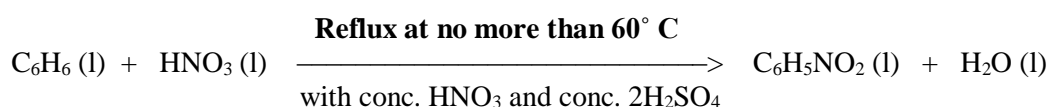


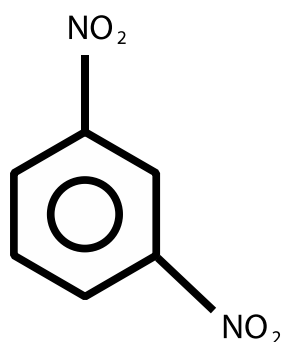
Year 2, Organic Chemistry, Chapter 12:

The EAS Nitration of Benzene

- This is an EAS reaction, **but no FC catalyst is involved**. At RTP, $\text{C}_6\text{H}_5\text{NO}_2$ is a yellow liquid.
- It may already be apparent to you that somewhere where you could obtain an “ NO_2^+ ” species would be from Nitric Acid, HNO_3 – and if this has occurred to you then well done. **That is exactly where you get the E^+ for this EAS reaction.**
- The reaction conditions are



- In order to maintain the temperature at 60°C you need to sit the flask that contains the reactants on a thermostatically controlled electric heater, and you use not H_2SO_4 but $\underline{2}\text{H}_2\text{SO}_4$ (and I will explain why in just a moment).
- However there are a couple of problems with this EAS reaction.. The first one is a trivial problem viz. different textbooks give different temperatures for the reaction. The temperatures quoted vary from 55° to 60°C therefore if I were you, in the exams, I would say “**at no more than 60°C** ”. The reason for keeping the temperature at no more than 60°C is that at higher temperatures (around 95°C) you would get $\text{C}_6\text{H}_4(\text{NO}_2)_2 (\text{s})$ i.e. you would get 1,3-dinitro benzene. **(NB Trinitrobenzene does not form.)**



- The second problem is that even though conc. HNO_3 is a poor nitrating agent, when in conjunction with conc. H_2SO_4 it turns out to be a very good nitrating agent. The explanation for this phenomenon puzzled chemists for a long time, and the solution involves some lovely Chemistry that goes well beyond the ‘A’ level syllabus and involves proton donation from the stronger acid to the weaker acid (something that we will cover in Inorganic Chemistry).

Nitration (where the attacking electrophile is “ NO_2^+ ”)

- Benzene is carcinogenic therefore you will NOT be allowed to (and should **not** be allowed to) use it in schools. In most cases you can use methyl benzoate at below 5°C (but my advice is just learn about it, and watch it on youtube – it is much safer that way)
- Sulphuric acid acts as both the solvent and as the catalyst in this reaction, but you must write “ H_2SO_4 ” when you write your reaction equation in the exam.
- As it happens, Nitration is another easy Benzene reaction where you can score the maximum marks available. All that you need to remember is that you need an electrophile, and that the electrophile “ NO_2^+ ” comes from Nitric Acid (HNO_3).¹
- It is obtained by H_2SO_4 donating a proton to the HNO_3 , and then H_2O^+ breaks away from the NO_2 by heterolytic bond fission thus creating H_2O and NO_2^+ .



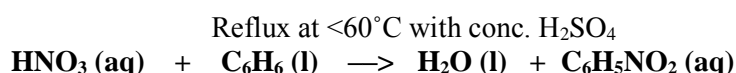
- A second H_2SO_4 molecule then donates a proton to the water molecule



