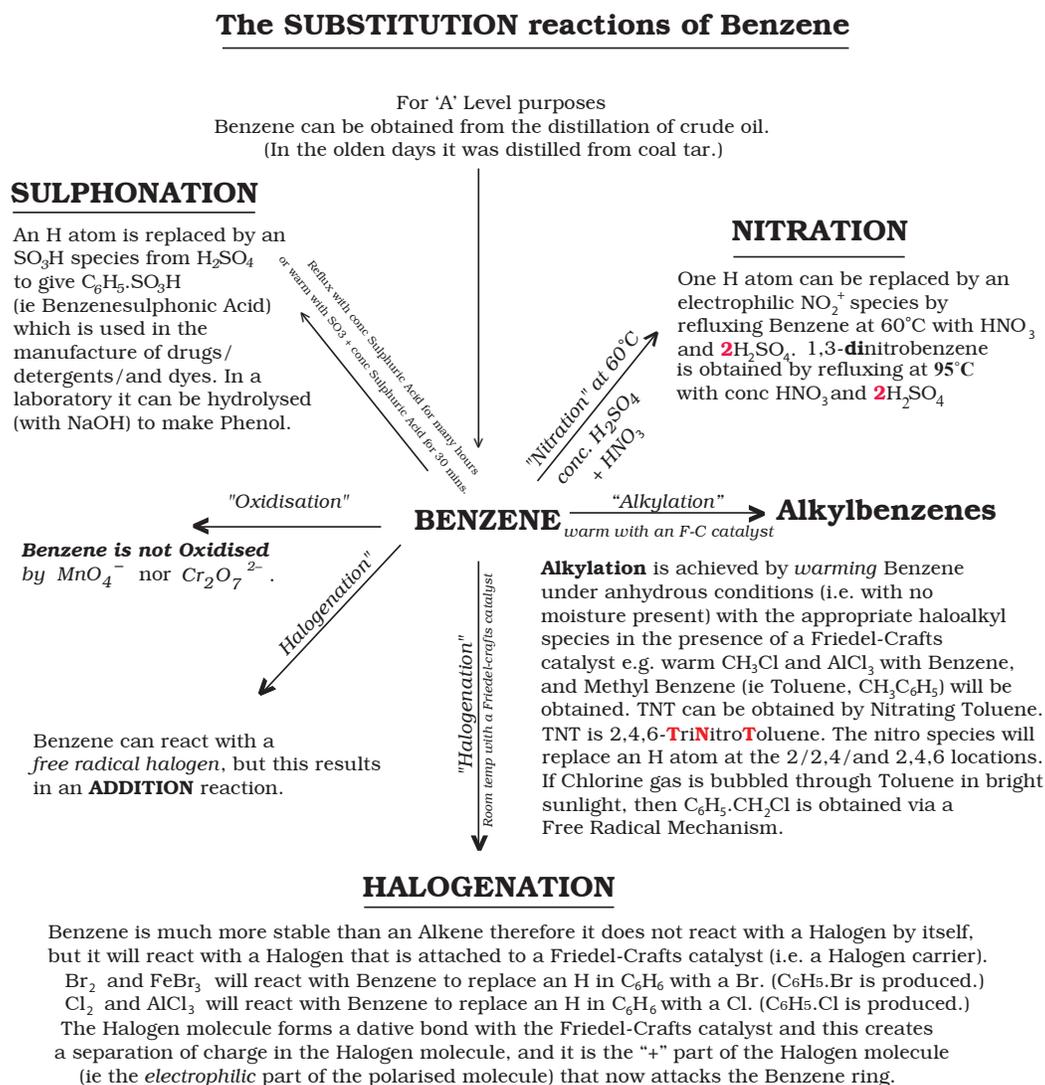


A Second Year blog on Benzene, The Nitration of C₆H₆, Part 2: 22nd Dec 2018

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

In the first blog on Benzene I told you about three EAS (Electrophilic Aromatic Substitution) reactions of Benzene that needed the use of a Friedel-Crafts' catalyst such as AlCl₃ or FeBr₃ in order for the reaction to be conducted in a reasonably short space of time (minutes rather than many hours or even days). The three reactions were the **Halogenation** (replacing an H atom with a Halogen atom)/the **Alkylation** (replacing an H atom with a "C_nH_{2n+1}" species)/the **Acylation** (replacing an H atom with an "R-C⁺=O" species) of Benzene, and this blog is about the **Nitration** of Benzene.

