



Benzene & Aromatic Compounds

Chapter 5

1432-2011

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Chapter Outlines

- Aromatic Compounds and Aromaticity.
- The physical properties of Benzene
- Hybridization of Benzene ring.
- Hückel's Rule.
- Nomenclature of Benzene and Aromatic Compounds.
- Electrophilic Substitution Reactions:
 - 1. Specific Electrophilic Aromatic Substitution reactions.*
 - 2. Side reaction of Aromatic compounds.*
 - 3. Disubstituted Benzene "Orientation in monosubstituted".*

Hydrocarbons

Aliphatic

Aromatic

will be discussed in this chapter

Alkanes

Alkenes

Alkynes

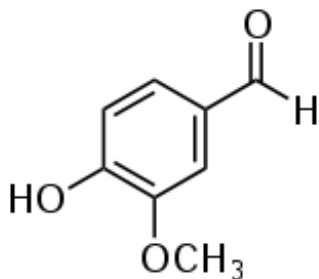
Have been discussed in previous chapters

Aromaticity and Aromatic compounds

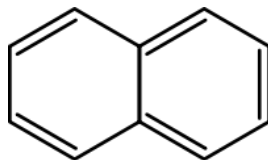
Aromatic word is derived from the Greek word '*aroma*' which means **fragrant smell**. For such reason, benzene and its derivative were originally classify as *aromatic compounds* as many of them have distinctive odors.

Here is some examples of aromatic compounds that have *distinctive odors*:

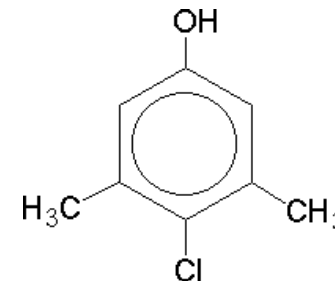
General Information



Vanillin



Naphthalene



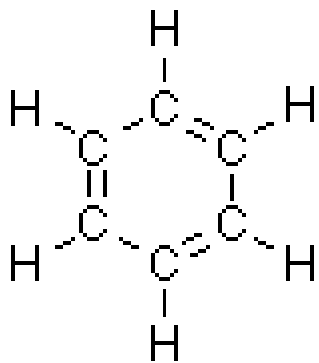
Dettol

4-hydroxy-3-methoxybenzaldehyde

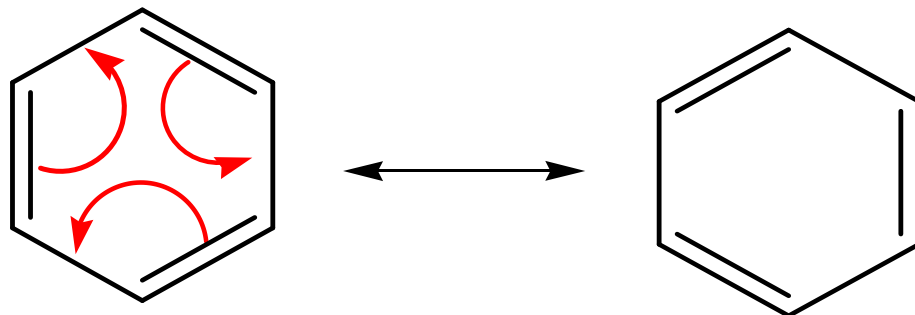
4-chloro-3,5-dimethylphenol

! Note, however, that "aromatic" hydrocarbons sometimes are **odorless**.

- There were several other structures proposed for **benzene**, but a much more satisfactory approach became possible when we began to understand that covalent bonds consist of **pairs of electrons shared between atoms**.
- In 1865 **Kekulé** proposed the structure for **benzene**. Which satisfied the molecular formula C_6H_6 and the **valence of carbon**. It also has only a **single kind of hydrogen**.



Kekulé suggested that the two compounds were in rapid equilibrium, so they could not be separated. Although this is not exactly correct, it was a pretty good answer for the time. Now we know that these are; the two resonance structure of the same compounds.



The true structure of benzene is a the RESONANCE MIXTURE or HYBRID of the two Lewis structures, with the dashed lines of the hybrid indicating the position of the π bonds.



The electrons in the π -bonds are delocalized around the ring

or in an abbreviated way

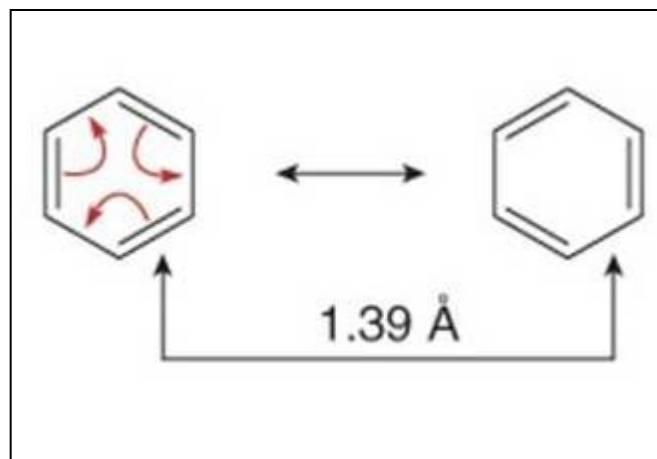
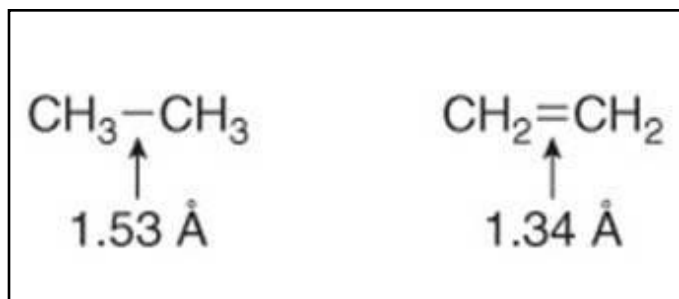


The circle represent six π -electrons distributed over the six atoms of the ring.

Circle-in-a-ring notation stands for resonance description of benzene (hybrid of two **Kekulé** structures)

Later spectroscopic evidence showed :

1. All bond lengths to be **equal** and **intermediate** between **single** and **double bond** lengths (**1.39 Å**).



2. It was also found that benzene was a **flat (planar)** molecule.
3. Further more, all **bond angles** in benzene are 120° , p electrons are **delocalised**.



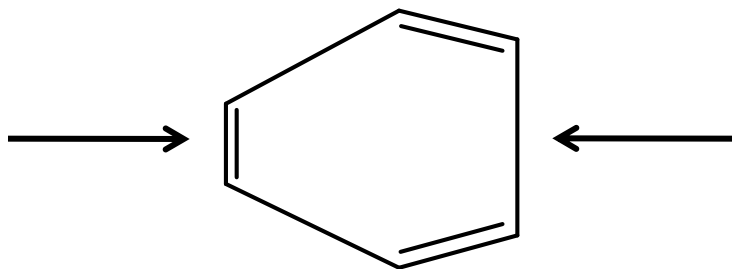
Delocalized electrons are electrons in a molecule that are not associated with a single atom or to a covalent bond. **Delocalized electrons** are contained within an **orbital** that **extends over several adjacent atoms**. ⁷

Argument in favour of Kekulé structure of Benzene

I. Argument in Benzene Kekulé structure

□ The **Kekulé** structures satisfy two of the three criteria of benzene (**planar & six membered ring**), because the third **having three alternating π bonds** means that benzene should have **three short double bonds** alternating with **three longer single bonds**.

Short bond
1.34 Å
(exaggerated)



Long bond
1.53 Å
(exaggerated)

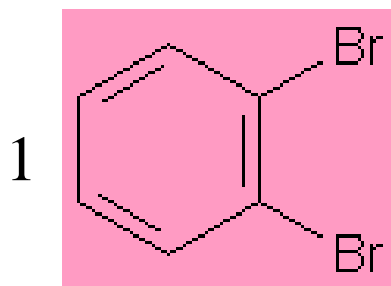
- Three short bonds
- Three long bonds

II. Argument in Resonance Benzene Kekulé Structure

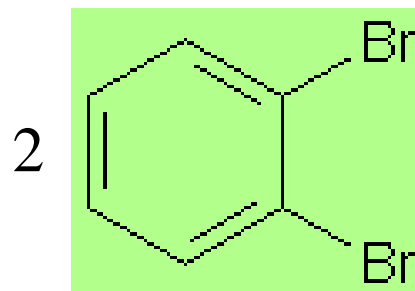
❑ If the double bonds in **benzene** were to be **localized**, such as the **Kekulé** formula indicates, substitution with bromine would yield two different **1,2-dibromobenzenes**.

However, **two 1,2-dibromobenzenes** that display **different chemical properties** are **actually not found**.

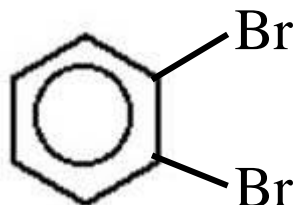
“**Kekulé** reasoned that there is a rapid establishment of equilibrium”.



1,2-dibromobenzenes



1,2-dibromobenzenes



Only **one** 1,2-dibromobenzenes

III. Argument Benzene type reactions according to Kekulé structure

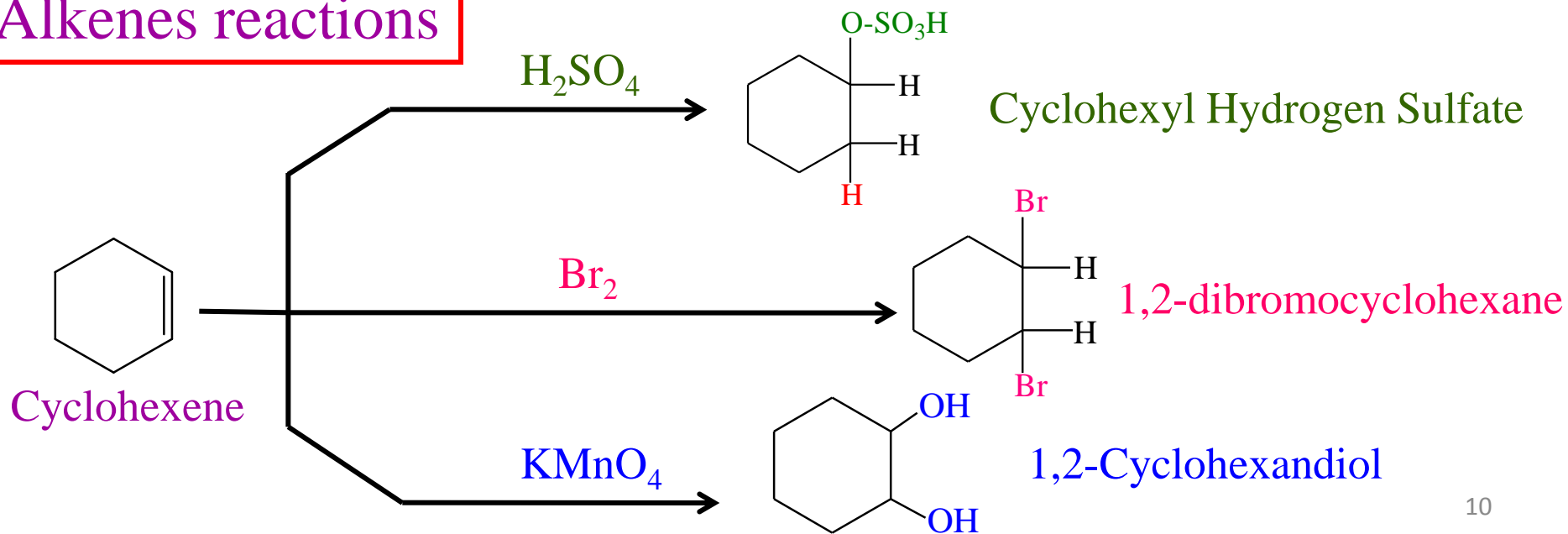
“Chemistry Argument”

- Because of the **three double bonds**, you might expect **benzene** to have reactions like **alkenes** such as; cyclohexene.

- **Alkene** undergoes **addition reactions** in which **one of the two bonds** joining the carbon atoms **breaks**, and **the electrons are used to bond with additional atoms**.

- **Benzene** rarely does this. Instead, it usually undergoes **substitution reactions** in which **one of the hydrogen atoms** is **replaced by** something new.

