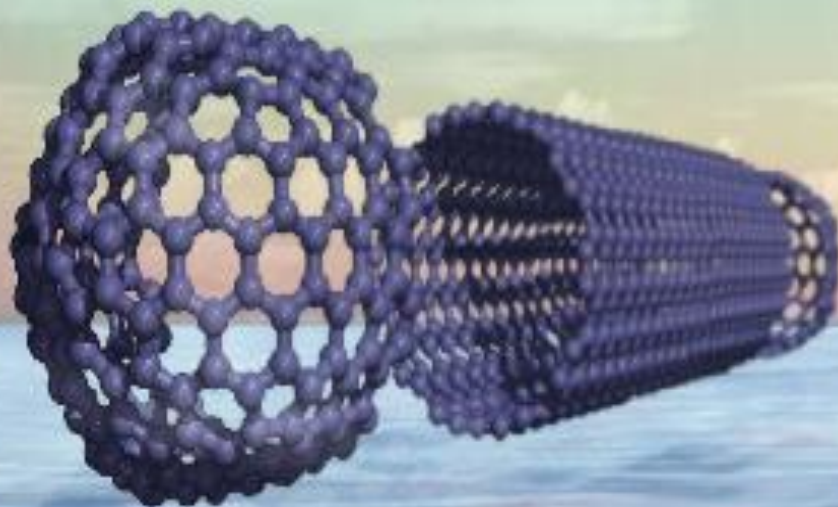


Organic Chemistry

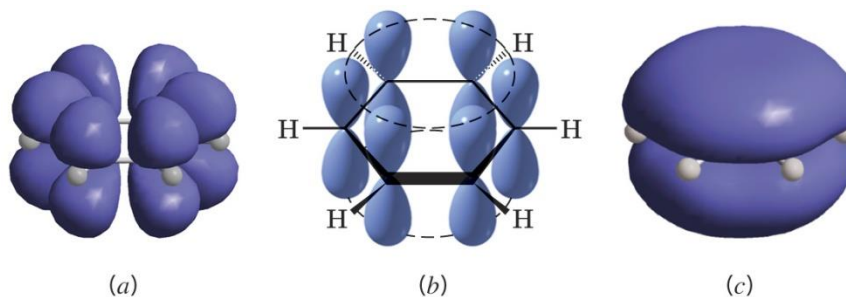


By
Dr. Assem Barakat

Chemistry Department, College of Science, King Saud University



Benzene & Aromatic Compounds



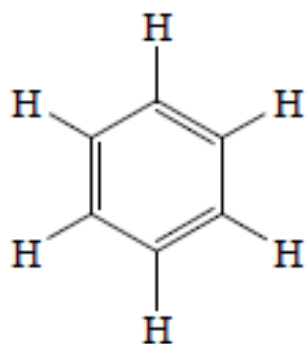


Introduction

- ▶ Name= **Benzene**
- ▶ Chemical formula= C_6H_6
- ▶ Structure = Cyclic planner
- ▶ Hybridization= SP^2
- ▶ Bond angles= 120°
- ▶ Bond Length= 1.39 A

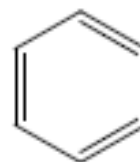


- ▶ 1) Benzene can be written as a six-membered ring with alternating single and double bonds (**Kekulé structure**).
- ▶ 2) Benzene reacts with substitution reactions not with addition reactions

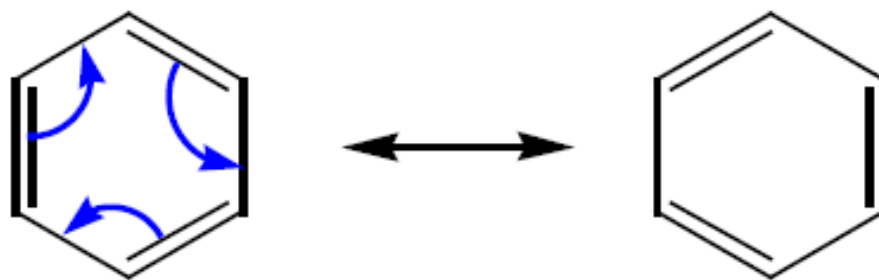


Kekulé structure

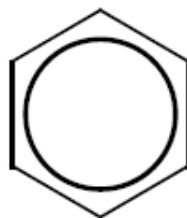
or



Bond-line representation



Two contributing Kekulé structures



A representation of the resonance hybrid

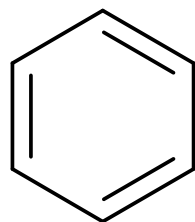


The Aromatic Character

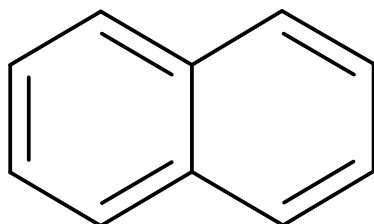
- ▶ When to say this compound is aromatic?
- ▶ 1) If it is cyclic
- ▶ 2) If it has π and σ alternating bonds
- ▶ 3) If it is planar
- ▶ 4) Reacts with substitution not addition reactions
- ▶ 5) Contain $(4n+2)$ π electrons



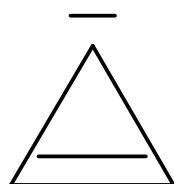
- **Huckel's Rule:** The $4n+2p$ Electron Rule
- Planar monocyclic rings with a continuous system of p orbitals and $4n + 2p$ electrons are aromatic ($n = 0, 1, 2, 3$ etc)
 - Aromatic compounds have substantial resonance stabilization
 - Benzene is aromatic: it is planar, cyclic, has a p orbital at every carbon, and 6 p electrons ($n=1$)



