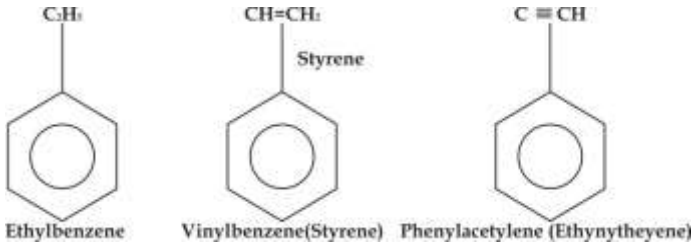
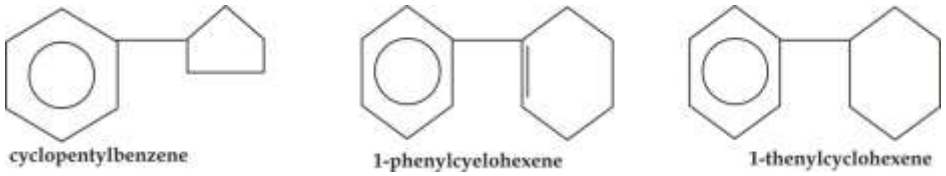
AROMATIC CHEMISTRY

Aromatic Hydrocarbons contains at least six-membered ring, within which appears three conjugated double bonds. They are considered to be a separate class of compounds called Arenes. We have four types of Aromatic hydrocarbons

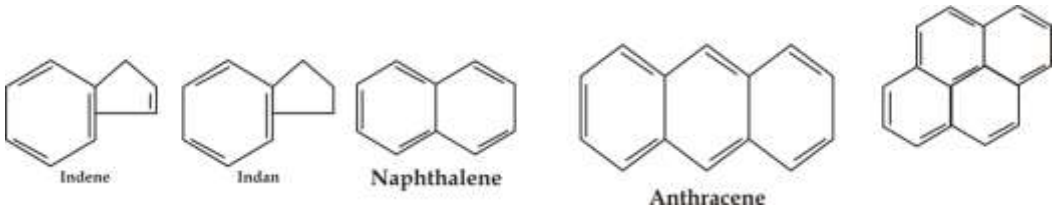
Type A comprises of benzene, alkylbenzene, alkenylbenzene(styrene) and alkynylbenzene.



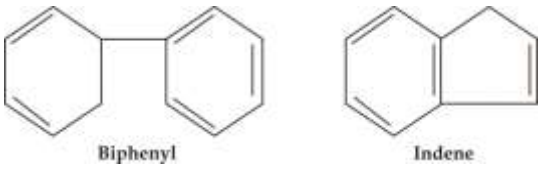
TYPE B included in this grp is cycloalkylbenzene (cyclopentylbenzene) and cycloalkenylbenzenes (phenylcyclohexenes)



TYPE C This are faced ring polynuclear Hydrocarbons example include: indene indan, naphthalens pyrene anthracene



TYPE D There are polynuclear aromatic Hydrocarbons having directly united rings e.g biphenyl



Benzene is the simplest member of the aromatic compounds. The world aromatic is derived from the greek word “aroma” pleasant smells are tagged “aromatic “. It si not all compounds which have pleasant smell that are tagged aromatic.

The structure of Benzene

The molecular formula of benzene is C_6H_6. A comparison of this formulate with that of corresponding (six membered) alkane alkane and alkyne suggestion that benzene is an unsaturated

