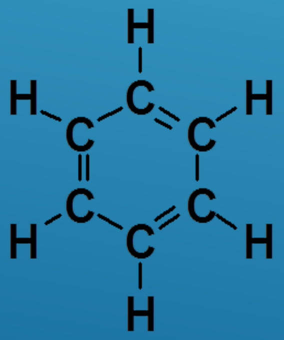
AROMATIC COMPOUNDS

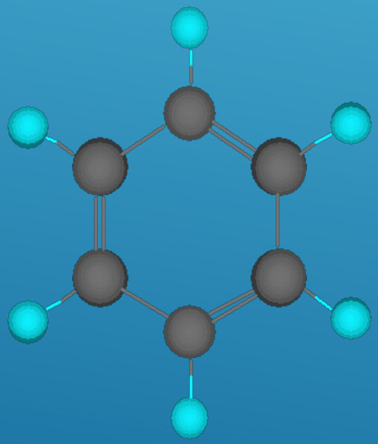
AROMATIC COMPOUNDS

- Aromatic compound: a hydrocarbon that contains one or more benzene-like rings.
- Arene: a term used to describe aromatic compounds.
- Ar-: a symbol for an aromatic group derived by removing an -H from an arene.
- Kekule's structure for benzene (1872).



A Kekulé structure
showing all atoms

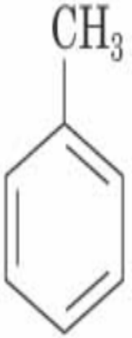
A Kekulé structure
as a line-angle formula



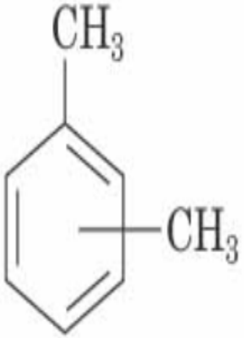
AROMATIC COMPOUNDS

- Aromatic was used to described some fragrant compounds in early 19th century.
- Not correct: however they are grouped as aromatics differed from other compounds in their chemical behavior (unsaturated compounds that undergo substitution rather than addition).

Benzene
(bp 80°C)



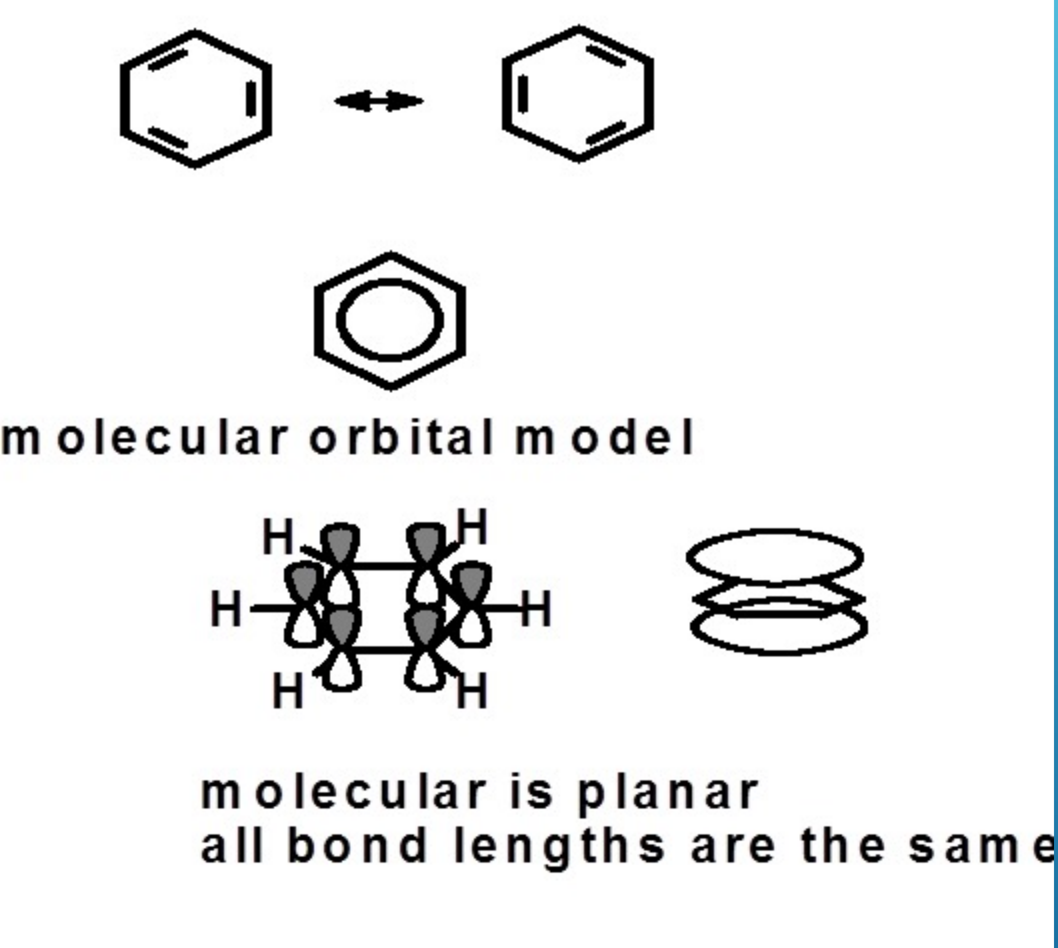
Toluene
(bp 111°C)



Xylene
(bp: ortho, 144°C; meta, 139°C; para, 138°C)

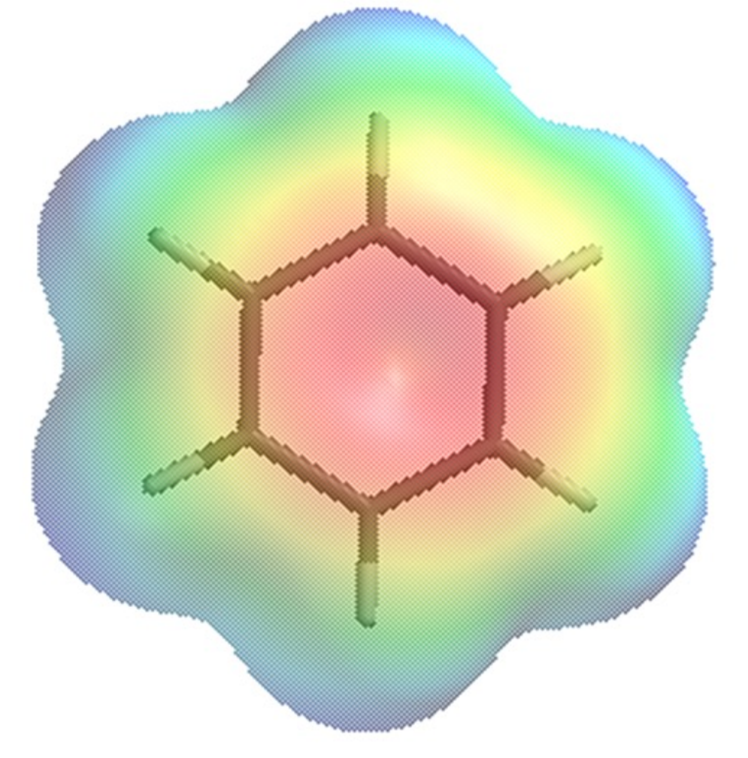
Indene
(bp 182°C)