$n = 1$ $(4 \times 1) + 2 = 6 \pi$ electrons aromatic



$n = 2$ $(4 \times 2) + 2 = 10 \pi$ elect. aromatic



$n = 0$ $(4 \times 0) + 2 = 2 \pi$ elect. not aromatic

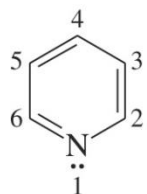


Heterocyclic Aromatic Compounds

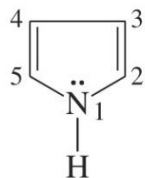
Heterocyclic compounds have an element other than carbon as a member of the ring

Example of aromatic heterocyclic compounds are shown below

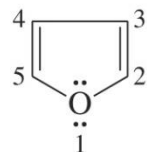
Numbering always starts at the heteroatom



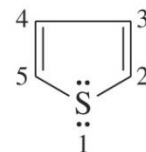
Pyridine



Pyrrole



Furan



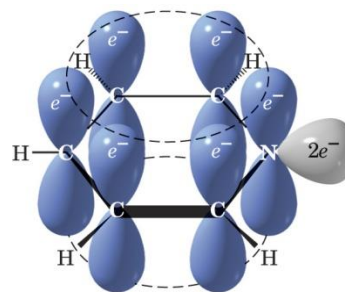
Thiophene

Pyridine has an sp^2 hybridized nitrogen

The p orbital on nitrogen is part of the aromatic p system of the ring

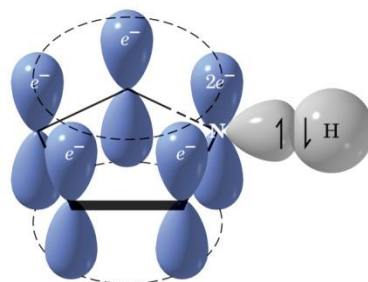
The nitrogen lone pair is in an sp^2 orbital orthogonal to the p orbitals of the ring; these electrons are not part of the aromatic system

The lone pair on nitrogen is available to react with protons and so pyridine is basic

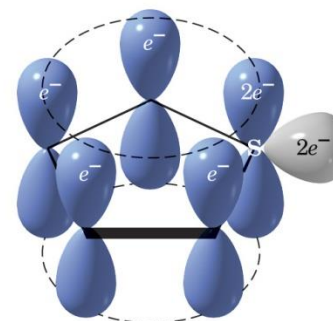
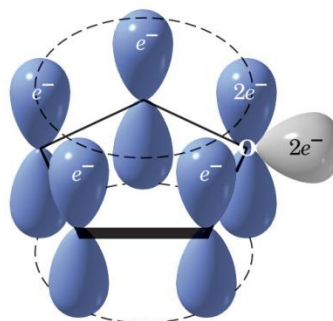




- The nitrogen in pyrrole is sp^2 hybridized and the lone pair resides in the p orbital
 - This p orbital contains two electrons and participates in the aromatic system
 - The lone pair of pyrrole is part of the aromatic system and not available for protonation; pyrrole is therefore not basic



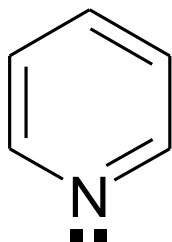
- In furan and thiophene an electron pair on the heteroatom is also in a p orbital which is part of the aromatic system



