positive sign in it. The C atom where substitution will occur is now *temporarily* bonded to both an H and the Electrophile.

Step 3

The Hydrogen atom that is bonded to the C atom to which the electrophile is attached breaks away (as a proton) leaving behind its electron – and this now recreates the Benzene π ring!

Step 4

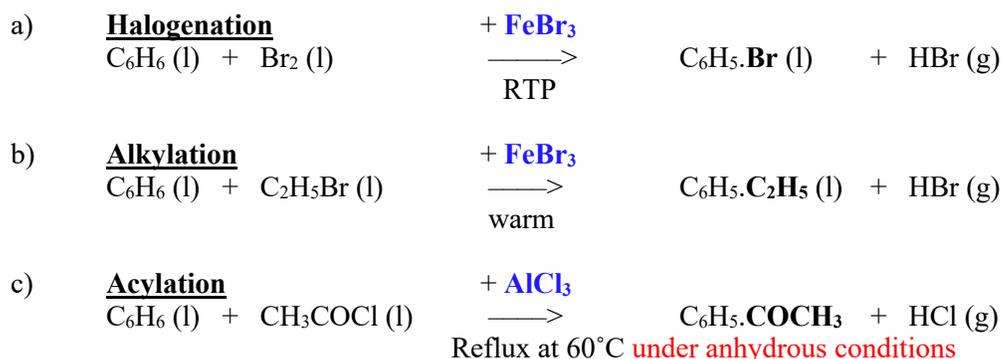
The reaction is now complete and the substitution reaction is finished. The proton that broke away will bond with the other “half” of the electrophile which at that stage is still attached to the FC catalyst.

In the case of

- Halogenation**, the molecule that reacts with the F-C catalyst will be either Chlorine or Bromine (it is *much* more difficult to react Iodine with Benzene³), while in the case of
- Alkylation** it is sensible to use $C_nH_{2n+1}-Hal$ to bond with the F-C catalyst (such as $AlCl_3/FeBr_3/etc$) to get the Alkyl Group “ $-C_nH_{2n+1}$ ” to bond with the Benzene, and in the case of
- Acylation** it is sensible to use $RCO-Hal$ for the **Hal** to bond with the FC catalyst, and the RCO to bond with the Benzene,

In this way, to accompany the E^+-Hal species, there will always be a Halogen atom in the molecule to bond with the FC catalyst.⁴

At ‘A’ Level you *are* required to know reaction equations as well as reaction mechanisms, and I now give you three typical reaction equations using an FC catalyst in each case.



² If the ring were not broken, then the C atom which now has the electrophile attached to it would have 5 bonds – and this it cannot have.

³ Iodobenzene can be obtained by reacting Benzenediazonium Chloride (BDAC) with Potassium Iodide. (“Azote” is the French name for Nitrogen, and that is where you get the term “diazonium” meaning two N atoms.)

⁴ I would therefore contend that the “halogen carrier” is actually carrying the *companion* species (but the term “companion” carrier would be ridiculously vague).

OK, it is clearly time now to talk about Friedel-Crafts (F-C) catalysts.

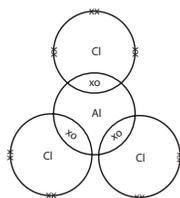
The area of high electron density above and below the Benzene molecule protects it from nucleophilic attack, and the delocalisation of the π ring in Benzene confers thermodynamic stability to it. Benzene will undergo electrophilic reactions (and usually Electrophilic *Substitution* reactions), but the stability that it possesses could mean that the reaction takes hours or even days to happen. To speed up the reaction, something called a **Friedel-Crafts' catalyst** is therefore used.

Friedel-Crafts catalysts/Lewis Acids

Some textbooks state that a Halogen carrier (and that name is self-explanatory viz. a species that carries a Halogen species) or a Friedel-Crafts' catalyst works by dative bonding. However, there is a lot more to Halogen carriers/Friedel-Crafts catalysts' that is insufficiently explained in 'A' Level textbooks, therefore I am going to describe their action in a bit more detail.

Friedel-Crafts' catalysts/halogen carriers are very (or indeed are most) often used in the halogenation/or the alkylation/or the acylation of an aromatic molecule⁵. Acylation is something that is dealt with mainly at University, but **halogenation** (using a Hal-Hal / "X-X" diatomic molecule) and **alkylation** (using an Alkyl-Hal / "R-X" species) are both part of the Advanced Level syllabus, but here let us just consider the **halogenation** of a Benzene molecule using a halogen-carrier. However, let me warn you that **benzyl halides are TOXIC** species. As far as you are concerned therefore, this is just *theoretical* stuff. **You will rightly not be allowed to go anywhere near this sort of stuff in your school/college labs.**

Friedel-Crafts' catalysts/carriers **must have** a diminished octet (6 bonding electrons instead of 8) because it is this that creates the situation where a totally empty or vacant orbital can be used for dative bonding. Examples of substances that have diminished octets are **AlCl₃ / AlBr₃ / FeCl₃ / FeBr₃** (and also BF₃ / BeCl₂ / TiCl₄ / SbCl₅ / SnCl₄ / and so on).