The structures below, were some of those postulated for benzene

$H_3C - C \equiv C - C \equiv C - CH_3$

$H_2C = C = CH - CH = C = CH_2$

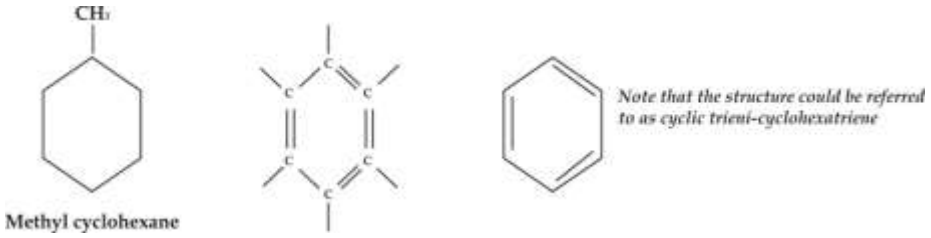
$H_2C = CH - C \equiv C - CH = CH_2$

$HC \equiv C - CH = CH - CH = CH_2$

$H - C \equiv C - CH_2 - CH_2 - C \equiv C - H$

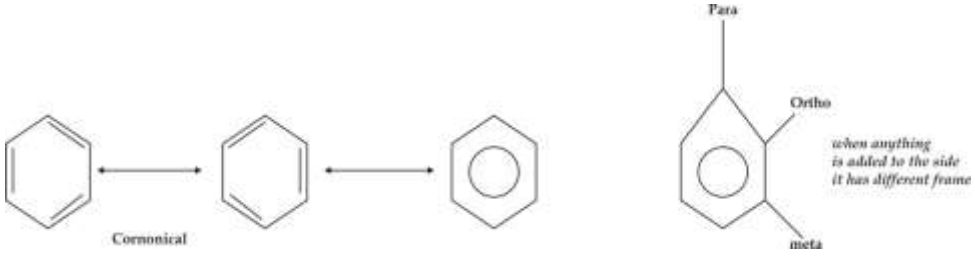
However, benzene does not undergo the usual addition reaction which other unsaturated Hydrocarbons like alkene and alkynes readily do it seems as if benzene has a special unsual type of unsaturation. A London chemical by name August Kekule in 1865 proposed an acceptable cyclic structure for benzenes.

It is often written as an hexagonal structure as follows;



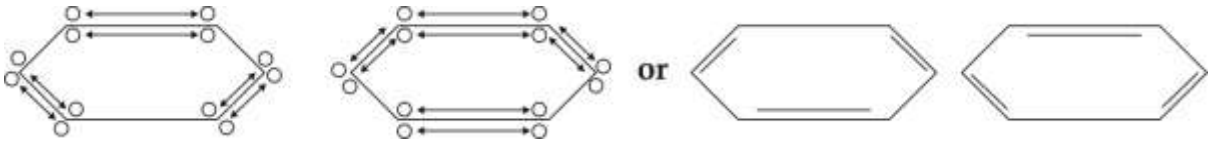
Objections to Kekule's structure

1. It failed to explain the peculiar stability of benzene to addition despite the presence of double bonds.
2. It failed to explain why only one di substituted benzene isomer is known
3. It failed to explain why benzene behave as a saturated Hc producing substitution reaction products rather than addition reaction products
4. Instead of 2 sets of bond length (3 short Ca = C) and (3-tiny C – C) over it was found that all c-c binds were equal in length
5. The heat of hydrogenation of benzene is less than the expected 3 times the heat of hydrogenation of a simple c – c double bind. Many at thou objectives were take care of by the illustration of the alternation of double bind and single binds in the Kekule's structure. Benzene is thou a resonance hybride of the 2 canonical (Kekule's forms and so is represented as follows

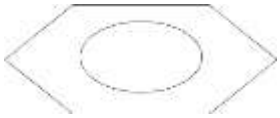


Modern molecular orbital picture of benzene

1. The carbon and hydrogen atoms and planer (they all lie in the same plane
2. Each carbon atom, being bounded to the other used sp^2-hybrodized orbital
3. Each bind angle is close to 120^0
4. The carbon atoms are arranged in the form of a regular hexagon
5. sp2 – sp2 hybridization is round with other carbon atoms in other side and one sigma bind sp1-s with is orbitals
6. at each sp2 hybridized carbon, these is an unhybridized p-orbital lying perpendicular to the plans of the 3 hybride orbital
7. The p orbital overlap laterally with each other to form 2 Kekule structure



All the p orbital can overlap to produce a continuously overlapping away of p – orbitals, leading to formation of p1 electron units



We say they are delocalization of pi-electron in benzene

Huckel 4n + 2 rule – Aromativity

Stability of aromatic compounds based in the delocalization is not enough, the number of p_1 electons prevent is of importance. Erich Huckel a German chemist proposed that for a compound be aromatic it must have (4n + 2) π electrons, where n is an integer. Benzene has 6 π electrons n is the number of ring in the molecule, naphthalene has 10 π electron and an Antracene has 14 π electrons

