Quadrant II – Notes

Programme: TY BSc

Subject: Chemistry

Paper Code: CHC-107

Paper Title: Organic Chemistry

Unit: 1 (Aromaticity, aromatic Hydrocarbons and Reactivity)

Module Name: Reactivity and Orientation

Module No: 6

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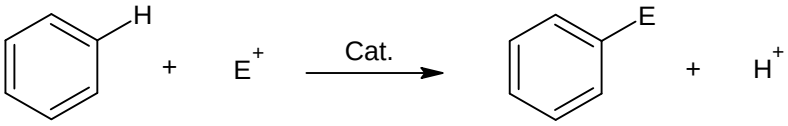
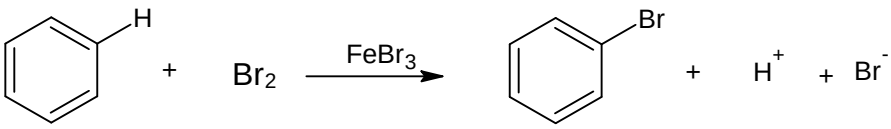
In this module on reactivity and orientation following points will be with regards to Reactivity of Benzene and Substituted Benzenes in electrophilic substitution.

- ✓ Comparison of reactivity of benzene with alkenes.
- ✓ Reactivity and Orientation in substituted benzenes with respect to nature of substituent.

It is known that in an electrophilic reaction on benzene, benzene reacts with electrophile in which electrophile replaces a aromatic hydrogen. Generally a suitable catalyst is necessary for this reaction.



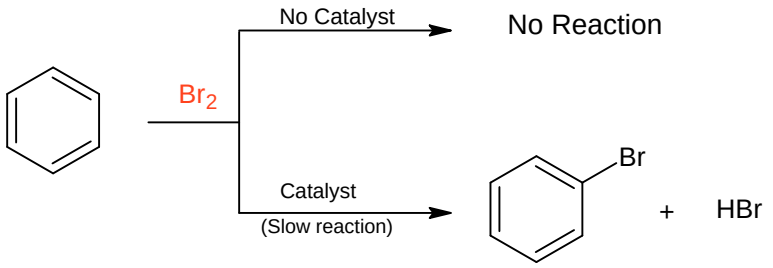
For e.g. bromination of benzene as shown below



This reaction is normally carried using catalyst like FeBr3

Let us now understand the reactivity of this reaction. Benzene contains three double bonds in the ring. An ordinary alkene is known to react with bromine very quickly to give dibromo addition product. In this reaction red colour bromine gets quickly decolorize. This reaction of alkene is used as test reaction in your laboratory work in organic spotting. Recall your Unsaturation test in Organic Spotting.

Do benzene gives this unsaturation test like an ordinary alkene? The answer is no.



Not Addition, but Substitution Product

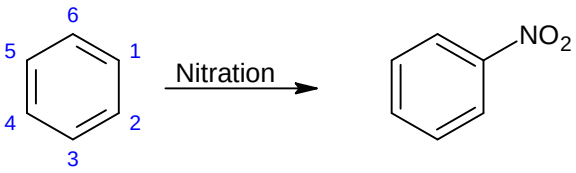
Benzene do not react with benzene like an alkene reacts, however if a suitable catalyst is used then benzene do react but this reaction is slow and produces substitution product and not addition product. Thus, unlike an alkene benzene undergoes electrophilic substitution than an electrophilic addition.

Let us now understand this reactivity in monosubstituted benzenes. In reactions of substituted benzenes, two things to look at

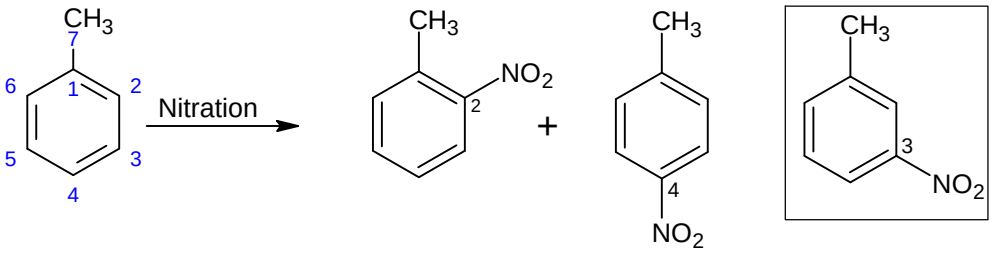
- ✓ Reactivity: How Fast/Slow the reaction is?
- ✓ Orientation: In which position Substitution takes place?

