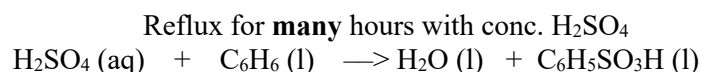


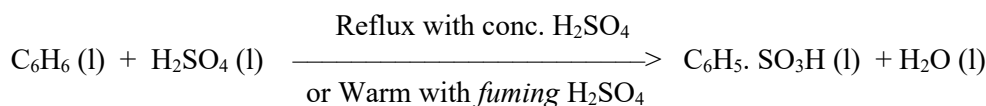
Year 2, Organic Chemistry, Chapter 13: The EAS Sulphonation of Benzene

- This is an EAS reaction **where no FC catalyst is involved**. $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ is a white waxy solid at RTP. The reaction equation for Sulphonation is

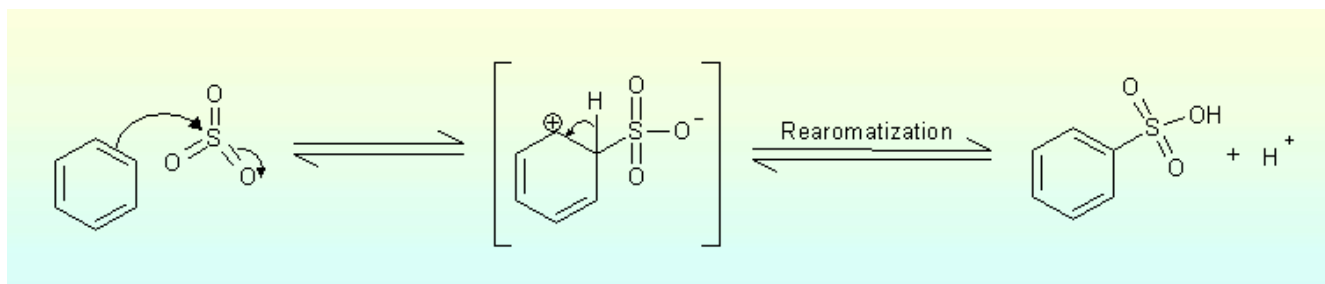


but it takes so long that Benzenesulphonic Acid is **not** produced in this manner.

- The reaction can be speeded up very considerably by refluxing Benzene with so-called “*fuming*” sulphuric acid (Oleum) which consists of $\text{SO}_3(\text{g})$ dissolved in $\text{H}_2\text{SO}_4(\text{l})$ to give $\text{H}_2\text{SO}_4 \cdot x\text{SO}_3$. This reaction is accomplished in minutes.



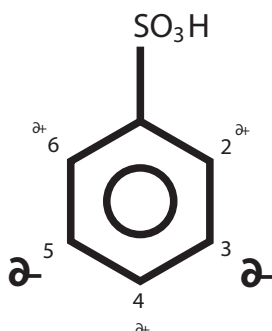
- Alternatively, Benzenesulphonic Acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ (also called Phenylsulphonic acid) can be made by reacting Benzene with $\text{SO}_3(\text{l})$.



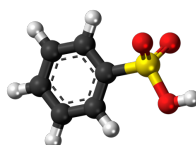
Source: University of Malta

- This is a good opportunity to remind you about ‘activation’ and ‘de-activation’ (and these two terms would have been better named “activation at 2/4/6” and “de-activation at 2/4/6 but activation at 3/5”).
- If a species has replaced an H atom on a Benzene ring then you must look to see what is attached to the atom that has attached itself to the C atom in the Benzene ring. The classic example is the difference between $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NO}_2$.
 - “H” is less electronegative than “N” therefore the electrons in N’s ‘p’ orbital get locked into Benzene’s delocalised π ring via the ‘+’ mesomeric effect, but because “O” is more electronegative than “N”, the electrons in N’s ‘p’ orbital get pulled towards the “O” atom, therefore the electrons in N’s ‘p’ orbital get locked into Benzene’s delocalised π ring via a **negative mesomeric effect**.
 - $\text{C}_6\text{H}_5\text{NH}_2$ activates the Benzene ring at 2/4/6, whereas
 - $\text{C}_6\text{H}_5\text{NO}_2$ activates the Benzene ring at 3/5.
- Now could you please work out where the Benzene ring will be activated with $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, and please remember that it is the “S” atom that becomes attached to the Benzene ring.

- The answer is that “O” atoms are more electronegative than “S” atoms, therefore the electrons in S’s ‘p’ orbital get pulled towards the **three** O atoms and the Benzene ring is de-activated but **activated at 3/5** thus

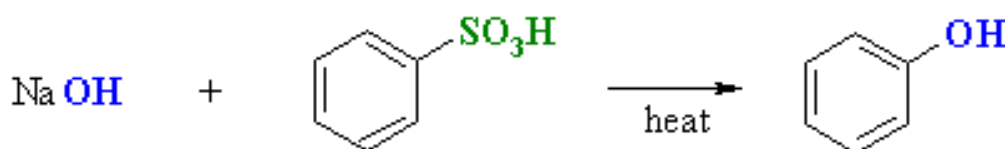


- In the diagram below, the S atom is coloured yellow, and the three O atoms are shown in red.