Assignment

Determine if the following is aromatic or not

1. cyclobutadiene
2. cyelectraletrance
3. cyclodecapentance

Sources of benzene and other aromatic compounds

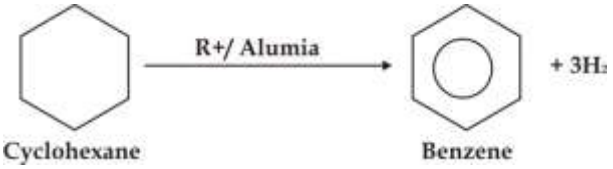
Coal and petroleum are the major sources of aromatic hydrocarbons. Destructive distillation of coal yields a mixture of gases and coal tar as the residue. Distillation of coal tar yields major fractions consisting o aromatic compounds, phenols, anlhracene, phenanthrene and so on.

Another source is petroleum. Catalytic reforming is applied to increase, the yield of benzene.

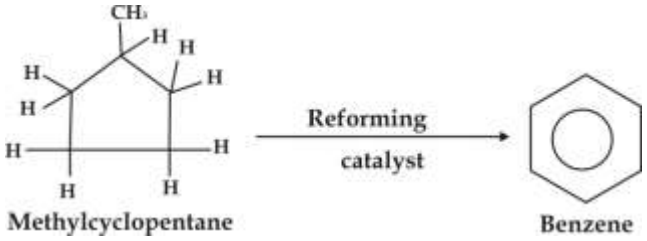
Preparation of benzene

Industrial preparation: the highest abundance of benzene is obtained industrially.

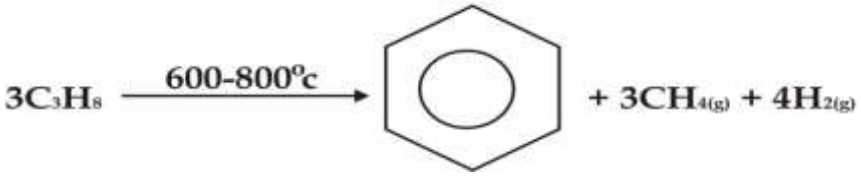
1. **Dehydrogenation of Naphthenes from petroleum:** Catalyst like platinium is used on acidified alumina support to generate benzene from naphthenes.



2. **Dehydroisomerization of Naphthenic from Petroleum:** Reforming catalyst are used to generate benzene from Naphthenes

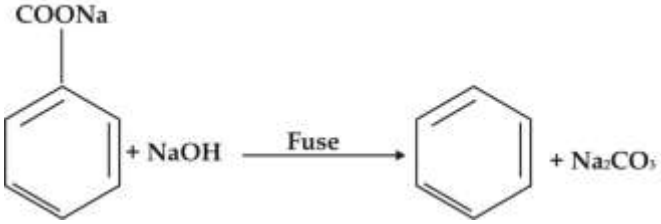


3. **High temperature thermal cracking of petroleum fractions:** Small Hydrocarbons may condensed to aromatics

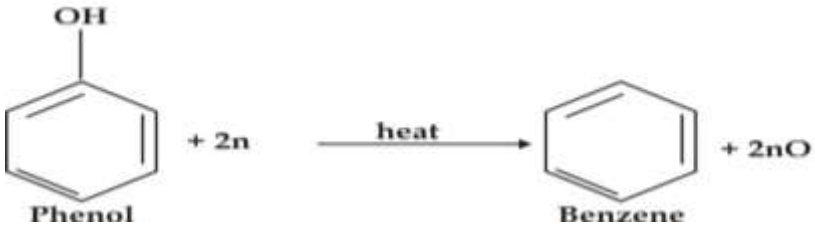


Laboratory preparations

1. **Decarboxylation of sodium salt):** The fusion of sodium benzene carboxylate with sodaline (CaO slaked with NaOH)



2. **From Phenol:** The passage of phenol vapour over heated zinc dust



3. **Polymerization of Ethyne:** Small **a**mount of benzene is produced when ethyne at 400^0C is under pressure but a large amount of benzene yield is observed when a complex organo-nickel catalyst is used at a 10 range of 60^0 – 70^0C

$$3CH \equiv CH \xrightarrow[60-70^oc]{complex\ organo-nickel} C_6H_6$$

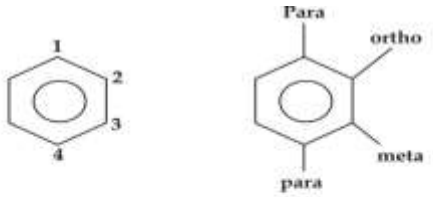
Ethyne **Benzene**

Physical properties

It is a colourless liquid which boils at 300^0C and melts at 550^0C it has a characteristic aromatic odour. It does not mix with water. Due to its highly unsaturated nature it burns with a smoky flame. Benzene is carcinogenic.