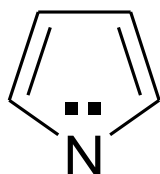


Exercise

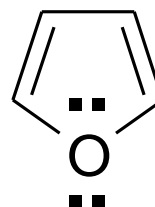
Apply Huckel,s rule to the following



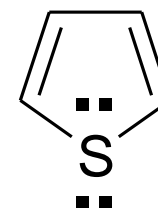
Pyridine



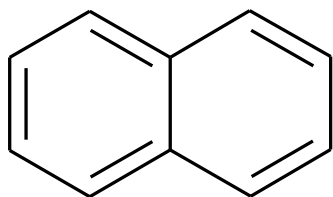
Pyrrole



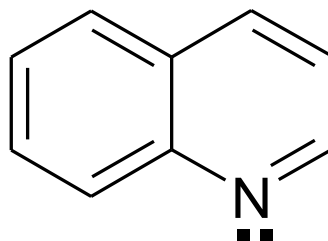
Furan



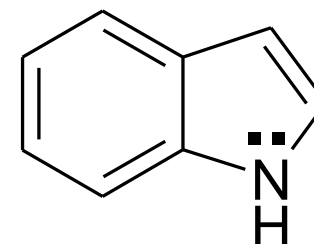
Thiophene



Naphthalene



Quinoline



1H-Indole

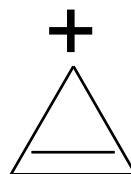


Some Aromatic Ions

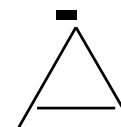
$n = 0$



not aromatic

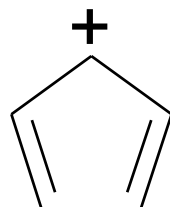


aromatic

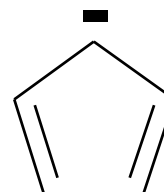


not aromatic

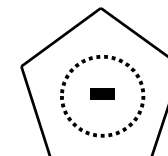
$n = 1$



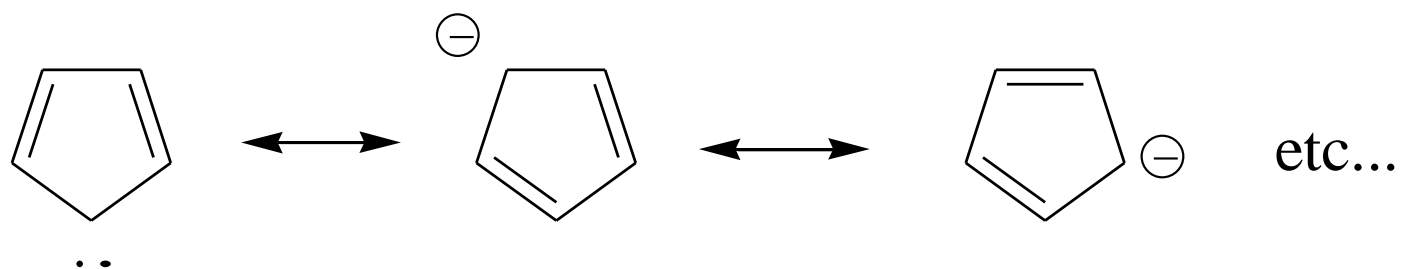
not aromatic



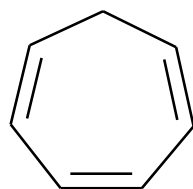
=



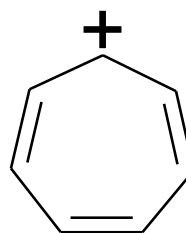
aromatic



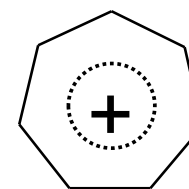
$n = 1$



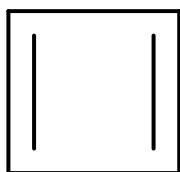
not aromatic



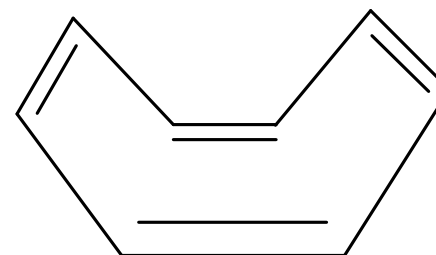
=



aromatic



Not aromatic (does not follow Huckel,s rule



Not aromatic (not planar)

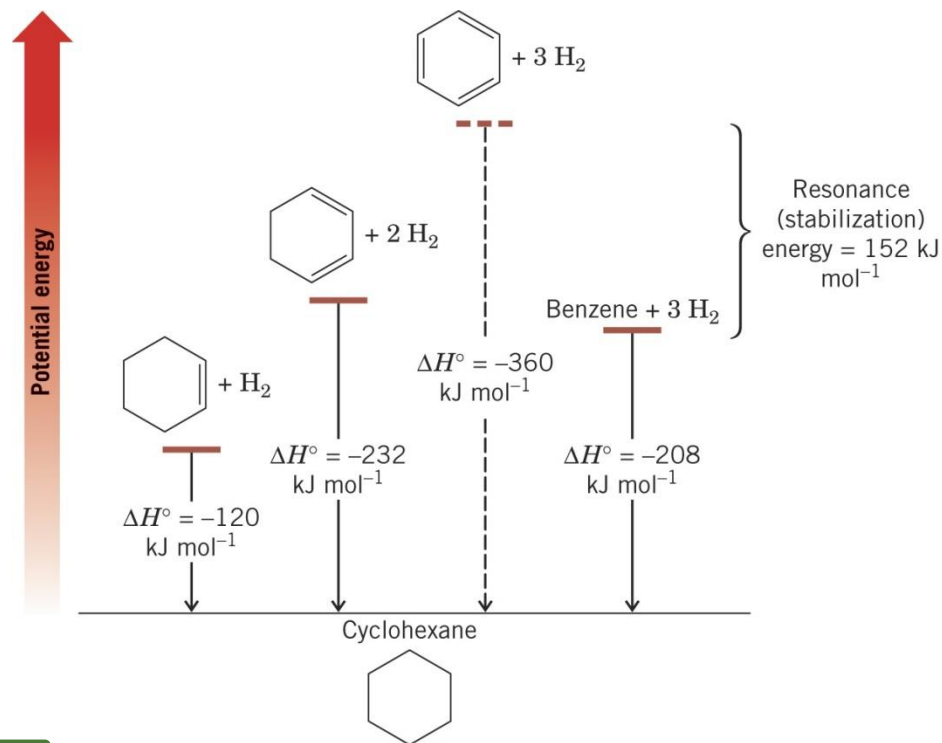
The Stability of Benzene

Benzene is much more stable than would be expected based on calculations for “cyclohexatriene”

A reasonable prediction for the heat of hydrogenation of hypothetical cyclohexatriene is -360 kJ mol^{-1} (3 times that of cyclohexene, -120 kJ mol^{-1})

The experimentally determined heat of hydrogenation for benzene is -208 kJ mol^{-1} , 152 kJ mol^{-1} more stable than hypothetical cyclohexatriene

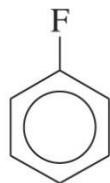
This difference is called the resonance energy



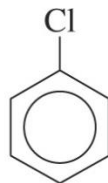


► Nomenclature of Benzene Derivatives

- Benzene is the parent name for some monosubstituted benzenes; the substituent name is added as a prefix



