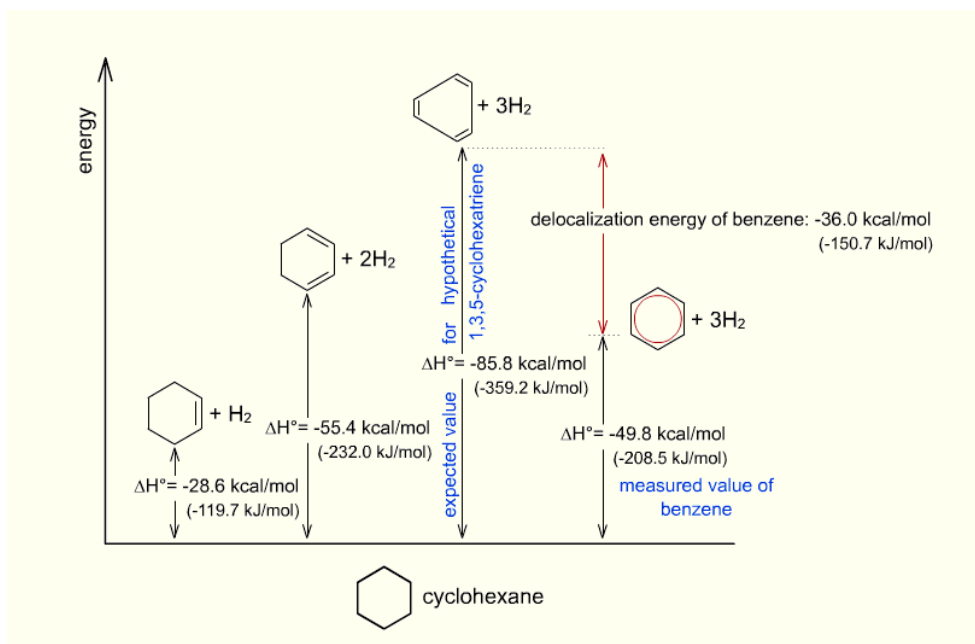


Year 2, Organic Chemistry, Chapter 14: The Electrophilic Addition Reactions of Benzene (These are **NOT** EAS reactions.)

- In certain circumstances Benzene can be regarded as a conjugated species with alternating double and single bonds. The double bonds should make Benzene react like a poly-alkene species. In theory this may be so, but in practice that is not the case because the delocalisation of Benzene's π ring confers considerable stability on it. (The stability involved is of the order of 151 kJ mol^{-1} .)



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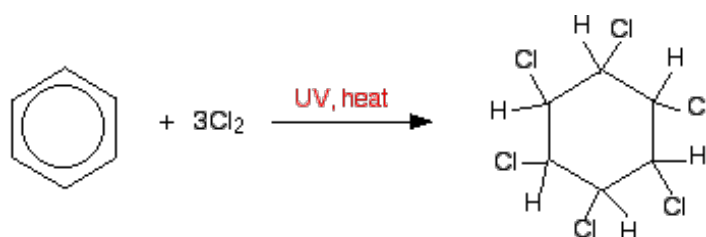
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- I have already told you that both Alkenes and Benzene (and Benzene's sister Aromatic compounds, the Arenes) have π bonds that are created by the overlap of unhybridised 'p' orbitals, and thus it is **not** surprising that Benzene in some circumstances 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 Arenes) will also react with Halogens – except that Aromatic compounds (because of the delocalisation of the electrons in the π ring) are normally *very* stable at room temperature and pressure (RTP) and therefore they react **much** less rapidly/much less easily than Alkenes do.
- In contrast to Alkenes, Arenes normally require much higher temperatures and pressures before they react and will exhibit the reactions of an Alkene sometimes only in the presence of a (very aggressive) 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 u.v. light**), and
 - Bromine** gas instantaneously in bright sunlight,
 so also **Benzene will react with Chlorine and Bromine, but only with a Halogen free radical and then minutely slowly at RTP (and over the period of about an hour with boiling Benzene in the presence of u.v. light).**

- Benzene **will** thus undergo Addition reactions, but I believe that it requires the considerable reactivity of a free radical to overcome the inherent stability of Benzene. 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*)¹.
- There are only three Addition reactions that you need to know about at 'A' Level
 - Halogenation
 - Hydrogenation, and
 - Oxygenisation (which is mainly combustion).