Nomenclature of benzene derivatives

Derivative of benzene are formed by the replacement of some hydrogen by a grp or atom. Removal of one hydrogen from benzene leave behind a group of atoms known as phenyl (ph) A mono substituted arene has no isomer, a disubtituted derivative has 3 isomers namely (a) 1, 2 ortho (O) derivative (b) 1, 3 or meta (m) derivative (c) 1,4 or para (p) derivative



Reactive of benzene

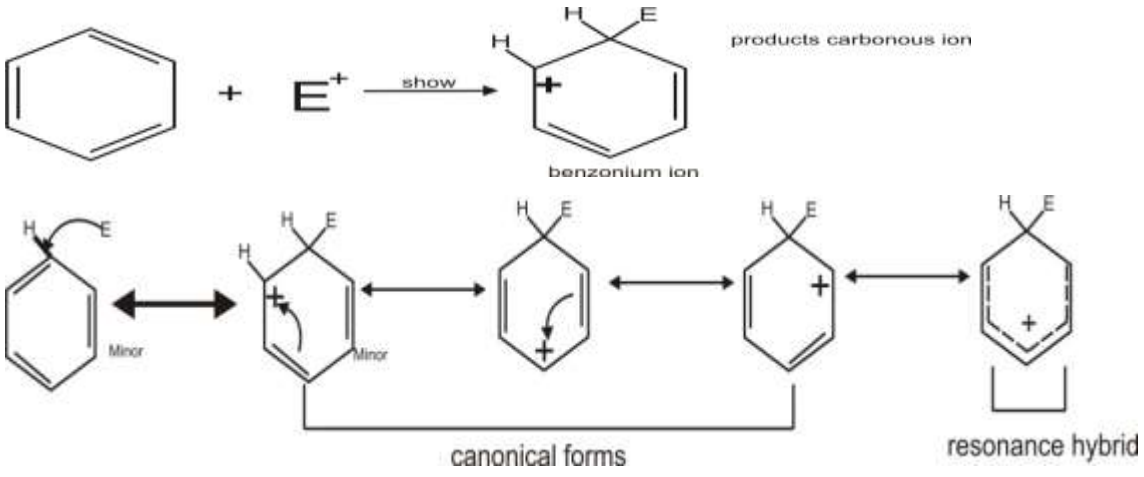
Benzene is a very rich sources for electrons, and it is attached by electron deficient reagents or species (electrophile) to seek for electrons. Due to the nature of the double bonds which is delocalized, benzene molecule resist any reaction that would destroy its aromatic character therefore it undergo electrophilic substitution. In Aromatic HCs with increasing numbers of fused rings there is an increasing tendecy for addition reaction rather than substitution reaction to occur. Due to its stability it requires more forcing conditions such as heat use of catalyst to react with halogens under severe condition it can be hydrogenated

Mechanism of Electrophilic Aromatic Substitution

The mechanism takes place in two steps.

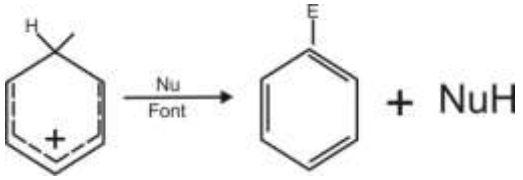
Step 1: Attach of the electrophilic reagent E^+ within II electron of the benzene ring

Shadow of the benzene



Although resonance stabilized, it is not as stable as benzene. The camonical forms are not as s stable as benzene, therefore a re-aromatisation stage as to take place which is the second step to enhance stability and restore the aromatic nature to the benzene ring.