Fluorobenzene



Chlorobenzene

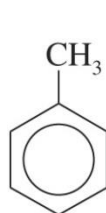


Bromobenzene

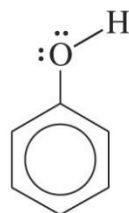


Nitrobenzene

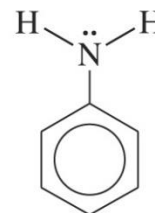
- For other monosubstituted benzenes, the presence of the substituent results in a new parent name



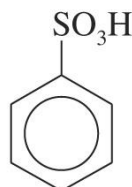
Toluene



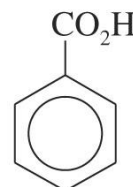
Phenol



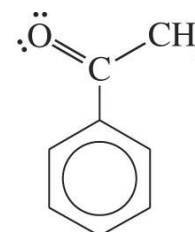
Aniline



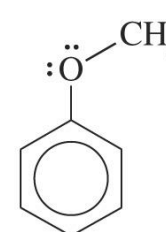
Benzenesulfonic acid



Benzoic acid



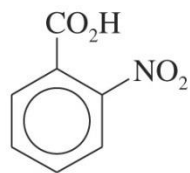
Acetophenone



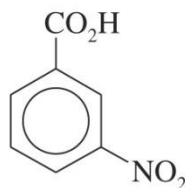
Anisole



- When two substituents are present their position may be indicated by the prefixes *ortho*, *meta*, and *para* (*o*, *m* and *p*) or by the corresponding numerical positions



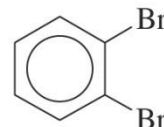
2-Nitrobenzoic acid
(*o*-nitrobenzoic acid)



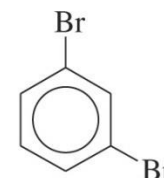
3-Nitrobenzoic acid
(*m*-nitrobenzoic acid)



4-Nitrobenzoic acid
(*p*-nitrobenzoic acid)



1,2-Dibromobenzene
(*o*-dibromobenzene)
ortho



1,3-Dibromobenzene
(*m*-dibromobenzene)
meta

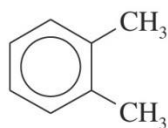


1,4-Dibromobenzene
(*p*-dibromobenzene)
para

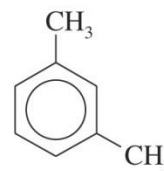
CH₃

CH₃

- Dimethyl substituted benzenes are called xylenes



1,2-Dimethylbenzene
(*o*-xylene)



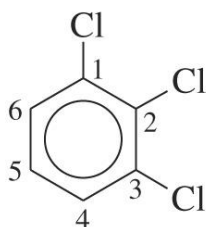
1,3-Dimethylbenzene
(*m*-xylene)



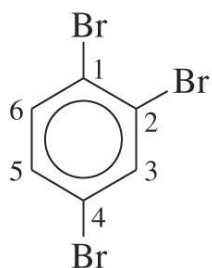
1,4-Dimethylbenzene
(*p*-xylene)



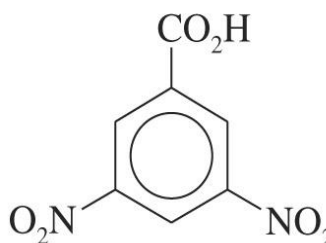
- Numbers must be used as locants when more than two substituents are present
 - The lowest possible set of numbers should be given to the substituents
 - The substituents should be listed in alphabetical order
 - If one of the substituents defines a parent other than benzene, this substituent defines the parent name and should be designated position 1



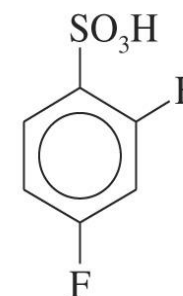
1,2,3-Trichlorobenzene



1,2,4-Tribromobenzene
(not 1,3,4-tribromobenzene)



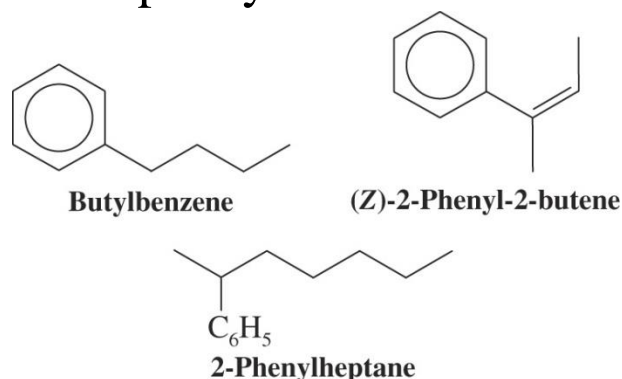
3,5-Dinitrobenzoic acid



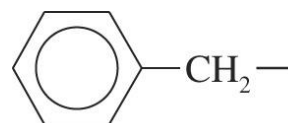
2,4-Difluorobenzenesulfonic acid



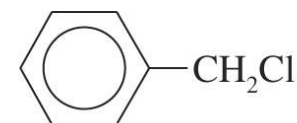
- The C_6H_5 - group is called phenyl when it is a substituent
 - Phenyl is abbreviated Ph or F
 - A hydrocarbon with a saturated chain and a benzene ring is named by choosing the larger structural unit as the parent
 - If the chain is unsaturated then it must be the parent and the benzene is then a phenyl substituent



- The phenylmethyl group is called a benyl (abbreviated Bz)



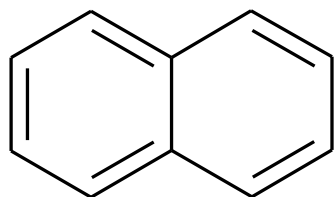
The benzyl group
(the phenylmethyl
group)