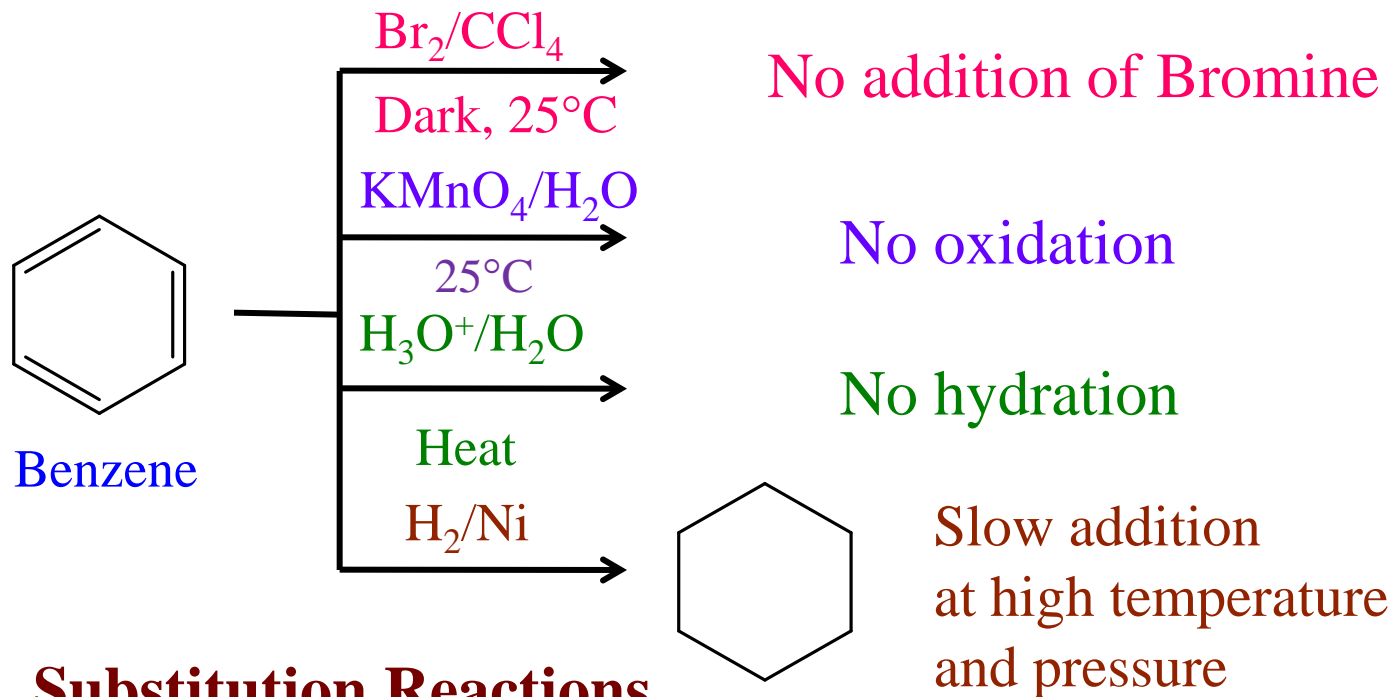
Alkenes reactions



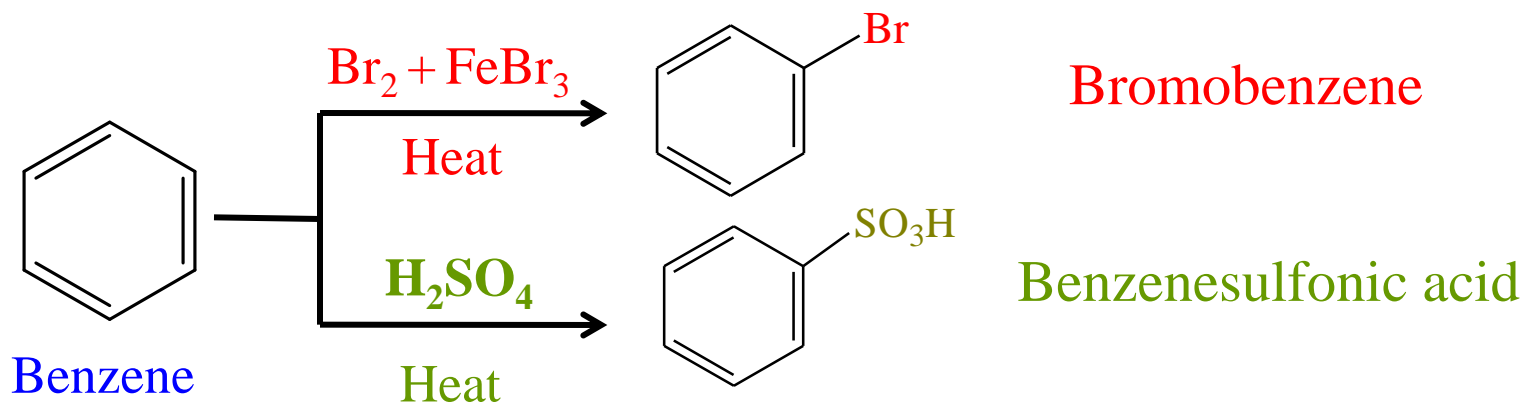
Benzene Reactions

Examples

a. Addition Reactions



b. Substitution Reactions



III. Argument in Benzene stability according to Kekulé structure

□ Although **Kekulé** had proposed a reasonable structure for **benzene**, it still did not address the **unusual stability** of **benzene**. The unusual stability of **benzene** (and related structures) is seen in both its *heat of hydrogenation* and its *chemical reactivity*, which differ appreciably from those usually observed conjugated **alkenes**, **dienes** and **trienes**.

Q1: Why *Benzene* is Highly Stable?

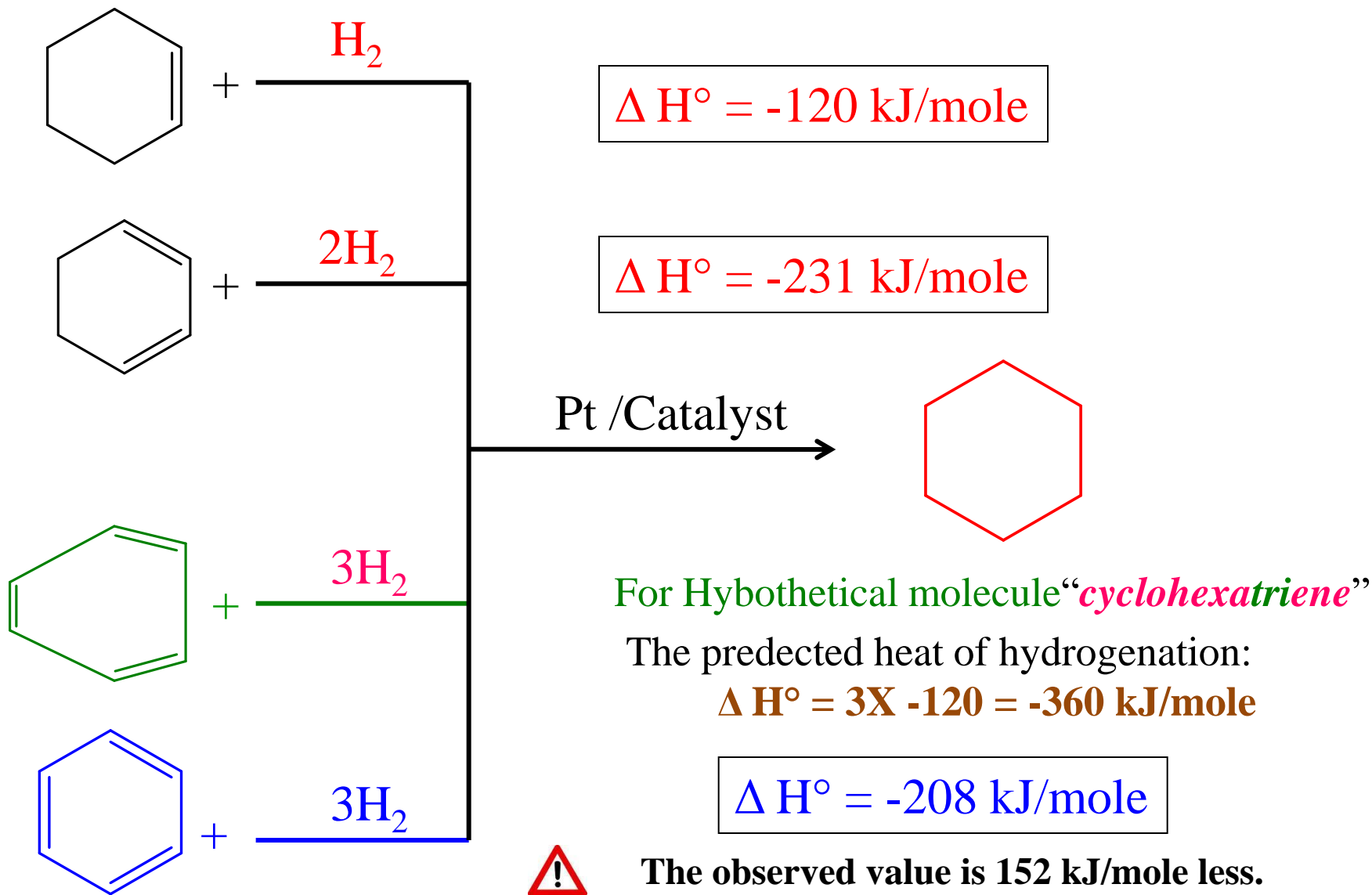
??????

Possibly it was a property of *cyclic molecule with alternating single and double bonds*.

Q2: How can we quantify the stability of *Benzene* relative to other unsaturated compounds?

Heat of hydrogenation

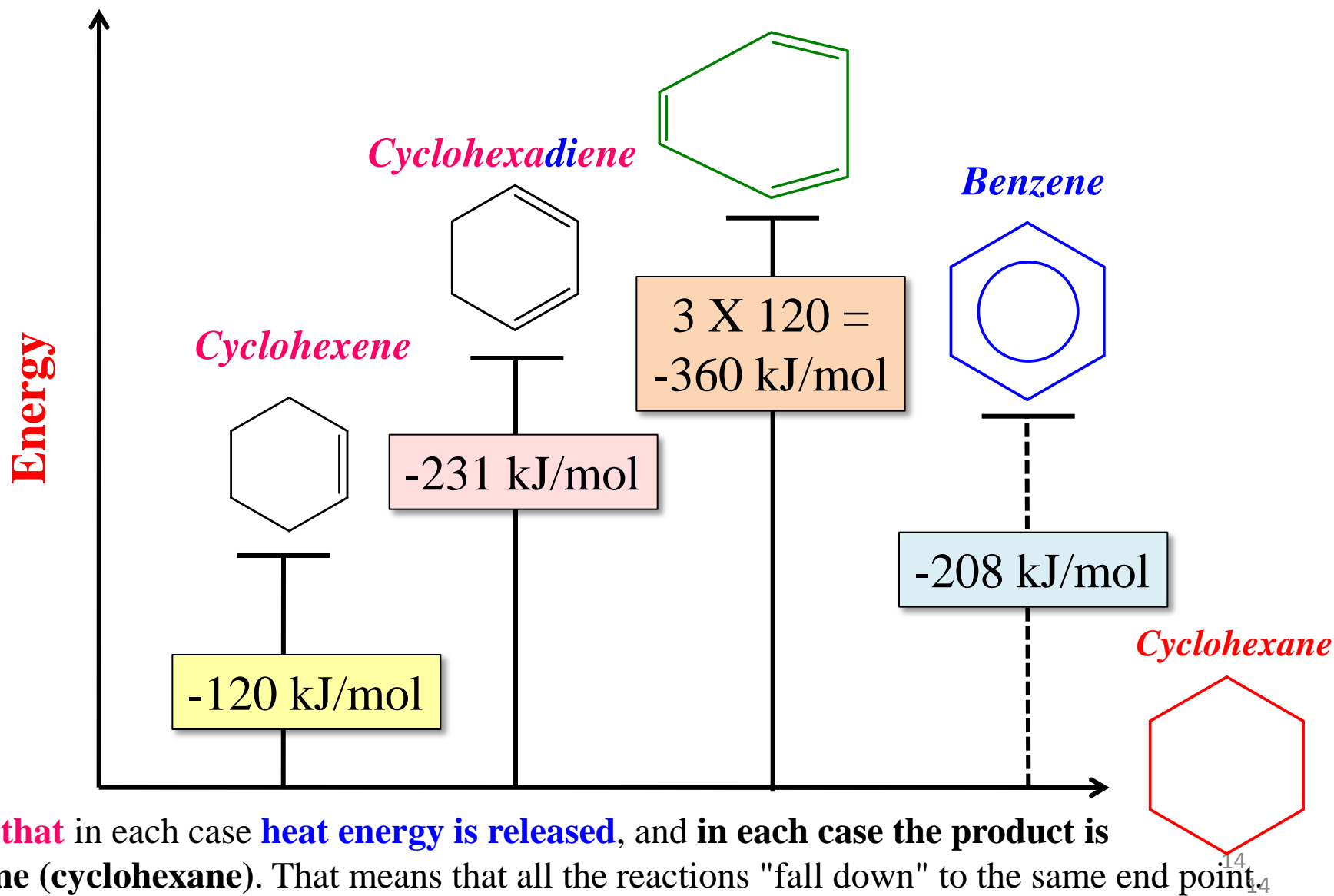
Quantification of stability-Heat of Hydrogenation



This energy difference is the stabilization of **benzene**. It is commonly referred as **the resonance stabilization** of **benzene**.

This is very much easier to see on **an enthalpy diagram**.

Hypothetical molecule
"cyclohexatriene"



Notice that in each case **heat energy is released**, and in each case the product is the same (cyclohexane). That means that all the reactions "fall down" to the same end point.

