Aromatic Hydrocarbons

Aliphatic and aromatic compounds

Chemists have found it useful to divide all organic compounds it two broad classes aliphatic and aromatic compounds.

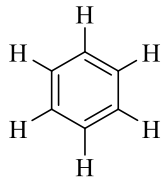
a. Aliphatic compounds are open- chains compounds and those cyclic compounds that resemble the open-chain compounds . the families we have studies so far are :- alkanes , alkenes , alkynes and their cyclic analogs are all members of the aliphatic class.
b. Aromatic compounds are benzene and compounds that resemble benzene in chemical behavior . aromatic properties are those properties of benzene that distinguish it from aliphatic hydrocarbons.

Benzene

Molecular formula . kekule structure

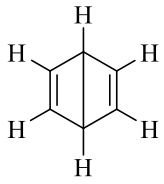
Benzene is the parent of a classes of especially stable compounds called **aromatic compounds .** It was first isolated by faraday in 1825 from compressed illuminating gas.

Different structures were suggested for benzene (C_6H_6) the regular conjugated hexagon structure was suggested by kekule in 1865.



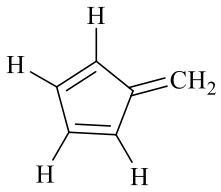
I

Kekule structure



II

Dewar formula



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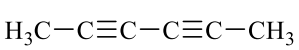
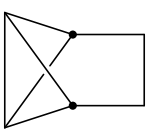
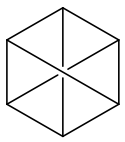


IV

V



Hukel benzene



Klaws benzene

From all these structures, kekule structure (I) was expected as the most nearly satisfactory.

Carbon –carbon double bond length in benzene

All carbon –carbon double bond in benzene are equal and are intermediate in length between single bond and double bonds .Bond length of C=C = 1.34 A°

Bond length of C- C =1.53A° (In ethane)

Bond length of C- C = 1.50 A° (In propylene)

Bond length of C- C = 1.48 A° (In butadiene)

if benzene actually possessed three single and three double bonds as in kekule structure ,we expect to find three short bonds (1.34 A°) and three long bonds (1.48A°) as in butadiene) Actually , x-ray diffraction studies show that six C- C bonds in benzene are equal and have a length of 1.39A° ,and are this intermediate between single and double bonds.

Aromatic Character , The Huckel Rule

We have defined aromatic compounds at those that resemble benzene . but just which properties of benzene must compound possess before we speak of it as being aromatic ? besides the compounds that contain benzene rings, there are many substance that are called aromatic ,yet some of these superficially bear little resemblance to benzene.

From theoretical stand point, to be aromatic a compound must have a molecule that contains cyclic clouds of delocalized л electrons above and below the plane of the molecule; furthermore the л clouds must contain a total of **(4n + 2) = л electrons .**

That is to say , for the particular degree of stability that characterization an aromatic compound, delocalization alone is not enough . these must be particular number of л electrons : 2 or 6 or 10 …etc. this requirement, called the **(4n + 2)** rule or named **Huckel Rule** is based on quantum mechanics.

Let us look at some of evidence supporting the Huckel Rule benzene has six л electrons , the aromatic sextet . six is , of course a Huckel number , corresponding to n =1.

Finally, the number of pi electrons must equal 2 plus a multiple of 4 (or $4n + 2$ pi electrons). Some of the possible numbers are as follows:

n	$4n + 2$	Number of pairs
0	2	1
1	6	3
2	10	5
3	14	7

Aromaticity

1) Cyclic , SP^2 , Plannar ⟶ X ⟶ Not Aromatic (Alkanes , Alkenes , Alkynes)

2) Obey Huckel's rule ⟶ X ⟶ Anti Aromatic

Obey ← Odd ← lone pair , - ve pi bond

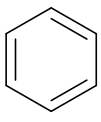
Not Obey ← even ← lone pair , - ve pi bond

