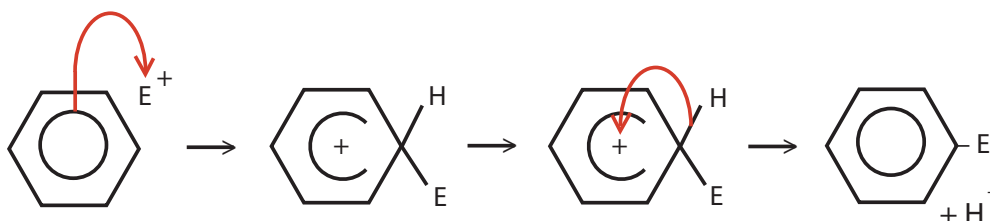


Year 2, Organic Chemistry, Chapter 13A: Essence/Summary of the EAS Reactions of Benzene

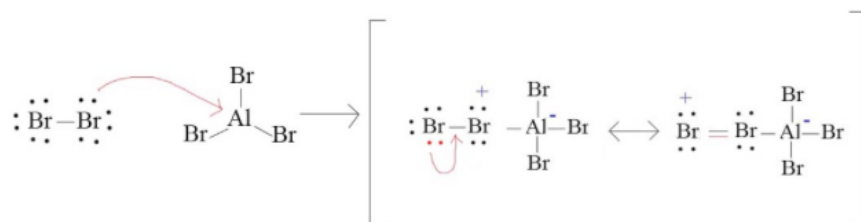
- Before leaving the subject of EAS reactions, let me summarise the things that you need to know about them.

- You need to know the [reaction mechanism](#), and I have drawn it for you thus



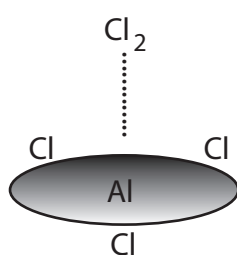
- You need to know the way that [Friedel-Crafts' catalysts act as Halogen carriers](#) (but do not forget that they are catalysts as well as Halogen carriers) – and the two most popular FC catalysts are AlCl_3 and FeBr_3 .

- You can draw it like this (where the species inside the brackets are resonance structures)



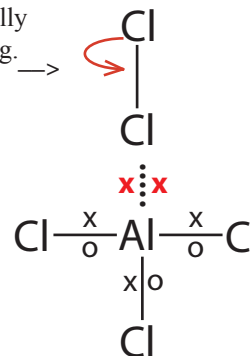
but you can **think** of it like this

I have drawn AlCl_3Cl_2 in only *one* of its Resonance forms



AlCl_3 is a trigonal **planar** species, and the Cl_2 approaches it either from above it or below it.

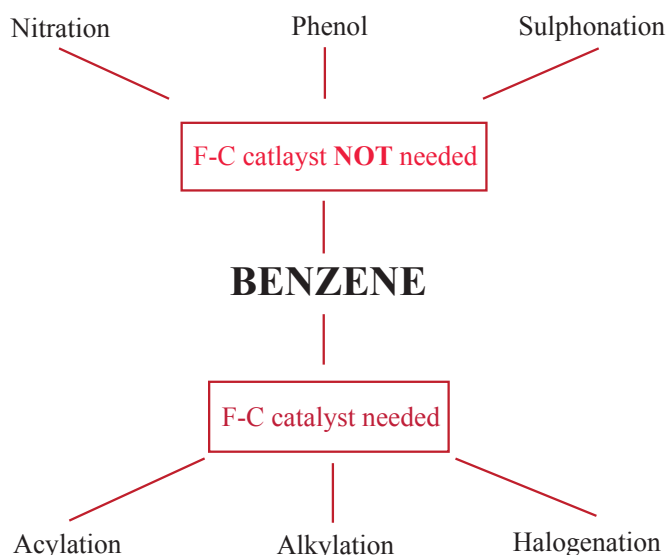
This bond will break heterolytically on collision with the Benzene ring. At that point the outer Cl species will become a Cl^+ species.



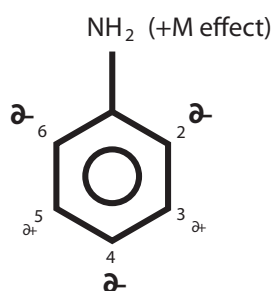
or if you are holding the AlCl_3 in the perpendicular plane, then the approach of the Cl_2 species is from one side or the other.

