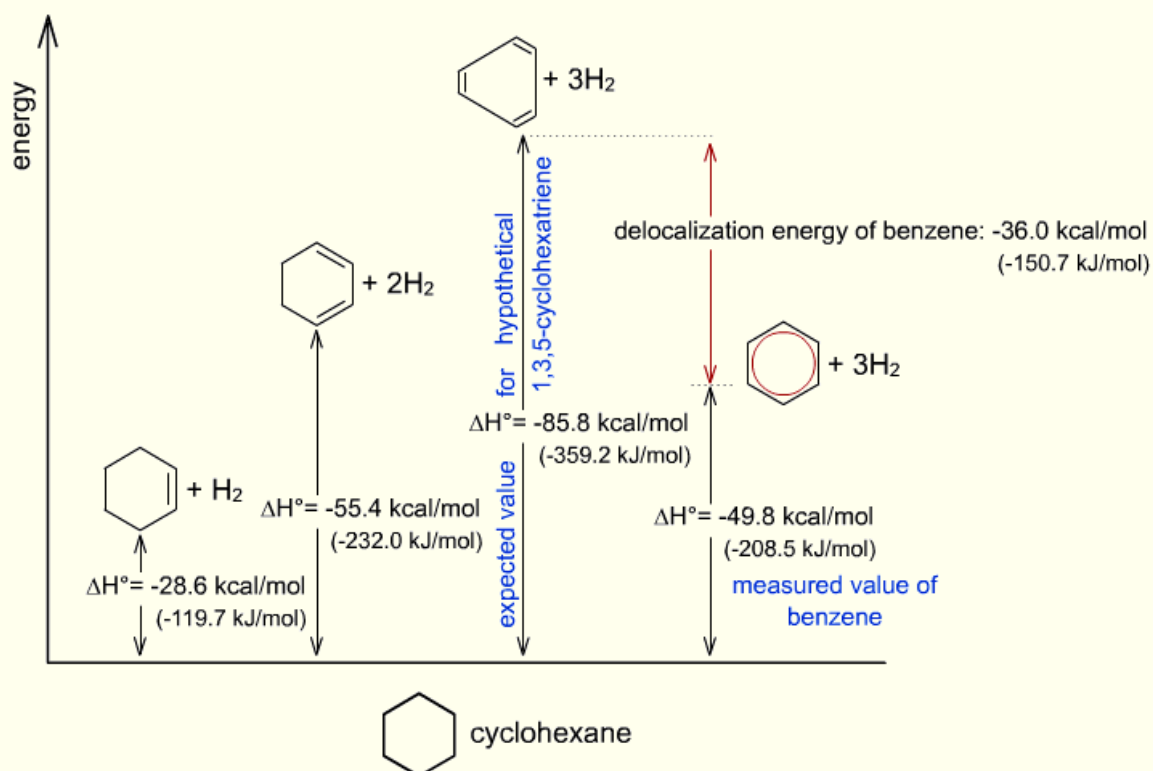


Year 2, Organic Chemistry, Chapter 11: The EAS Halogenation of Benzene

- Actually, **you** could now write this Chapter very easily.
- The only thing that you do not know is that there are both
 - **Substitution** Halogenation reactions, and there are
 - **Addition** Halogenation reactions
 and I am dealing with all the substitution (EAS) reactions of Benzene that you need to know first, and then **I will put together all the Addition reactions for Benzene in a different Chapter (Chapter 14)**. (I trust that you have not forgotten that C_6H_6 resembles an Alkene in that it can be considered to be a conjugated (alternating double-bond-and-single bond) species. Therefore whatever an Alkene does, an Arene can probably be made to do – albeit by putting in a lot of energy into the reaction.
- The stability of the delocalised π ring in Benzene confers a stability of about 151 kJ mol^{-1} of energy on C_6H_6 , and it therefore requires that amount of energy to ‘persuade’ C_6H_6 to do what an Alkene would otherwise do. I have shown you the following diagram before.



Source :

http://www.chemgapedia.de/vsengine/vlu/vsc/en/ch/12/oc/vlu_organik/aromaten/aromaten/benzol_stabilitaet.vlu/Page/vsc/en/ch/12/oc/aromaten/aromaten/stabilitaet/stabilitaet.vscml.html

- You are going to need to know the normal reactions of an Alkene, so please go back and read Chapter 5 of last year's Organic Chemistry book. Please make sure that you are thoroughly familiar with the mechanisms of all the different reactions, because you will be tested on them in your A2 exams and you will need to know them for some bits of Benzene. Last year I told you the following.