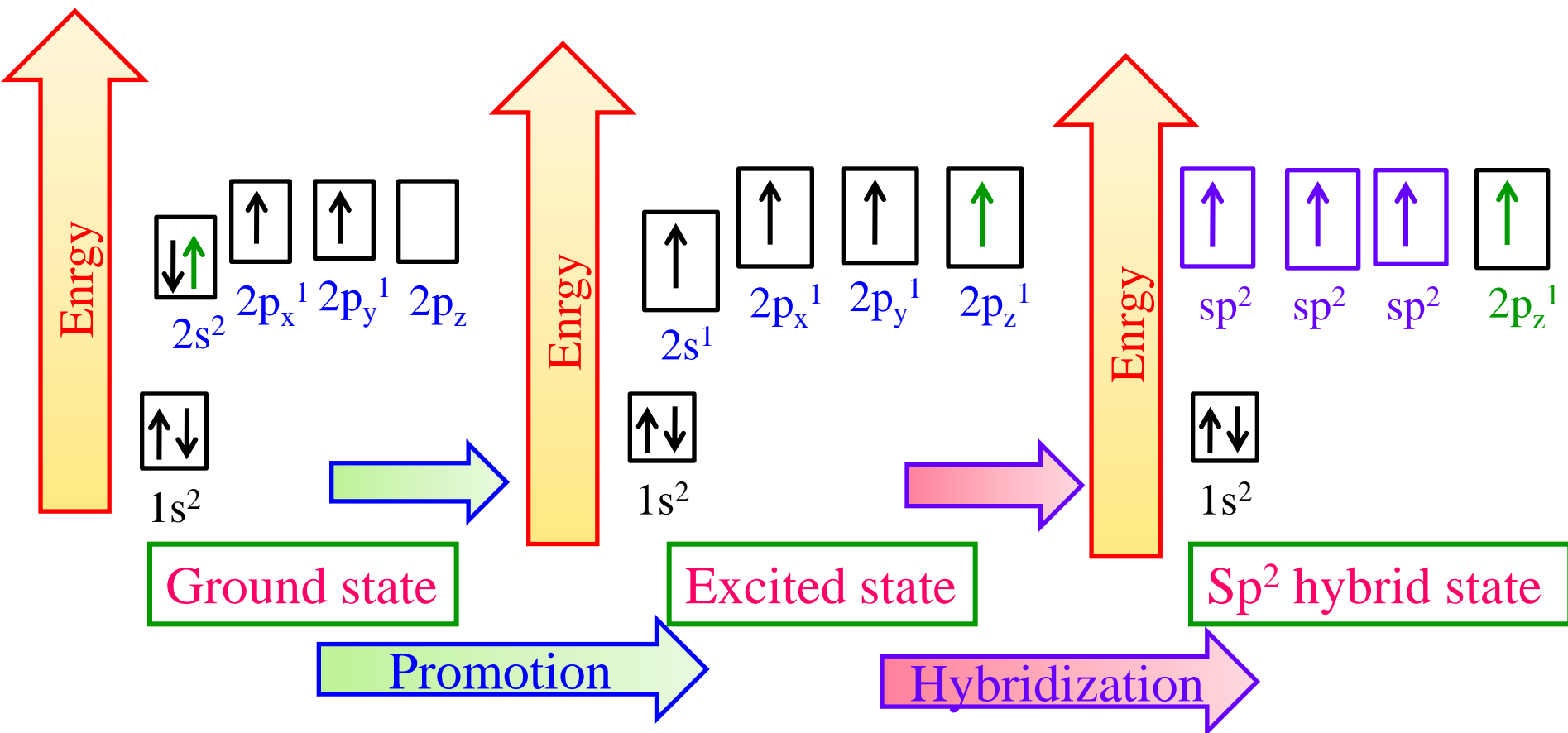
The physical properties of Benzene

- 1) Benzene is a **colorless** liquid.
- 2) Benzene is **soluble in** organic solvents but **immiscible** in water.
- 3) It is an aromatic compound so it has a typical aromatic odor.
- 4) Benzene is **highly inflammable** and burns with sooty flame.
- 5) Benzene is **toxic** and **carcinogenic** in nature.

Hybridization of Benzene ring.



The Simplest Aromatic Compound; “*The parent Aromatic compound*”.

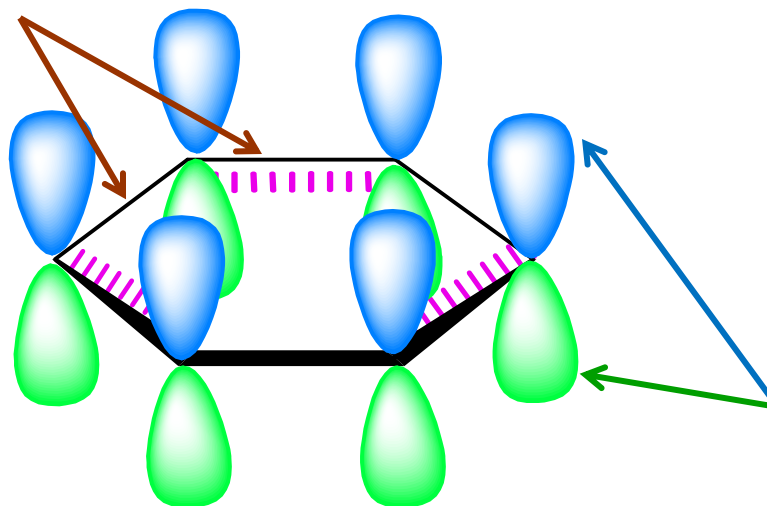


Benzene is built from **hydrogen** atoms ($1s^1$) and **carbon** atoms ($1s^2 2s^2 2p_x^1 2p_y^1$). Each **carbon atom** has to join to **three other atoms** (one hydrogen and two carbons) and **doesn't have enough unpaired electrons** to form the required number of bonds, so it needs **to promote** one of the $2s^2$ pair into the empty $2p_z$ orbital.

Summary

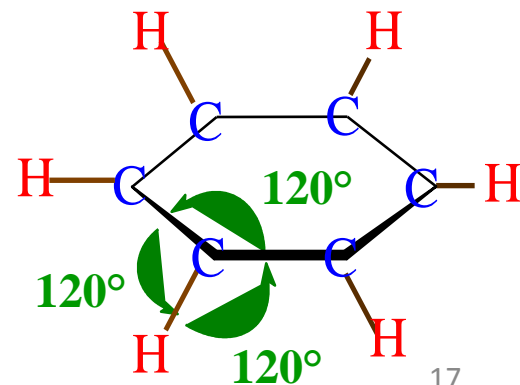
- **Benzene** has **3 sp^2 -hybridized** for each **C** atoms, Each carbon atom uses the sp^2 hybrids to form sigma bonds with **two other carbons** and **one hydrogen atom**.

σ bond formed from sp^2 hybrid orbitals .



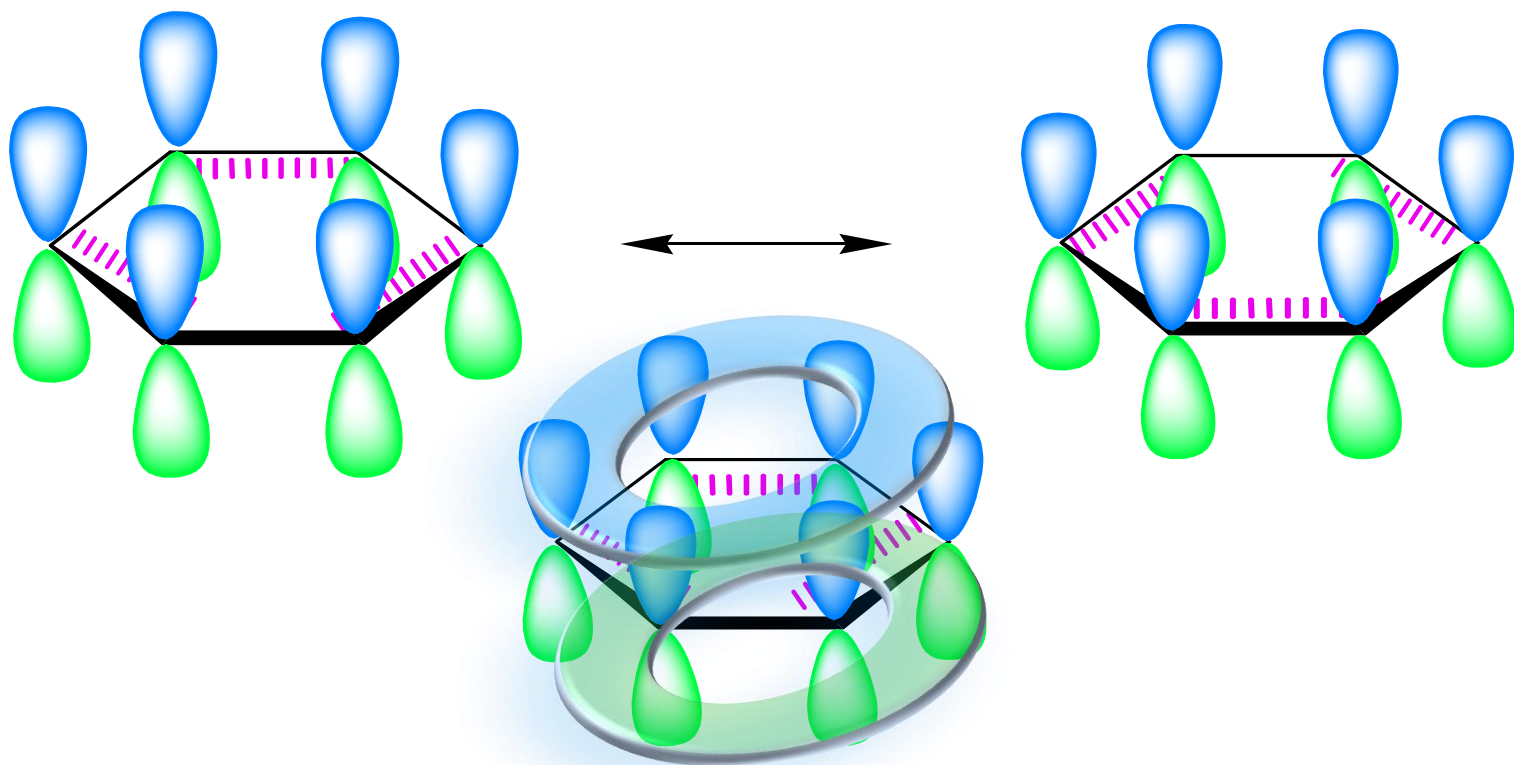
P_z unhybrid orbital above and below the plan of the ring.

- The **three sp^2 hybrid orbitals** arrange themselves as far apart as possible which is at 120° to each other in a **plane**.



Summary

The lobes of these atomic orbitals meld together to form **circular rings of electron density** *above* and *below* the plane of the molecule. Because **the electrons are no longer held between just two carbon atoms**, but are spread over the whole ring, the electrons are said to be *delocalised*. The two of these together constitute the "**second half**" of the carbon-carbon double bonds in **benzene**.



Hückel's Rule

Erich Hückel proposed a series of rules that would predict whether compounds would be **unusually stable** like **benzene**. These compounds are called **aromatic**, and *if they meet these requirements* are **much more stable** than expected for a similar **non-aromatic** structure.

Aromatic structural requirements :

- ✓ The molecule must be **cyclic**.
- ✓ Every atom in the ring must possess a **p-orbital** (**sp^2 hybridized**).
- ✓ The molecule must be **planar** so that all of the **p-orbitals** are **parallel**.
- ✓ The molecule must have **$4n+2$ π -electrons** (electrons in the π -orbitals), where **n** is an **integer** (**0,1,2,3, etc**). Thus the aromatic molecule will have **2, 6, 10, 14, etc. π -electrons** .

• **Hückel** also found that, If the molecules meet **the first 3 conditions** (**Cyclic**, **Planar**, and **fully Conjugated**), **but** only have **$4n$ π -electrons** (4, 8, 12, etc) they are **unusually unstable**. These compounds are called ***anti-aromatic***.

How does the $4n+2$ Rule Work?

To apply the $4n+2$ rule,

first count the number of π electrons in the molecule.

Then, set this number equal to $4n+2$ and solve for n .

If n turns out to be **0** or any positive integer (**1, 2, 3,...**), the rule has been met.

For; **$4n+2$ π** electrons ($n = 0, 1, 2, 3, \dots = 2, 6, 10, 14, 18$) is **Aromatic**

For; **$4n$ π** electrons ($n = 0, 1, 2, 3, \dots = 4, 8, 12, 16,$) is **Anti-Aromatic**

 Note that;

Molecules that **doesn't follow** any of the first three ***aromatic criteria*** are called ***Non-Aromatic***.

Summary

Aromatic	Anti-Aromatic	Non-Aromatic
Cyclic	Cyclic	Not Cyclic
Planar (Flat)	Planar (Flat)	Not Planar (Flat)
Completely Conjugated	Completely Conjugated	Not completely conjugated
2, 6, 10, 14... π electrons	4,8,12,16, ... π electrons	-----

Following is *decreasing order of stability* of aromatic, anti-aromatic and non-aromatic compounds.

