

Year 2, Organic Chemistry, Chapter 10:

The EAS Acylation of Benzene

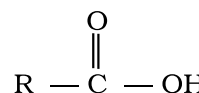
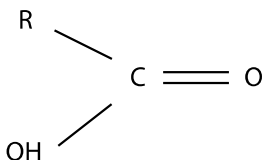
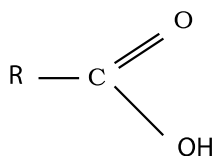
At <https://www.chemguide.co.uk/mechanisms/elsub/fcacyl.html> Jim Clark says the following

An acyl group is an alkyl group attached to a carbon-oxygen double bond. If "R" represents any alkyl group, then an acyl group has the formula RCO-. Acylation means substituting an acyl group into something - in this case, into a benzene ring.



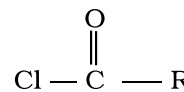
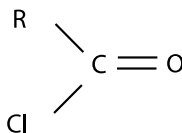
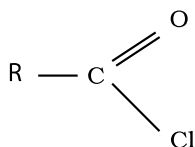
The Acylation of Benzene

- Let me start with one of the representations of a Carboxylic Acid that I did for you last year.



This is the way that examiners often draw it in the exam

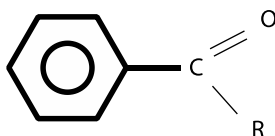
- However, if I now replace the “-OH” species in the acid with a “Cl”, then we would have an “Acyl Chloride”.



This is the way that examiners often draw it in the exam

– and that is the species that I am going to use here (together with an FC catalyst) in the Acylation of Benzene .

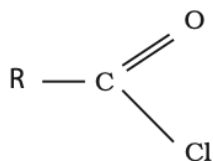
- Do you remember that I have told you that you would need an FC catalyst such as AlCl_3 for the **Alkylation**, the **Acylation** and the **Halogenation** of Benzene? Well here I have an acyl chloride, **R.(C=O).Cl** , and the “Cl” species in the acyl chloride will attach to the FC catalyst to form “ $\text{AlCl}_4^-.\text{RC}^+=\text{O}$ ” (cf. footnote¹) and it is the “ $\text{RC}^+=\text{O}$ ” Acyl species that will be the electrophile (E^+) that attacks the area of electron density that protects the Benzene ring above and below the horizontal plane of the C_6H_6 molecule. An EAS reaction will then occur.



← This could be $\text{C}_6\text{H}_5.(\text{C}=\text{O})\text{Cl}$

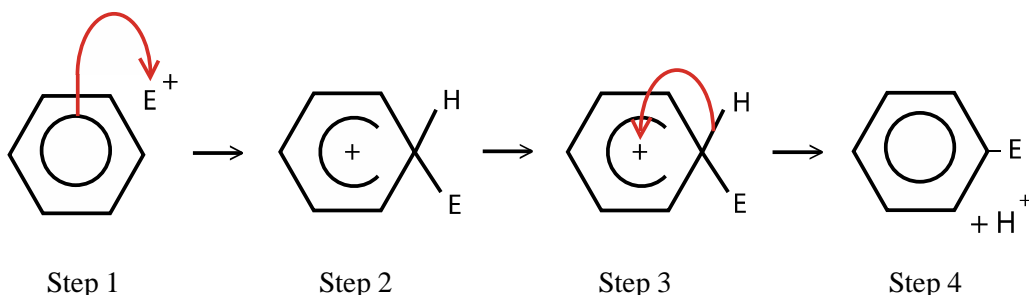
¹ If you say this species as the “R C double-bond O cation” or “R C double-bond O electrophile” species, then you will be using the appropriate wording to describe what is written in front of you.

- Remember, this is the basic mechanism for the conversions that we have been discussing. For Acylation, we will use



and an FC catalyst AlCl_3 / FeBr_3 / etc. The halogen anion (Cl^- in this case) will then join on to the FC catalyst leaving the $\text{R}-\text{C}^+=\text{O}$ anion to react with the Benzene as E^+ .

- 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 broken² 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

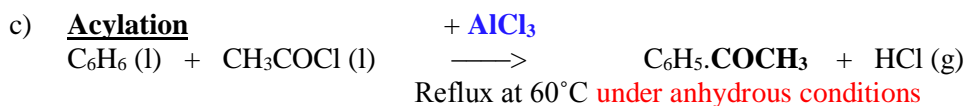
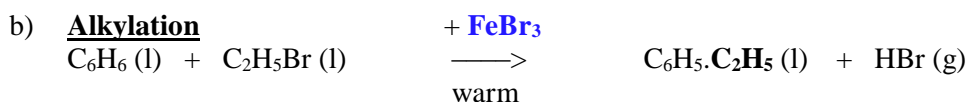
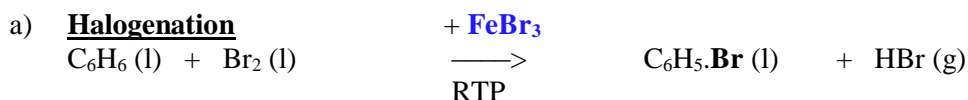
The Hydrogen atom that is bonded to the C atom to which the electrophile is attached breaks away (as a proton) leaving behind its electron – and this now recreates the Benzene π ring!

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.

² 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 Benzene³), 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.⁴
- 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**).

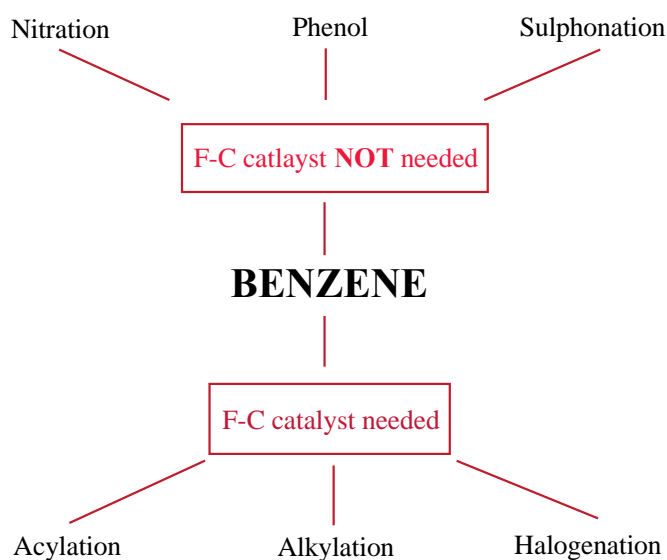


³ Iodobenzene can be obtained by reacting Benzenediazonium Chloride (BDAC) with Potassium Iodide. (“Azote” is the French name for Nitrogen, and that is where you get the term “diazonium” meaning two N atoms.)

⁴ I would therefore contend that the “halogen carrier” is actually carrying the *companion* species (but the term “companion” carrier would be ridiculously vague).

- 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.

EAS Reactions of Benzene



- **Have you noticed that things have been getting easier and easier.** That is because you are now beginning to be familiar with all the principles that are involved in EAS (Electrophilic Aromatic Substitution) reactions. OK, “*all*” is a bit of an exaggeration (because for a degree in Chemistry you would need to know a huge amount more), but you now know miles more than you would know if you had learnt it all by heart and understood not a single thing. Therefore, no matter what they throw at you in the exam, **you should be able to answer any question in seconds!**