Huckel's Rule

4n + 2 = resonance electrons

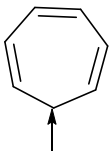
n = 0 ,1 , 2 . 3 ⟶ Obey

n= 1/2 , 1/4 . 3/4 ⟶ Not Obey

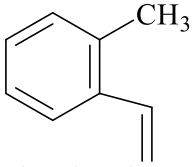


4n +2 = 6
n = 1
Aromatic

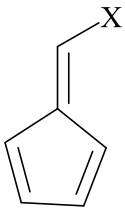
4n + 2 = 4
n= 1/2
Anti Aromatic



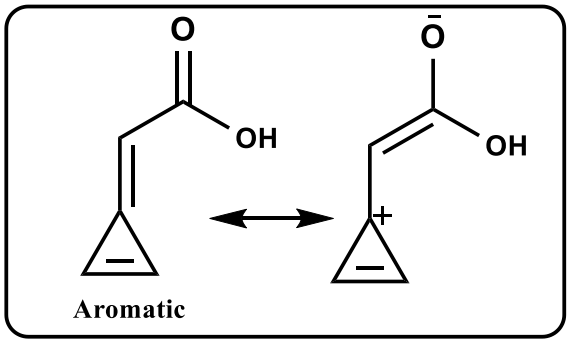
SP^3
Not Aromatic



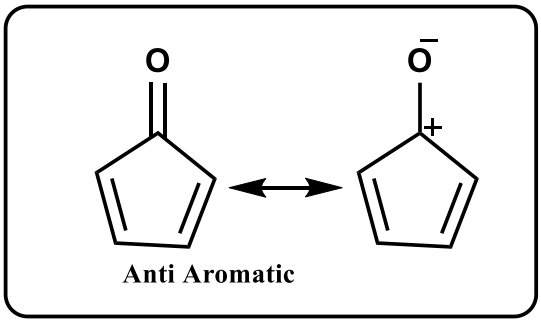
4n +2 = 6
n = 1
Aromatic



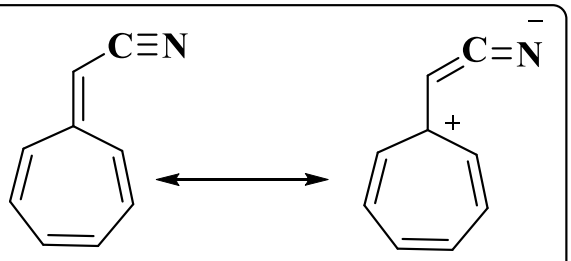
X = EWG or EDG



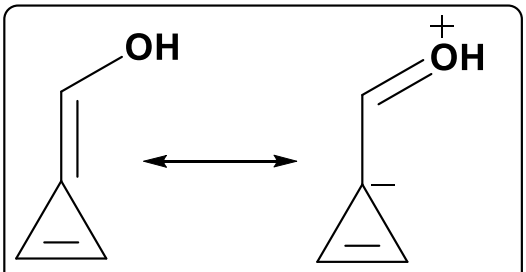
Aromatic



Anti Aromatic



Aromatic



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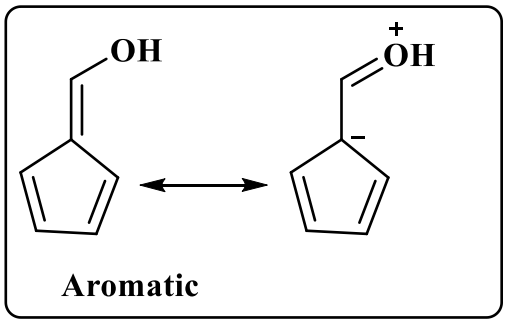
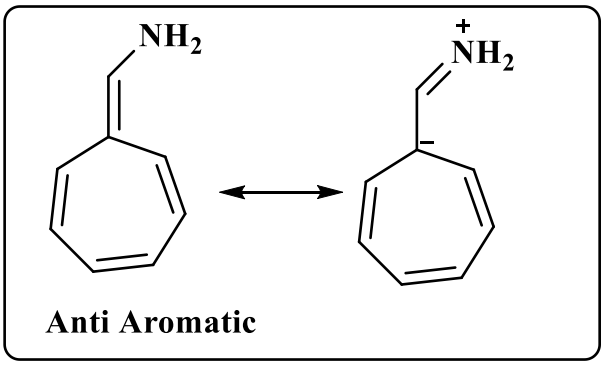
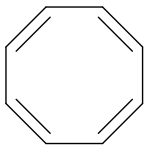


Aromatic



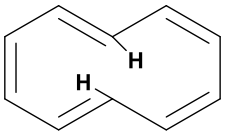
Anti Aromatic

Not Aromatic " Not Plannar "

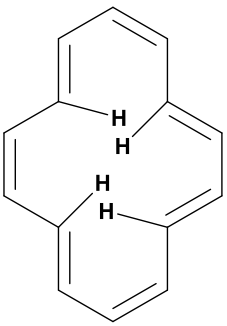


[8] annulene

Due to crowdness of Hydrogen atom

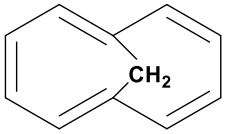


[10] annulene



[14] annulene

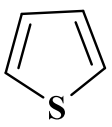
To be aromatic :- Replace the two hydrogen by a bridge as methylene bridge, Oxygen or nitrogenic bridge