Step 2: loss of a proton H+ from the intermediate ion which is accepted by a nucleophile

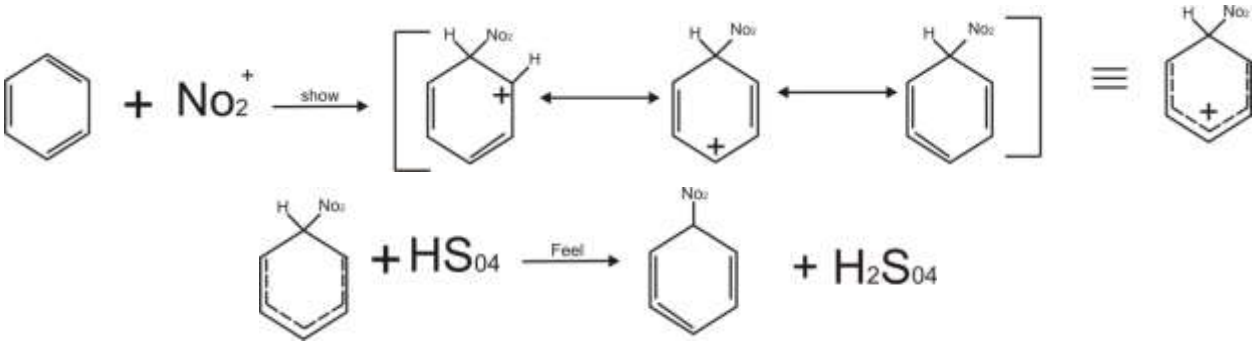


Nitration of benzene

Nitration refers to the attachment of the nitro group-NO_2 to a hydrocarbon. Equal mixture of concentrated H_2SO_4 and HNO_3 (nitration mixture) converts benzene to nitrobenzene at a temperature of 55-60^{0}C . NO_2^+ is generated which attacks the benzene

Step 1 $HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$

Step 2 the slow attack of NO_2^+ on benzene to form benzenonium ion

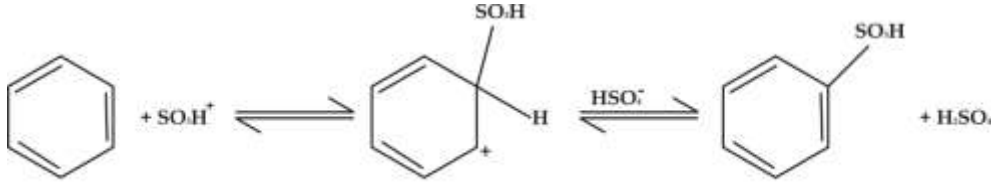


Sulphonation of Benzene

$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4$

This is the introduction of sulphonic acid grp – SO_3H, to a hydrocarbon residue. The hydrocarbon can be sulphonated by oleum fuming H_2SO_4 [sulphur trioxides, oleum)]. The reactive eletrophilic is either HSO_3+ or SO_3.

$2H_2SO_4 \rightleftharpoons HSO_3^+ + H_3O^+ + HSO_4^-$

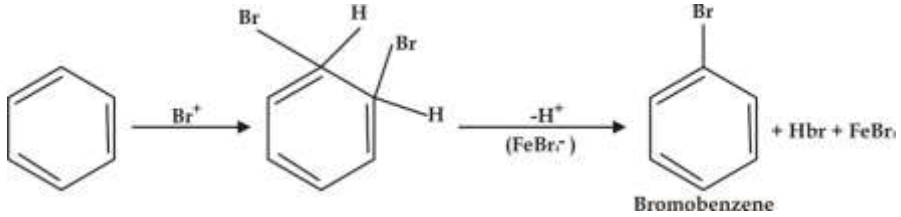


benzenesulphonic acid

Halogenation of Benzene

This is the introduction of hydrogen atom into a hydrocarbon residue. The reagents are Br and FeBr, the attaching electrophile is Br^+

$Br_2 + FeBr_3 \rightleftharpoons Br^+ + FeBr_4$



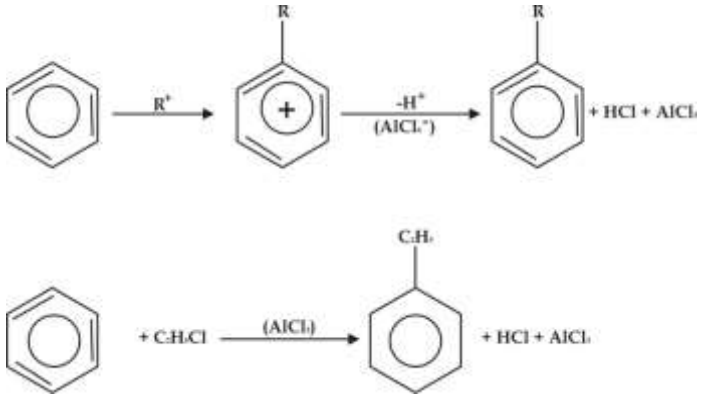
Bromobenzene

Friedel Craft's Alkylatin of Benzene

Two chemist, Friedel and crafts, discovered the alkylation and acylation reaction. Alkylation is the in introduction of alky grps, i.e R, in to a benzene nucleus.