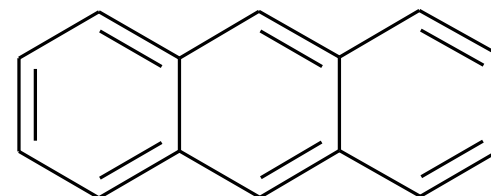
Benzyl chloride
(phenylmethyl chloride
or BzCl)



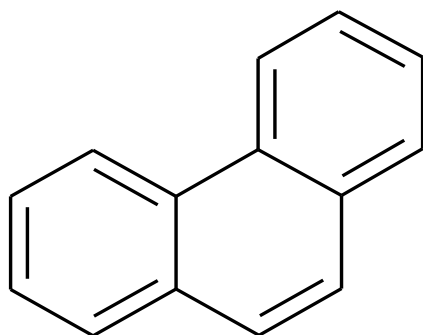
Polynuclear Aromatic Hydrocarbons



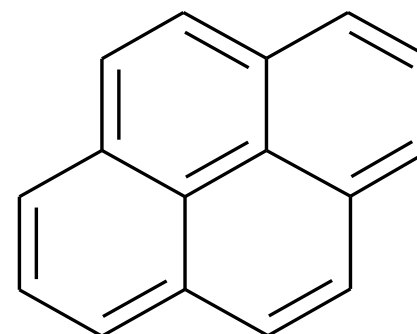
Naphthalene



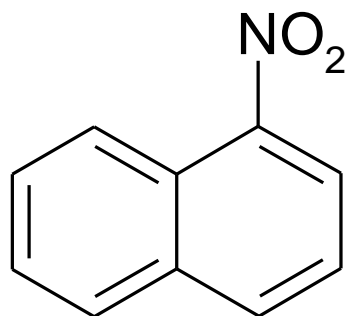
Anthracene



Phenanthrene



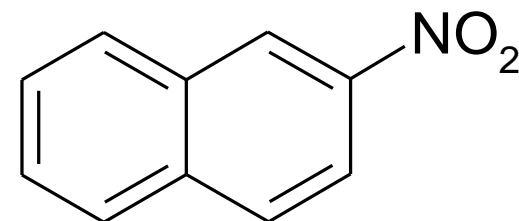
Pyrene



1-Aminonaphthalene

α -Naphthylamine

A weak carcinogen



2-Aminonaphthalene

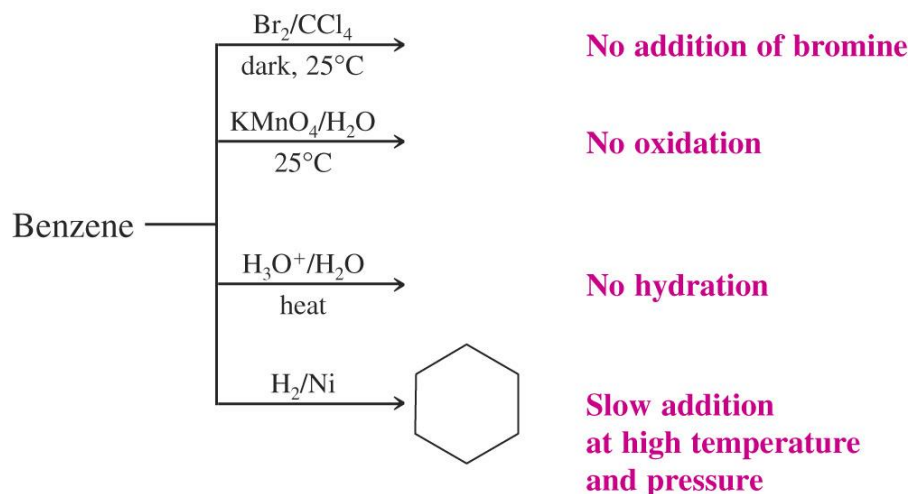
β -Naphthylamine

A strong carcinogen



► Reactions of Benzene

- Even though benzene is highly unsaturated it does not undergo any of the regular reactions of alkenes such as addition or oxidation