EWG = NO_2 > $\overset{+}{N}$ > CF_3 > O=S=O > C≡N > C=O > F > Cl > Br > I

EDG = O > N " Resonance" except " NO_2 , N=O , $\overset{+}{N}$

Alkyl group



thiophene

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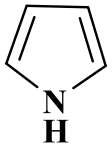

pyrrole

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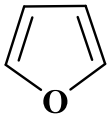


furane

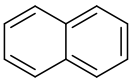
Due to S < N < O

↑ Electronegativity

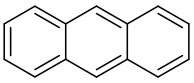
↓ Aromaticity

In aromaticity

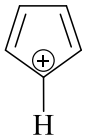
6e
aromatic



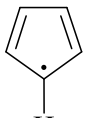
naphthalene
10e
aromatic



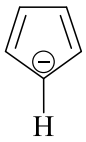
anthracene
14e
aromatic



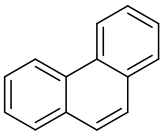
4e
Anti-aromatic



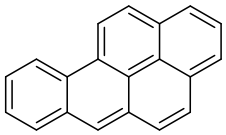
5e
Anti-aromatic



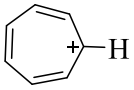
6e
aromatic



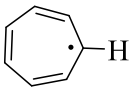
phenanthrene
14e
aromatic



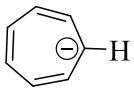
benzo[*pqr*]tetraphene
20e
Anti-aromatic



6e
aromatic



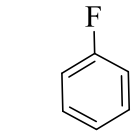
7e
Anti-aromatic



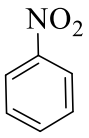
8e
Anti-aromatic

Nomenclature of benzene derivatives:-

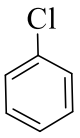
Naming the benzene derivatives by prefix the name of substituent group the word –benzene .for example chlorobenzene, flourobenzene, bromobenzene, nitrobenzene



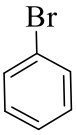
fluorobenzene



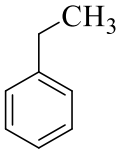
nitrobenzene



chlorobenzene

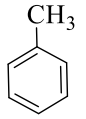


bromobenzene

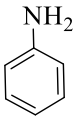


ethylbenzene

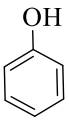
There are other derivatives, which have a special name such as:



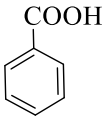
toluene



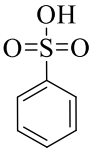
aniline



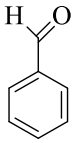
phenol



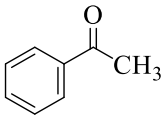
benzoic acid



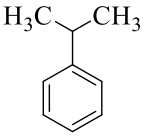
benzene sulfonic acid



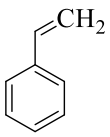
benzaldehyde



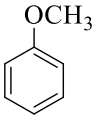
acetophenone



cumene

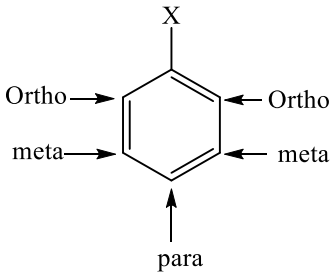


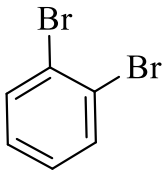
styrene



anisole

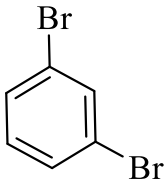
If several groups are attached to the benzene ring, we must indicate the position and the name of the groups. Only for disubstituted benzene we can use ortho , meta and Para to indicate the relative position 1,2- ,1,3- and 1,4- di substituted benzene.





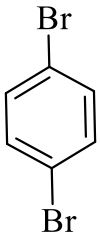
1,2-dibromobenzene

o-dibromobenzene



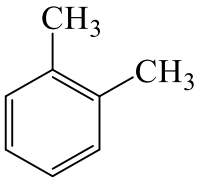
1,3-dibromobenzene

m-dibromobenzene

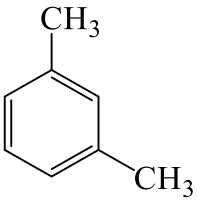


1,4-dibromobenzene

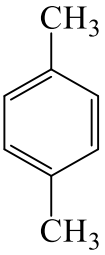
p-dibromobenzene



o-xylene



m-xylene

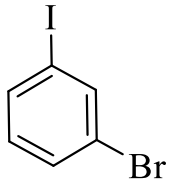


p-xylene

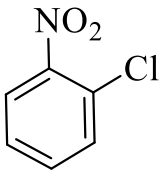
Assigning Priority

Halogen, NO_2 < alkanes < alkenes < amines < OH < Ketone < aldehyde < acid < Ester

If there is different group, we simply naming the two groups with their position and ending the word with benzene.