The reagents used in alkylation are alkyl chloride and aluminium chloride, acting as a catalyst called lewis acid

$R - Cl + AlCl_3 \rightleftharpoons R^+ + AlCl_4^-$

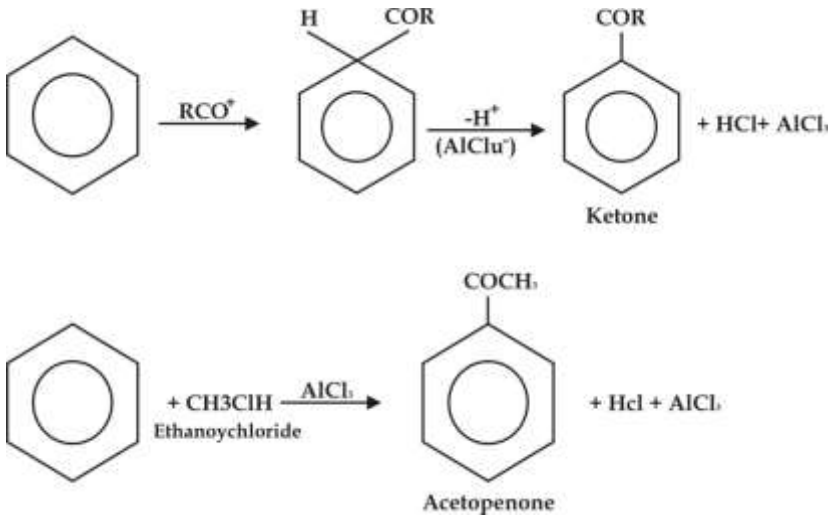


Other suitable catalysts include stannic fluoride (SuF_4) Boron trifloride (BF_3) Ferric chloride ($FeCl_3$) zinc chloride ($ZnCl_2$) and hydrogen Flouride (HF).

Friedol Crafts Acylation

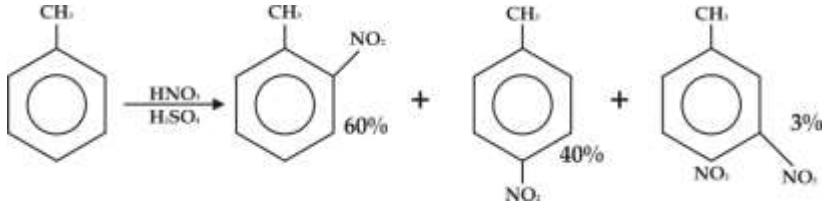
This is the introduction of an acyl grp -COR into the benzene nucleus. The reagents are an acyl chloride and $AlCl_3$

$RCOCl + AlCl_3 \rightleftharpoons RC \equiv O^+ + AlCl_4^-$



Effects of Substituents Groups on Benzene

Toluene (methybenzene) react faster than benzene because the methyl grp is slightly electron donating and has the effect of activating the ring. Further substituents are directed to the ortho and para positions.



But nitrobenzene reacts slower than benzene because the nitro grp with electron withdrawing, deactivates the ring meta directing. Electron donating are activating while electron withdrawing are deactivating to electrophilic reagents.

1. Activating to o/p directing
   a. Strong activating NH_2, NHR, NR_2, -OH
   b. Moderately activating OCH_3, OC_2H_5, $NHCOCH_3$
   c. Weakly activating CH_3, C_2H_5, C_6H_5.
2. Deactivating- Meta directing

   $-NO_2$, $+N(CH_3)_3$, CN, COOH- (COOR), SO_3H, CHO, COR

3. Deactivating grp having ortho and para directing effect F, Cl, Br, I. A partial explanation relies on the balance of 2 effects inductive and resonance effects.