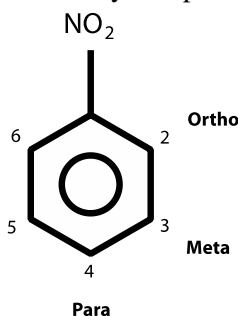


Year 2, Organic Chemistry, Chapter 06: More introductory stuff about Benzene

(Benzene and its sister Aromatic compounds with delocalised π rings are called "Arenes")

The naming of Benzene derivatives

- The very first thing that you need to grasp is how to name the different derivatives of Benzene, and for that you need the little Mnemonic **OMP** "Oh My Pappa"¹. **O** (for 'ortho') **M** (for 'meta') and **P** (for 'para') stand for the Latin names for positions 2/3/and 4 on a Benzene ring. To this I hope you will say "But since Benzene is a symmetrical hexagonal structure, from where are you starting your numbering?" – and to which I will reply "That is a very good question".
- For the moment, let me dodge that question (because I want to tell you about **OMP**). In the diagram below I have chosen Nitrobenzene as my compound to illustrate OMP



and as you can see my "Pappa" is in position '4'.

- As it happens half a century ago I spent two years doing all my studies in Latin when I was studying to be a priest², but I cannot see the point of using Latin in Chemistry if it is not necessary. I therefore do not use the OMP numbering system. **I use the 1/2/3/4/5/6 Arabic numbering system** – but whichever system you choose to use, the rule is the same "Start your numbering with No1 being the position of the base chemical, and after that it does not matter whether you count clockwise or counter-clockwise" because *that will depend merely on where you are in space in relation to the molecule*. If I am standing on one side of the above Nitrobenzene molecule and you are standing on the opposite side of the molecule, then my "clockwise" will be your "counter-clockwise" and *vice versa*. In fact, just as with all numbering in Chemistry, the numbering system you choose must be the one that gives the lowest numbers in the name of the species. In other words, there is no such thing as 6-methyl nitrobenzene. The correct name for the molecule will be 2-methyl nitrobenzene, or if you want to be pedantic, then you could call it ortho-methyl nitrobenzene (or "o-methyl nitrobenzene") – but I do not use such nomenclature.

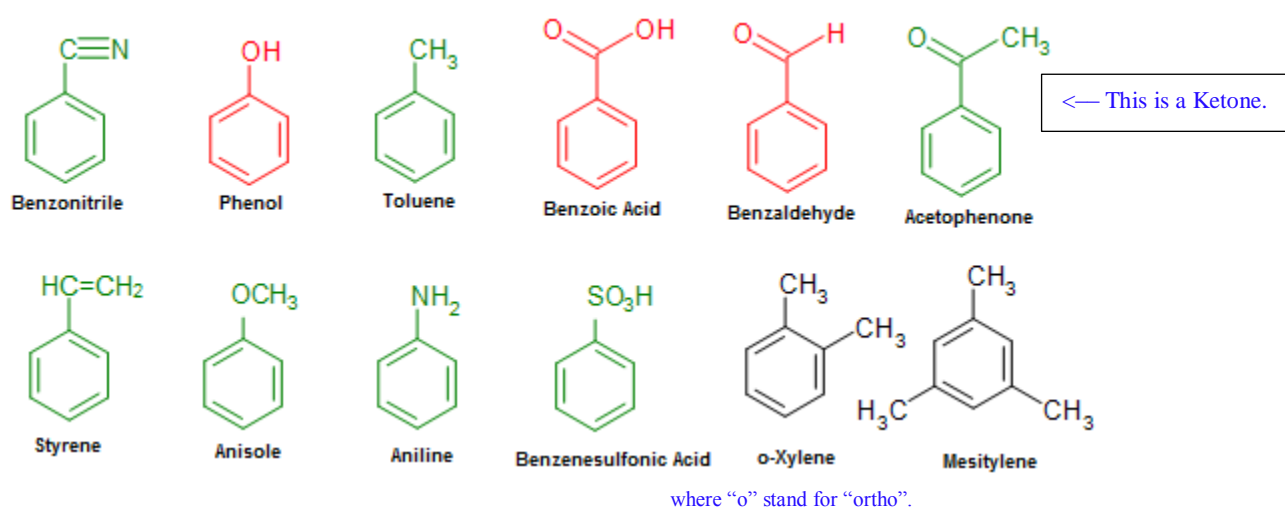
¹ A song made famous by Eddie Fisher in 1954. (The original song "Oh Mein Pappa" was written in 1939 for a German musical).