Aromatic > **Non-aromatic** > **Anti-aromatic**

Applications of Hückel rules:

(a) Homocyclic Systems.

(b) Heterocyclic Systems.

(c) Polycyclic Systems.

(1) Neutral Compounds.

(2) Aromatic Ions.

Aromatic Ions.

Hückel's rule also applies to **ions**, as long as a compound has $4n+2 \pi$ - **electrons**. It doesn't matter if the molecule is *neutral* or has a *charge*.

Pi electrons are counted as follows:

each double bond counts as two pi electrons

each (+) charge counts as zero pi electrons,

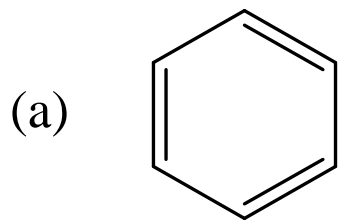
each (-) charge counts as two pi electrons,

each radical counts as one pi electron.

Set the total number of pi electrons as equal to $4n + 2$; solve for **n**.

Examples

“Neutral Aromatic compounds”

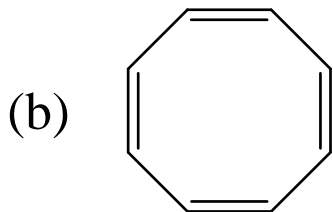


Benzene

$3\pi\text{-bonds} = 6 \text{ pi electrons}$

$$4n+2=6; n=1$$

☺ **Aromatic**

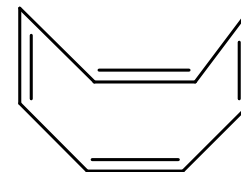


Cyclooctatetraene

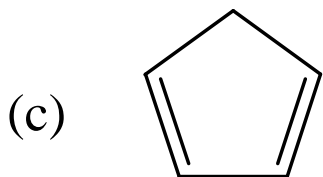
$4\pi\text{-bonds} = 8 \text{ pi electrons}$

$$4n+2=8; n=3/2$$

☹ **Non-aromatic**



Tub-shap

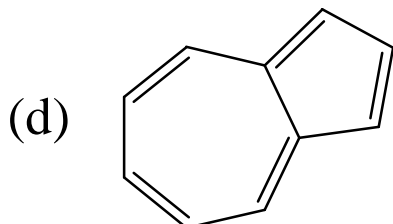


Cyclopentadiene

The hybridization of the top C is sp^3

Not planar, not fully conjugated

☹ **Non-aromatic**



Azulene

$5\pi\text{-bonds} = 10 \text{ pi electrons}$

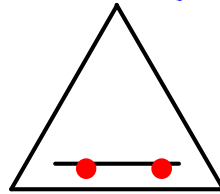
$$4n+2=10; n=2$$

☺ **Aromatic**

Excercise

The hybridization of the top "C" is sp^3 i.e. No p-orbital

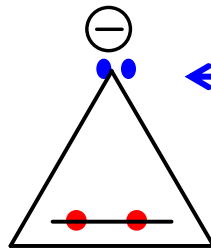
Case 1



Cyclopropene

The compound is **Non-aromatic**

Case 2



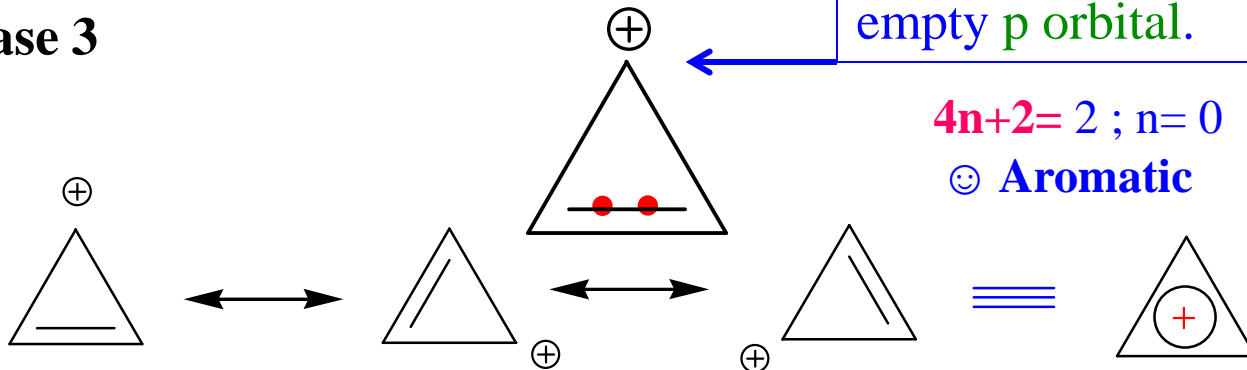
-ve charge atom has **2 pi** electrons

$$4n+2=4; n=1/2$$

☹ **Anti-aromatic**

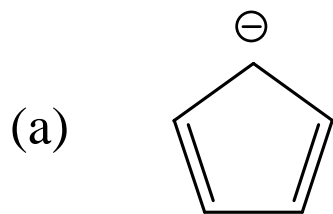
+ve charge atom empty p orbital.

Case 3

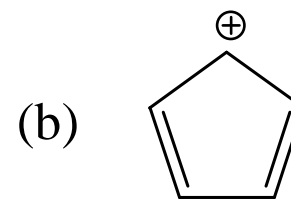


Examples

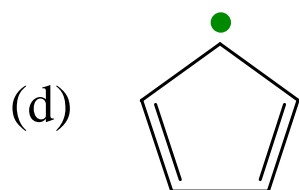
“Aromatic Ions”



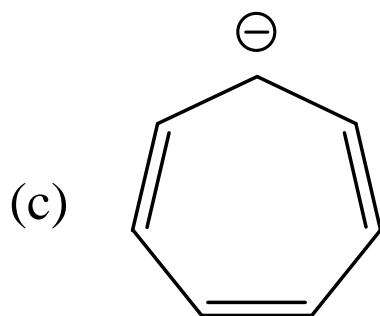
Cyclopentadienylanion



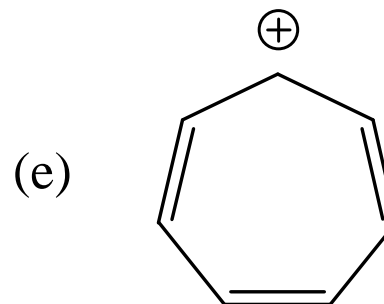
Cyclopentadienylcation



Cyclopentadienylradical



Cycloheptatrieneanion



Cycloheptatrienecation
(*tropylium ion*)

Heterocyclic Systems

Heterocyclic compounds are compounds in which **one** or **more carbons** in the ring are replaced by other atoms (*heteroatoms*). Heteroatoms in organic compounds are usually **nitrogen**, **oxygen**, or **sulfur** atoms. Heterocyclic aromatic compounds are heterocycles that are **planar**, **cyclic**, **fully conjugated** molecules that follow Hückel's rule.

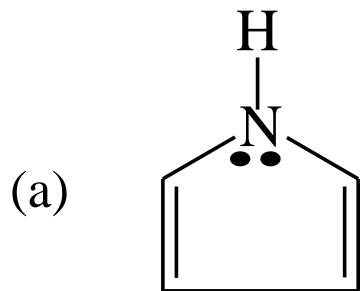
How to count the # lone pair(s) on hetero atom?

- A **single lone pair** can be found with atoms in the nitrogen group such as **nitrogen** in ammonia,
- **Two lone pairs** can be found with atoms in the **chalcogen** group such as **oxygen** , **sulfur** in water

Examples

“Heterocyclic compounds”

Predict which of the following structures accord to Hückels rule for aromaticity:

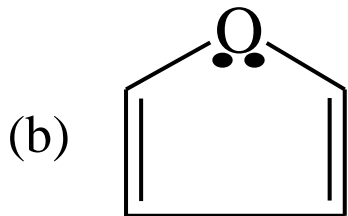


Pyrrol

2π -bonds + 1 lone pair = 6 pi electrons

$$4n+2=6 ; n=1$$

☺ **Aromatic**

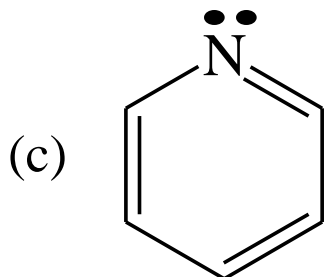


Furan

2π -bonds + 1 lone pair = 6 pi electrons

$$4n+2=6 ; n=1$$

☺ **Aromatic**



Pyridine

the lone pair is perpendicular to the π -system

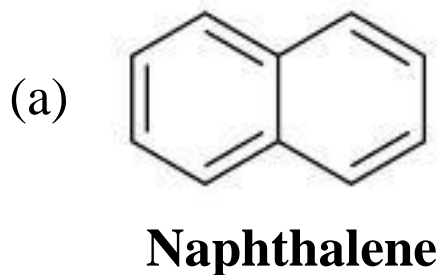
2π -bonds + 0 lone pair = 6 pi electrons

$$4n+2=6 ; n=1$$

☺ **Aromatic**

Polycyclic Systems

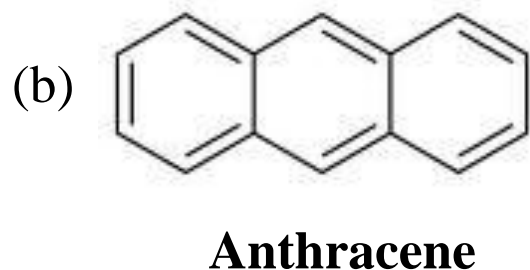
Predict which of the following structures accord to Hückels rule for aromaticity



5π -bonds = 10 pi electrons

$$4n+2=10 ; n=2$$

☺ **Aromatic**



7π -bonds = 14 pi electrons

$$4n+2=14 ; n=3$$

☺ **Aromatic**

H.W(5-a)

Page: 126; problems 5.2

Page: 129; problem 5.4

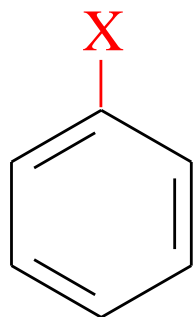
Page:130; problem 5.5



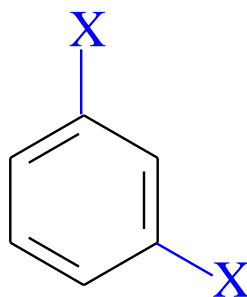
Nomenclature of Benzene derivatives

Benzene derivatives are divided into three classes :

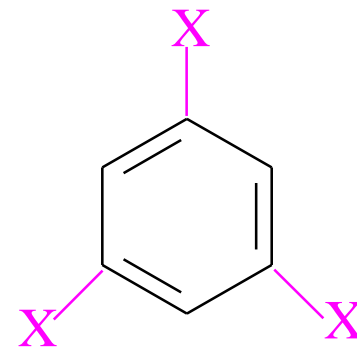
MonoSubstituted
Benzene



DiSubstituted
Benzene



Tri or Poly-
Substituted
Benzene



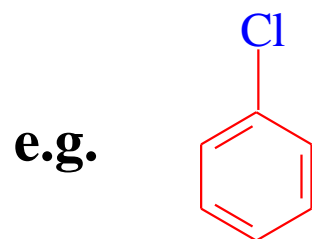
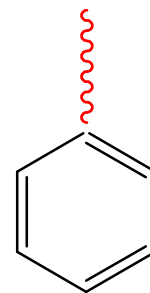
IMPORTANT NOTES:

- Aryl = Ar = Aromatic group

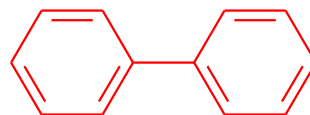
“It is a broad term, and includes *any aromatic* rings”

- Phenyl = Φ or Ph = C_6H_5-

You get a phenyl group, C_6H_5 , by removing a **hydrogen** from a benzene ring, C_6H_6 .



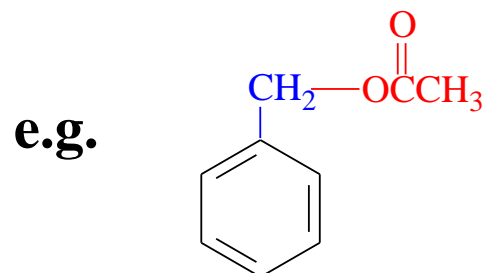
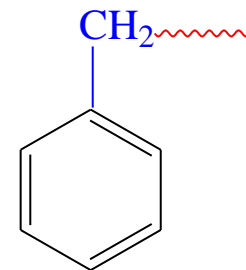
Phenylchlorid



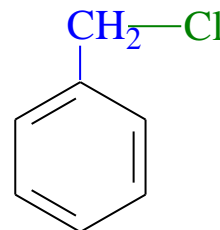
biphenyl

- Benzyl = Bn = $C_6H_5CH_2-$

You get a benzyl group, $C_6H_5CH_2-$, by removing a **hydrogen** from the **methyl** on the benzene ring.



Benzylacetate



Benzylchloride

(a) Monosubstituted Benzene

Two systems are used in naming *monosubstituted* benzene.

Case 1.

Benzene is a **parent name** for some **monosubstituted** benzenes the substituent name is added as prefix. (**Combined name**).