MODEL REPRESENTATION OF BENZENE



molecular orbital model

molecular is planar
all bond lengths are the same



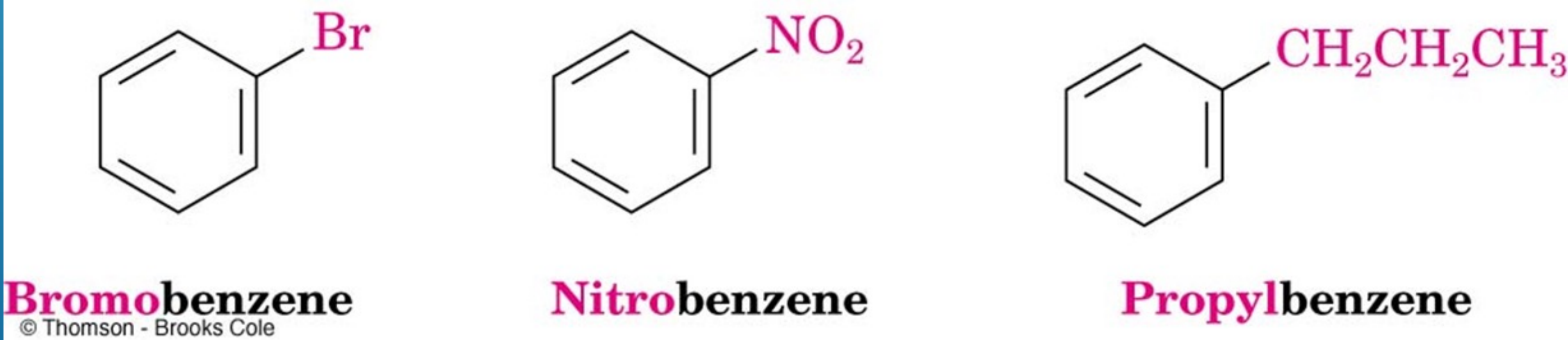
NOMENCLATURE OF AROMATIC COMPOUNDS

- Many common names (toluene = methylbenzene; aniline = amino benzene)
- Monosubstituted benzenes systematic names as hydrocarbons with –benzene

C_6H_5Br = bromobenzene

$C_6H_5NO_2$ = nitrobenzene, and

$C_6H_5CH_2CH_2CH_3$ is propylbenzene



Bromobenzene **Nitro**benzene **Propyl**benzene

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AROMATIC COMPOUNDS

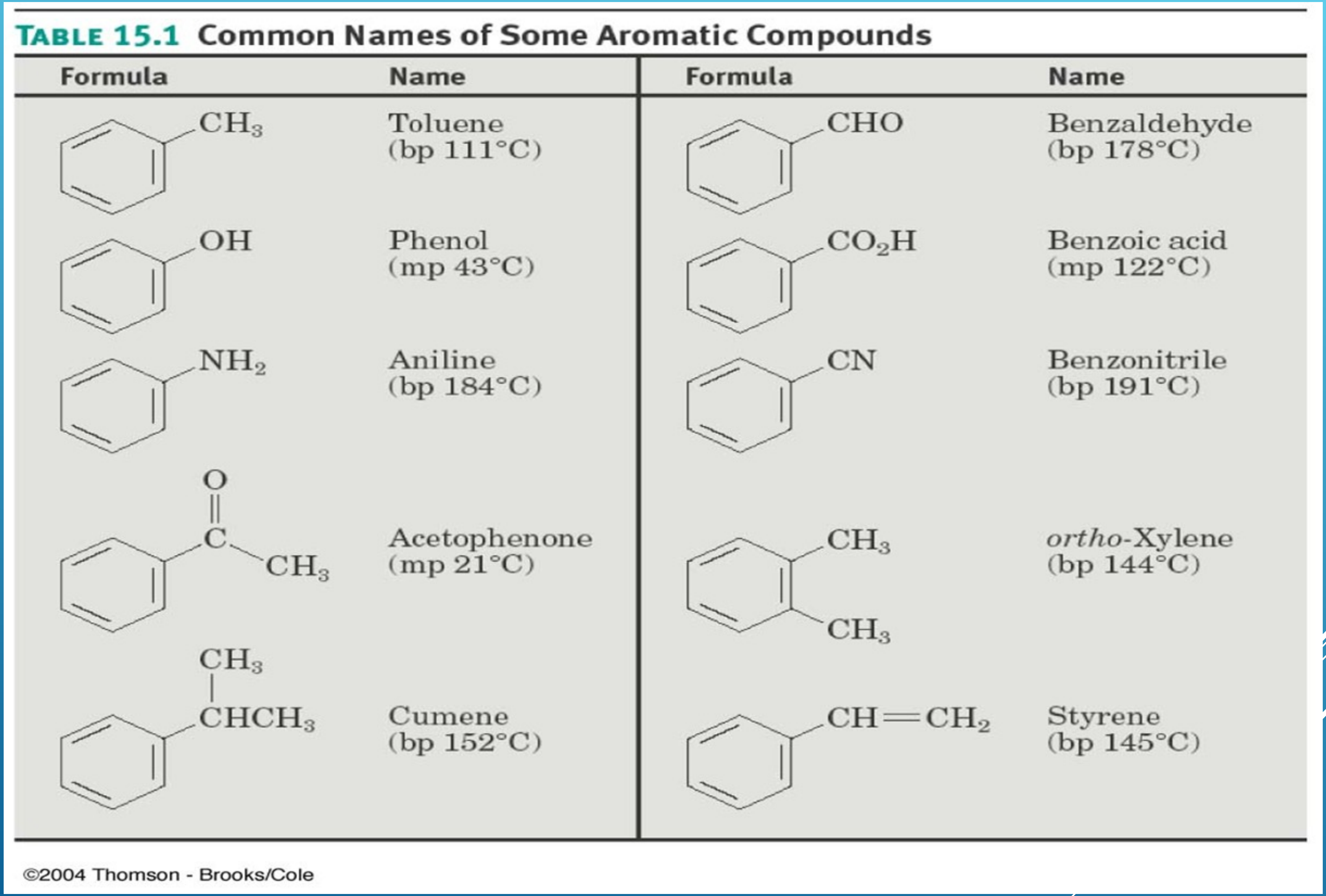

TABLE 15.1 Common Names of Some Aromatic Compounds

Formula	Name	Formula	Name
CH_3	Toluene (bp 111°C)	CHO	Benzaldehyde (bp 178°C)
OH	Phenol (mp 43°C)	CO_2H	Benzoic acid (mp 122°C)
NH_2	Aniline (bp 184°C)	CN	Benzonitrile (bp 191°C)
$\overset{O}{\overset{\|}{C}}CH_3$	Acetophenone (mp 21°C)	CH_3 CH_3	*ortho*-Xylene (bp 144°C)
$\overset{CH_3}{\overset{\|}{C}}HCH_3$	Cumene (bp 152°C)	$CH{=}CH_2$	Styrene (bp 145°C)

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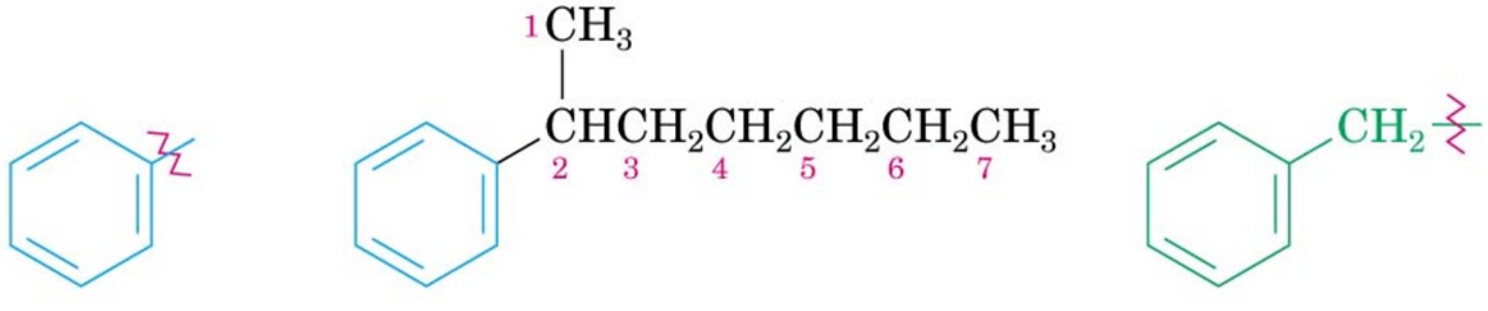
PHENYL GROUP

-phenyl group (C_6H_5- or Ph-): the substituent group derived by loss of an H from benzene.