The Electrophilic Addition Halogenation reaction of Benzene

- In Chapter 11, when we were talking about the EAS reactions of Benzene, I told you that Benzene can be persuaded to decolourise Bromine water without heating when it is accompanied by an FC catalyst – and then substitution would occur only at one point on the Benzene ring (whereas every single double bond in a poly-alkene would get broken).
- However, boiling Benzene in the presence of u.v. light would undergo Addition reactions with both Chlorine and Bromine. Jim Clark on his excellent *chemguide* website shows it thus



and please note that C₆H₆Cl₆ **now has no delocalised π ring**. The reaction above was with Chlorine, but it would equally well take place with Bromine.

The Electrophilic Addition Hydrogenation reaction of Benzene

- I hope that you will remember that a gentleman called “Murray Raney” perfected a preparation of sponge-like Nickel that gave a very large surface area for the use of Ni as the catalyst in the manufacture of margarine from vegetable oils.
- Cyclohexane, C₆H₁₂, is a ring alkane with no delocalised π ring, and it is created by reacting Hydrogen gas with Benzene at about 150°C in the presence of finely divided Nickel or Raney Nickel.

¹ Where the catalyst adsorbs the Hydrogen gas and weakens the intramolecular bond thus creating Hydrogen free radicals.

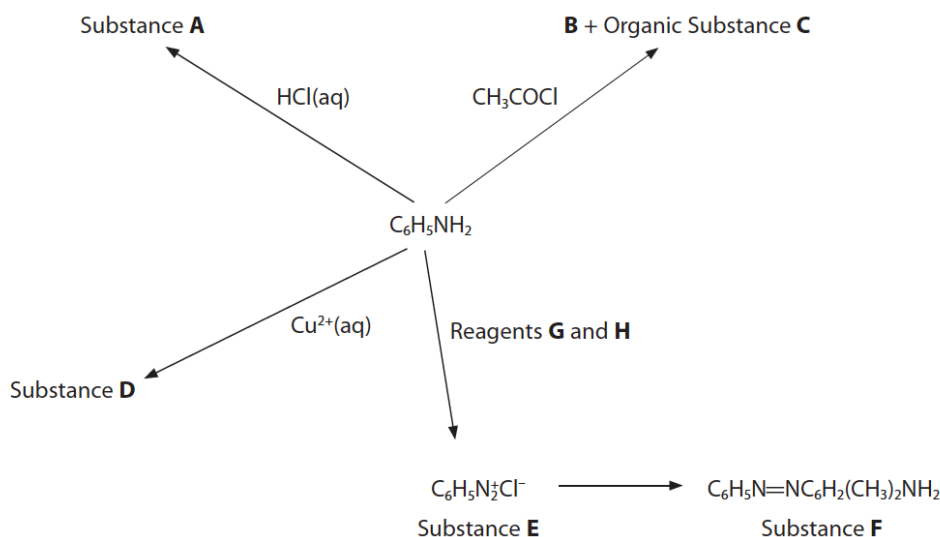
The Electrophilic Addition Oxygenisation reaction of Benzene

- Benzene occurs naturally in crude oil, and in earlier times it was a by-product in the manufacture of “town gas” from coke.²
- Benzene combusts in Oxygen with a bright light³ and a smoky flame. Because it is carcinogenic, the amount of Benzene permitted in petrol/gasoline is very strictly controlled by law in most countries.
- I taught you how to do combustion equation calculations last year.
- Benzene will react with Ozone at RTP to form Benzene triozoneide – but the chance of you getting a question on that in the ‘A’ Level exams is about the same as you winning the Lottery.

You do not need to know anything else about the Electrophilic Addition reactions of Benzene.

- Let me do an excerpt from an exam paper for you. It was a lovely question that tested a large amount of your comprehension of both Organic and Inorganic Chemistry.
- Q24(b) in the June 2015 Edexcel Unit5(6CH05) exam paper contained the following, and just in case you do not recognise the “C₆H₅” and the Phenyl element of a Benzene ring, the examiners actually tell you that the substance in the middle of the diagram is Phenylamine (or as it is also called “Aniline”)⁴.
- The trick with questions like this is to see what it is that is going to react. Do that for each one of the reactions A/B/C/D/E/F/G/H.

(b) Some reactions of phenylamine are shown below.



² Town gas was the ‘mains’ gas that was piped into all our cookers until we switched from ‘town gas’ to ‘natural gas’ from the North Sea in the 1960s/1970s.

³ That is why the adjective for $-\text{C}_6\text{H}_5$ is “phenyl” (from the ancient Greek word for light/to shine).

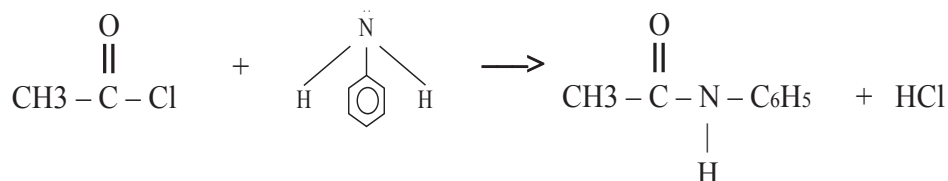
⁴ The “A” in the name of the huge German chemicals company BASF comes from “Aniline” because the name of the company used to be “Badische Anilin und Soda Fabrik”.