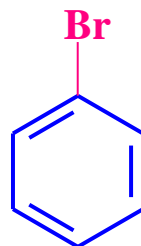
Case 2.

For other **monosubstituent** benzenes, the presence of substituent result in a **new parent name**. (**Singular Name**)

For the 1st Case

There are usually **two equivalent names** for each **benzene-based compound**, one with *phenyl* as the root and one with *benzene*.

(a) Functional group **suffix** = *-benzene*



Bromobenzene

(b) Functional group **prefix** = *phenyl-*

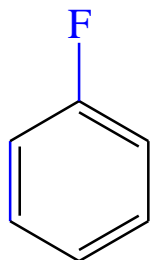


Phenylbromid

(1) Benzene as a Parent Name

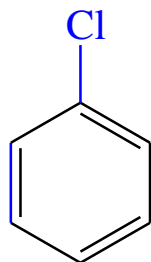
The IUPAC system of naming **mono-substituted** benzene derivatives uses the name of the **substituent** as a **prefix** to the name benzene.

Examples



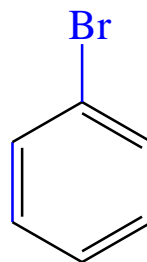
Fluorobenzene

Phenyl fluoride



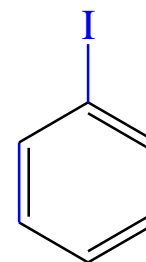
Chlorobenzene

Phenyl chloride



Bromobenzene

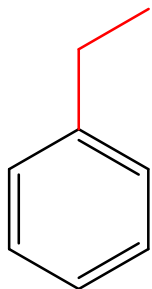
Phenyl Bromide



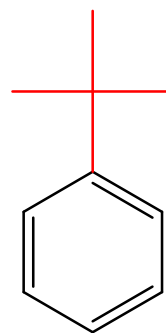
Iodobenzene

Phenyl Iodide

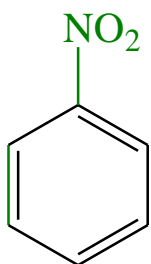
Examples



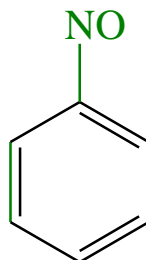
Ethylbenzene



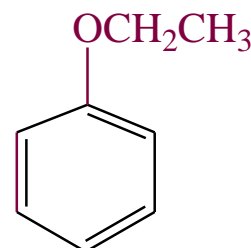
t-Butylbenzene



Nitrobenzene



Nitrosobenzene



Ethoxybenzene

Note:

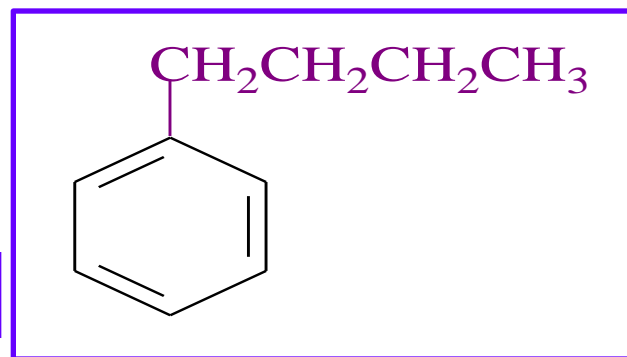
Because all six positions in benzene are *equivalent*, there is no need to specify by a **position number of a substituent** for **monosubstituted benzene**.

Notes that:

When **the aliphatic part** of a molecule is **more complex** than **the aromatic**. The name of the compound may be derived from the aliphatic part using **prefix**, **Phenyl**, to indicate benzene substitution.

1. $R \leq 6$ benzene ring as **parent name**
“alkyl-substituted benzene”

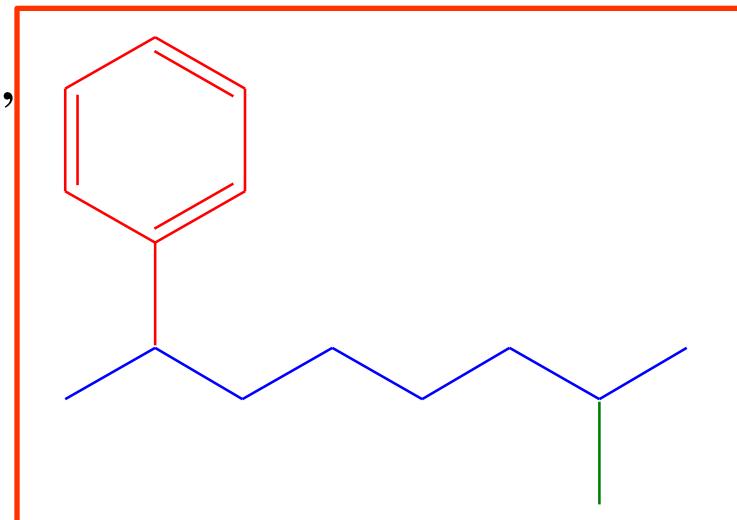
Butylbenzene



2. $R > 6$ (or R containing a functional group),
benzene ring as **substituent**.

“Phenyl-substituted hydrocarbon”

2-methyl-7-phenyloctane

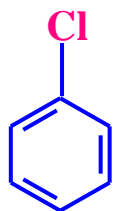


Cases where the name is based on *phenyl*

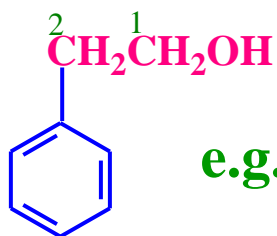
Is substituent higher than C₆?

No

Use the phenyl group naming,
Phenyl + **substituent**



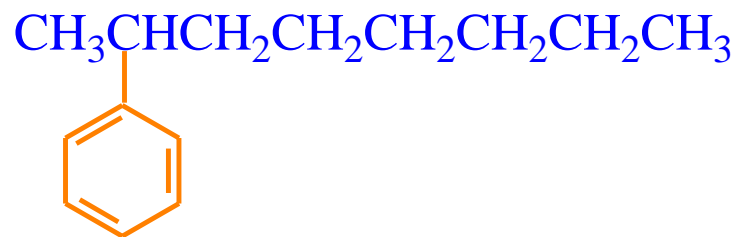
e.g. **phenylchlorid**



e.g. **2-phenylethanol**

Yes

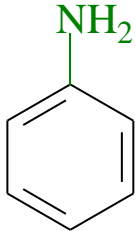
Use the ***phenyl*** as **substituent**,
& the root contains the principle
functional group.



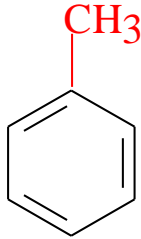
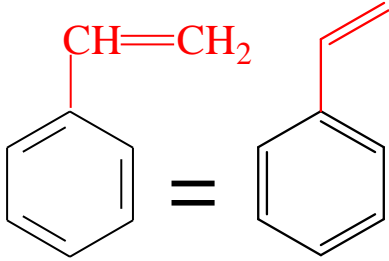
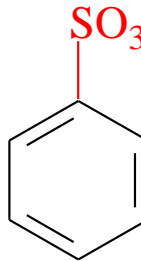
e.g. **2-phenyloctane**

(2) Benzene Derivative Common Name Singular Name

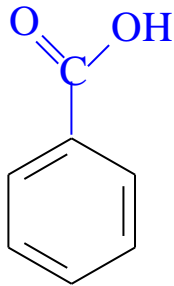
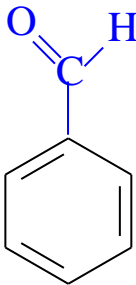
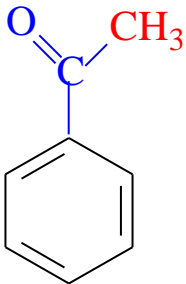
A few **mono-substituted benzene** have names wherein the substituent and benzene ring taken together constitute a ***new parent name***.

Function group	Structure	Name
—NH ₂		Aniline
Amino		

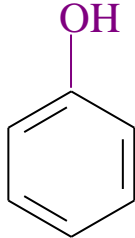
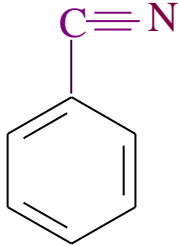
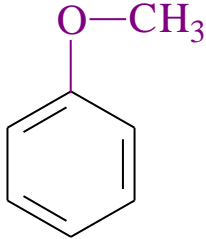
Examples

Function group	Structure	Name
$-\text{CH}_3$		Toluene
Methyl		
$-\text{CH}=\text{CH}_2$		Styrene
Vinyl		
$-\text{SO}_3\text{H}$		Benzenesulfonic acid
Sulfo		

Examples

Function group	Structure	Name
—C(=O)OH		Benzoic acid
Carboxyl group		
—C(=O)H		Benzaldehyde
Aldehyde group		
—C(=O)CH_3		Acetophenone
Carbonyl group “ Keton”		

Examples

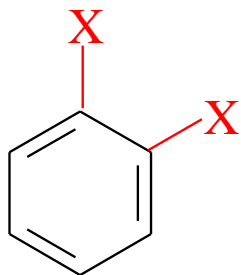
Function group	Structure	Name
—OH		Phenol
Hydroxyl		
$\text{—C}\equiv\text{N}$		Benzonitrile
Nitrile		
—O—CH_3		Anisol
Methoxy		

Disubstituted Benzene

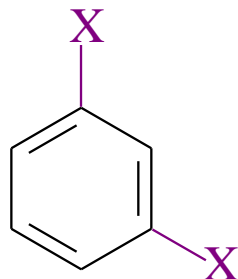
□ When two substituents, either the *same* or *different*, are attached to benzene ring, three isomeric structures are possible.

1- When the two substituents are the same:

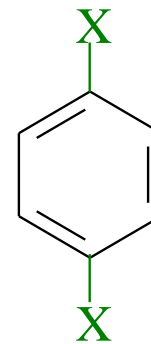
We locate the substituents either by numbering the atoms of the ring or by using locators *ortho* (*o-*), *meta* (*m-*), and *para* (*p-*).



1,2- = *ortho-*
(abbreviated, *o-*)



1,3- = *meta-*
(abbreviated, *m-*)



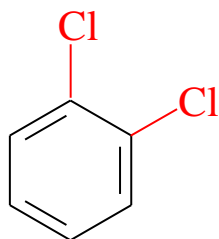
1,4- = *para-*
(abbreviated, *p-*)

Note that:

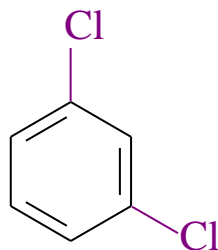
1,2- are equivalent to *ortho*; (Greek: straight), 1,3- to *meta*; (Greek: after), and 1,4- to *para* (Greek: beyond).

• The locators *ortho*, *meta*, and *para* can be used with *similar* as well as *different* di-substituents.

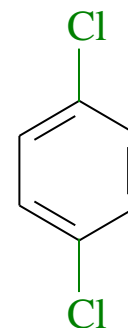
Examples:



ortho-chlorobenzene
or *o*-
1,2- Dichlorobenzene

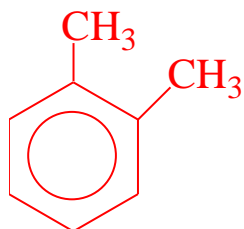


meta-chlorobenzene
or *m*-
1,3- Dichlorobenzene

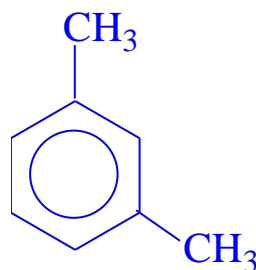


para-chlorobenzene
or *p*-
1,4- Dichlorobenzene

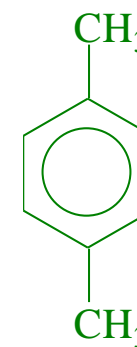
□ A benzene ring bearing **two methyl groups** is a situation that generates a new special base name. such compounds has **three isomers**.



o-Xylene
or 1,2- Dimethylbenzene



m-Xylene
or 1,3- Dimethylbenzene



p-Xylene
or 1,4- Dimethylbenzene

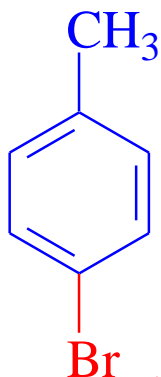
2- When the two substituents are **different** :

a. One group imparts a special name

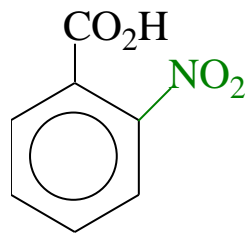
□ If one of the two substituents in a disubstituted benzene impart a *special name* to the compound (as example; $-\text{CH}_3 = \textit{toluene}$),

- Name the compound as a **derivative of that parent molecule**.
- Assume that the substituent occupies ring position number 1.