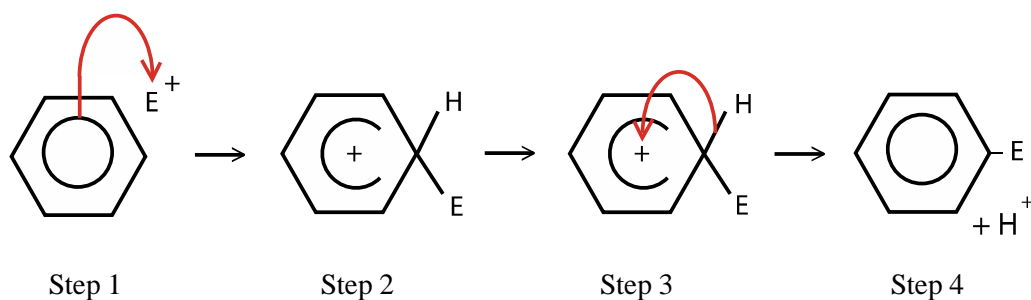
A classic test for an unsaturated Carbon compound

- Bromine can be decolourised **either** by an Alkane **or** by an Alkene.
- An Alkane will decolourise Bromine very **slowly in sunlight** (via a Free Radical Substitution Mechanism) – but an Alkene will decolourise Bromine **IMMEDIATELY even in the dark**, even in sub-zero temperatures (via an Electrophilic Addition Reaction Mechanism). *The fact that the reaction occurs in the dark and in the extreme cold demonstrates that the mechanism is **not** a Free Radical Substitution mechanism involving an Alkane (because in a Free Radical Substitution mechanism reaction either (i) u.v. light or (ii) energy would be needed to break the Br–Br bond to produce the free radical species).*
- A **SIMPLE** test (as opposed to a complicated test) for deciding whether a particular Carbon compound is saturated or unsaturated is therefore **the decolourisation of Bromine**. If the decolourisation is immediate, even in the cold and in the dark, then the Carbon compound was unsaturated!
- Bromine gas/liquid Bromine/and aqueous Bromine all have the characteristic brown colour of Bromine, and if an unsaturated Carbon compound comes into contact with Br (g)/ Br (l) / or Br (aq) then the compound will **immediately (even in the dark and without any heat)** undergo an electrophilic addition reaction with the Br – and the Bromine will immediately become decolourised i.e. it will become colourless.
- If therefore, in an exam you are asked for a simple test for an unsaturated Carbon compound, all that you have to do is to say that **you would add the given Carbon compound to Bromine** (dissolved in a solvent such as CCl₄) **or to Bromine water** (i.e. an aqueous solution of Bromine) and **if the Bromine/Bromine water is decolourised IMMEDIATELY, even in the dark and in the cold, without the attendant production of HBr** (a fuming pungent gas), **then the Carbon compound was an unsaturated Carbon compound!** (An Alkane would not be able to do this in the dark or without heat. *Energy from somewhere would be needed to break the Halogen–Halogen bond.*)
- Well, now I can tell you that even though Benzene can be regarded as a conjugated species with alternating double and single bonds, **Benzene will NOT decolourise bromine water in the dark and definitely not at ice cold temperatures**. The stability conferred by its delocalised π ring will prevent any such occurrence.
- However, Benzene can be persuaded to decolourise Bromine water without heating when it is accompanied by an FC catalyst – and then only at one point on the Benzene ring (**whereas every single double bond in a poly-Alkene would get broken**).
- Many chemists tend to favour FeBr₃ as the catalyst/Halogen carrier for the EAS bromination reaction of Benzene, and AlCl₃ for the **EAS** chlorination reaction of Benzene, and the results would be C₆H₅.Br and C₆H₅.Cl. (Please remember that in this Chapter we are talking about the EAS Halogenation of Benzene.)



The reaction mechanism for the EAS Halogenation of Benzene

- 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.