Let us understand this by taking example by comparing nitrations of Benzene and Toluene.

When you carry out mono notration of benzene you obtain nitrobenzene as product as shown below. Is there any other possibility of the product in this reaction. No, All the carbons in benzene are equivalent, Therefore substitution at any of these carbons will lead to Only One Possible Product i.e. Nitrobenzene



Let us now think of a same reaction on toluene (i.e. methyl benzene). Out of the six carbons of the aromatic ring one carbon is blocked from any further substitution by the methyl group. Thus there are five other carbons from where aromatic H can be replaced by nitro group hence there are three isomeric products possible as orthonitrotoluene, metanitrotoluene and paranitrotoluene.



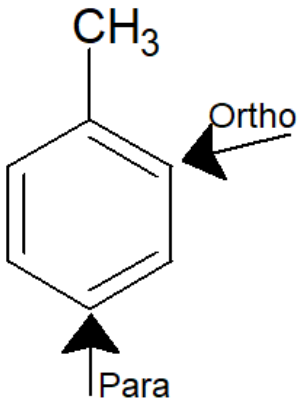
When you experimentally perform this reaction following are the observations made.

- ✓ Mixture of ortho and para substituted products are formed
- ✓ Reacts faster than Benzene

Let us put our infrences from the above observations.

The first observation tells us that the Presence of methyl group directs the electrophilic substituent to either ortho or para position giving mixture of two products. Therefore, we can substituent like a Methyl group is o/p director.

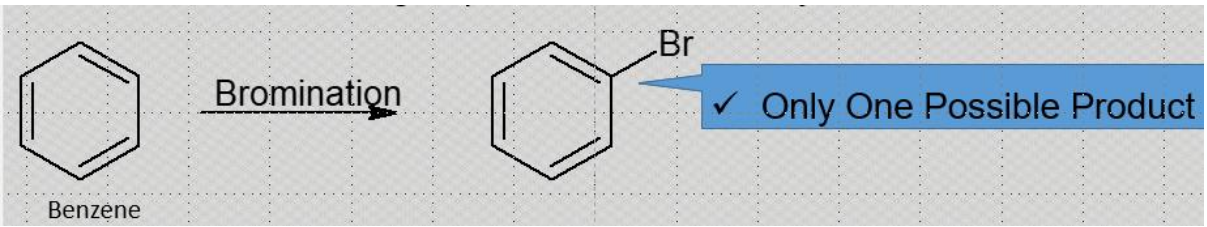
Second observation informs us that Methyl group increases the rate of reaction because of which toluene reacts faster than benzene. Therefore methyl group is said to be activating group.



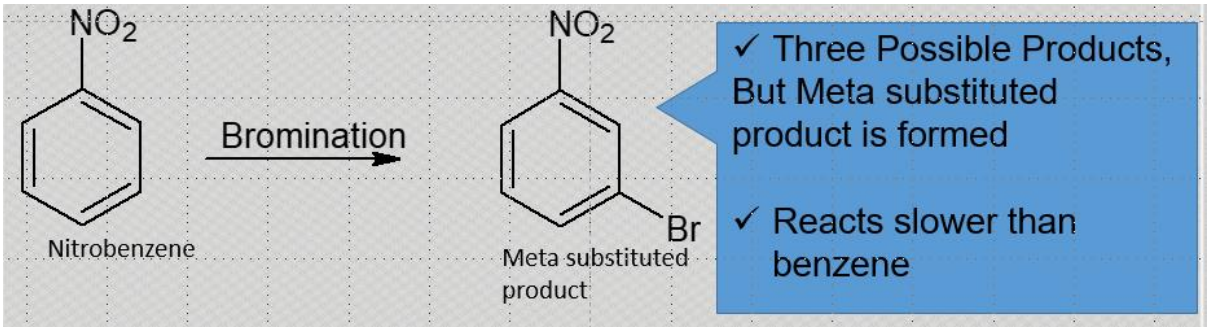
Overall we can say that a Substituent can be activating and ortho/para directing.