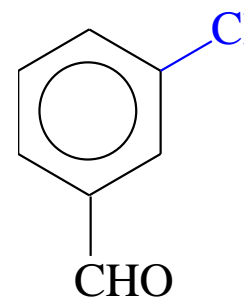
Examples



4-Bromotoluene
(Not; 1-Bromo-4-toluene)



2-Nitrobenzoic acid
o-Nitrobenzoic acid

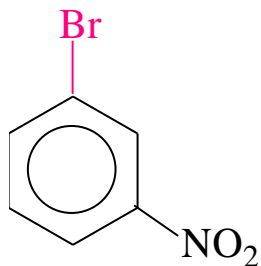


3-Chlorobenzaldehyde
m-Chlorobenzaldehyde

b. Neither substituent group impart a special name

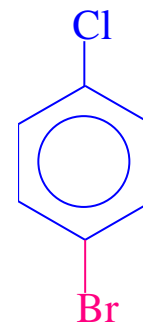
- The substituents are cited in **alphabetical order** before the ending **-benzene**.
- The **carbon of the benzene ring** bearing the substituent with **alphabetical priority** becomes **carbon 1**.

Examples



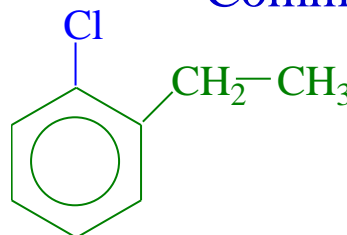
IUPAC: 1-Bromo-3-nitrobenzene

Common: *m*-Bromonitrobenzene



IUPAC: 1-bromo-4-chloro-benzene

Common: *para*-Bromochlorobenzene

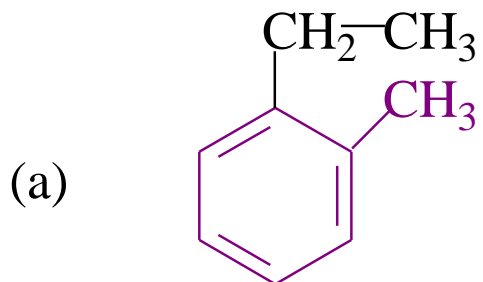


IUPAC: 1-Chloro-2-ethylbenzene

Common: *o*-Chloroethylbenzene

Not; 2-Chloro-1-ethylbenzene

Practice:

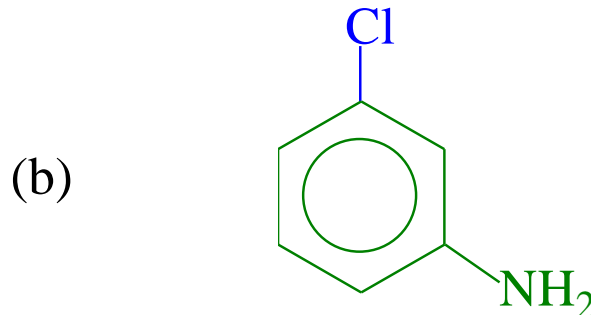


2-Ethyltoluene

or

ortho-Ethyltoluene

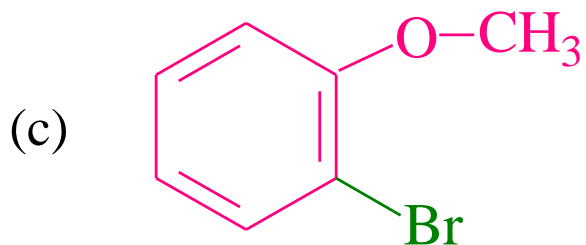
(Not; 1-Ethyl-2-methylbenzene)



3-chloroaniline

or

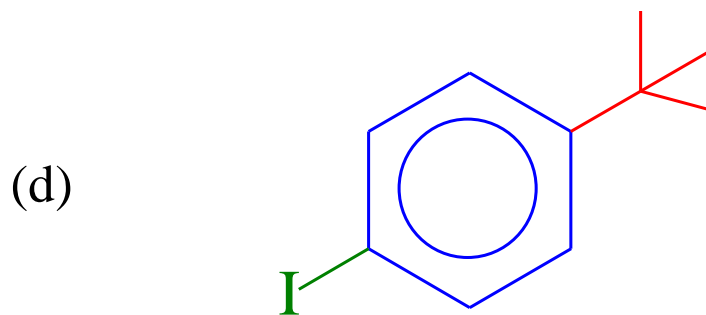
m-chloroaniline



2-Bromoanisole

or

o-Bromoanisole



4- Iodo-t-butylbenzene

= 1-t-butyl-4-iodobenzene or

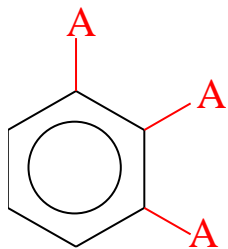
p- Iodo-t-butylbenzene

Benzene derivatives with three or more substituents

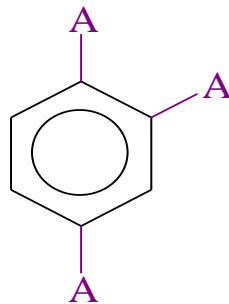
□ In the case of tri-substituted derivatives, the nature of the substituted groups determine the number of arrangements. their positions are indicated by *numbers*.

1- When the three substituents are the same:

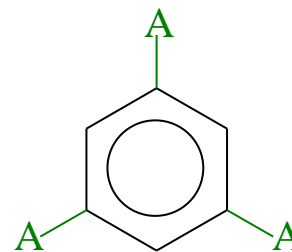
When the three substituent groups are identical (say, A), three arrangements are possible. These are termed as follows.



Vicinal
(vic-)

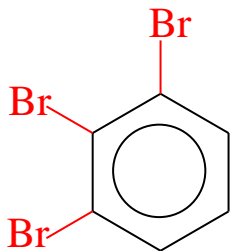


asymmetrical
(asym-)

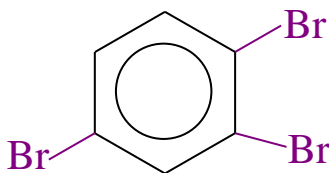


Symmetrical
(sym-)

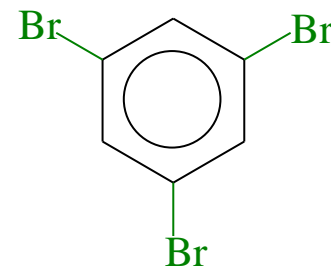
Examples:



1,2,3-Tribromobenzene
vic- Tribromobenzene



1,2,4-Tribromobenzene
as- Tribromobenzene

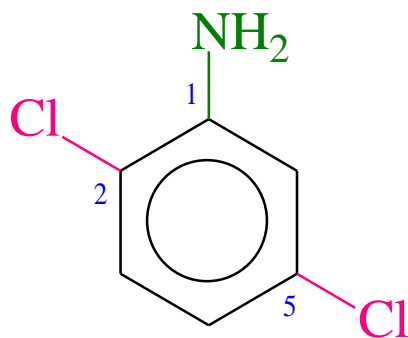


1,3,5-Tribromobenzene
s- Tribromobenzene

2- When the three substituents are different:

- The ring is numbered in such a way as to obtain *the lowest possible numbers* for the carbon atoms that have substituents.
- If there is a choice of numbering (*two systems give the same lowest set*), then the group that *came first alphabetically* is given *the lower number*.

a. One group imparts a special name

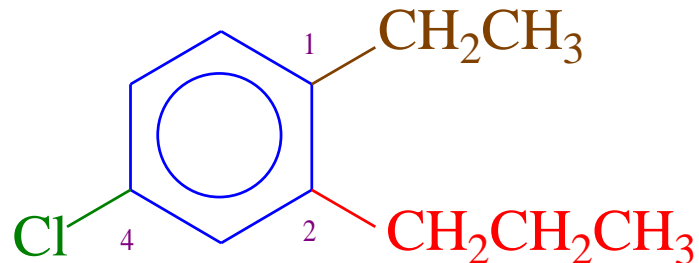


- Name the molecule as derivative of the common root **aniline**.
- Designate the position of the **NH₂ group** as “1”, and then assign the lowest possible set of numbers to the other substituents.

2,5- dichloroaniline.

b. None of the substituents groups impart a special name

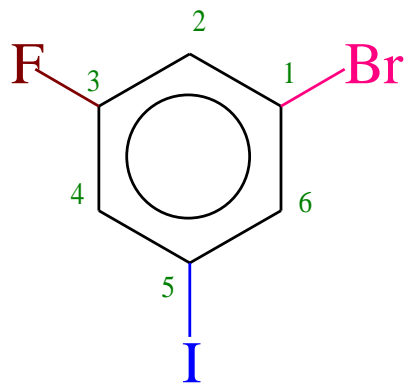
(a)



- Assign the lowest set of numbers.
- Alphabetize the names of all the substituents.

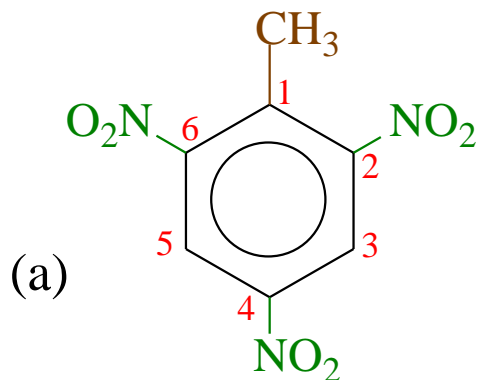
4-Chloro-1-ethyl-2-propylbenzene

(b)



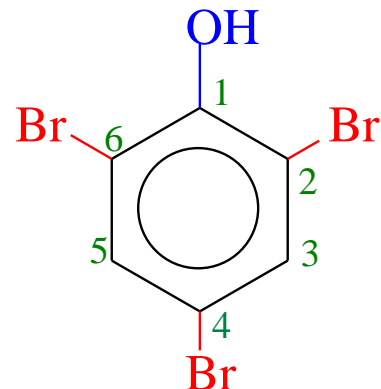
1-Bromo-3-fluoro-5-iodobenzene

Examples:

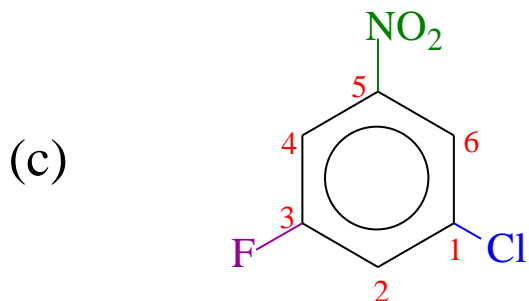


2,4,6-Trinitrotoluene (TNT)
“CH₃ on Carbon 1”

(b)

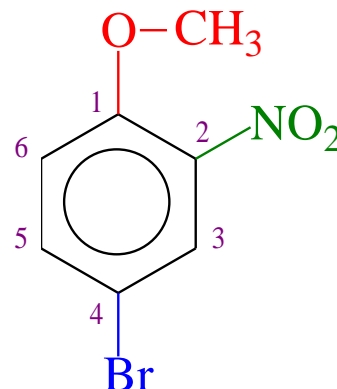


2,4,6-Tribromophenol
“OH on Carbon 1”



1-Chloro-3-fluoro-5-nitrobenzene
“alphabetical order”

(d)

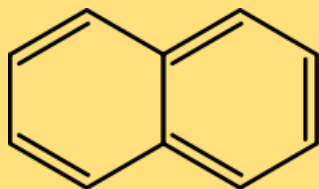


Common: 4-Bromo-2-nitroanisole
4-Bromo-1-methoxy-2-nitrobenzene

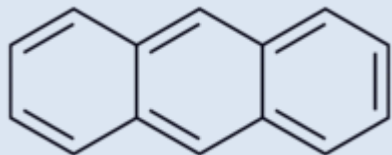
Polynuclear Aromatic Hydrocarbons

Benzene rings may be fused together to form *polynuclear aromatic hydrocarbons*.