² and I may well be one of the few people left in the UK who has read Aquinas' "Summa Theologica" in Latin. Aquinas was the greatest theologian the Catholic Church has ever had, and it is interesting that he quoted Islamic scholars such as Avicenna/Averroes/et alii *with great reverence*. How times have changed in just 1,000 years! I wish that American Presidents knew a bit more about History, and I am deeply ashamed that a liar (Blair) was once the Prime Minister of this formerly great nation.

- Earlier on I fended off the question about where to start numbering a Benzene ring, but let me attempt to answer the question now. You can adopt either the alphabetical order of importance and start with the substituent that has the earliest alphabetical occurrence, or if the emphasis is on a particular base molecule, then that is where you start your numbering. For example if I have both a “-CHO” (an Aldehyde) and an “-NH₂” (an Amine) substituent on the Benzene ring, if it is the reaction of the Amine on which I am concentrating, **then my base molecule will be the Amine** (and that will be position No1) – but if I am concentrating on the reaction of the molecule as an Aldehyde, *then my base molecule will be the Aldehyde* (and that will be position No1). All this will become clearer over the course of the next few weeks.

- On a number of occasions last year I mentioned the website “LibreTexts” to you. It is an outstanding Chemistry website, and I cannot recommend it to you highly enough. The diagram below is taken from

[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)



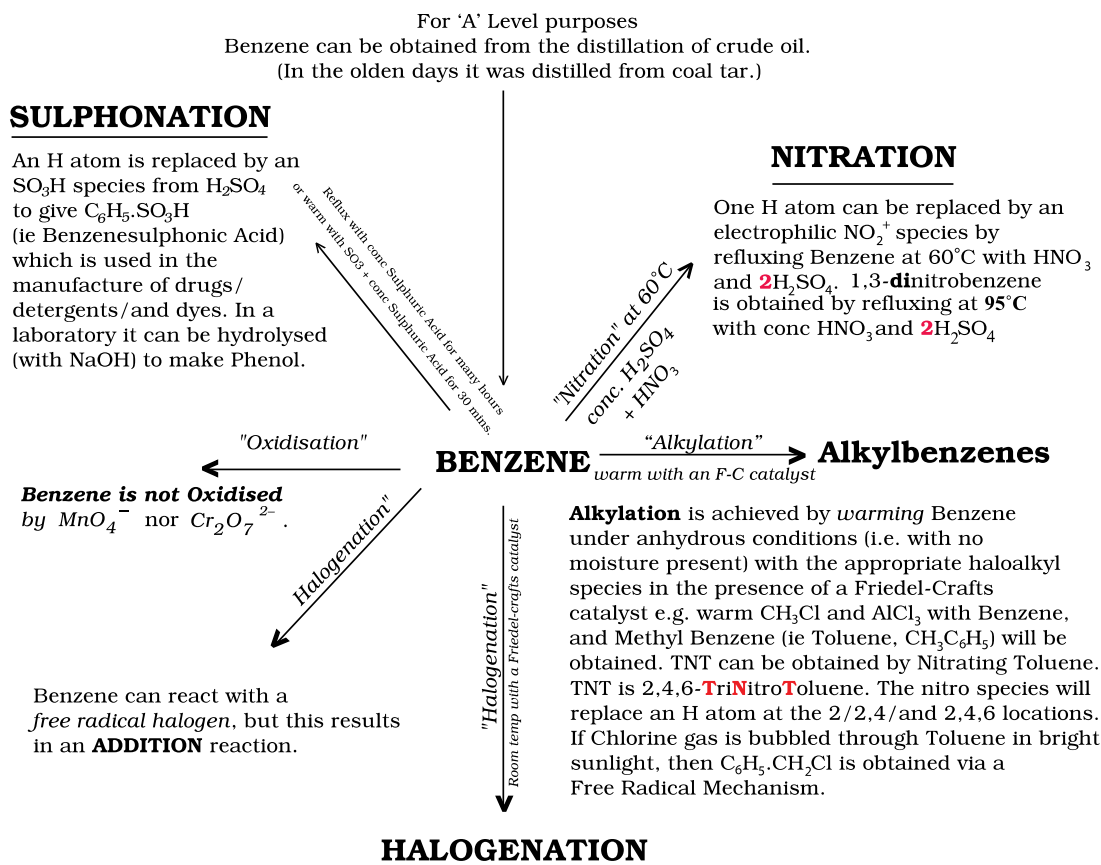
and at ‘A’ Level you **will** encounter (alphabetically)