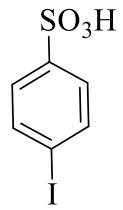


m-bromo iodobenzene

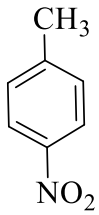


o-chloro nitrobenzene

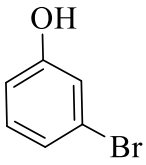
For di substituted benzene with groups of special name: for example



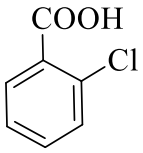
P-iodobenzenesulfonic acid



1-methyl-4-nitrobenzene
p-nitro toluene

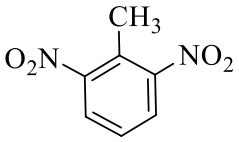


m-bromophenol

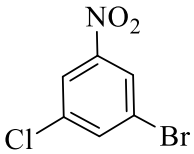


o-chlorobenzoic acid

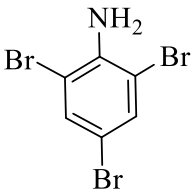
If there are more than two groups attached to the benzene ring, number must be used to indicate their relative position



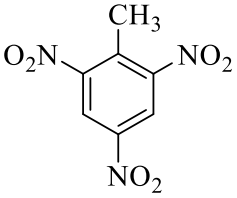
2,6-dinitrotoluene



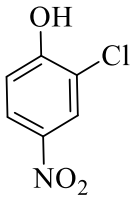
1-bromo-3-chloro-5-nitrobenzene



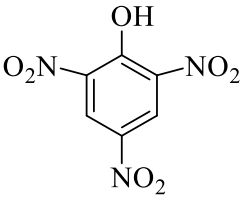
2,4,6-tribromoaniline



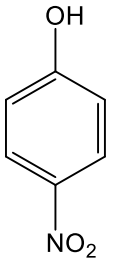
2,4,6-trinitrotoluene



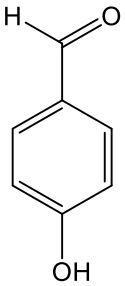
2-chloro-4-nitrophenol



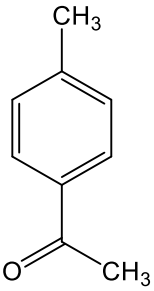
2,4,6-trinitrophenol
(picric acid)