Reaction A : Phenylamine is basic and HCl is acidic, therefore this is just an acid/base reaction
(The lone pair on the N atom makes Phenylamine into a Lewis **base** and HCl is an **acid**.)

- The N atom in Phenylamine/Aniline/Aminobenzene has its required three bonds (one to “C₆H₅”, and one each to the two H atoms), but the N atom still has a lone pair of electrons and it uses that lone pair to form a dative bond with the H⁺ in the HCl(aq) to form the cation “C₆H₅.NH₃⁺”. (Please draw it and you will follow what I have just said.) This cation and the anion “Cl⁻” then form a straightforward ionic substance **C₆H₅.NH₃⁺. Cl⁻**. This is called Aniline Hydrochloride or Phenyl-ammonium Chloride.
- However, please note that the electron density on the N atom is locked into Benzene’s π ring through the +M effect, therefore its ability to attract and hold onto the H⁺ from HCl is not as large as it would be as say NH₃ or even an alkyl amine, C_nH_{2n+1}.NH₂. Phenylamine/Aniline/Aminobenzene is therefore a very *weak* base with 0.1 mol dm⁻³ Phenylamine having a pH of 9 compared to Ammonia of the same strength having a pH of more like 11.

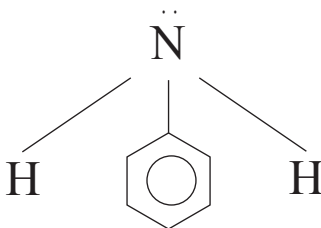
Substance B and an Organic Substance, C : this is the ACYLATION reaction of Phenylamine
(A Friedel-Crafts’ catalyst is not needed because Phenylamine is 2,4,6-activated where Benzene is not.)

- “CH₃.C=O(Cl)” is an Acyl Chloride (in this case Acetyl Chloride), and as we shall see later, if you react it with Phenylamine then you get the following.



- On my interpretation of the Edexcel Syllabus, strictly speaking the Acylation reactions of Phenylamine are not in the syllabus; but, as I have pointed out elsewhere, the Examining Boards make the rules and they mark your exam papers, so my job is to teach you enough Chemistry, and your job is to remain cool/calm/collected and use the stuff that I have taught you and the brains that you were born with, **and you will be able to answer this question.**
- Once again I want to draw your attention to the fact the N atom in Phenylamine has its required three bonds (one to “C₆H₅”, and one each to the two H atoms), but the N atom still has a lone pair of electrons and it uses that lone pair to form a dative bond.
- Let me draw it for you and you will see the point that I am making.

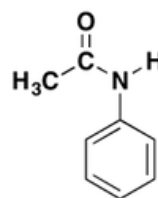
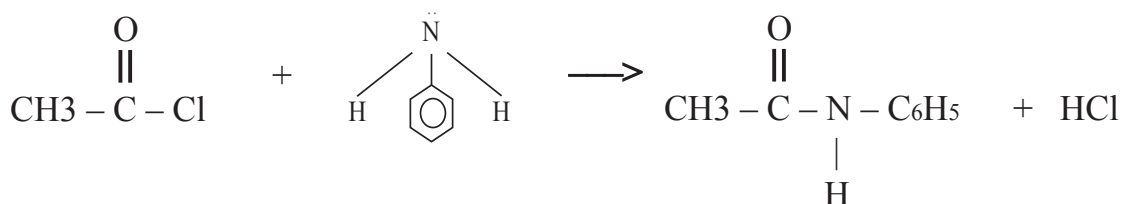
Don’t look at the “Phenyl” bit, **concentrate on the AMINE bit**



- What is going to happen in this reaction is that the “Cl” in the Acetyl Chloride (a hugely reactive substance) will break away heterolytically as “Cl⁻” thus leaving the Acetyl bit as a positively charged cation “CH₃.C⁺=O” (it is *short* of electron density). On the other hand, Phenylamine has the lone pair of electrons that I have talked about, therefore it is *long* on electron density. This therefore is going to lead to the classic “**electrophile reacting with a nucleophile**” reaction.
- One of the H species will break away as a proton and bond with the Cl⁻ to form HCl and we thus get the following species that the question mentioned.

