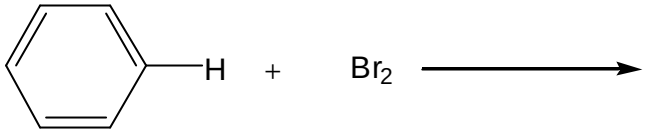
Electrophilic Aromatic Substitution of Benzene

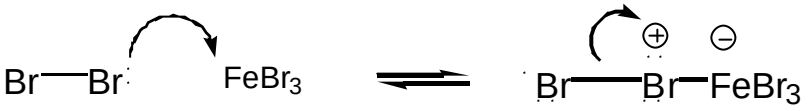
1. Halogenation of Benzene

While bromine dissolved in carbon tetrachloride reacts rapidly with alkenes at room temperature benzene requires harsh conditions, liquid Br_2, no solvent, and a Lewis acid $FeBr_3$ catalyst.

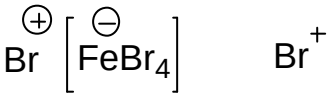


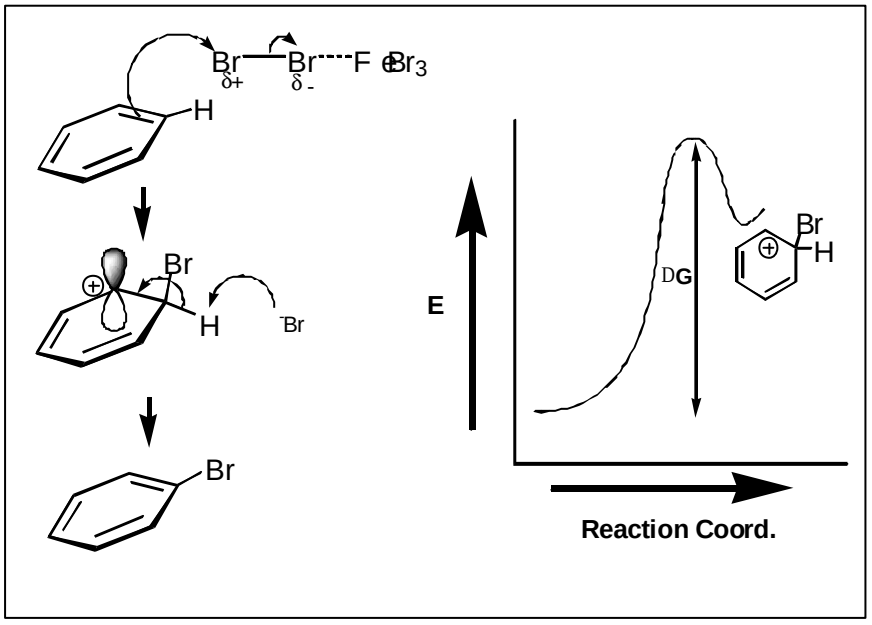
Unlike addition of halogen to an alkene bromine susbstitutes hydrogen on the aromatic ring, [Not like addition of Br_2 to ethylene].

The aromatic ring is more stable than an alkene. For bromination to take place a Lewis acid catalyst is required. By complexing with the bromine the Lewis acid makes it more elctrophilic by generating the species Br^+:-