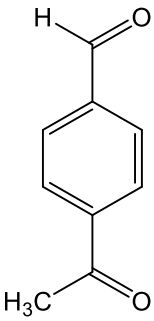
4-nitrophenol



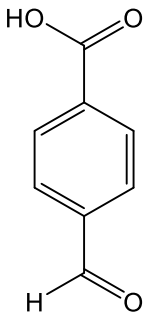
4-hydroxybenzaldehyde



4-methylacetophenone

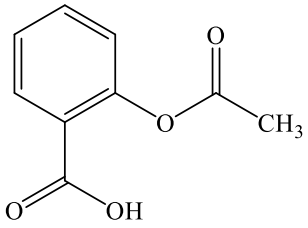


4-acetylbenzaldehyde

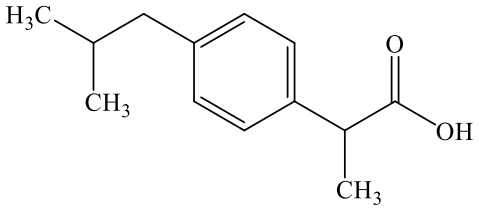


4-formylbenzoic acid

Aromatic compounds in nature and health

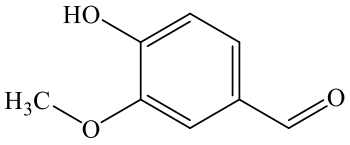


2-acetoxybenzoic acid
Aspirin



2-(4-isobutylphenyl)propanoic acid

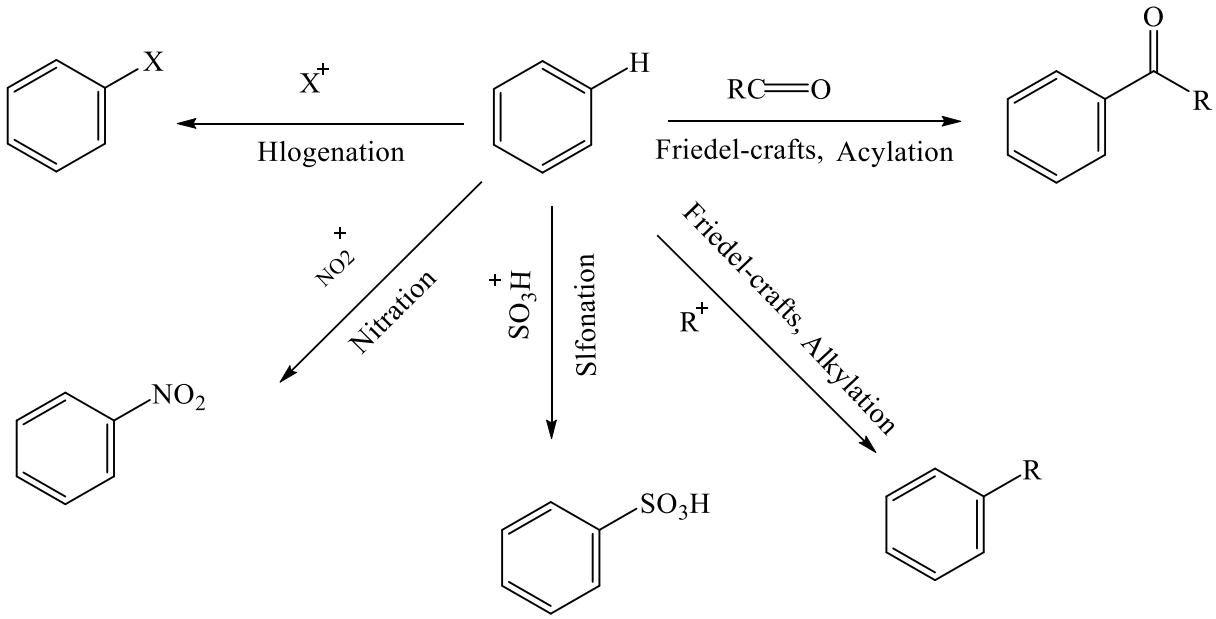
Ibuprofen



4-hydroxy-3-methoxybenzaldehyde

Vanilin

Electrophilic Aromatic substitution



Reactivity of substituted Benzene

1- Substituents effects the reactivity of aromatic rings.

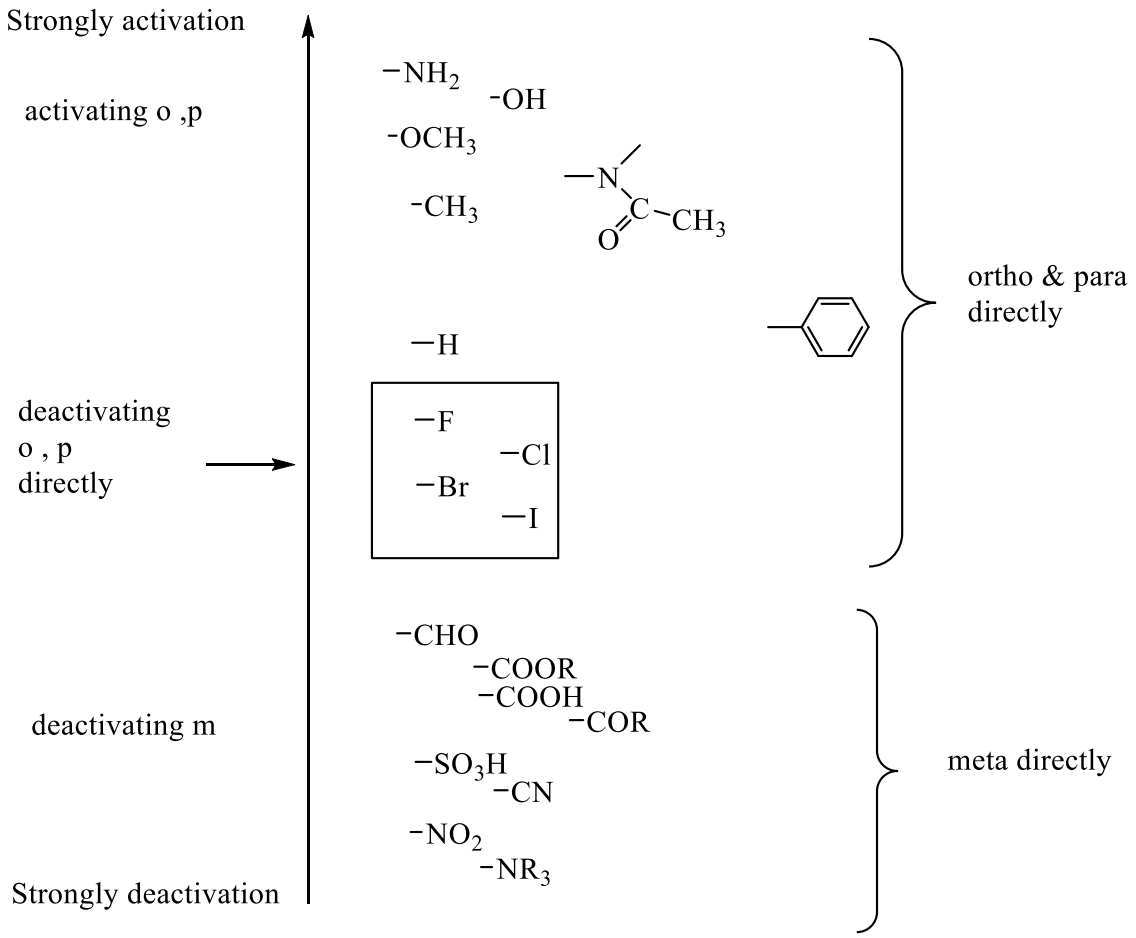
2- Substituents also effect the orientation or radiochemistry of the reaction .