This is my info tree of the reactions of Benzene.



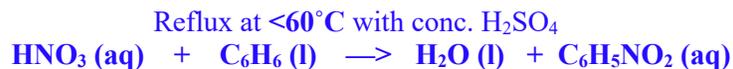
ADDITION REACTIONS

- Benzene will react with **Hydrogen** gas at 150°C in the presence of finely powdered Nickel to give C₆H₁₂.
- 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 -CH₃ group in *Toluene* will be oxidised by an alkaline manganate ion to give Benzoic Acid (C₆H₅COOH).

The Nitration of Benzene

This is the essence of what you need to remember.



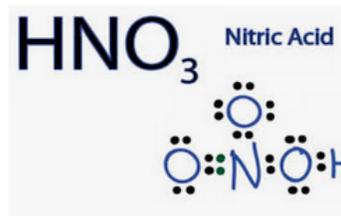
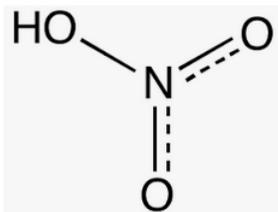
In your first year I talked about HNO_3 as an acid (*viz. a substance that dissociates protons when in aqueous form*), and the reaction equation for that is $\text{HNO}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{NO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$.

However, because you are now beginning to get the hang of things you will immediately say to me that NO_3^- cannot react with Benzene because it is a negatively charged species and it would be repulsed by the area of high electron density that lies above and below the Benzene ring, and if that was your immediate reaction, then well done. **Well done indeed!** I therefore now want to draw your attention to another possible equation for Nitric Acid.



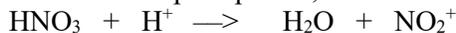
Could you now as Revision draw a dot-and-cross diagram of HNO_3 , but dot-and-cross diagrams are more GCSE stuff than 'A' Level stuff, so could you draw also the Lewis structure for HNO_3 (and if you get stuck, then as further revision could you type "Dr Wayne Breslyn, Lewis structure for HNO_3 " into the search engine of your computer and remind yourself of how to do a Lewis structure).

When you have done that, you will get the following (where the dashed line represents delocalisation).

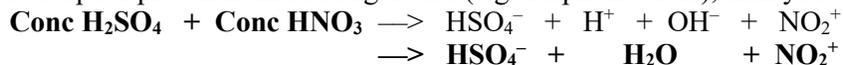


The representation on the left is more accurate, but Dr Breslyn's depiction on the right shows you that every single O atom in HNO_3 has at least one lone/one unbonded pair of electrons on it.

If the O atom that is bonded to the H atom accepts a proton, then it will break away as water as follows.



If HNO_3 therefore accepts a proton from a stronger acid (e.g. Sulphuric Acid), then you will get



OK, that is the basis for what I am now going to talk about.

The Nitration of Benzene (where the attacking electrophile is “-NO₂⁺”)

Benzene is carcinogenic therefore you will NOT be allowed to (nor should you be allowed to) use it in English schools (nor in any school for that matter).

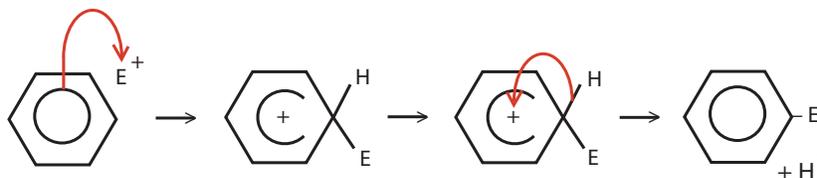
As it happens, Nitration is an easy Benzene reaction where you can score the maximum marks available in an exam. All you need to remember is that you need an electrophile, and that the electrophile “-NO₂⁺” comes from Nitric Acid (HNO₃). HNO₃ → OH⁻ + NO₂⁺.

H₂SO₄ is a stronger acid than HNO₃, and when Sulphuric Acid donates a proton to Nitric Acid you get

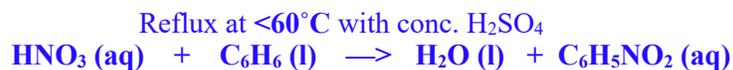


and it is the electrophilic NO₂⁺ that reacts with the nucleophilic C₆H₆.