If we examine AlCl₃ we can see that there are only three electron pairs on the central Al atom, and the Al atom in the AlCl₃ species therefore lacks the stability imparted by the Noble Gas Configuration of sharing in **FOUR electron pairs** (which is why AlCl₃ often forms the dimer Al₂Cl₆)⁶.

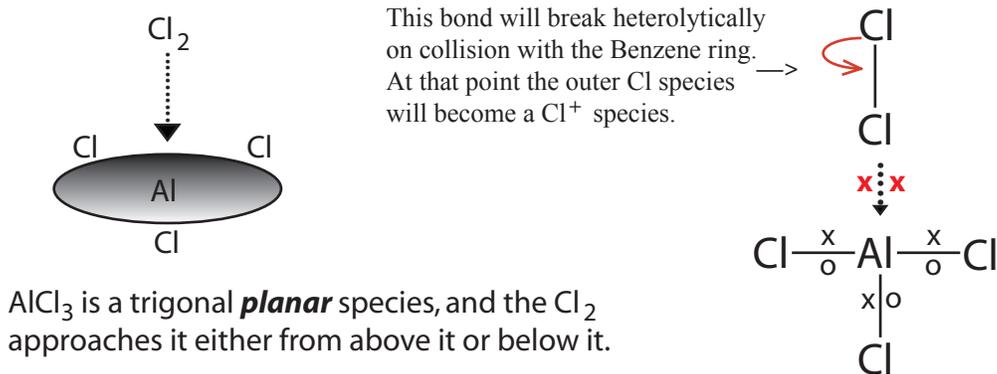
Al is in Group III, and in order to form three bonds, Al in AlCl₃ promotes one electron from 3s to 3p to form three sp² hybridised atomic orbitals which it uses to form sigma bonds, one with each of the Cl atoms. This leaves its 2p_z unhybridised orbital able to accept a lone pair of electrons from a fourth Cl atom from, for example, a Cl-Cl molecule (to become, temporarily, AlCl₄⁻ and Cl⁺, cf. next page). Because F/Cl/and Br (but not Iodine) are sufficiently more electronegative than Al (Iodine is not sufficiently more electronegative than Aluminium, then the four Cl (or whichever halogen) atoms in the AlCl₄⁻ part of AlCl₄⁻Cl⁺ each become Cl⁻ species and the Al atom therefore becomes an Al^{δ+} species. In fact, because **four** Cl⁻ species are each drawing electron density off the Al species, the Al species becomes (almost) an Al^{δ+δ+δ+δ+} species!

⁵ Aromatic in the sense of a derivative of Benzene or any Arene molecule.

⁶ "Dimers" have cropped up in 'A' Level exams. A dimer is a conjoined pair of similar *molecules* that exist together for greater stability. "Diatomic" means two conjoined atoms, and a "dimer" consists of two conjoined *molecules*.

Any diatomic Halogen molecule⁷ such as Cl–Cl that approaches the Al in the AlCl₃ species *in the same plane as its existing Cl^{δ-} species*, will be hindered in its planar approach by one of the existing three physically big Cl^{δ-} species, and the diatomic Halogen molecule can therefore approach the AlCl₃ species **only either from above or from below** AlCl₃.⁸

I have drawn AlCl₃Cl₂ in only *one* of its Resonance forms



If you look at Br₂ on the next page you will see a second possible resonance structure for Br₂ or Cl₂.

The Cl atom nearer the AlCl₃ species will then become partially polarised by the Al^{δ+} species, and it will thus become a Cl^{δ-} species, and its companion Cl atom will thus automatically become a Cl^{δ+} species – **and it is THIS Cl^{δ+} species that will be attracted to the area of high electron density that encircles the Benzene molecule.**

Other than in very rare circumstances, it is only an electrophile that can bond easily with a Benzene molecule – and that is precisely what Cl^{δ+} is. It is an **ELECTROPHILE** and it will be attracted to the nucleophile Benzene. **All the other four Cl species are Cl^{δ-} species, and they cannot bond with Benzene.**