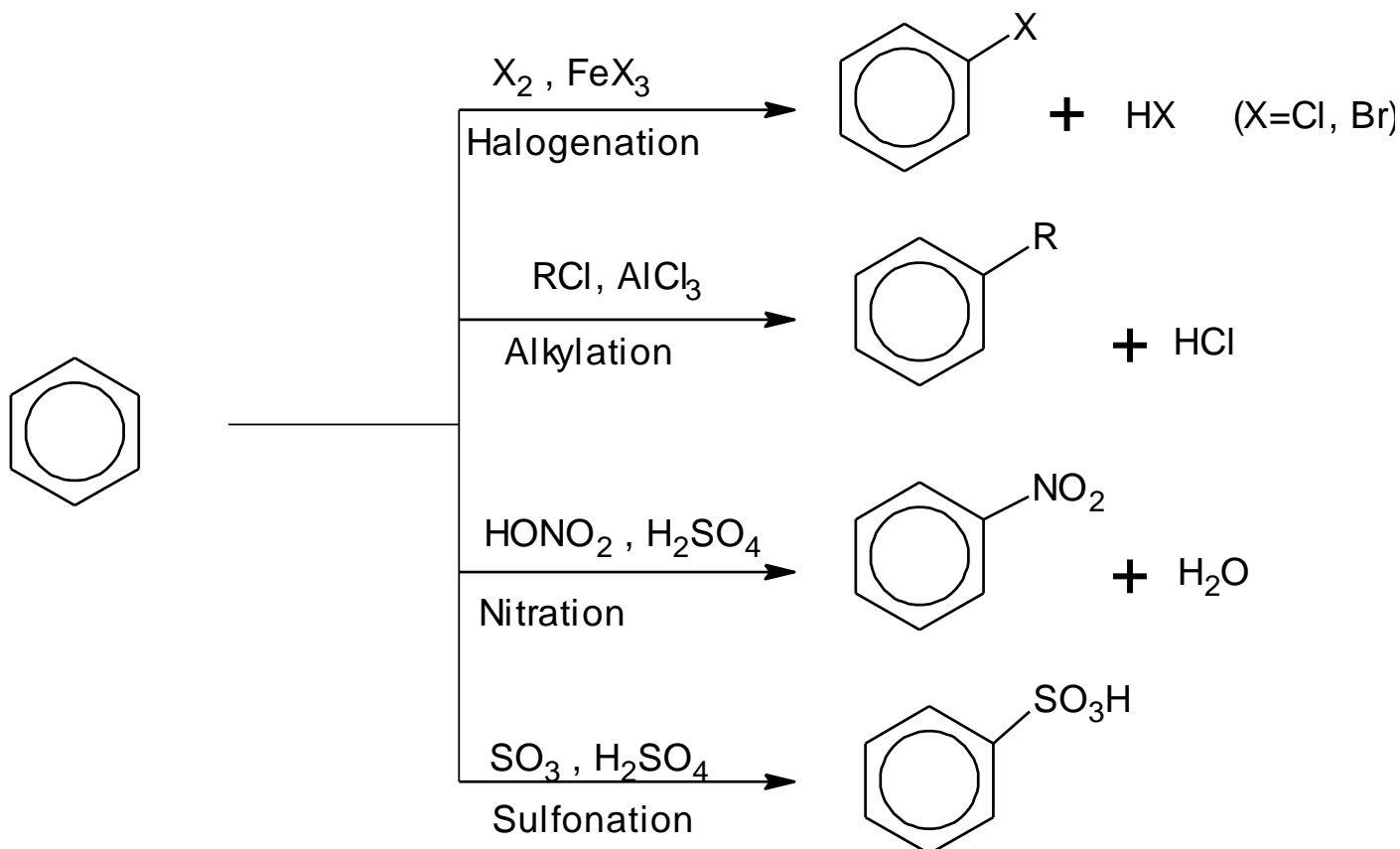


- Benzene can be induced to react with bromine if a Lewis acid catalyst is present however the reaction is a *substitution* and not an addition
 - Benzene produces only one monobrominated compound, which indicates that all 6 carbon-hydrogen bonds are equivalent in benzene





Specific Electrophilic Aromatic : Substitution Reactions





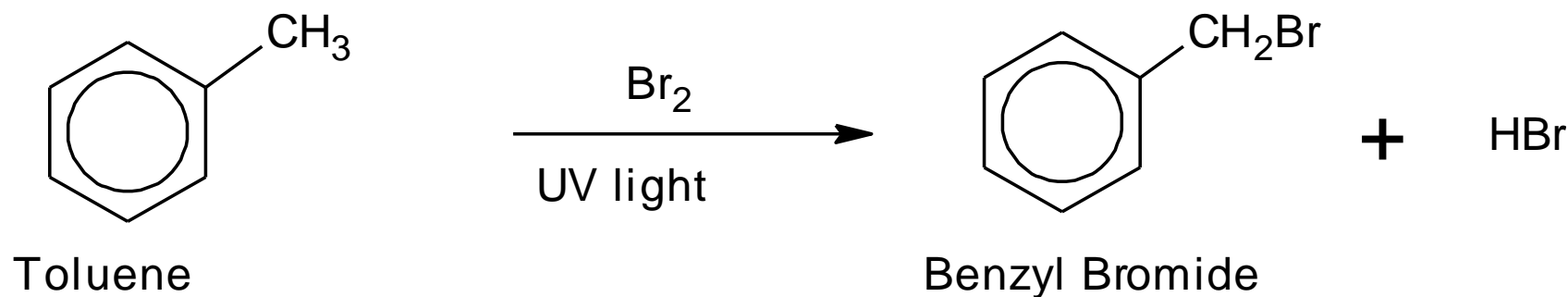
Summary of the electrophilic substitution reactions

Reaction Type	Typical Equation			Electrophile $E^{(+)}$
Halogenation:	$C_6H_6 + Cl_2$ & heat $FeCl_3$ catalyst	\longrightarrow	$C_6H_5Cl + HCl$ Chlorobenzene	$Cl^{(+)}$ or $Br^{(+)}$
Nitration:	$C_6H_6 + HNO_3$ & heat H_2SO_4 catalyst	\longrightarrow	$C_6H_5NO_2 + H_2O$ Nitrobenzene	$NO_2^{(+)}$
Sulfonation:	$C_6H_6 + H_2SO_4 + SO_3$ & heat	\longrightarrow	$C_6H_5SO_3H + H_2O$ Benzenesulfonic acid	$SO_3H^{(+)}$
Alkylation: Friedel-Crafts	$C_6H_6 + R-Cl$ & heat $AlCl_3$ catalyst	\longrightarrow	$C_6H_5-R + HCl$ An Arene	$R^{(+)}$
Acylation: Friedel-Crafts	$C_6H_6 + RCOCl$ & heat $AlCl_3$ catalyst	\longrightarrow	$C_6H_5COR + HCl$ An Aryl Ketone	$RCO^{(+)}$