- Benzaldehyde $C_6H_5.CHO$
 - Benzenecarboxylic acid (Benzoic acid) $C_6H_5.COOH$
 - Benzenesulphonic acid (also called Benzene mono-sulphonic acid) $C_6H_5.HSO_3$
 - Benzonitrile $C_6H_5.CN$
 - 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 $C_6H_5.NH_2$
- I hope that you never encounter Tri-Nitro Toluene, TNT (because I abhor all sorts of violence). TNT used to be called 2,4,6-trinitrotoluene, or 2,4,6-trinitromethylbenzene $C_6H_2(NO_2)_3CH_3$. However, just to show you how complicated the subject of naming can get, TNT is now called 2-methyl-1,3,5-trinitrobenzene.
 - OK, I am going to leave the subject of naming Benzene compounds (and as we develop our knowledge of this topic, you will pick it up as we go along).
 - I want now to give you a birds’ eye view of what we are going to need to know about Benzene and its reactions for ‘A’ Level purposes.

- I have constructed an Information Tree that I believe covers all the reactions of Benzene that you need to know for all the UK 'A' Level Syllabuses³. It is vitally important that, in the exams, you do not have to think about how you go from Benzene to any of its derivatives. If you have to do so, **then you will be wasting valuable time and you may not be able to finish all the questions on the exam paper.** *That would not just be sad, it would be TRAGIC!* **If you have the potential to shine, then let your light shine through bright and clear.** Do not get hung up on things that will waste your time.

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

The SUBSTITUTION reactions of Benzene



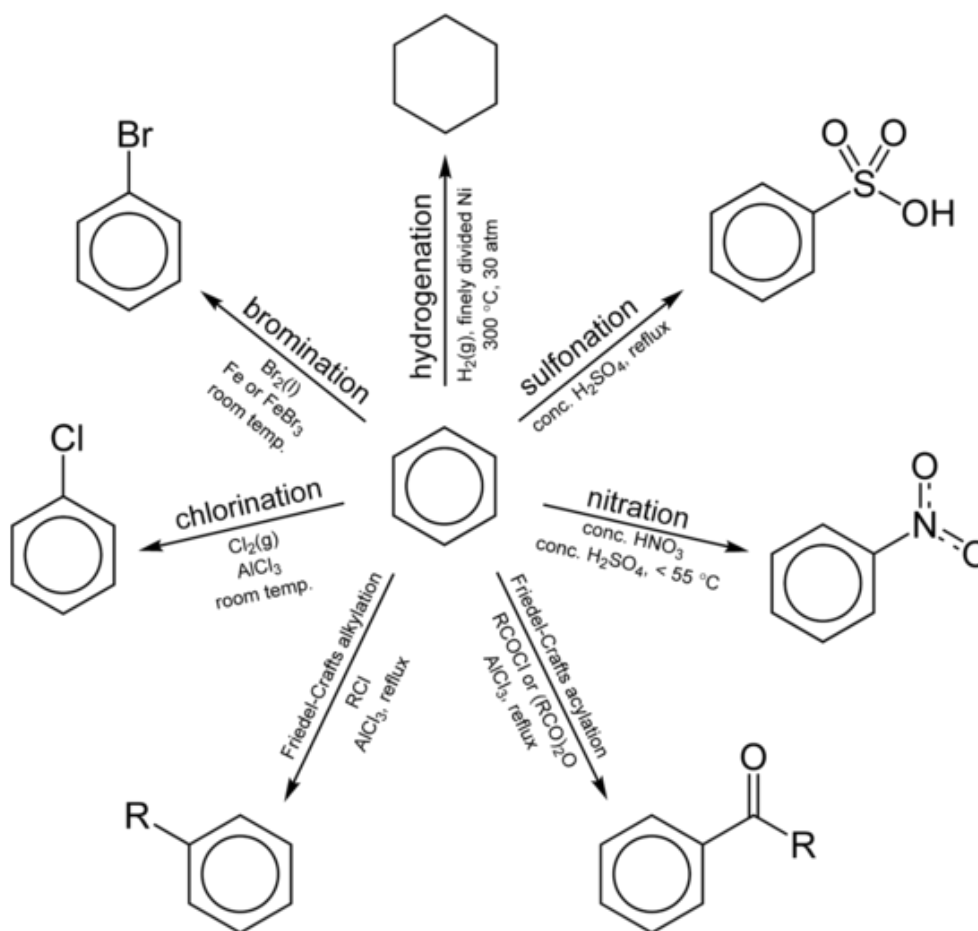
ADDITION REACTIONS

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

³ The plural form of the original Latin word *syllabus* is *syllabi*, and the plural form of the Anglicised word is Syllabuses.