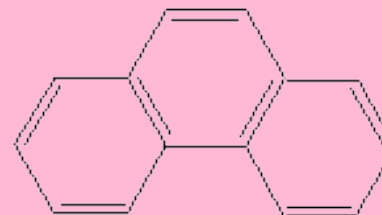
Examples for polynuclear aromatic hydrocarbons containing **two**, **three** and **four** rings are:



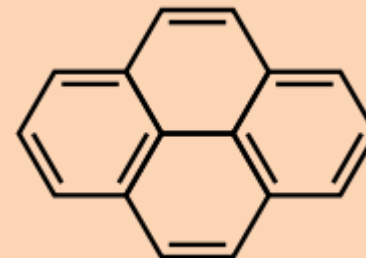
Naphthalene



Anthracene



Phenanthrene



Pyrene

Electrophilic Substitution Reactions:

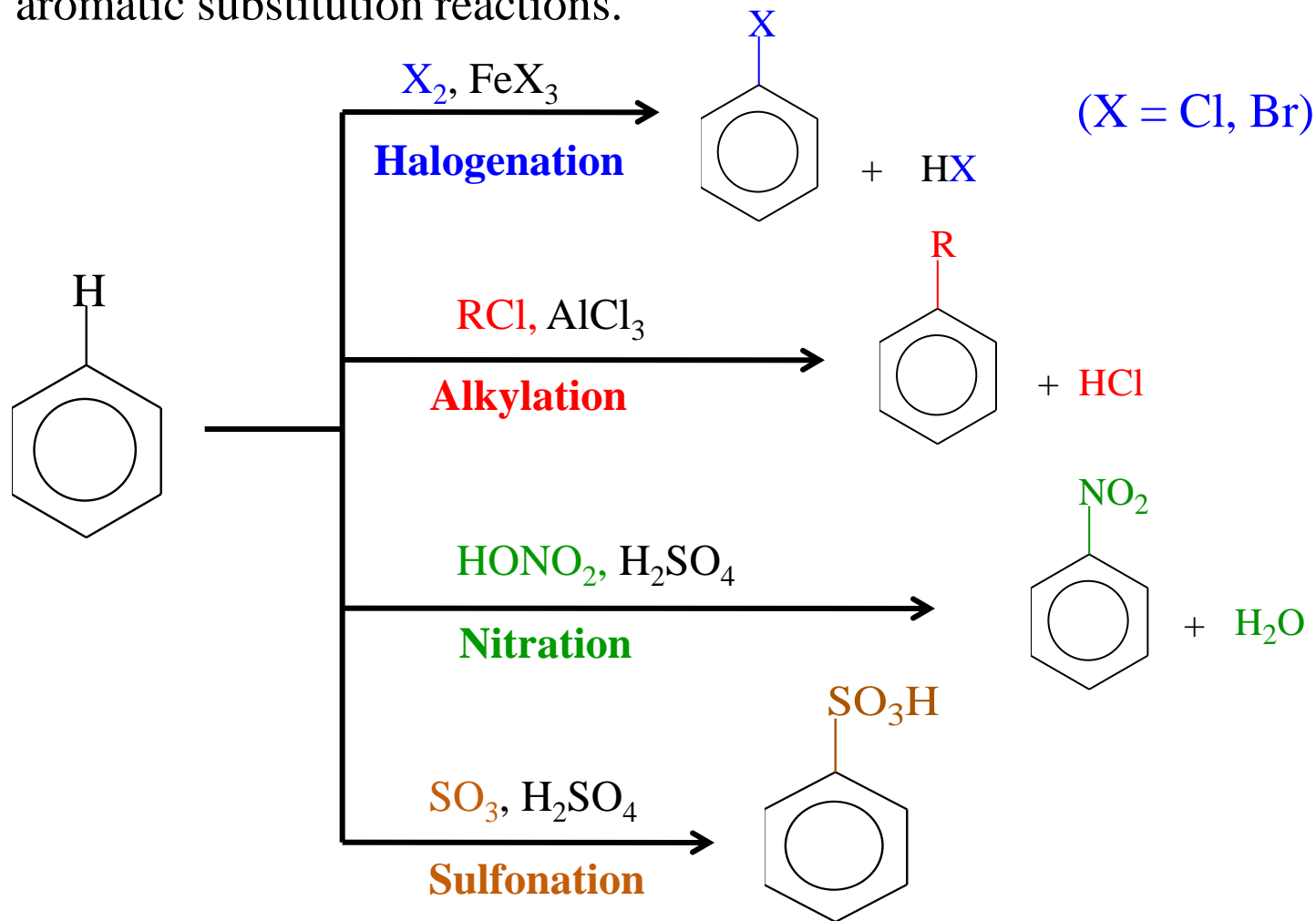
In *electrophilic substitution reactions*, an electrophile (E^+) is substituted for a **hydrogen** in the aromatic(benzene) ring.

The Electrophiles in Common Aromatic Substitution Reactions:

Electrophile	Name of Reaction
Cl^+ or Br^+	Halogenation
R^+	Alkylation
NO_2^+	Nitration
SO_3H^+	Sulfonation

1. Specific Electrophilic Aromatic Substitution reactions.

Halogenation, **alkylation**, **nitration**, and **sulfonation** are the typical electrophilic aromatic substitution reactions.



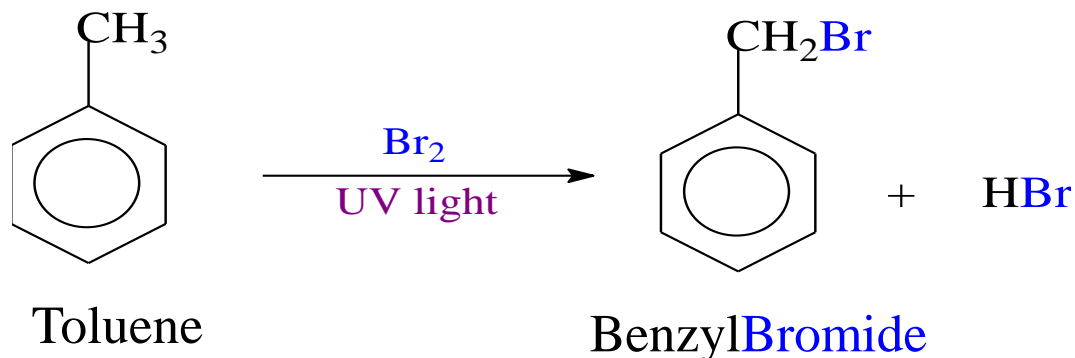
Note that; in each reaction **the net result** of replacement of a hydrogen in benzene by **one of the electrophiles**

2. Side reaction of Aromatic compounds.

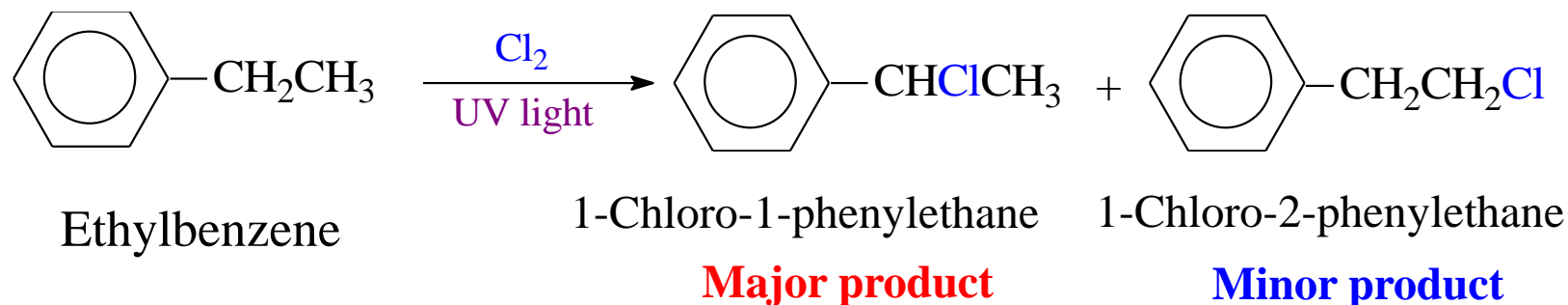
A. Halogenation of an alkyl Side chain

An **alkylbenzene** contains both an **aliphatic** and **aromatic** portion, we may expect the aliphatic portion (the alkyl side chain) to undergoes **the alkane substitutions**.

Example 1. Bromination of toluene in the presence of UV light



Example 2. Chlorination of ethylbenzene in the presence of UV light

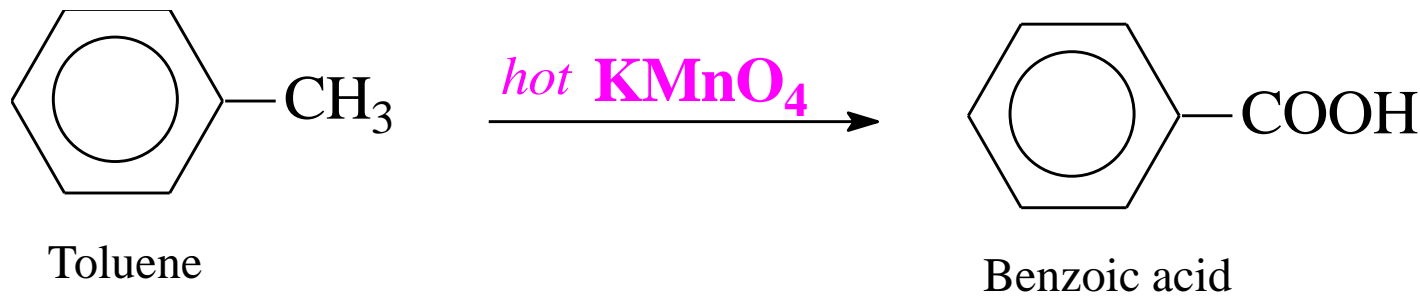


2. Side reaction of Aromatic compounds.

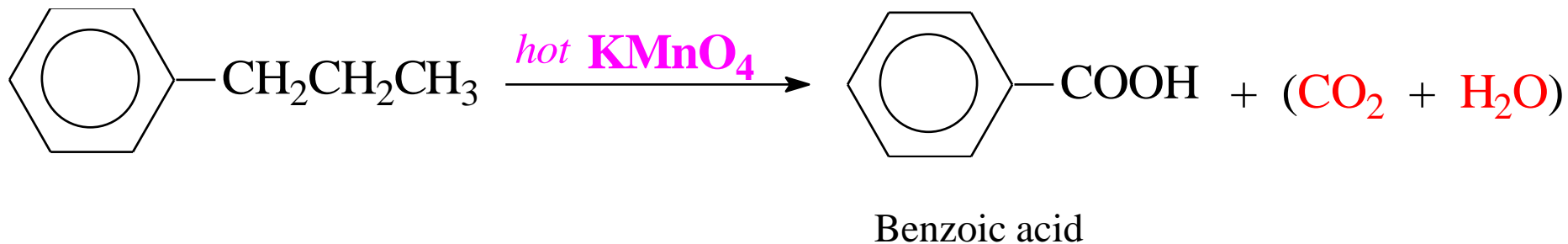
B. Oxidation of an alkyl Side chain

Another reaction of the alkyl side chain is the conversion into a *carboxyl group*, COOH , by treatment with hot potassium permanganate.

Example 1.

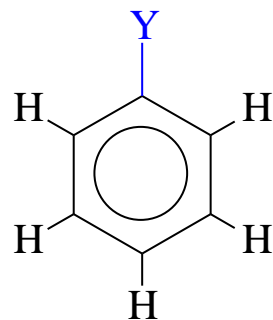


Example 2.

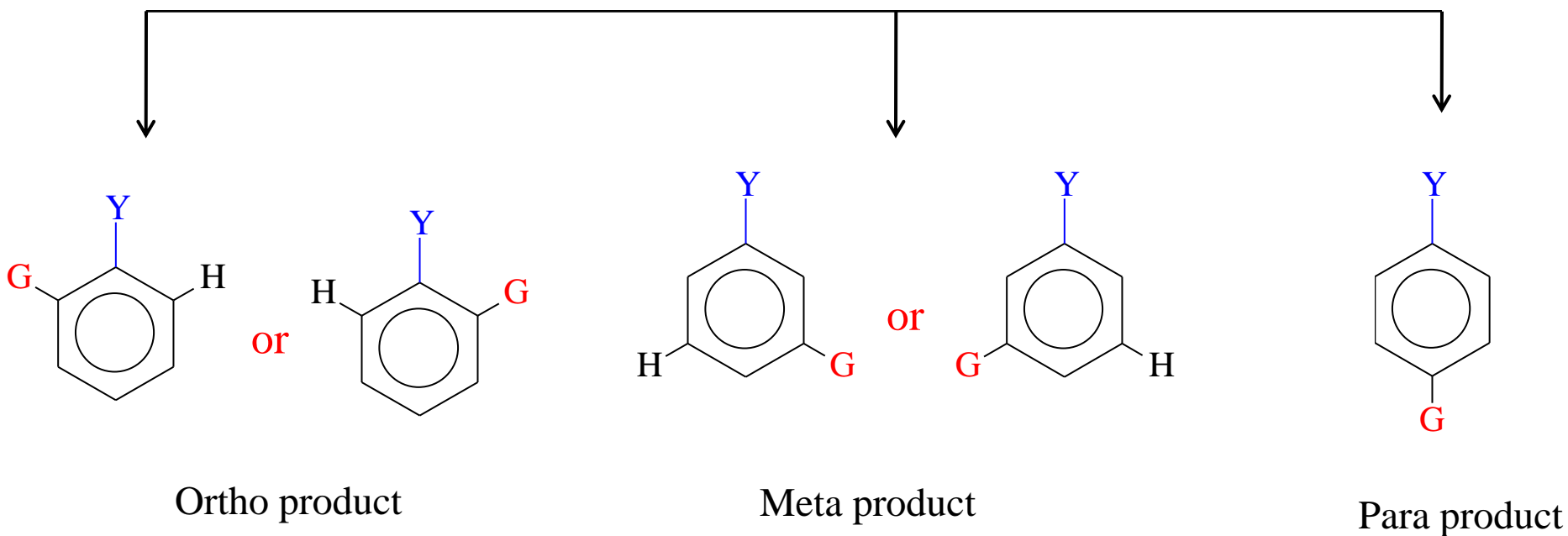


3. Disubstituted Benzene “Orientation in monosubstituted”.

The monosubstituted benzene C_6H_5-Y , has **5 replaceable hydrogens**.