You may also see “Ph” or “Φ” in place of “C_6H_5-”

Benzyl” refers to “$C_6H_5CH_2$-



A phenyl group **2-Phenylheptane** **A benzyl group**

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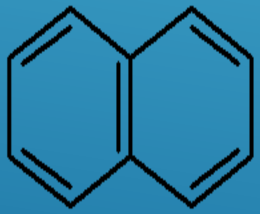
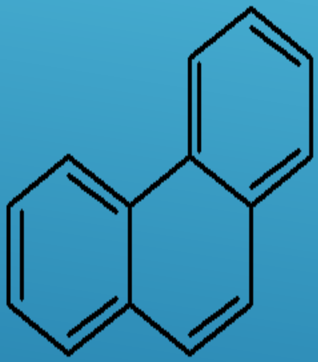
POLYNUCLEAR AROMATIC COMPOUNDS

- Polynuclear aromatic hydrocarbon (PAH).
- A hydrocarbon that contain two or more benzene rings, with each pair of rings sharing two adjacent carbon atoms.

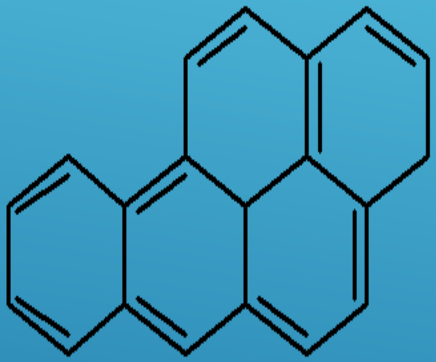


Naphthalene

Anthracene



Phenanthrene

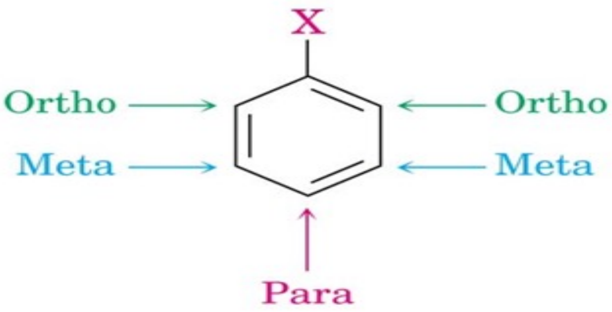


Benzo[a]pyrene

DISUBSTITUTED BENZENES

Relative positions on a benzene ring:

- *ortho*- (*o*) on adjacent carbons (1,2)
- *meta*- (*m*) separated by one carbon (1,3)
- *para*- (*p*) separated by two carbons (1,4)



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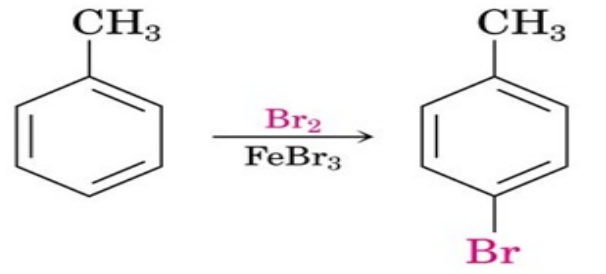
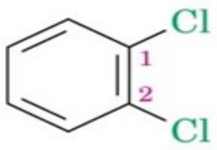
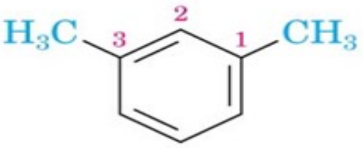


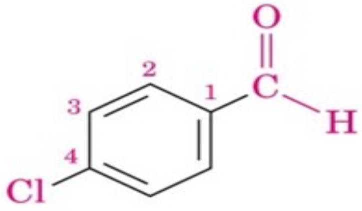
Toluene ***p*-Bromotoluene**



***ortho*-Dichlorobenzene**
1,2 disubstituted



***meta*-Xylene**
1,3 disubstituted



***para*-Chlorobenzaldehyde**
1,4 disubstituted

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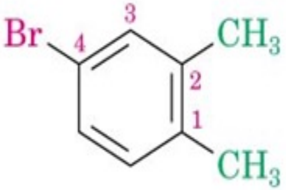
NAMING BENZENES WITH MORE THAN TWO SUBSTITUENTS

- When there are 2 or more substituents, they are numbered to give the lowest numbers (substituents are listed alphabetically).
- Disubsituted benzenes are also named by the common prefixes ortho, meta and para.



4-Bromo-1,2-dimethylbenzene

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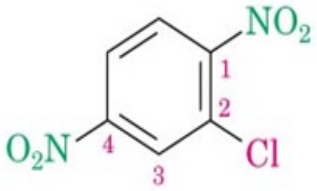
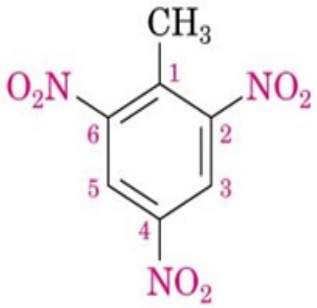
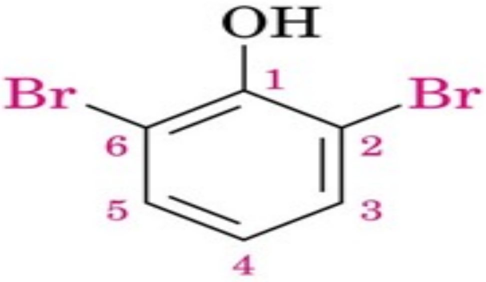


2-Chloro-1,4-dinitrobenzene



2,4,6-Trinitrotoluene (TNT)



2,6-Dibromo*phenol*

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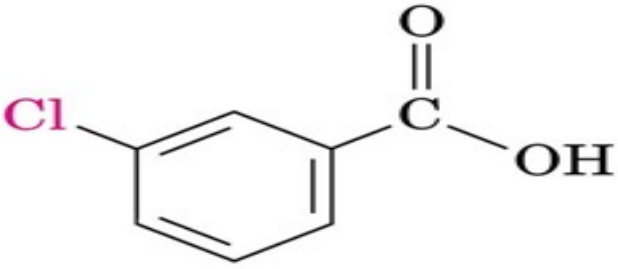
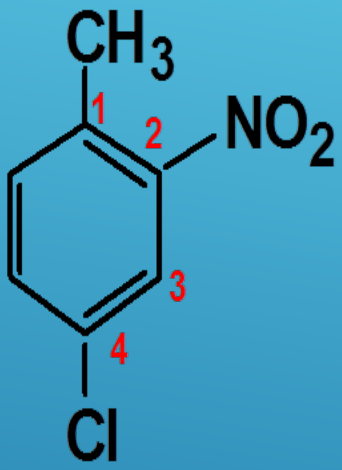
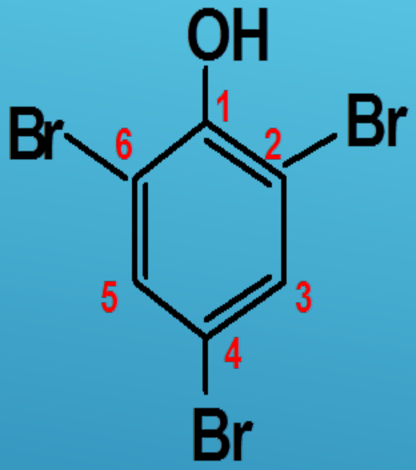