- We have covered **six EAS reactions of Benzene** and three of them required an F-C catalyst (AlCl_3 or FeBr_3) and three of them did not (and you have to look at the detailed Benzene info tree for the reaction conditions for each reaction).

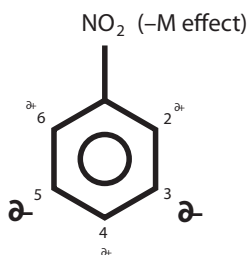
EAS Reactions of Benzene



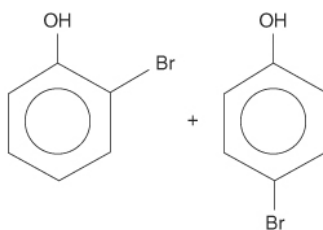
- In order to understand where and how substitution occurs on the Benzene ring, it is first necessary to understand the **Inductive** and the **Mesomeric** effects (and these are explained at considerable length in the relevant Chapters).
- In essence however, the **Mesomeric** effect occurs when the unhybridised 'p' orbital of a species (let us call it species 'R') that substitutes for an "H" species on the Benzene ring overlaps with the unhybridised 'p' orbital of the Carbon atom onto which it has bonded. This causes the electron in the unhybridised 'p' orbital of X to join onto the delocalised π ring of the C_6H_5 species. If nothing pulls the electron density off X (as is the case with " $\text{C}_6\text{H}_5.\text{NH}_2$ "), then the electron density on the C_6H_5 species has been increased and a **+M effect** has occurred – and the Benzene ring has been **activated** at positions 2/4/6.
- However, if X has something attached to it that pulls the electron density off it via a π bond (as is the case with " $\text{C}_6\text{H}_5.\text{NO}_2$ "), then there will be a "**–M effect**" and the electron density on the C_6H_5 species will be diminished, and the Benzene ring will be **deactivated** at 2/4/6 (but activated at 3/5).
- The term "**Activation**" thus indicates that activation has taken place at 2/4/6 e.g.



and “**Deactivation**” indicates that 2/4/6 have now become ‘ δ^+ ’ but that 3/5 have become ‘ δ^- ’ viz. 3 and 5 have become activated¹.

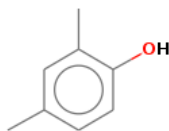


- An ‘activated’ Benzene species undergoes EAS reactions at much lower energy levels than does Benzene.
- Activation does not necessarily mean that substitution occurs at 2, 4 and 6. It could occur at just 2 or just 4, or 2 and 4, (but please remember that 2 and 6 are exactly the same unless tri-substitution occurs).
- Substitution can take place at 2 or at 4 e.g.



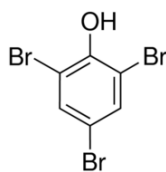
and in this instance 2-bromophenol and 4-bromophenol are obtained.

- Substitution can also take place at 2 and 4 (and here 2 and 4 are located *counter-clockwise* from the “-OH” species).



This is 2,4-dimethylphenol. (I have deliberately chosen a diagram above where you have to count ‘counter-clockwise’, and please remember that the convention is that you do not show the C atoms and the C–H bond lines in the skeletal diagrams in Organic Chemistry therefore you cannot see the ‘-CH₃’ species in the 2 and the 4 positions).