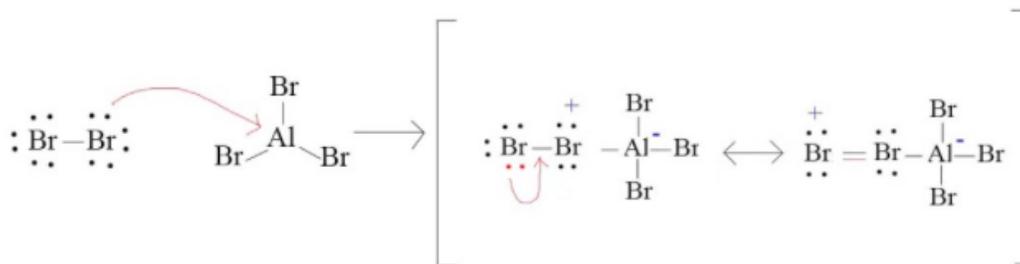
On impact with the Benzene molecule, the diatomic Cl–Cl molecule that has become a partially polarised molecule will break by **heterolytic bond fission** with the Cl^{δ-} species becoming a full Cl⁻ species, and the **Cl^{δ+} species breaks away as a full Cl⁺ electrophile** – and it is **THIS** species that then takes part in the electrophilic substitution reaction with Benzene.

That is what Halogen carrying is all about!

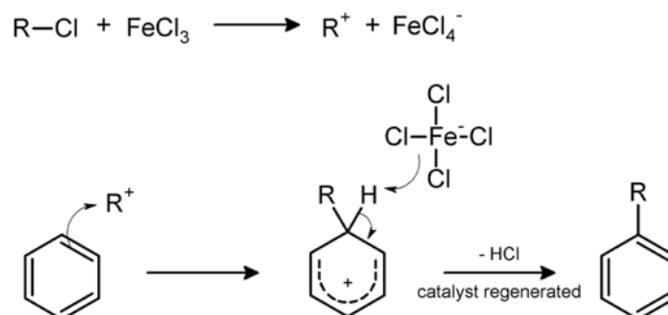
The University of California (Davis) shows the use of Bromine in an FC catalyst as overleaf

⁷ or Alkyl-Hal/R-X.

⁸ Some chemists talk of this and similar spatial reactions as a “backside” reaction. I do not do so because I find such terminology rather vulgar. If you insist on using such terminology, then please use the terms “frontal” attack, and “attack from the rear”. I have chosen to draw the attack as occurring from **above** the plane of AlCl₃.



and Wikipedia shows the action of an FC catalyst thus (where R is the E⁺ that you want to add to C₆H₆).



but so far I have explained only the first line in Wikipedia's representation.

I have told you that Benzene is given considerable stability by its delocalised π ring – and it is therefore normally **not** reactive at room temperature and pressure (RTP).

However, with a suitable Friedel-Crafts' catalyst acting as a Lewis acid (i.e. a species that accepts a lone pair of electrons) *the attacking electrophile will be made more reactive* and Benzene will *then* react with the attacking electrophile at RTP. Equally there are things that can be done to Benzene (e.g. we can increase the density of the electron cloud that surrounds the Benzene molecule by replacing an H atom on Benzene with a species that will “donate” electron density to Benzene (e.g. an Alkyl group/–NH₂/–OH/ etc)⁹ *to make it more reactive*, and that will then make the Benzyl compound much more reactive.¹⁰

We will talk about increasing the electron density of Benzene in future blogs, but could you please note that it is not really sensible to call a Friedel-Crafts (FC) catalyst simply a “halogen carrier” because an FC catalyst can also be used to make an *alkyl species* react with Benzene, and alkyl species are not halogens! *An FC catalyst thus may or may not be a halogen carrier.* My advice to you therefore is **not to use the term “halogen carrier” at all**. Catalysts such as AlCl₃ and FeBr₃ are more correctly called **Friedel-Crafts' catalysts**, or alternatively they can be described as **Lewis Acids** (but then you lose the importance of their function as catalysts).

⁹ An “activator” makes Benzene more reactive while a “deactivator” makes it less reactive (but the attacking species will still be an electrophile).

¹⁰ Imperial College London says “(Auguste) Laurent, proposed that due to it being discovered in illuminating gas, it should instead be called pheno, from the Greek *phainein*, meaning to shine. This name never really gained acceptance, but persists to this day as phenyl - the name for the “C₆H₅–” group – and nowadays when “Benzene” is used as an adjective we do call it a “phenyl” or “benzyl” species.

OK, that is enough about Friedel-Crafts' catalysts for the moment – and next week we need to start studying some of the other reactions of Benzene.

NB I told you that the Second Year of your 'A' Level studies would be more demanding than your First Year, and from now on I am going to be *much* more demanding of you intellectually than I was of you in your First Year. When you leave here to go to University, I want you, **YOU** to be the one who is streets ahead of everybody else (and not the other way around).

I would very much like to train you to use your brain to solve anything that life may throw at you.