***m*-Chlorobenzoic acid**

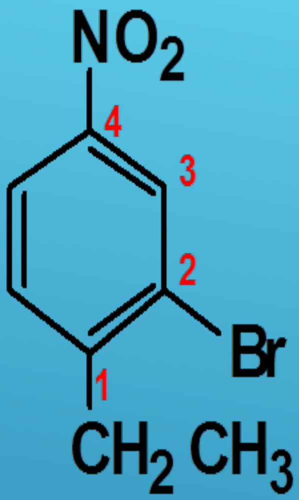
EXAMPLES



4-Chloro-2-nitrotoluene



2,4,6-Tribromophenol



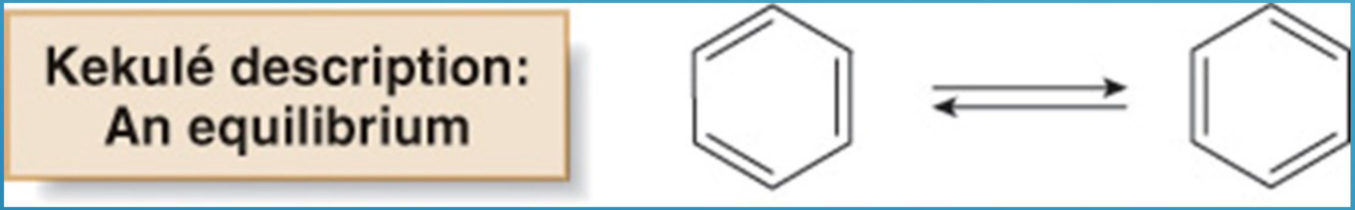
2-Bromo-1-ethyl-4-nitrobenzene

STRUCTURE OF BENZENE

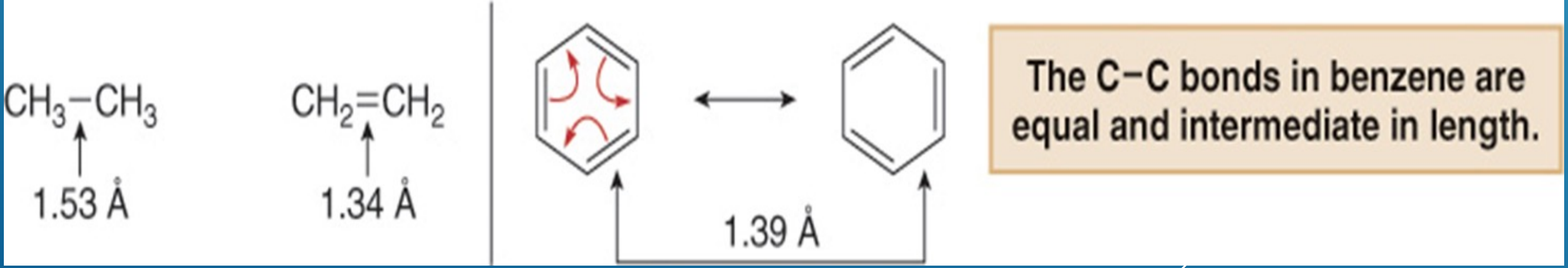
August Kekule’s proposed that benzene was a rapidly equilibrating mixture of two compounds, each containing a six-membered ring with three alternating π bonds.

In the Kekule’s description, the bond between any two carbon atoms is sometimes a single bond and sometimes a double bond.

These structures are known as Kekule’s structures.


Kekulé description: An equilibrium

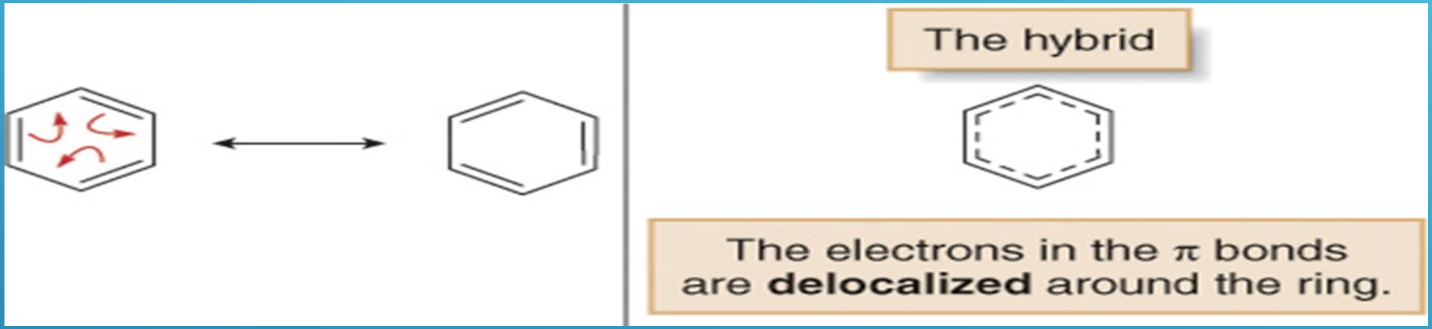
In benzene, the actual bond length (1.39 Å) is intermediate between the carbon—carbon single bond (1.53 Å) and the carbon—carbon double bond (1.34 Å).



The C–C bonds in benzene are equal and intermediate in length.

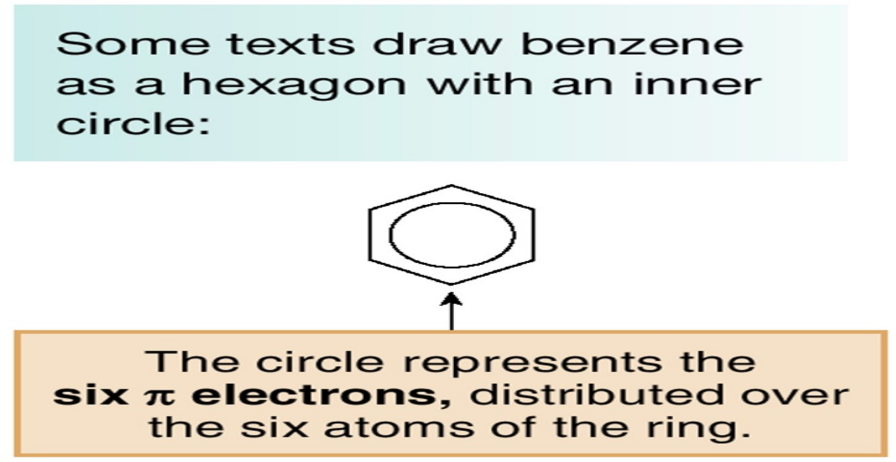
STRUCTURE OF BENZENE

The true structure of benzene is a resonance hybrid of the two Lewis structures, with the dashed lines of the hybrid indicating the position of the π bonds. Each π bond has two electrons, benzene has six π electrons.