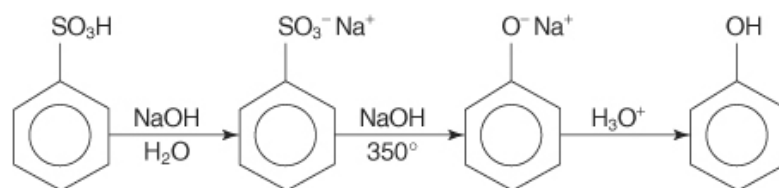


Source: Wikipedia

- Interestingly, Wikipedia says “*Benzenesulfonic acid is prepared from the sulfonation of benzene using concentrated sulfuric acid. This conversion illustrates aromatic sulfonation, which has been called “one of the most important reactions in industrial organic chemistry”.*
- That is Wikipedia’s statement and not mine, and sadly, I know next to nothing about Industrial Chemistry therefore I cannot comment on the claim, but the Encyclopaedia Britannica says the following “The sulfonic acids are among the most important of the organosulfur compounds; the free acids are widely used as catalysts in organic syntheses, while the salts and other derivatives form the basis of the manufacture of detergents, water-soluble dyes and catalysts, sulphonamide pharmaceuticals, and ion-exchange resins. Aromatic sulfonic acids are particularly useful as intermediates or starting materials in synthesis – for example, in the preparation of phenols”.
- Benzenesulphonic acid gives a very easy route into Phenol where the “–SO₃H” is replaced by hydrolysis to give C₆H₅OH. The cursory explanation (below) of the reaction is that of McGraw-Hill

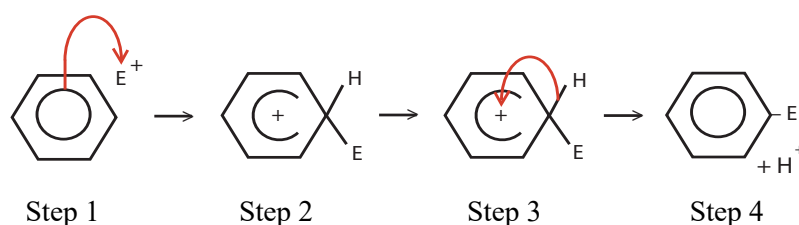


but a fuller description is shown overleaf



Source: cliffsnotes

- 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 broken¹ 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

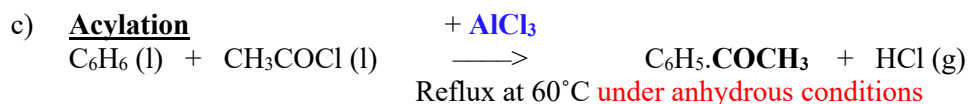
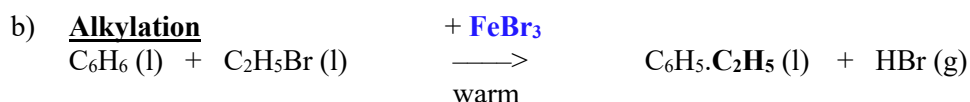
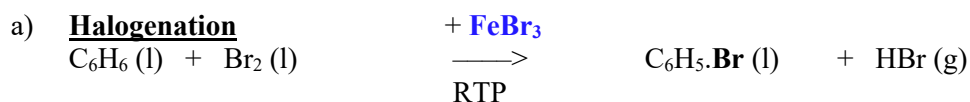
The Hydrogen atom that is bonded to the C atom to which the electrophile is attached breaks away (as a proton) leaving behind its electron – and this now recreates the Benzene π ring!

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.

¹ 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.

- In the case of
 - a) **Halogenation** the molecule that reacts with the FC catalyst will be either Chlorine or Bromine (it is *much* more difficult to react Iodine with Benzene²), while in the case of
 - b) **Alkylation** it is sensible to use $C_nH_{2n+1}-Hal$ to bond with the FC catalyst (such as $AlCl_3/FeBr_3$ /etc) to get the Alkyl Group “ $-C_nH_{2n+1}$ ” to bond with the Benzene, and in the case of
 - c) **Acylation** it is sensible to use $RCO-Hal$ for the $RC=O$ to bond with the FC catalyst.
- In this way, to accompany the E^+ species, there will always be a Halogen atom in the molecule to bond with the FC catalyst.³
- 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 $60^\circ C$ 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.

² 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 “**diazonium**” meaning two N atoms.)

³ I would therefore contend that the “halogen carrier” is actually carrying the *companion* species (but the term “companion” carrier would be ridiculously vague).

EAS Reactions of Benzene