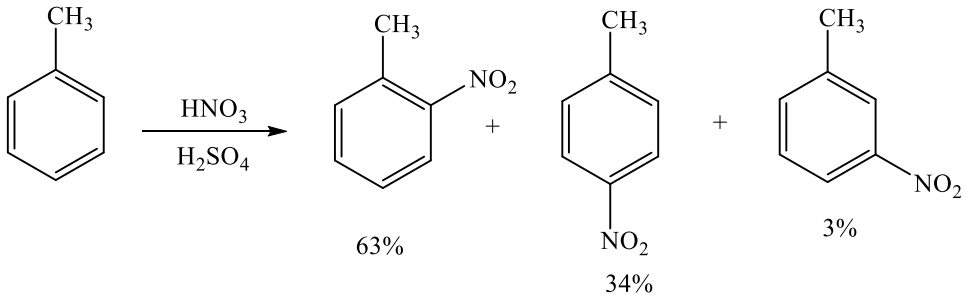
Classification of substituent groups:-

The groups that attached to benzene ring have a great effect on the electrophilic substitution, and nearly all groups fall into one of two classes.

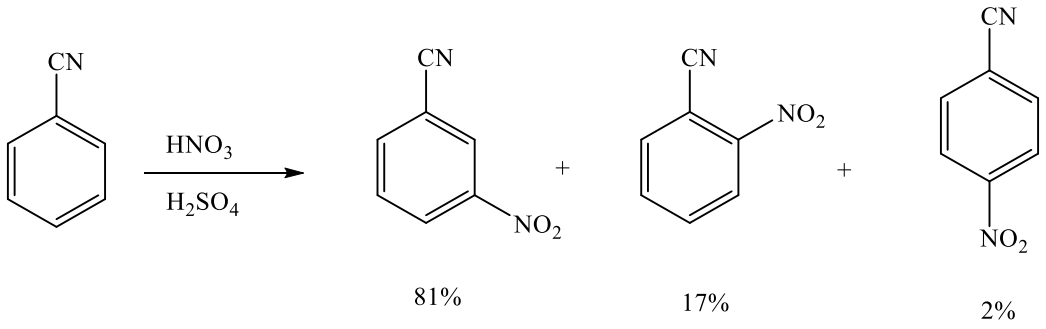
1- Activating and ortho ,Para directly
2- Deactivating and meta directly
3- Halogens are deactivating but ortho, Para directly.

The following table shows the effects of groups on the electrophilic aromatic substitution.