The hybrid

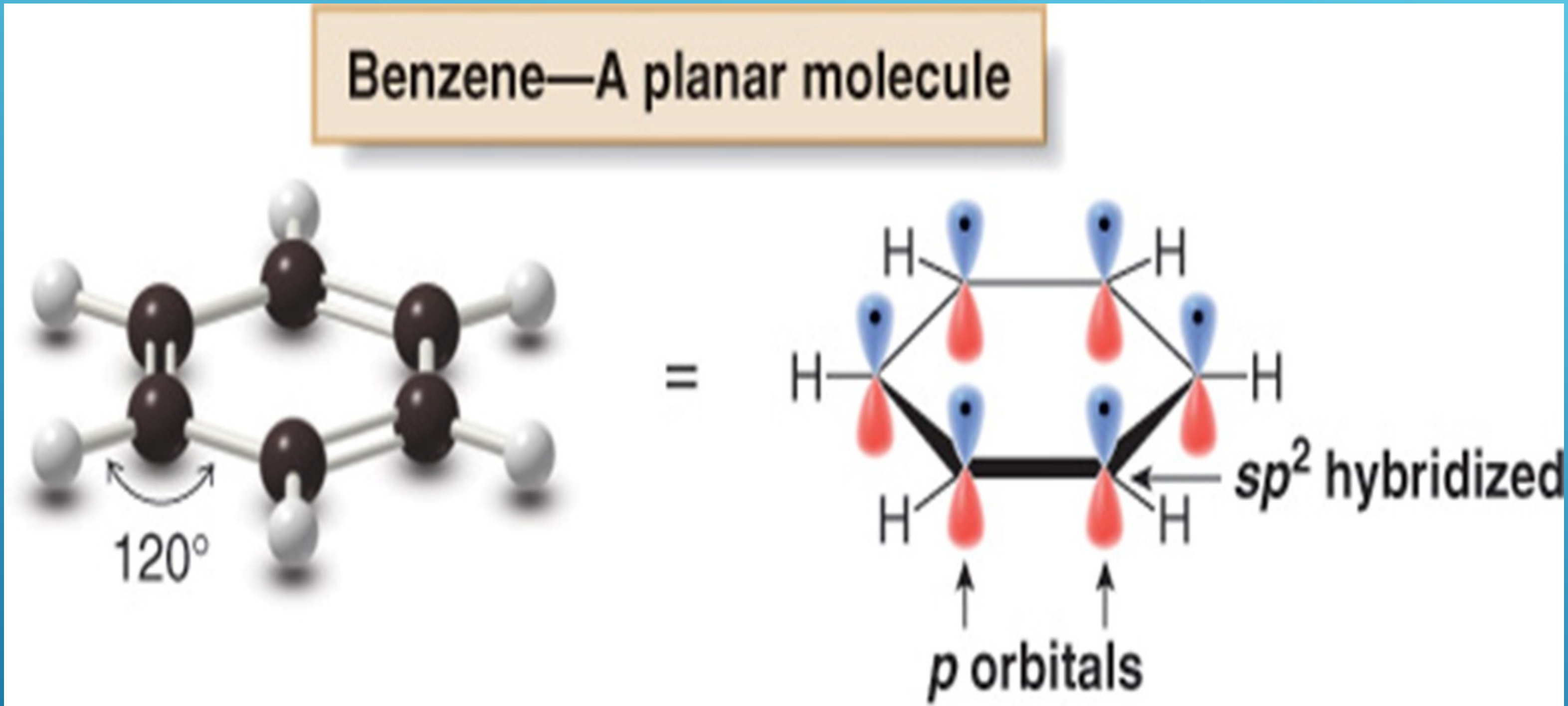
The electrons in the π bonds are **delocalized** around the ring.



Some texts draw benzene as a hexagon with an inner circle:

The circle represents the **six π electrons,** distributed over the six atoms of the ring.

STRUCTURE OF BENZENE

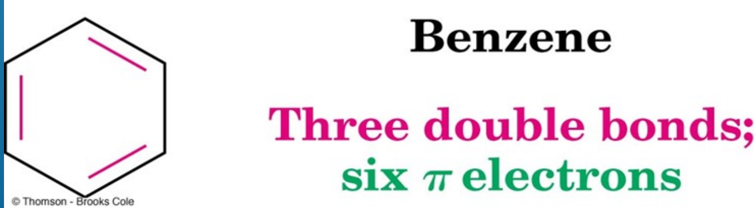


AROMATICITY

The underlying criteria for aromaticity were recognized in the early 1930s by Erich Huckel, based on MO calculations.

To be aromatic, a compound must;

- be cyclic.
- have one p orbital on each atom of the ring.
- be planar or nearly planar so that there is continuous or nearly continuous overlap of all p orbitals of the ring.
- have a closed loop of (4n + 2) π electrons in the cyclic arrangement of p orbitals.
- Huckel’s rule, based on calculations – a planar cyclic molecule with alternating double and single bonds has aromatic stability if it has (4n+ 2) π electrons (n is 0,1,2,3,4).
- For n=1: 4n+2 = 6; benzene is stable and the electrons are delocalized.



Benzene

Three double bonds; six π electrons

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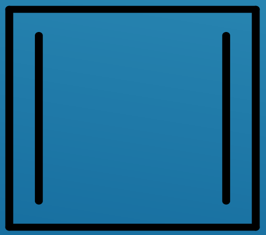
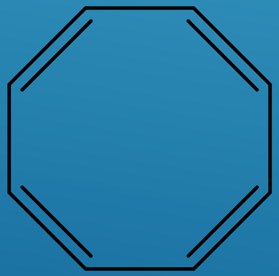
COMPOUNDS WITH 4N ∏ ELECTRONS ARE NOT AROMATIC (MAY BE ANTIAROMATIC)

- Planar, cyclic molecules with 4 n π electrons are much less stable than expected (anti-aromatic).
- They will distort out of plane and behave like ordinary alkenes.
- 4- and 8-electron compounds are not delocalized (single and double bonds).
- Cyclobutadiene is so unstable that it dimerizes by a self-Diels-Alder reaction at low temperature.
- Cyclooctatetraene has four double bonds, reacting with Br_2, $KMnO_4$, and HCl as if it were four alkenes.



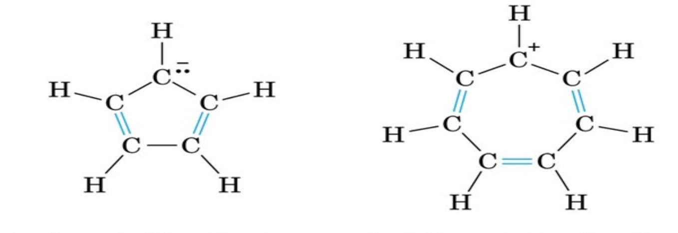
Cyclobutadiene



Cyclooctatetranene

AROMATIC IONS

- The 4n + 2 rule applies to ions as well as neutral species.
- Both the cyclopentadienyl anion and the cycloheptatrienyl cation are aromatic .
- The key feature of both is that they contain 6 π electrons in a ring of continuous p orbitals.
- Cyclopentadienyl anion is aromatic, as it is a cyclic, planar molecule with complete conjugation of 6 π electrons.