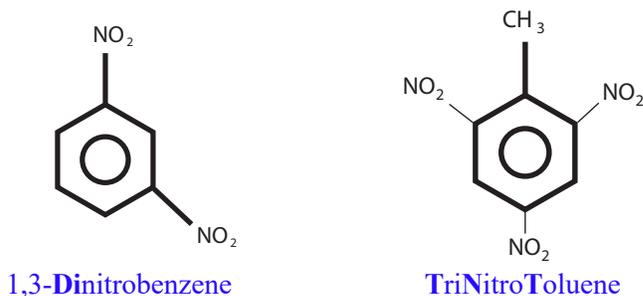
If you designate NO₂⁺ as the Electrophile “E⁺”, then you get the mechanism that we discussed in last week’s blog viz.



The NO₂⁺ has now replaced an “H” from C₆H₆, and the displaced H⁺ regenerates the Sulphuric Acid. The Sulphuric Acid is thus just a catalyst. *Most* exam boards are perfectly happy to accept the statement



If the reactants are refluxed at 95°C then 1,3-**D**initrobenzene will be obtained. To obtain the high explosive **TriNitroToluene** (TNT) an *activating* group¹ such as “-CH₃” must first be attached to a Benzene ring (to give a compound called Toluene, C₆H₅.CH₃) and then Toluene must be Nitrated to give CH₃.C₆H₂-2,4,6-(NO₂)₃.

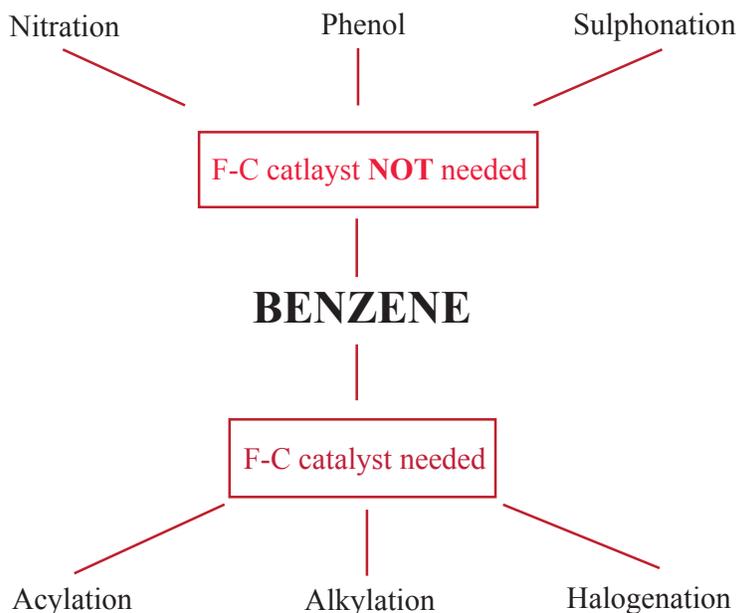


OK, that gives you the **Nitration** (replacing an H atom with an “NO₂⁺” species) of Benzene, and last week we looked at the **Halogenation** (replacing an H atom with a Halogen atom)/the **Alkylation** (replacing an H atom with a “C_nH_{2n+1}” species)/and the **Acylation** (replacing an H atom with a “R-C⁺=O” species) of Benzene.

¹ I will talk about “activation” and “deactivation” in next weekend’s blog.

Let me therefore now give you an info tree for the reactions of Benzene that shows the reactions that need an F-C catalyst.

EAS Reactions of Benzene



In next week's blog on Benzene I will tell you about "activation" and "deactivation" and then how you go from Benzene

- to something called **BenzeneDiAzoniumChloride** (BDAC) and then
- to Phenol, or
- to Azo dyes

but now I want to tell you about the **Addition** as opposed to the **Substitution** reactions of Benzene and please remember that this is meant to be just a revision summary of the important facts on Benzene.

You are meant to have read and mastered the Chapters on Benzene in the Second Year Organic Chemistry book for yourself.