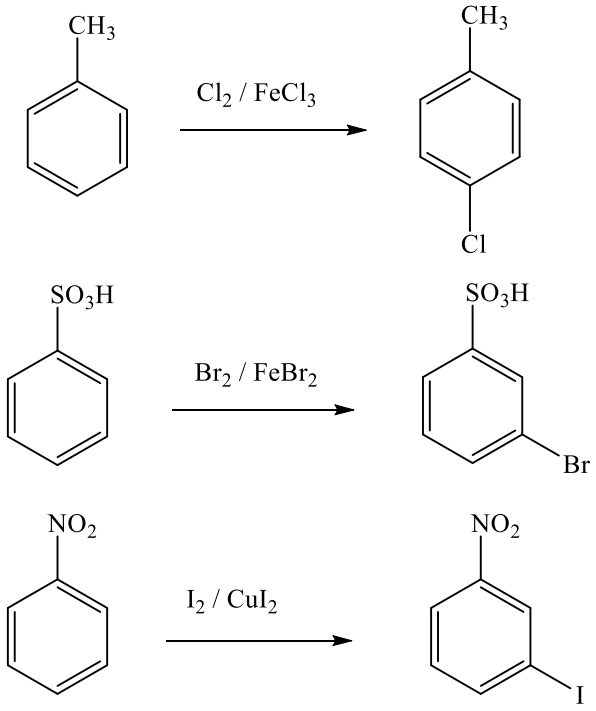


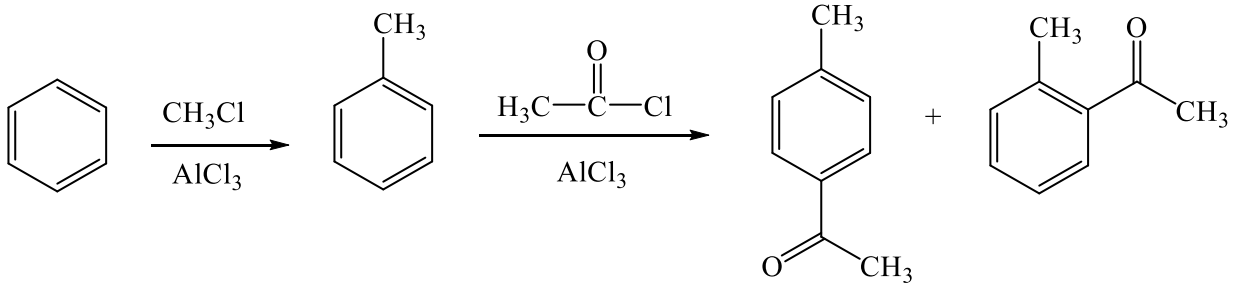
The alkyl group is activating and increases electron density in the ortho and Para position thus nitration generates predominantly ortho and Para products.



The cyano group is deactivating: nitration generates predominantly Meta product.