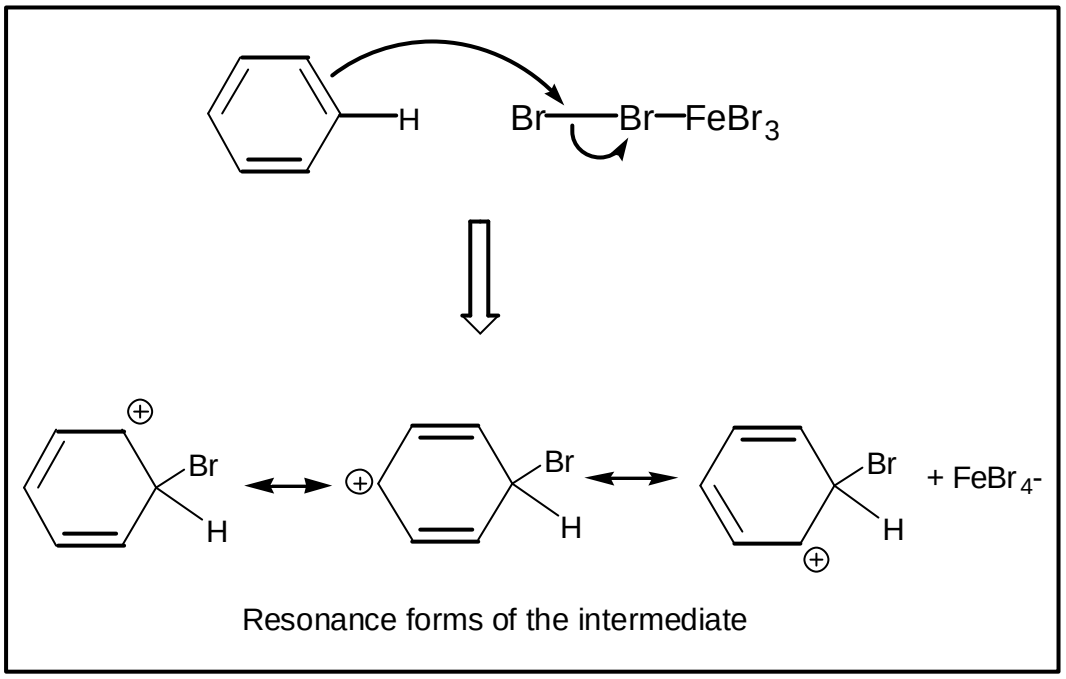


Does not go this far but behaves as if had:



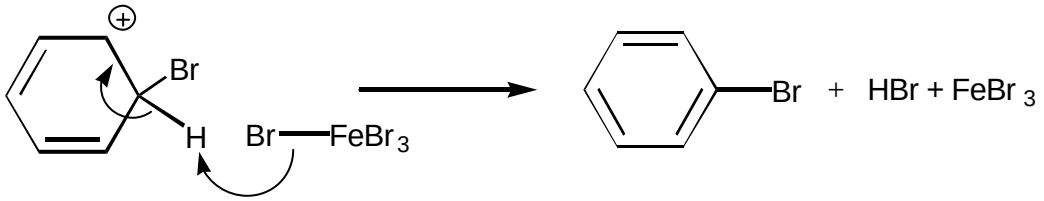


The π electrons of the benzene ring attack the activated bromine. However because the benzene ring is stabilized by aromaticity and the delocalization of 6 π electrons, the reaction has a high activation energy and the reaction is slow and requires heat. Although the intermediate carbocation is resonance stabilized aromaticity has been lost.

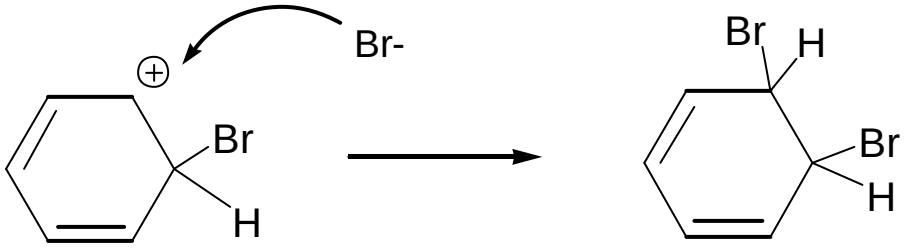


Resonance forms of the intermediate

In the final step of the mechanism the bromide ion forms HBr by reacting with the hydrogen at the substituted carbon centre.



Why is the carbocation not attacked by Br^- as shown below (similar to what we see for Br_2 attack on an alkene.?



Does not happen!!

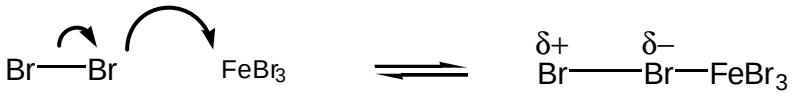
Because the resulting product is not aromatic this type of product is not formed.
Instead Br^- acts as a base to remove the ring proton. Loss of H^+ is a typical reaction of carbocations and here it generates the stabilization of aromaticity.