giving the overall equation as



- However, *some* exam boards are perfectly happy to accept the statement



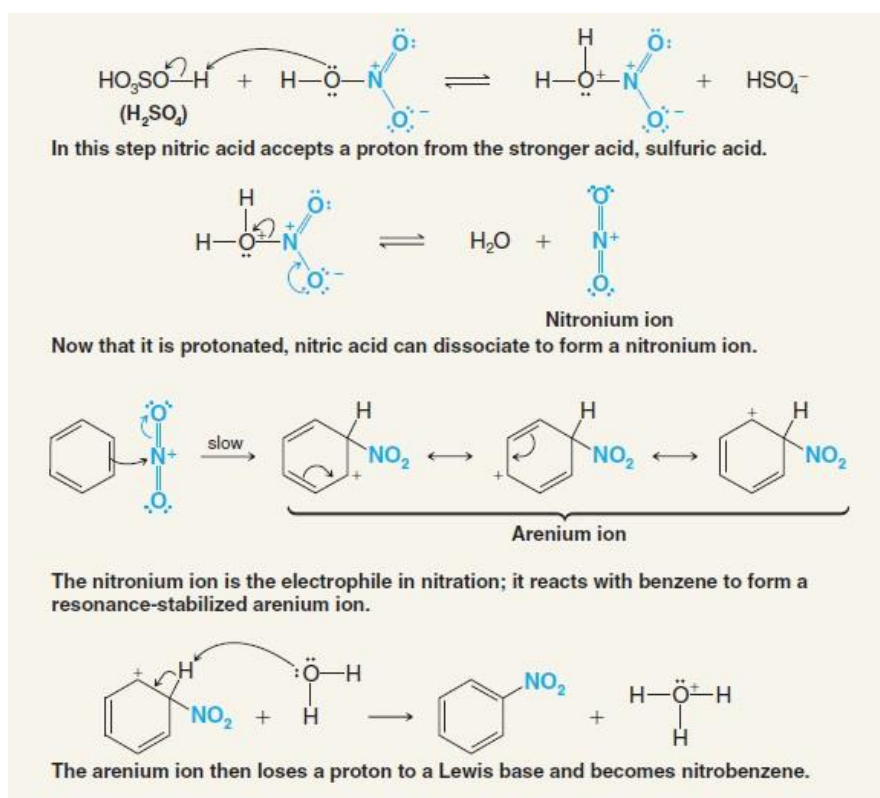
- If the reactants are refluxed at 95°C then **1,3-Dinitrobenzene** will be obtained. For a reason that I told you about in Chapter 8 (the process can involve either Activation or Deactivation) *the Nitro group deactivates the Benzene ring*, making Nitrobenzene less reactive than Benzene. To obtain the high explosive **TriNitroBenzene** (TNT) an *activating* group such as “ $-\text{CH}_3$ ” must first be attached to a Benzene ring (to give a compound called Toluene, $\text{C}_6\text{H}_5\text{CH}_3$) and then Toluene must be Nitrated to give $\text{CH}_3\text{C}_6\text{H}_2\text{-(2,4,6-(NO}_2)_3$).

¹ $\text{HNO}_3 \longrightarrow \text{NO}_2^+ + \text{OH}^-$.

- The following is a nice little explanation of what is happening. I found it on

<https://chemistry.stackexchange.com/questions/14883/why-does-a-br%C3%B8nsted-lowry-acid-accept-proton-from-stronger-acid>

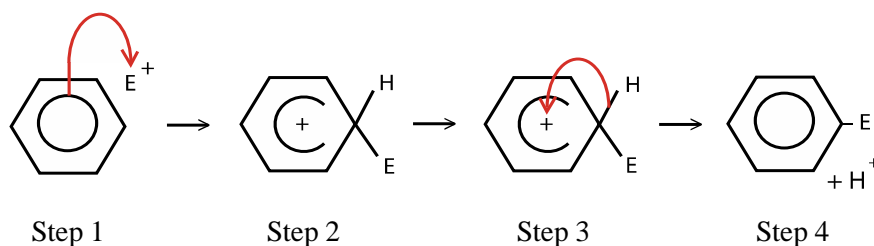
- Please do not let the direction of the arrows fool you into thinking that the Nitric Acid is doing something to the Sulphuric Acid. It is in fact the other way around. It is the Sulphuric Acid that is donating a proton to the Nitric Acid. **Look at the whole of the first line of the diagram carefully and you will see that the Sulphuric Acid is donating a proton to the Nitric Acid. The “Nitronium ion” is the NO_2^+ species.** The Arenium ion is labelled clearly in the third line of the diagram. (Being an ‘ion’ it must have a charge.)²



- “The first step of the mechanism would not, on its own, happen to a large extent (protonating nitric acid is unfavorable,) so the equilibrium would lie far to the left. However, the second step of the mechanism is highly favorable (entropically), so it quickly consumes what little H_2NO_3^+ is produced by the first step. This drives the overall reaction forward by Le Chatelier's principle.”*
- I imagine that the author was an American gentleman because the spelling is not English but American. I have put it in here because very soon we will need to start talking about Inorganic A2 Chemistry and things like “slow steps” and fast steps”, and Entropy.