- You may prefer Wikipedia's version of the info tree (below).



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)

- In the next couple of weeks we are going to learn all the reactions of Benzene that we need to know for the 'A' Level Syllabus. However, before I finish this Introductory Chapter on Benzene let me
 - show you some of the things in the info trees and then
 - I will tell you about the Addition reactions of Benzene
 and I will do so because the double bonds in Benzene make it modestly similar to an Alkene, therefore Arenes will do some of the things that Alkenes will do (except under different reaction conditions).
- I guess that the English 'A' Level Syllabus constitutes fairly standard required knowledge for 17-18 year olds because California State University, Dominguez Hills gives much the same sort of required reaction knowledge in one of its presentations (overleaf) where "Ar-H" means "I am going to take an H atom from an Aromatic compound and replace it with". In the study of Benzene, "Ar" would stand for the Arene "Benzene".

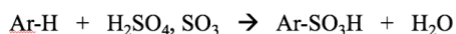
Electrophilic Aromatic Substitution (Aromatic compounds)

Ar-H = aromatic compound

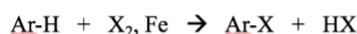
1. Nitration



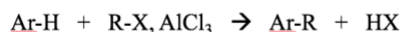
2. Sulfonation



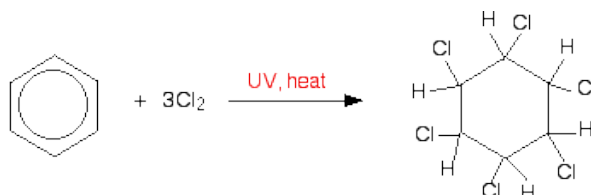
3. Halogenation



4. Friedel-Crafts alkylation

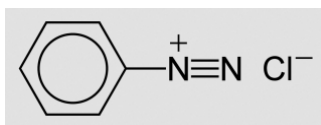


The info trees talk about the halogenation of Benzene, and the little diagram below shows you how to create C₆H₆Cl₆, Benzene-1,2,3,4,5,6-hexachloride. (Bubble the Halogen gas through boiling Benzene in bright sunlight.) The technically correct name for C₆H₆Cl₆ is *1,2,3,4,5,6-hexachlorocyclohexane*.

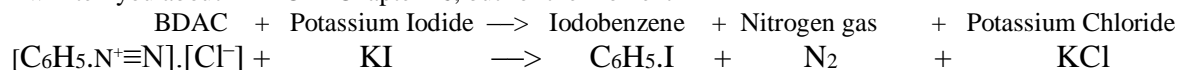


The Addition reactions of Benzene

- Both Alkenes and Benzene (and Benzene's sister Aromatic compounds) have π bonds 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 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 Halogen free radical and then minutely slowly at RTP (and 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 + Potassium Iodide.



I will tell you about BDAC in Chapter 16, 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. Benzene will also react with Hydrogen gas in the presence of an *adsorbitive* catalyst such as finely divided Nickel/Platinum/Rhenium/etc (*finely divided so as to provide a large surface area*)⁴.
- I hope that you will by now have noticed that since Benzene can be regarded as a conjugated species (in a sense possessing alternating double and single bonds) 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).
- Benzene will also undergo an addition reaction with Ozone (but that is well beyond the ‘A’ Level Syllabus).
- Where I have talked about Benzene, everything that I have said applies equally well to the other 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)

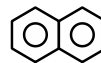
- Benzene (C_6H_6)
(and Benzene compounds)



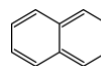
or



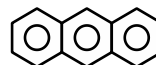
- Naphthalene ($C_{10}H_8$)⁵
(and Naphthalene compounds)



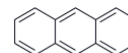
or



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



or



- OK, I think that I have now given you a fairly good introduction to Benzene, therefore let us now start talking about the reactions of Benzene in modest detail.

⁴ Where the catalyst adsorbs the Hydrogen gas and weakens the intramolecular bond thus creating Hydrogen free radicals.

⁵ There is far too much detail for you in it, but would you like to try clicking on to

<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 always think that they are in the right, even when they may possibly be in the wrong!