2. Electrophilic Aromatic Substitution

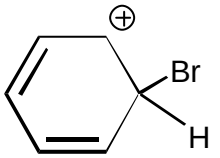
Halogenation is just one of the many reactions typical of benzene Electrophilic Aromatic Substitution.
H is substituted by Br.

Electrophilic - involves reaction of an electrophile or Lewis Acid with π electrons.
Bromination promoted by Lewis acid catalyst, the elctrophilic species is "Br^+"
S_N1 or S_N2 Nucleophilic substitution reaction involve a nucleophile which is Lewis base.
In Electrophilic Aromatic substitution – a Lewis acid or electrophile is substitution group.
Electrophilic aromatic substitution is the most common reaction of benzene.
General Steps in such reactions:

Step 1: Generation of Electrophile, E^+



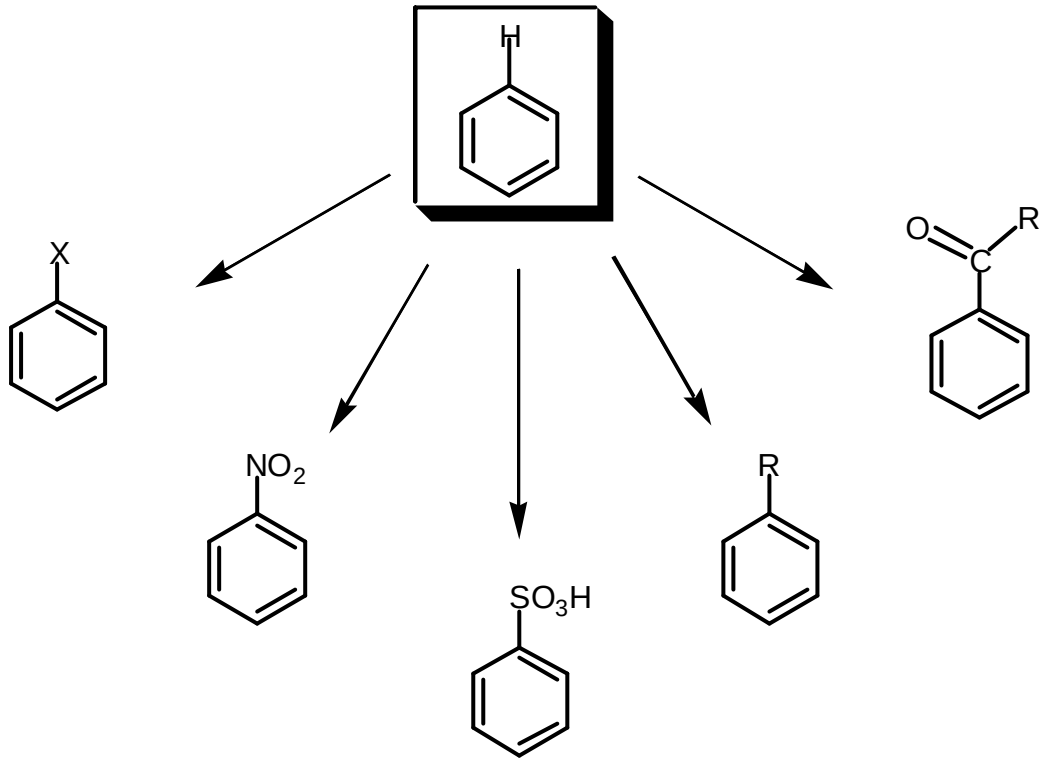
Step 2: Attack of π electrons of benzene on the electrophile and formation of resonance-stabilized carbocation



Electrophile approaches π electron cloud.
Carbon becomes sp^3 hybridized.

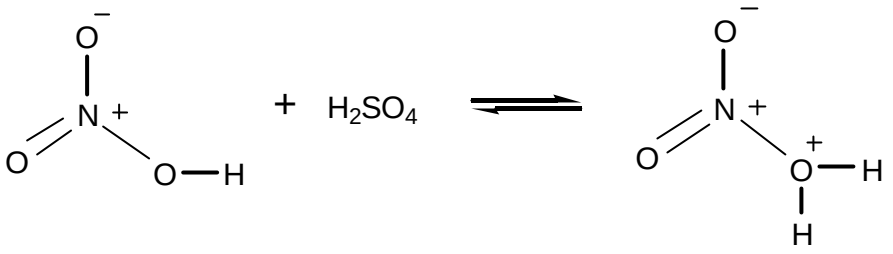
Step 3: Loss of proton from carbocation to reform aromatic.