Examples:-

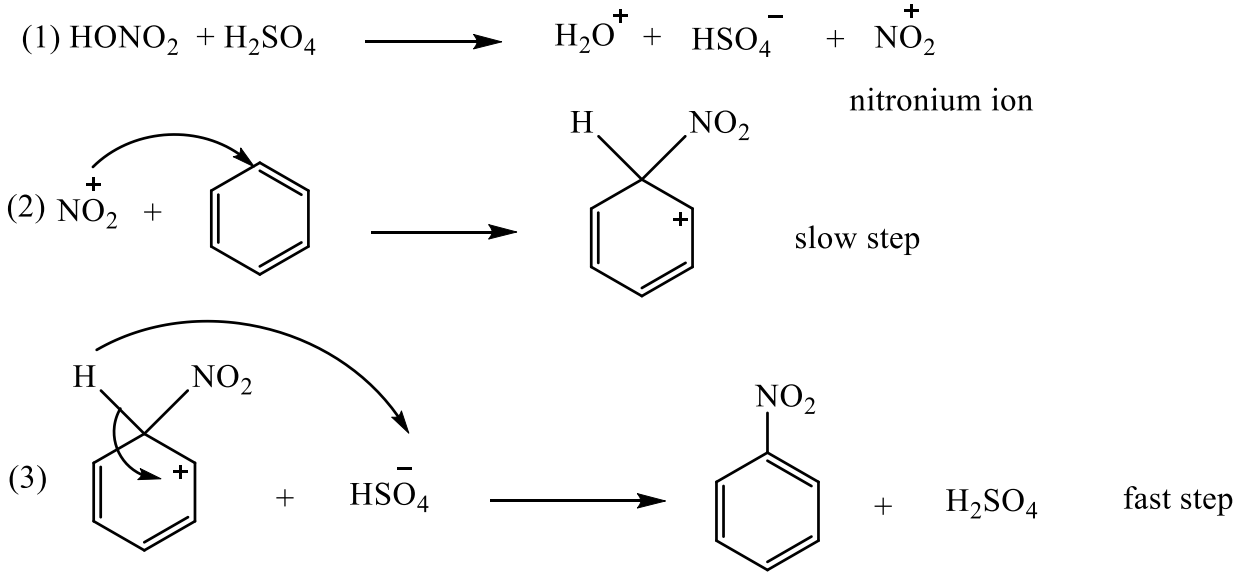




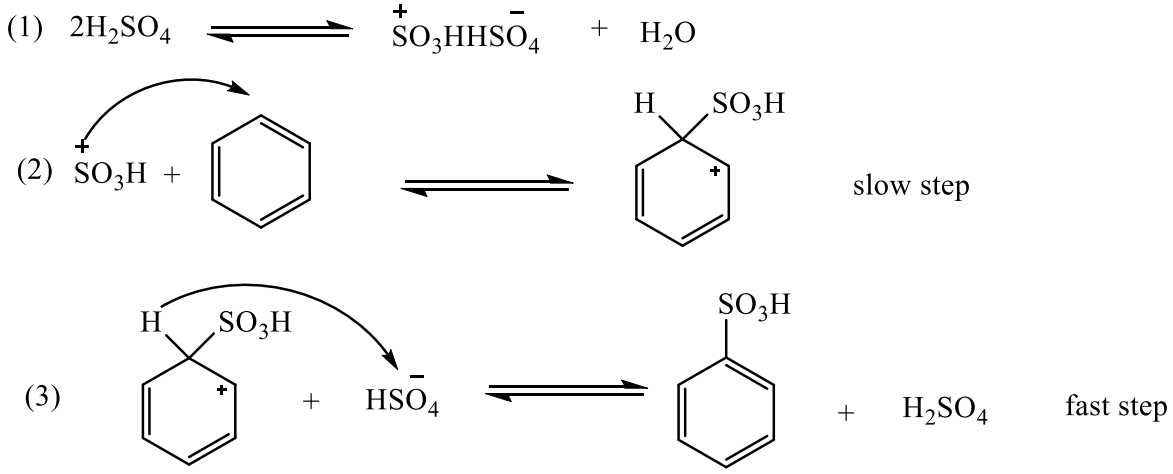
The Mechanisms:-

Now that we have seen the effects that substituent groups exert on orientation and reactivity in electrophilic aromatic substitution, let us see how we can account for these effects. The first step in doing this is to examine the mechanism for the reaction. Let us being with nitration. Using benzene as the aromatic substance.

(A) Mechanism of nitration

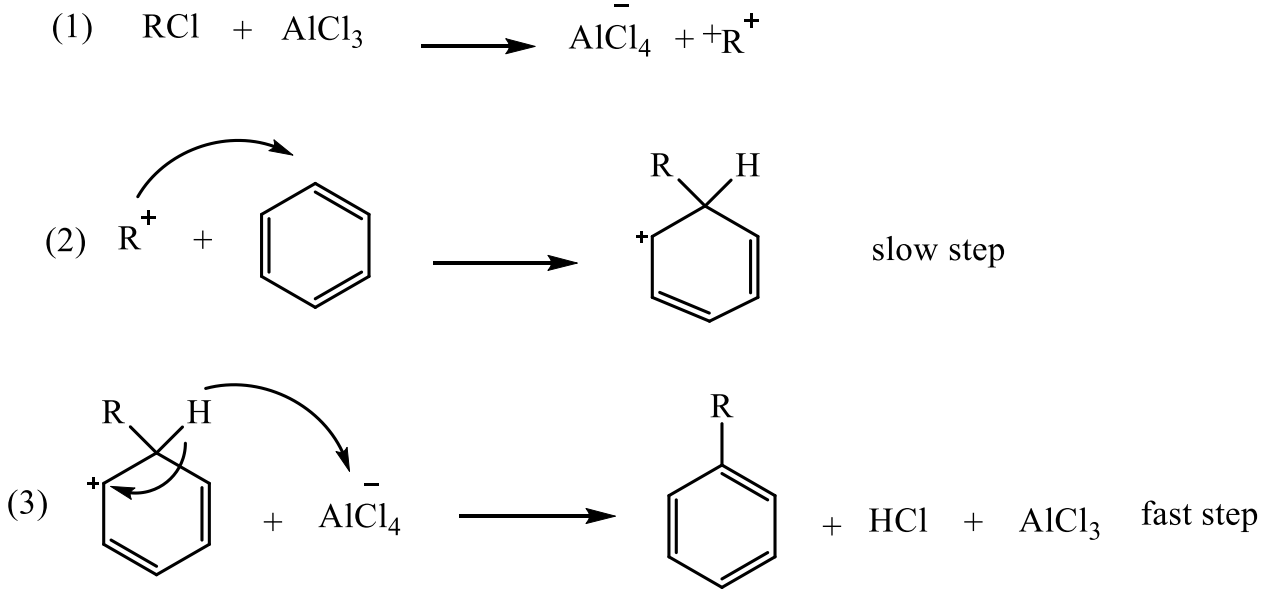


(B) Mechanism of sulfonation



(C) Mechanism of Friedal – crafts alkylation

In Friedal crafts alkylation. The electrophilic is typically a carbonium ion is R^+



(D) Mechanism of halogenation

Aromatic halogenation, illustrated for chlorination, involves the following steps:-