The Addition reactions of Benzene

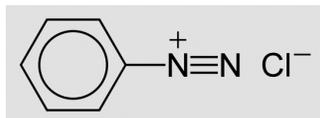
Alkenes and Benzene (and Benzene's sister Aromatic compounds such as Naphthalene/Anthracene/etc) have π bonds created by the overlap of unhybridised 'p' orbitals, and it is thus **not** surprising that Benzene in some circumstances will act a bit like an Alkene! You will remember that the classic test for an Alkene is the **decolourisation of Bromine water**. Well, it will not surprise you that Benzene (and its sister compounds) will also react with Halogens – except that Aromatic compounds are normally *very* stable at room temperature and pressure (RTP) and therefore react **much** less rapidly than Alkenes do.

In contrast to Alkenes, Aromatic compounds normally require much higher temperatures and pressures before they react (and will exhibit the reactions of an Alkene only with a free radical).

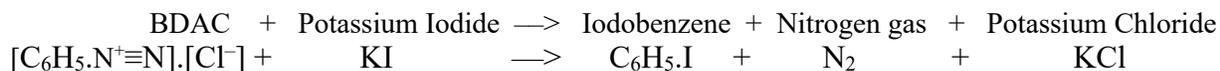
Therefore where an **Alkene** will react with

- Fluorine** gas explosively (even in the dark and even at sub-zero temperatures)
- Chlorine** gas explosively in bright sunlight (but not explosively in **filtered uv light**), and
- Bromine** gas instantaneously in bright sunlight,

so also Benzene will react with Chlorine and Bromine, but only with a reactive Halogen free radical and then minutely slowly at RTP (but over the period of about an hour with *boiling* Benzene in the presence of uv light). Benzene boils at 80°C. It is more difficult to react Benzene with Iodine, but Iodine will react with **BenzeneDiazoniumChloride** (BDAC).

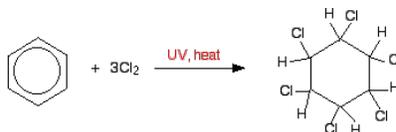


I will tell you about BDAC in a future blog, but for the moment



Boiling Benzene will thus undergo **addition** reactions, but it requires heat and the considerable reactivity of a free radical to overcome the inherent stability of Benzene.

Boiling Benzene in the presence of u.v. light will undergo Addition reactions with both Chlorine and Bromine. Jim Clark on his excellent *chemguide* website shows it thus



and please note that $\text{C}_6\text{H}_6\text{Cl}_6$ (1,2,3,4,5,6-Hexachlorocyclohexane) **now has no delocalised π ring**. The reaction above was with Chlorine, but it would equally take place with Bromine. Benzene will also react with Hydrogen gas in the presence of an **adsorbitive** catalyst such as finely divided Nickel/Platinum/Rhenium/etc (*finely divided to provide a large surface area*)².

I hope that you will by now have noticed that Benzene can be regarded as a conjugated species (in a sense possessing alternating double and single bonds) and it is now reacting exactly like an Alkene does when the Alkene reacts with Hydrogen gas in the presence of "Raney" Nickel (and we talked about that last year when we talked about the manufacture of margarine).

² Where the catalyst **adsorbs** the Hydrogen gas and weakens the intramolecular bond thus creating Hydrogen free radicals.

Where I have talked about Benzene in this blog, everything that I have said applies equally well to the Arenes.

Aliphatic compounds

- Alkanes
- Alkenes
- Alkynes

Alicyclic compounds

Cyclical organic substances
with **no** delocalised π ring

- Cyclical Alkanes
- Cyclical Alkenes

Aromatic compounds/Arenes

(these **do** have delocalised π rings)

- Benzene (C_6H_6)
(and Benzene compounds)



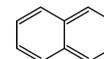
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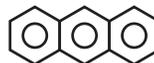
- Naphthalene ($C_{10}H_8$)³
(and Naphthalene compounds)



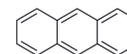
or



- Anthracene ($C_{14}H_{10}$)
(and Anthracene compounds)



or



³ There is far too much detail for you in it, but would you like to try clicking on
<http://en.wikipedia.org/wiki/Naphthalene>

It is good practice for you to see how other people describe/view things. Be flexible in your thought processes and always try to develop an “open” mind. The reason that human beings spend so much time killing each other is because they have closed minds – and they always think that they are in the right, even when they may possibly be in the wrong! Mind you, *even if you are in the right*, why should you kill anyone just because you are right and they are wrong!