Cyclopentadienyl anion **Cycloheptatrienyl cation**

Six π electrons; aromatic ions

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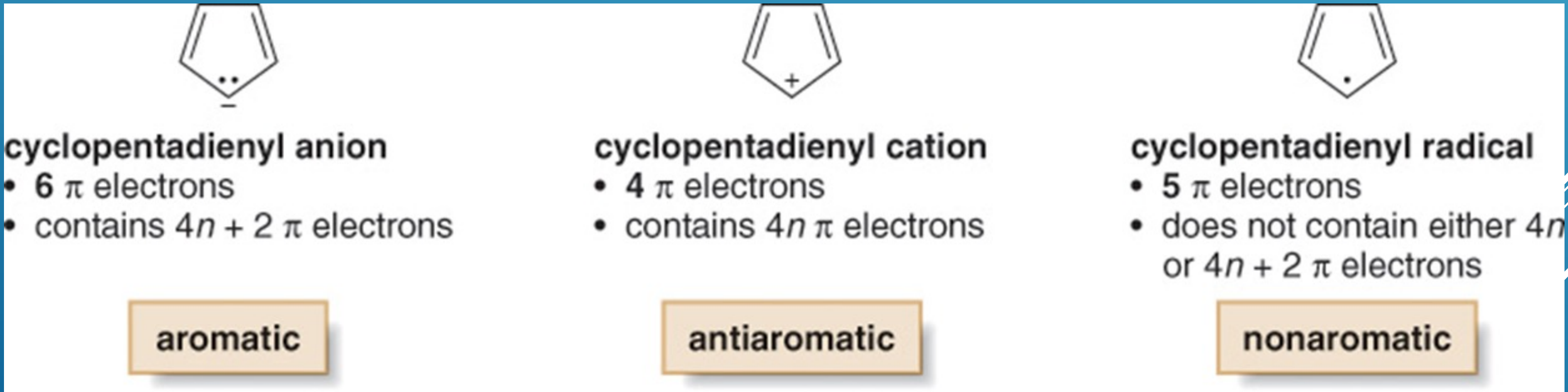


cyclopentadienyl anion
- **6 π electrons**
- contains 4*n* + 2 π electrons

aromatic

cyclopentadienyl cation
- **4 π electrons**
- contains 4*n* π electrons

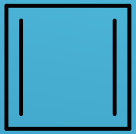
antiaromatic

cyclopentadienyl radical
- **5 π electrons**
- does not contain either 4*n* or 4*n* + 2 π electrons

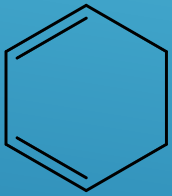
nonaromatic

WHICH OF THE FOLLOWING COMPOUNDS ARE AROMATIC?

A.

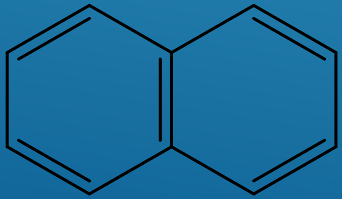


B.



C.

D.

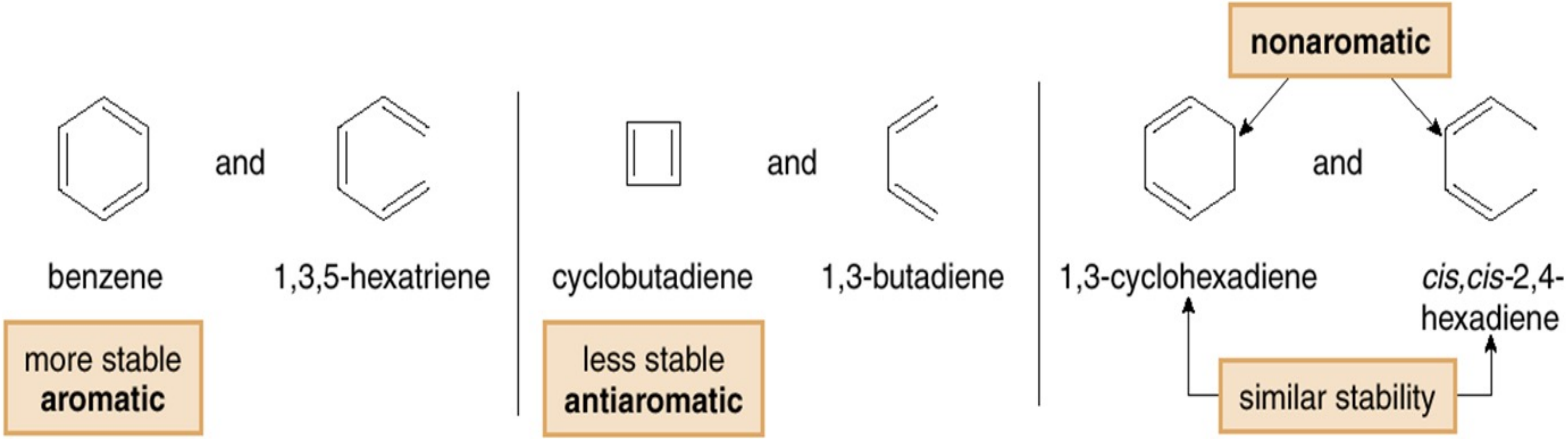


CRITERIA FOR AROMATICITY

- An aromatic compound is *more* stable than a similar acyclic compound having the same number of π electrons. Benzene is more stable than 1,3,5-hexatriene.

- An antiaromatic compound is *less* stable than an acyclic compound having the same number of π electrons. Cyclobutadiene is less stable than 1,3-butadiene.

- A compound that is not aromatic is *similar* in stability to an acyclic compound having the same number of π electrons. 1,3-Cyclohexadiene is similar in stability to *cis,cis*-2,4-hexadiene, so it is not aromatic.



SUBSTITUTION REACTIONS OF BENZENE AND ITS DERIVATIVES

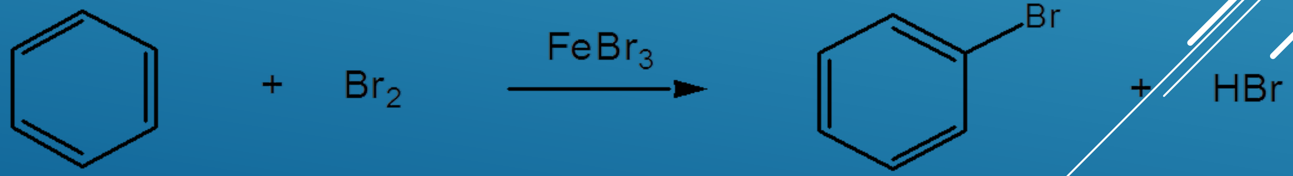
- Aromatic compounds do not undergo addition reactions because they would lose their special stability (aromaticity).
- Instead, they undergo substitution reactions, which allow them to retain their aromaticity.
- We will study three types of substitution reactions of benzene: halogenation, nitration and sulfonation.

Addition:

Aromatic

Loses aromaticity

Substitution:

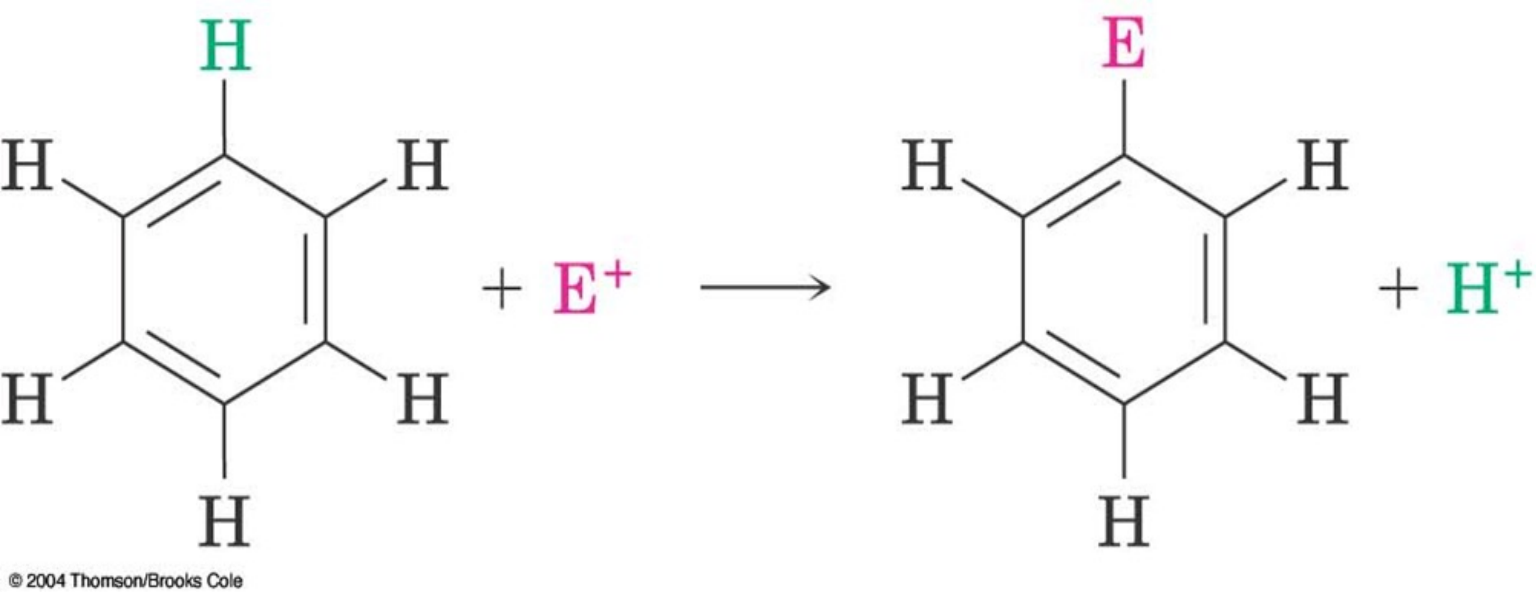


Aromatic

Retains Aromaticity

ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

- Benzene is aromatic: a cyclic conjugated compound with 6 π electrons.
- Reactions of benzene lead to the retention of the aromatic core.
- Electrophilic aromatic substitution replaces a proton on benzene with another electrophile .



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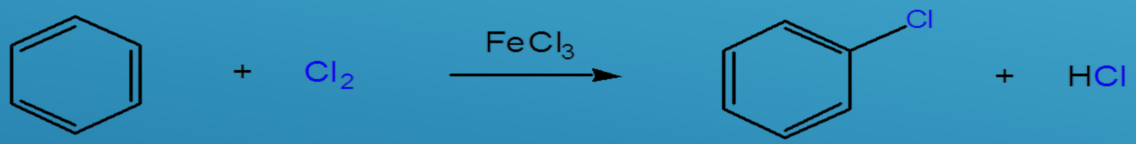
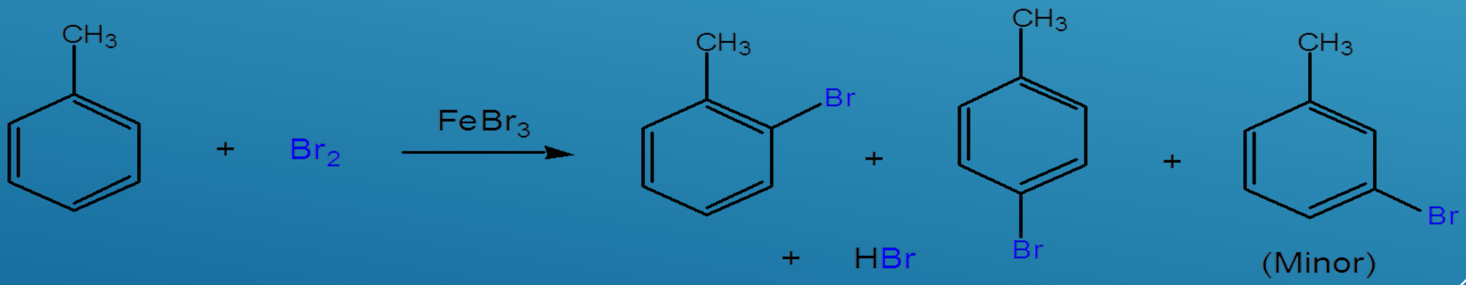
HALOGENATION OF BENZENE

- Br_2 or Cl_2 can react with benzene, using a catalyst, to form bromobenzene or chlorobenzene.
- Only the monohalogenation product is produced
- When Br_2 or Cl_2 reacts with toluene, a mixture of isomers is produced.
- Ortho and para isomers are the major products, and meta isomer is the minor product.

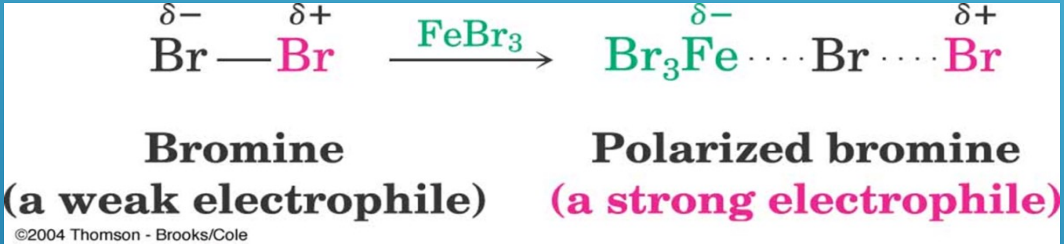
Examples:





HALOGENATION OF BENZENE

- Benzene's π electrons participate as a Lewis base in reactions with Lewis acids.
- The product is formed by loss of a proton, which is replaced by bromine.
- $FeBr_3$ is added as a catalyst to polarize the bromine reagent.