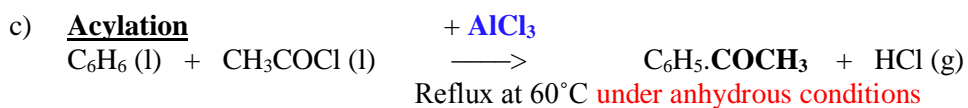
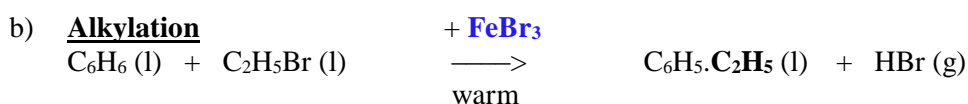
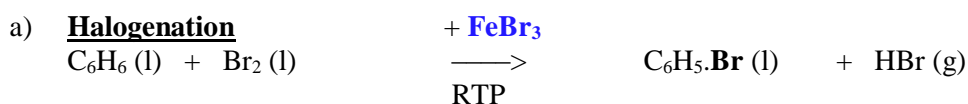
- In the case of

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.

- 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**).

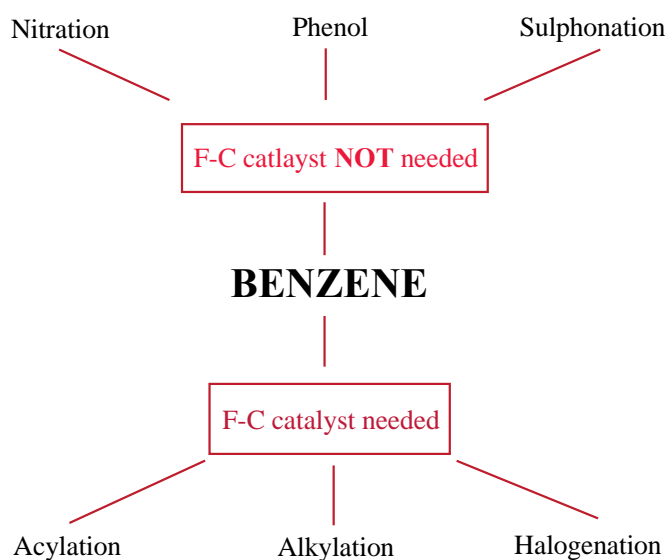


² Iodobenzene can be obtained by reacting Benzenediazonium Chloride (BDAC) with Potassium Iodide. (“Azote” is the French name for Nitrogen, and that is where you get the term “diazonium” meaning two N atoms.)

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

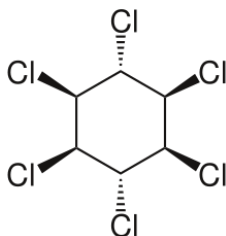
- In the exam, if you are asked about any of these three electrophilic substitution reactions of Benzene you will now be able to score 3 or 4 marks **within seconds** (and you **do** need to be able to answer questions *within seconds* or else you will not finish all the questions on the exam paper)!
- 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

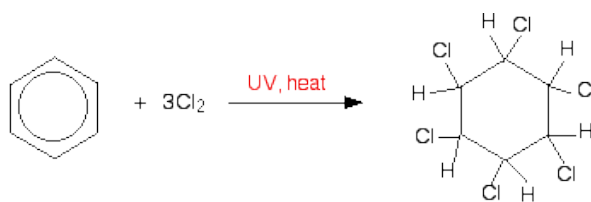


The Electrophilic Addition reaction of Benzene (described in Chapter 14)

- In the Electrophilic Arene **Addition** reaction of Benzene (in Chapter 14) with a Halogen (such as Chlorine) the result would be 1,2,3,4,5,6-hexachlorocyclohexane, but please remember that **this compound is NOT the result of an EAS reaction** (it will be the result of an **Addition** reaction)



and please also remember that the convention when drawing organic skeletal diagrams is NOT to show C atoms nor H atoms – therefore at each of the six vertices/apices of $C_6H_6Cl_6$ there are C atoms and (omitted bond lines to) H atoms. If you drew in the bond lines to the H atoms you would get



- I do not want to get into the complexities of the stereo-isomers of $C_6H_6Cl_6$, but the one that I have shown above is the dangerous chemical called Lindane (and it is also called gamma-hexachloro-cyclohexane) and if you want to go into Medicine when you leave here, then you might want to type the name into your search engine.
- In his excellent website Jim Clark points out that it is much *cheaper* to use Iron filings and the appropriate Halogen in the **EAS Halogenation of Benzene**, because this is a much cheaper industrial route than buying an FC catalyst and then mixing it with Benzene and the Halogen. Mr Clark is absolutely correct to also point out that in this methodology the Halogen carrier is being formed and used *in situ* (“*in situ*” is Latin for on the spot/there-and-then).
- Inevitably, there is a lot more to the Halogenation of Benzene, but now you already know more than you need to know for ‘A’ Level purposes.
- Let us now talk about Nitration in Chapter 12.