- However, substitution can take place at 2, 4 and 6

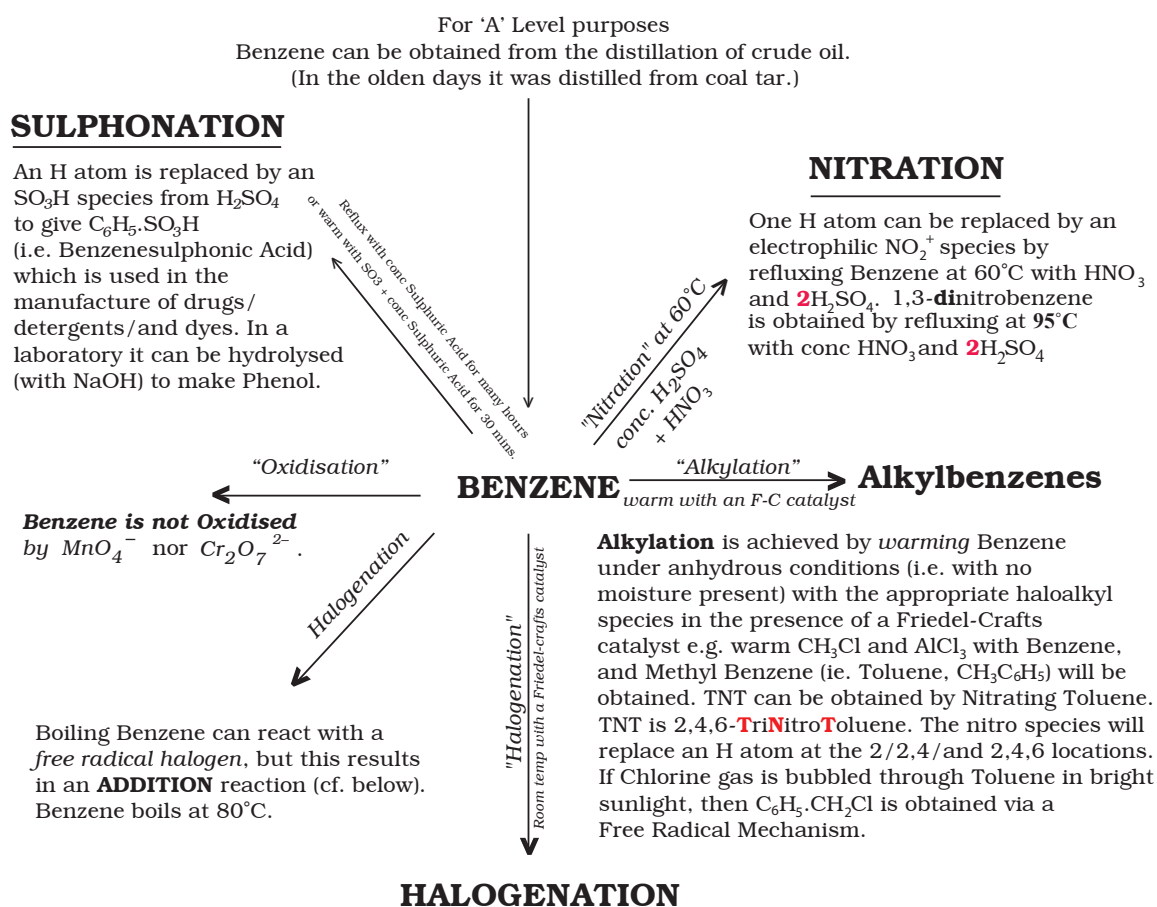


and this is 2,4,6-tribromophenol.

¹ 3 and 5 can be interchangeable and so can 2 and 6.

- I repeat therefore, that **activation does not necessarily mean that substitution will occur at 2, 4 and 6 but that it can occur at 2, 4 and 6 or at one or more of these positions** – and it is merely a matter of using the appropriate reaction conditions to achieve whatever it is that you require.
- Please remember that substitution reactions are not the only sort of reactions that can occur for Benzene. Benzene can be thought of as a conjugated species of alternating double and single bonds, and Benzene can therefore undergo the same sort of reactions as can an Alkene (as can be seen below).

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 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 ($\text{C}_6\text{H}_5\cdot\text{COOH}$).

- Michigan State University gives this little summary of the EAS reactions of Benzene, and it may serve as an '*aide memoire*'. I am not at all sure why they choose to show the positive charge on the electrophile in brackets. In the UK we certainly do **not** do so.

Reaction Type	Typical Equation			Electrophile E ⁽⁺⁾
Halogenation:	C ₆ H ₆ + Cl ₂ & heat FeCl ₃ catalyst	→	C ₆ H ₅ Cl + HCl Chlorobenzene	Cl ⁽⁺⁾ or Br ⁽⁺⁾
Nitration:	C ₆ H ₆ + HNO ₃ & heat H ₂ SO ₄ catalyst	→	C ₆ H ₅ NO ₂ + H ₂ O Nitrobenzene	NO ₂ ⁽⁺⁾
Sulfonation:	C ₆ H ₆ + H ₂ SO ₄ + SO ₃ & heat	→	C ₆ H ₅ SO ₃ H + H ₂ O Benzenesulfonic acid	SO ₃ H ⁽⁺⁾
Alkylation: Friedel-Crafts	C ₆ H ₆ + R-Cl & heat AlCl ₃ catalyst	→	C ₆ H ₅ -R + HCl An Arene	R ⁽⁺⁾
Acylation: Friedel-Crafts	C ₆ H ₆ + RCOCl & heat AlCl ₃ catalyst	→	C ₆ H ₅ COR + HCl An Aryl Ketone	RCO ⁽⁺⁾