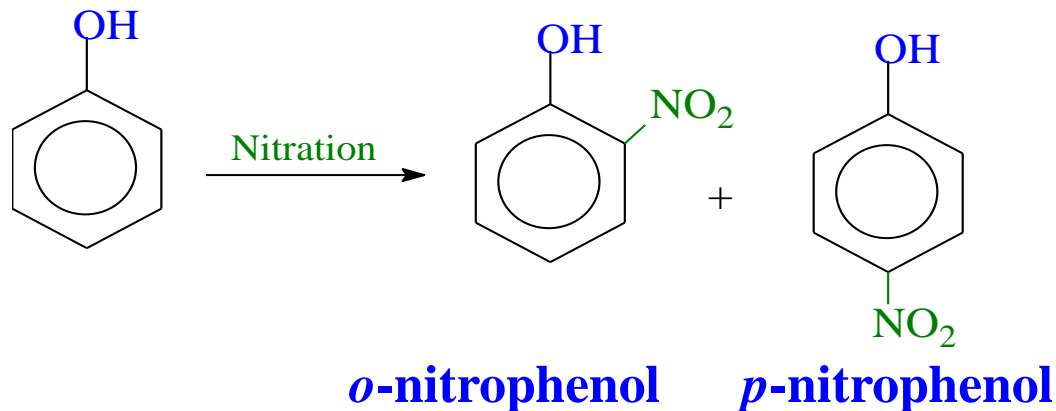
Further substitution
G = second substituent



The actual **distribution** depends on *the nature of the first substituents*, Y, and Falls into only two categories.

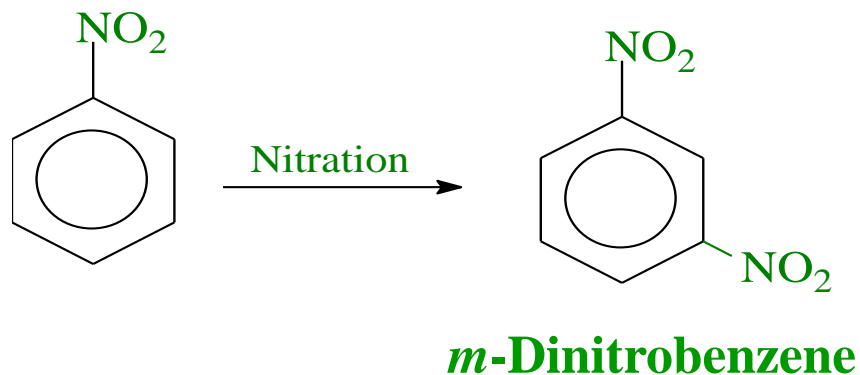
- Certain Ys direct the second substituent G, regardless of what G, into **ortho** and **para** positions.

*The -OH
Is said to be
ortho, para
director*



- Other Ys direct the second substituent G, regardless of the nature of G, into **meta** positions.

*The -NO₂
Is said to be
meta
director*



Orientation Effects of substituents **Y** in Electrophilic aromatic substitution

Ortho & Para directors	Meta directors
-OH, -OR	-NO ₂
-NH ₂ , -NHR, -NR ₂	-SO ₃ H
-C ₆ H ₅	-COOH, -COOR
-CH ₃ , -R (alkyl)	-CHO, -COR
-F, -Cl, -Br, -I	-CN

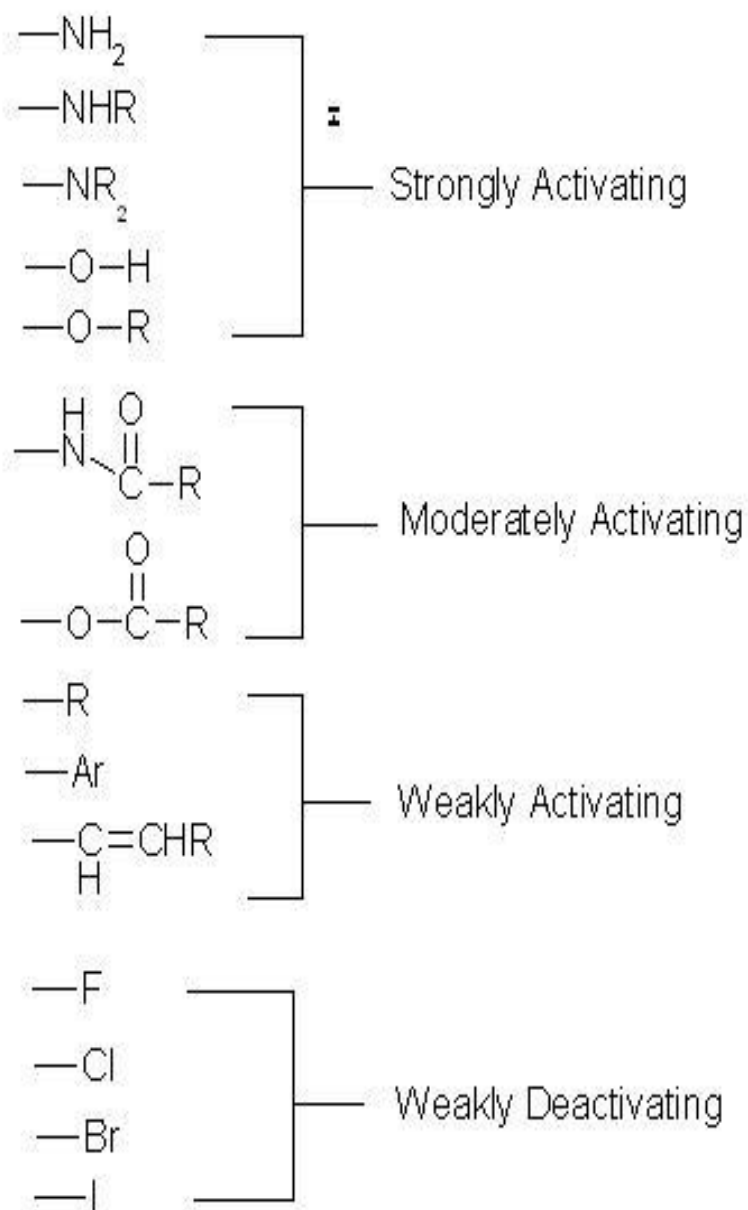
Activating groups

- donate those unshared electrons to the *pi* system.
- activates the benzene ring toward electrophilic substitution reactions.

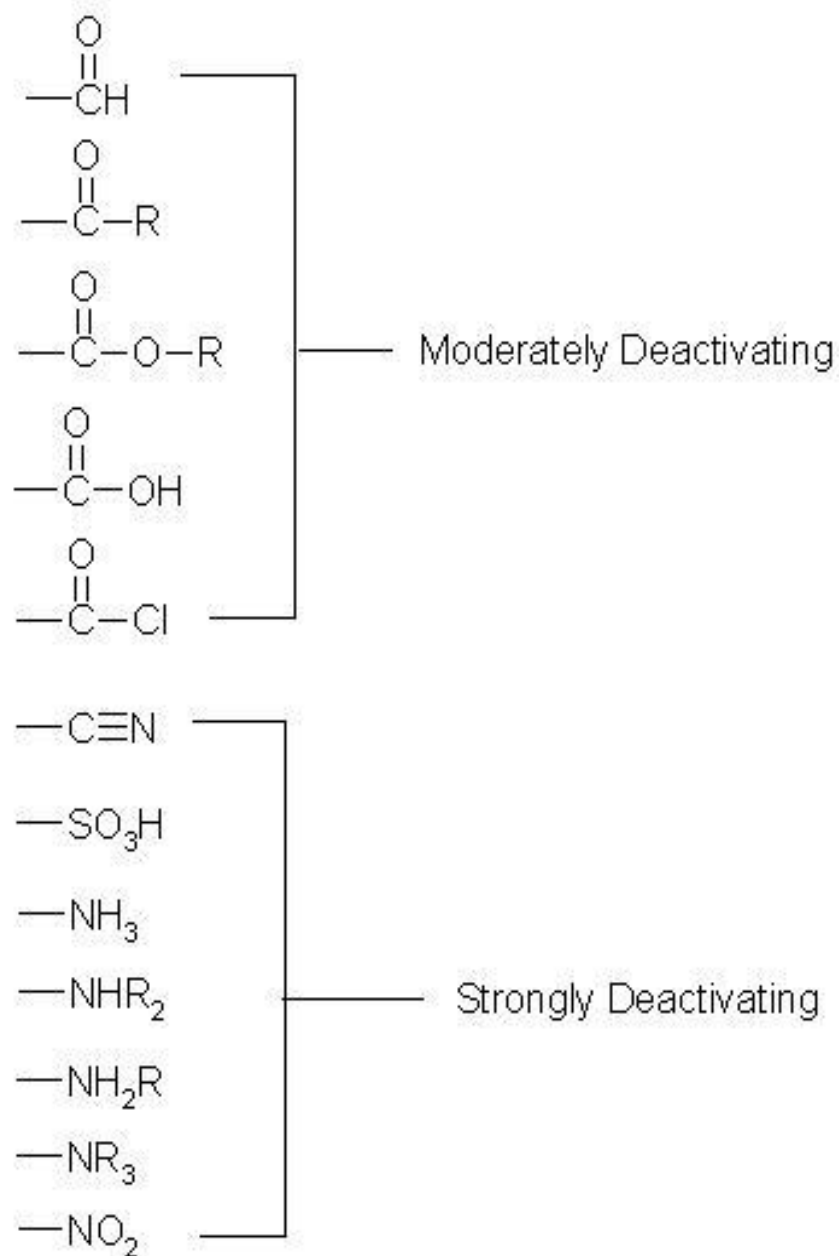
Deactivating groups

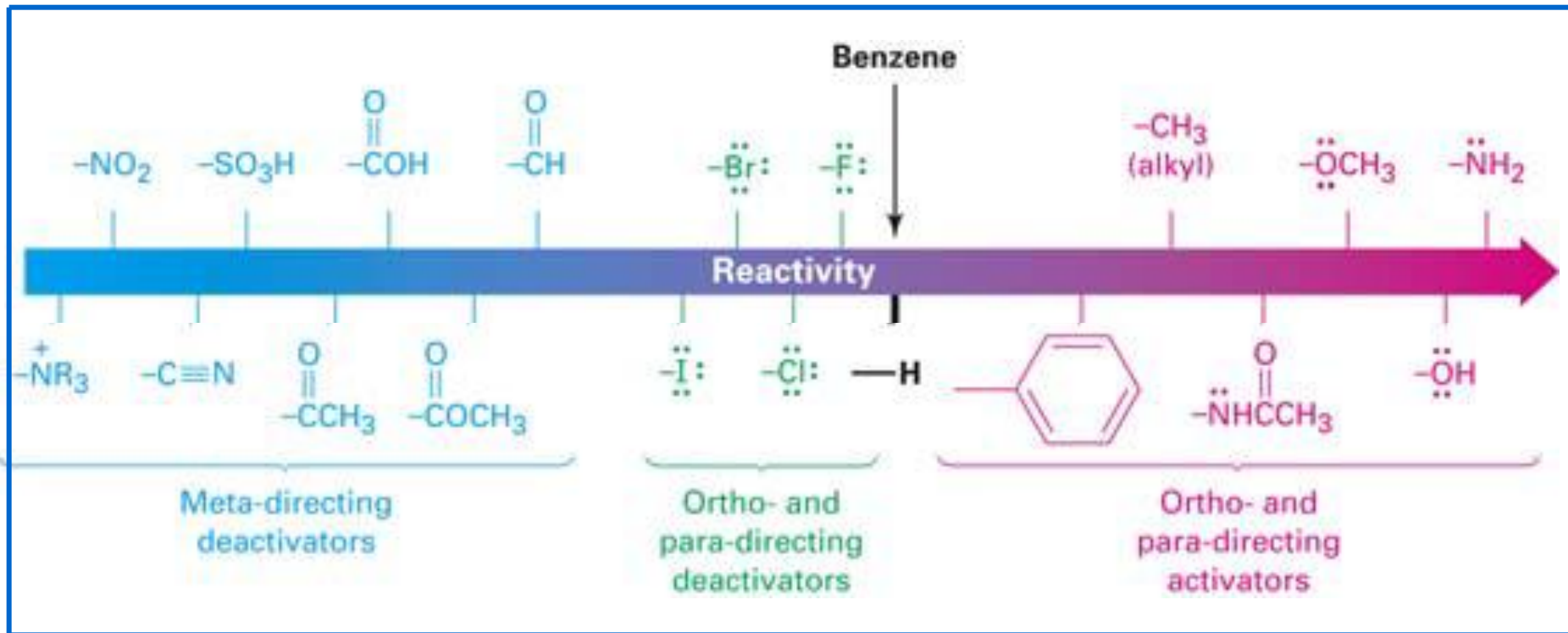
- Removes the electron density from the benzene ring.
- Making the electrophilic substitution reactions slower.

Common Ortho / Para directing substituents



Common Meta Directing Substituents





Conclusion:

Substituent Effects in Electrophilic Aromatic Substitution

Substituents already present on an aromatic ring have two effects:

1. Substituents affect the **reactivity of the aromatic ring**:

- **Activate**
- **Deactivate**

2. Substituents affect the **orientation of the reaction**:

- **Ortho**, **meta**, and **para**