Let us now discuss another substituent nitro about its effect in aromatic electrophilic substitution reactions.

Benzene on bromiation gives bromobenzenze.

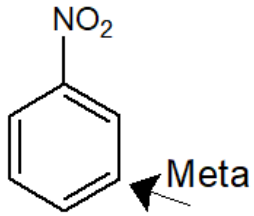


Similarly bromination of nitrobenzene can lead to three possible products namely orthobromonitrobenzene, parabromonitrobenzene, and metabromonitrobenzene, however only metabromonitrobenzene is formed.

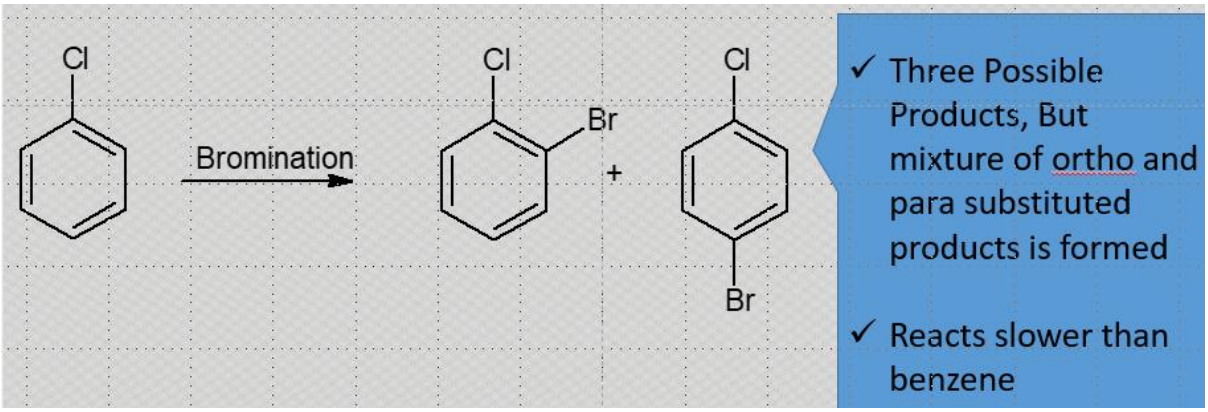


So we can say that Presence of Nitro group directs the electrophilic substituent to only meta position giving only one major product. Therefore Nitro group is meta director (meta directing group)

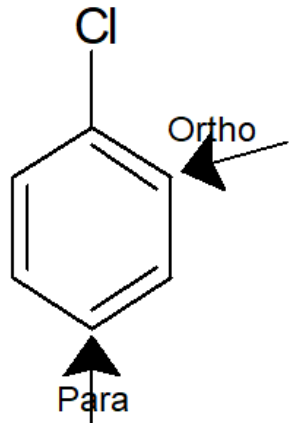
Secondly, Nitro group is found to decrease the rate of reaction compared to bromination of benzene hence Nitrobenzene reacts slower than benzene. Thus Nitro group is said to be deactivating group. A Substituent therefore can be deactivating and meta directing.



Let us now take another case of substituent i.e halogens. If the bromination is carried out on chlorobenzene then it is found that cholorobenzene reacts slower than benzene, just like nitrobenzene, however the products obtained are mixture of ortho and para substituted.



So what we understand is that a substituent can be deactivation and ortho/para directing like halogens.



A thought might just to a learner's mind that can there be substituent that activating and meta directing. Such a substituent does not exist.

To summarize, the substituent on the aromatic ring can be of three types as list below

Group (example)	Reactivity (effects on reaction rate)	Orientation (Regioselctivity)
Methyl	Activating	ortho/para
Nitro	Deactivating	meta
Chloro	Deactivating	ortho/para

Note that methyl, nitro and chloro are just the representative examples of the three types of substituents. Students can find through literature many more examples of these types.