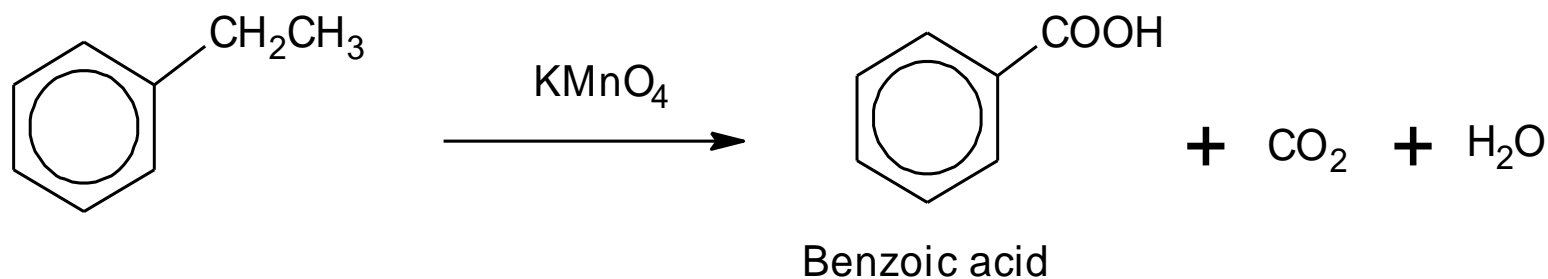
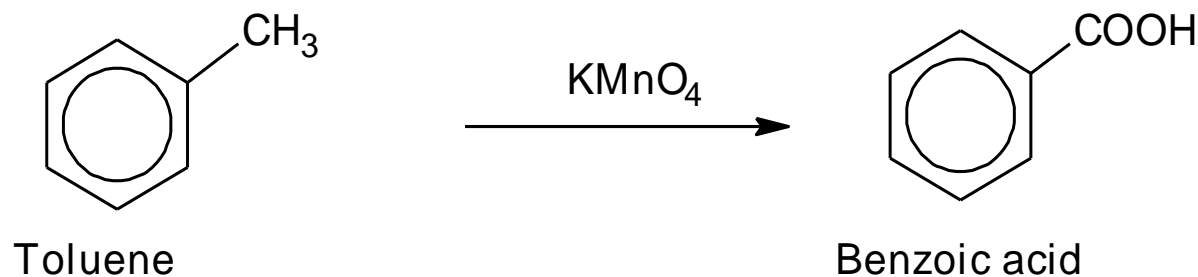
Side-Chain Reactions of Aromatic Compounds

A. Halogenation of an Alkyl Side Chain





B. Oxidation of an Alkyl Side Chain

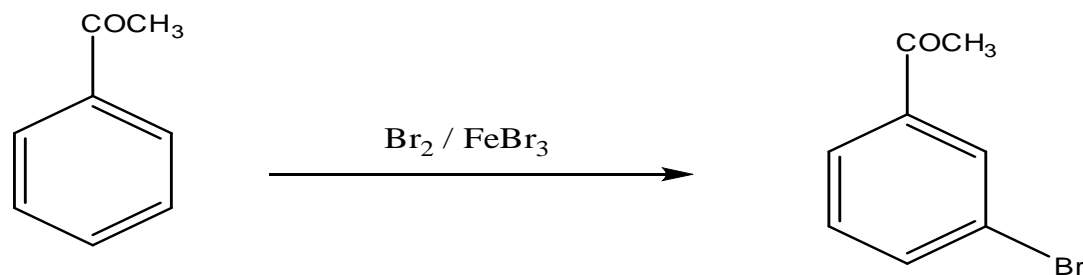
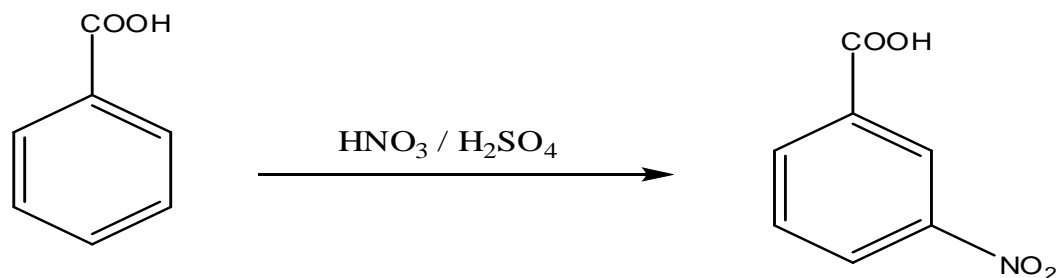
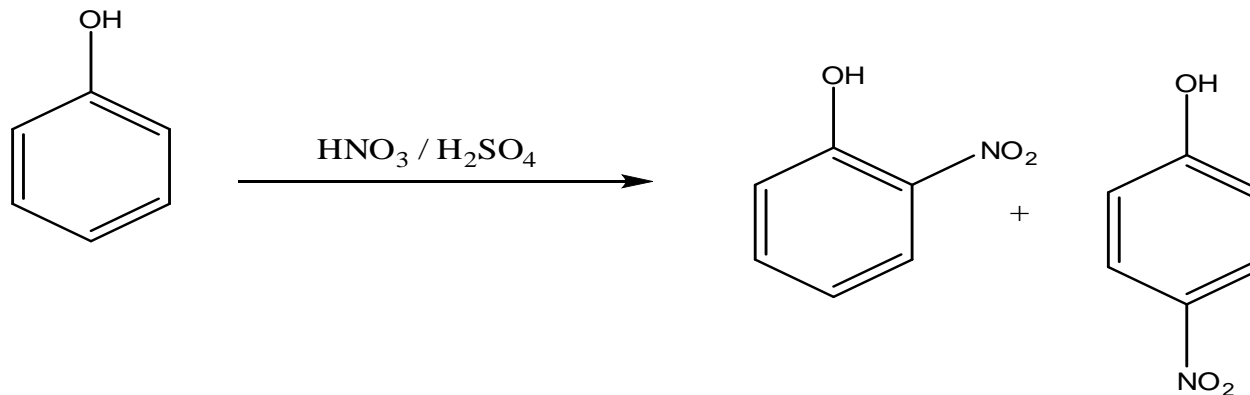