² I have a strong feeling that the “Ar” in Arenes comes from the word “Aromatic” which is where Benzene compounds were first discovered.

- The common reaction mechanism for the Halogenation, Alkylation, Acylation and the Nitration of Benzene is thus



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

Step 1

The electrophile E⁺ attached to the FC 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 broken³ and 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.

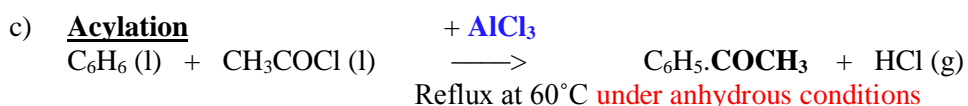
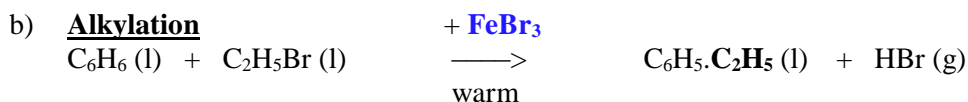
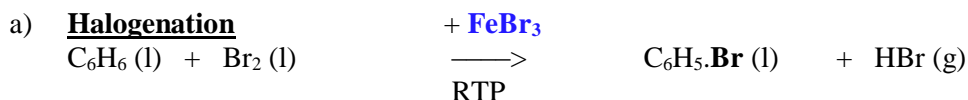
- In the case of
 - Halogenation** the molecule that reacts with the FC catalyst will be either Chlorine or Bromine (it is *much* more difficult to react Iodine with Benzene⁴), while in the case of
 - Alkylation** it is sensible to use **C_nH_{2n+1}-Hal** to bond with the FC catalyst (such as AlCl₃/FeBr₃/etc) 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 **RC=O** to bond with the FC catalyst.

³ 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.

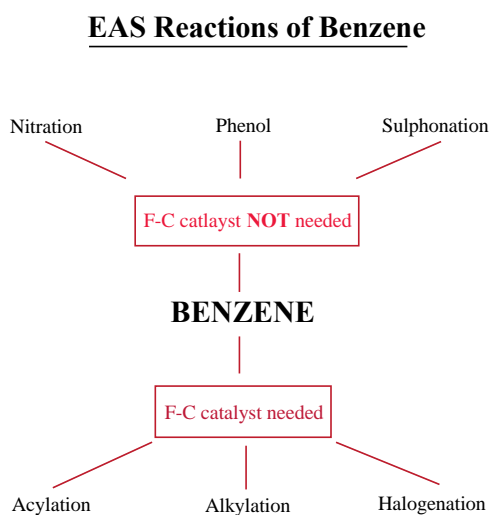
⁴ Iodobenzene can be obtained by reacting Benzenediazonium Chloride (BDAC) with Potassium Iodide. ("Azote" is the French name for Nitrogen, and that is where you get the term "di**azon**ium" meaning two N atoms.)

- In this way, to accompany the E^+ species, there will always be a Halogen atom in the molecule to bond with the FC catalyst.⁵

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



- In the exam, if you are asked about any of these three electrophilic substitution reactions of Benzene you will now be able to score 3 or 4 marks **within seconds** (and you **do** need to be able to answer questions *within seconds* or else you will not finish all the questions on the exam paper)!
- Halogenation will take place at RTP, but you would need to reflux the mixture at 60°C for **Acylation**, (whereas **Alkylation** with an FC catalyst should require nothing but warming).
- In Chapter 5 we talked about FC catalysts, and this little schema might be of help to you.



- OK, let us move on to Sulphonation in Chapter 13.

⁵ I would therefore contend that the “halogen carrier” is actually carrying the *companion* species (but the term “companion” carrier would be ridiculously vague).