Organic substance C

Substance B

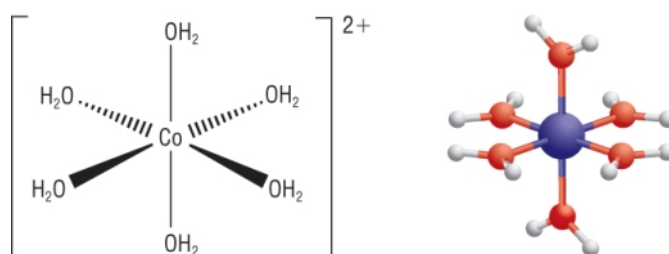


- This then is the classic case of the **Acylation of Phenylamine/Aniline/Aminobenzene**. There are two C atoms therefore the name of the substance will be derived from “Ethane”. The “-C₆H₅” species is attached to an N atom, therefore the name of the substance will have “N-phenyl” in it, and since the substance has “R-C=O (N)” in it, the name of the substance will have “amide” in it. The **substance C** in the exam question is in fact called “**N-phenylethanamide**”, and substance B is Hydrochloric Acid.

Substance D : This is all about the complexes formed by aqueous Transition Metals

(Cu²⁺ is the cyan coloured complex formed by Cu²⁺ and six molecules of Water: [Cu(H₂O)₆]²⁺)

- In Chapter 12 of Year 2, Inorganic Chemistry, I showed you the following complex. It was for Cobalt, but all that you need to do is substitute Copper for Cobalt.



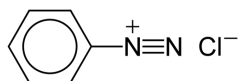
- When we talked about Transition Metals and their Complexes, I talked at some length about the reaction of Complexes with Ammonia. Complexes are formed by the donation of a lone pair of electrons by a ligand to a central metal ion, and what Ammonia does is to replace one by one the H₂O ligands with NH₃ ligands (if you need to do so, please read the Chapter on Transition Metals in Inorganic Chemistry again). Well, here the N atom in Phenylamine has a lone pair of electrons that it can donate, therefore it acts exactly as Ammonia does i.e. as a ligand.

- In the exam, I know that a number of candidates were cursing and swearing wondering how many of the (big) Phenylamine molecules they could fit in round the Copper central atom – and the examiners were **EXTRAORDINARILY** remiss for not having foreseen this problem but, as it happens, all that the examiners wanted was for candidates to say that **a Copper complex would be formed**.

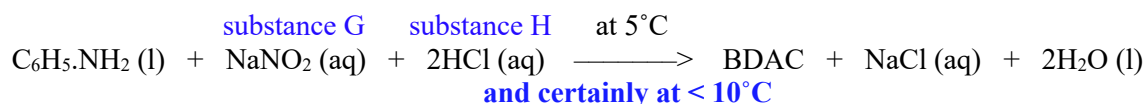
Substance E is BDAC

Phenylamine ($\text{C}_6\text{H}_5\text{NH}_2$) \rightarrow Benzenediazoniumchloride (BDAC)

(Using NaNO_2 and 2HCl : Chapter 16, Year 2, Organic Chemistry, Azo reactions.)

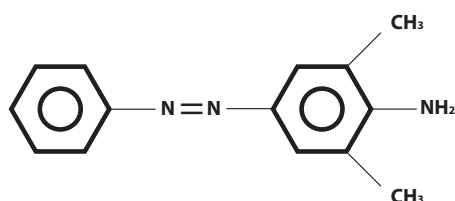


- When we get to Chapter 16 you will see that BDAC can be obtained by reacting Phenylamine with “Nitrous acid” (HNO_2) – **but nitrous acid is very unstable and decomposes very quickly**, therefore the nitrous acid has to be made and used on-the-spot (*in situ*) by reacting $\text{NaNO}_2(\text{aq})$ with $2\text{HCl}(\text{aq})$ and we would thus get



Substance F: $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_2(\text{CH}_3)_2\text{NH}_2$

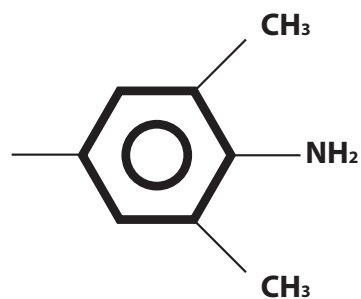
- Let me start by drawing substance “F” for you, and then you will see that it will be easy to make it from BDAC. This is what $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_2(\text{CH}_3)_2\text{NH}_2$ looks like. I have not drawn all the angles correctly. I have just drawn it all in a straight line.



- If you look carefully at the substance, there are two bits to it.



I hope that you can see that this bit is derived from BDAC



and this bit would be driven from 2,4,6-trimethyl phenylamine except that the third methyl group is no longer on position No 6 because it has been reacted with BDAC.

- We will talk more about BDAC in Chapter 16.