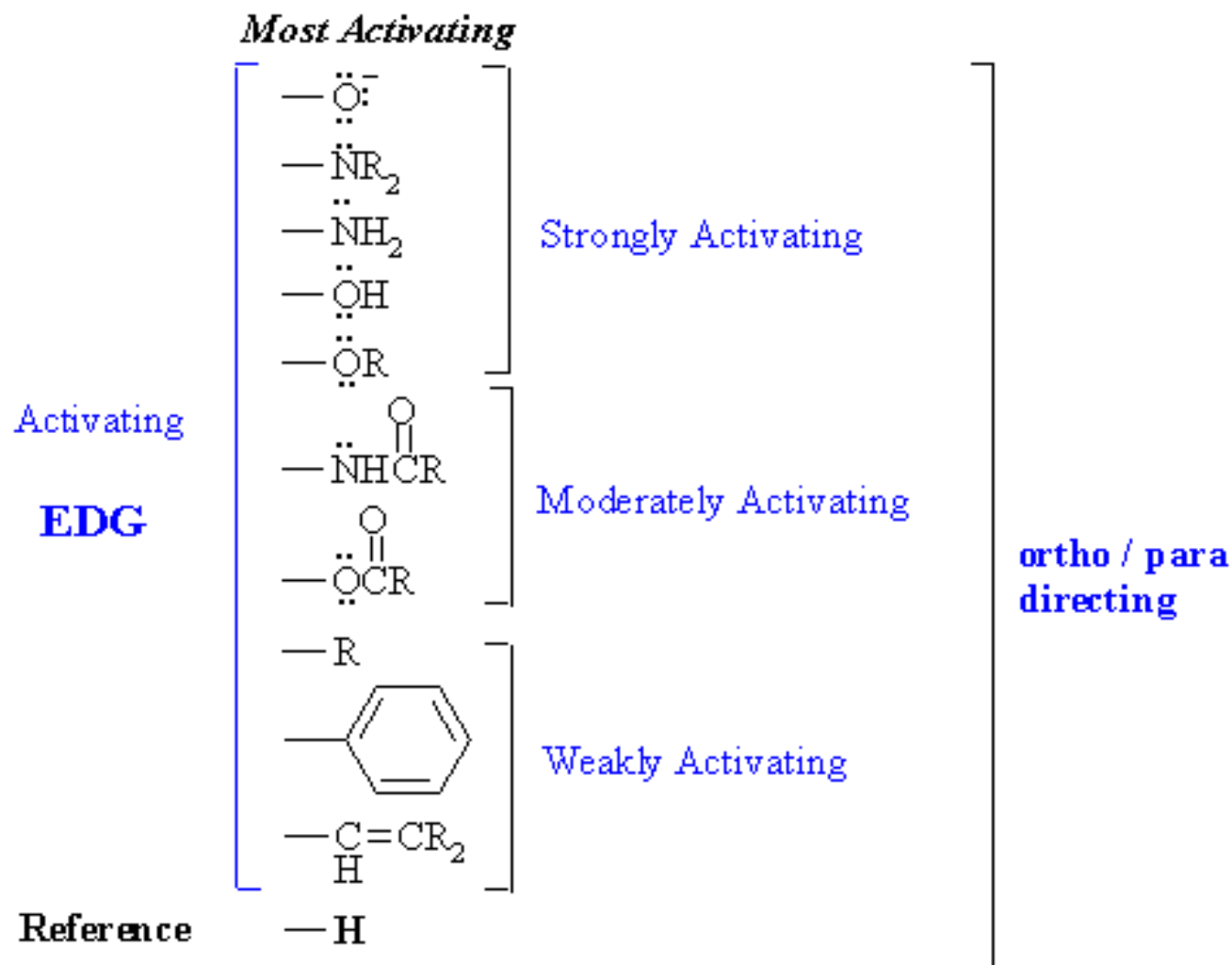


Disubstituted Benzenes : Orientation

Orientation Effects of Substituents in Electrophilic Aromatic Substitution :

<i>Ortho</i> , <i>Para</i> directing groups	<i>Meta</i> directing groups
<ul style="list-style-type: none">-OH, -OR-NH₂, -NHR, -NR₂-C₆H₅-CH₃, -R (alkyl)-F, -Cl, -Br, -I	<ul style="list-style-type: none">-NO₂-SO₃H-COOH, -COOR-CHO, -COR-CN





Most Deactivating



- ▶ Here are some **general pointers** for recognizing the substituent effects:
- ▶ The **H** atom is the standard and is regarded as having no effect.
- ▶ **Activating** groups increase the rate
- ▶ **Deactivating** groups decrease the rate
- ▶ **EDG** = **electron donating group**
- ▶ **EWG** = **electron withdrawing group**
- ▶ **EDG** / activating groups direct *ortho* / *para*
- ▶ **EWG** / deactivating groups direct *meta*
- ▶ **except** halogens (-X) which are deactivating **BUT** direct *ortho* / *para*