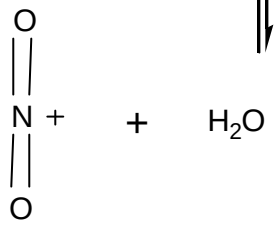
3. Other Electrophilic Substitution Reactions

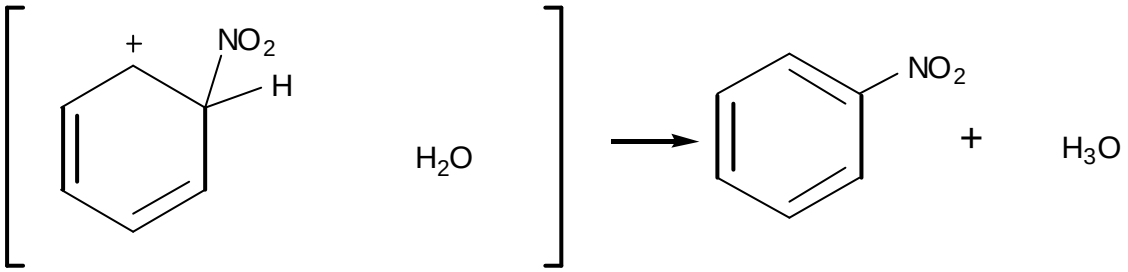


4. Nitration

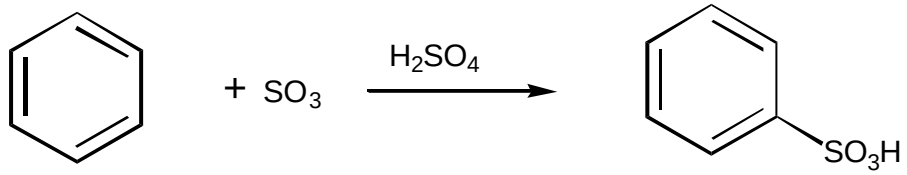
Aromatic rings can be nitarted by a mixture of concentrated sulphuric acid and nitric acids. The sulphuric acid generates the electrophilic reagent NO_2^+.



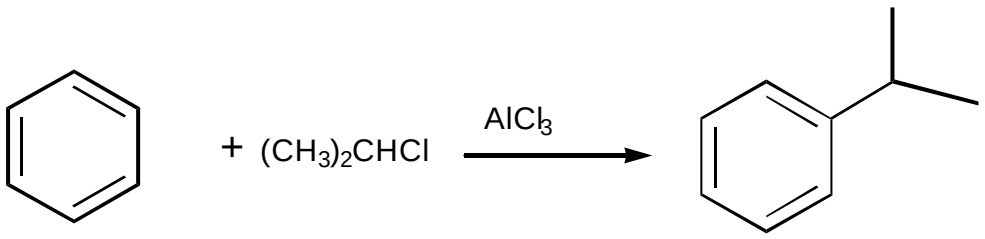


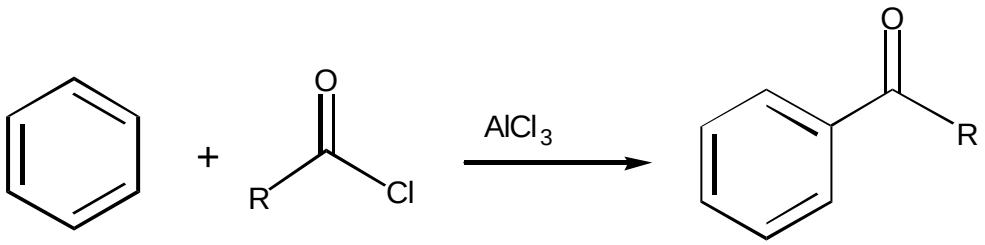


5. Sulphonation



6. Friedal-Craft Reaction





Friedal-Craft reaction acyl group is derived from an acid chloride reaction procedes in the presence of a Lewis acid $AlCl_3$. The electrophile is an acylium carbocation.