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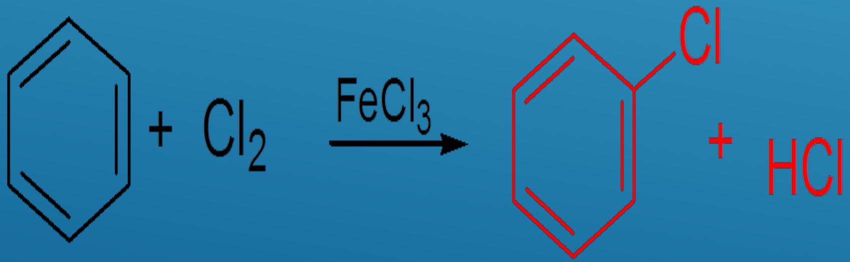
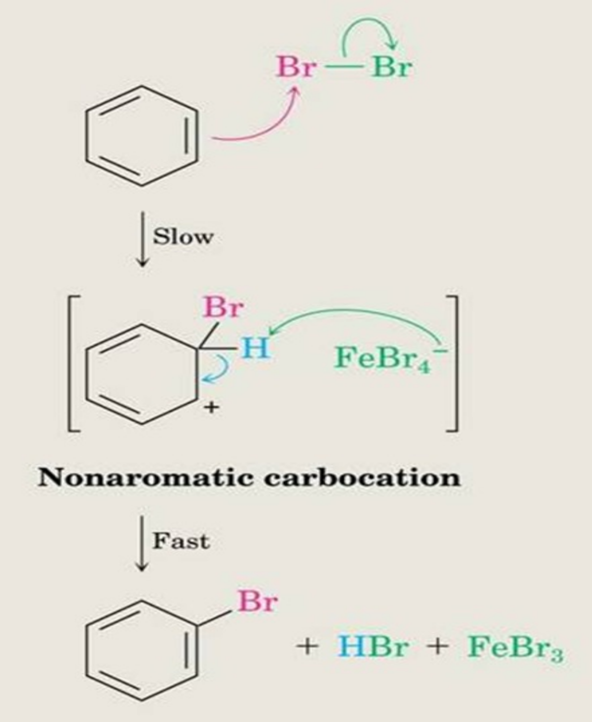
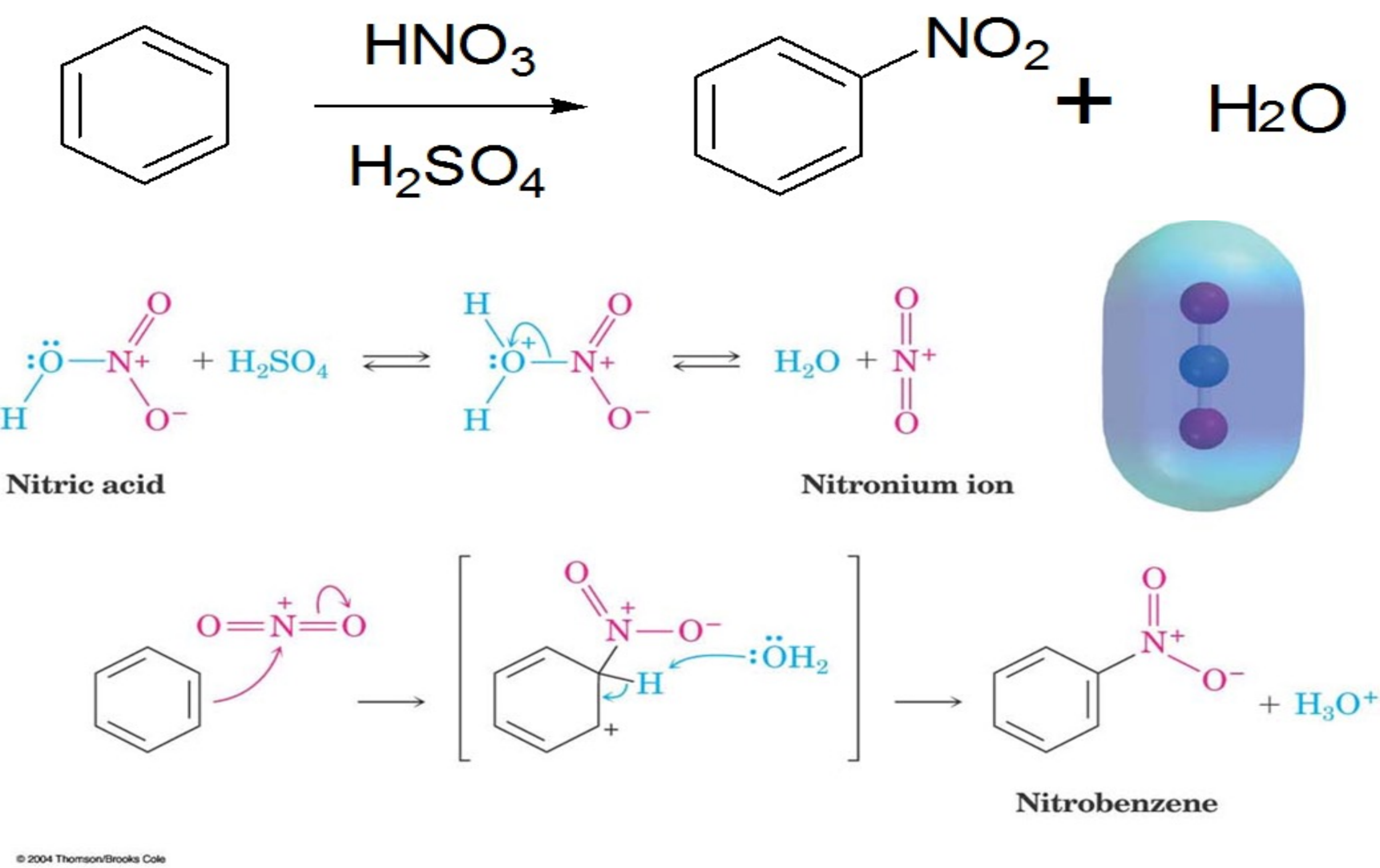




NITRATION OF BENZENE

- The combination of nitric acid and sulfuric acid produces NO_2^+ (nitronium ion).
- The reaction with benzene produces nitrobenzene.



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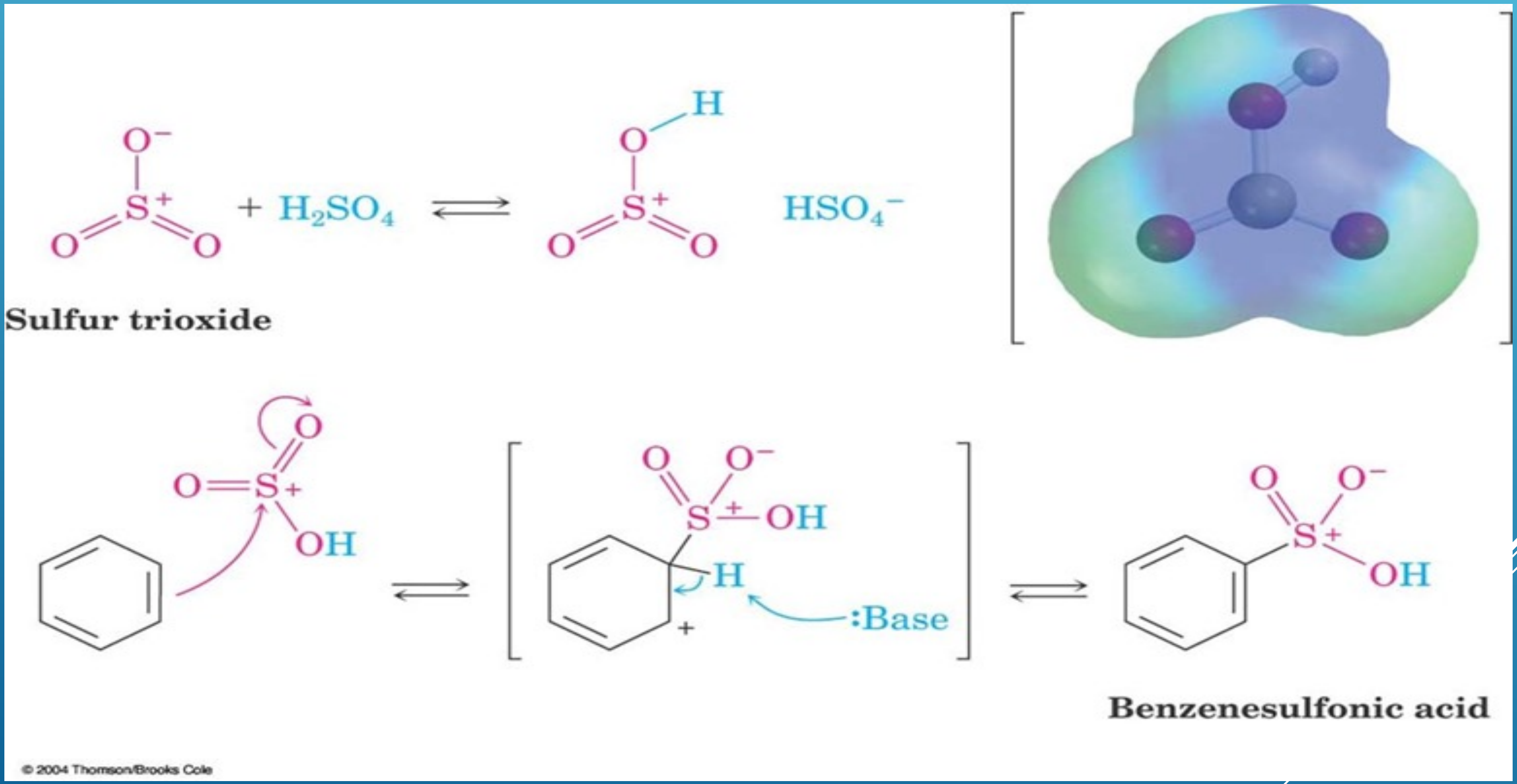
SULFONATION OF BENZENE

- Fuming sulfuric acid – combination of SO_3 and H_2SO_4.
- Electrophile is HSO_3^+ or SO_3.
- The product formed is Benzene sulfonic acid.



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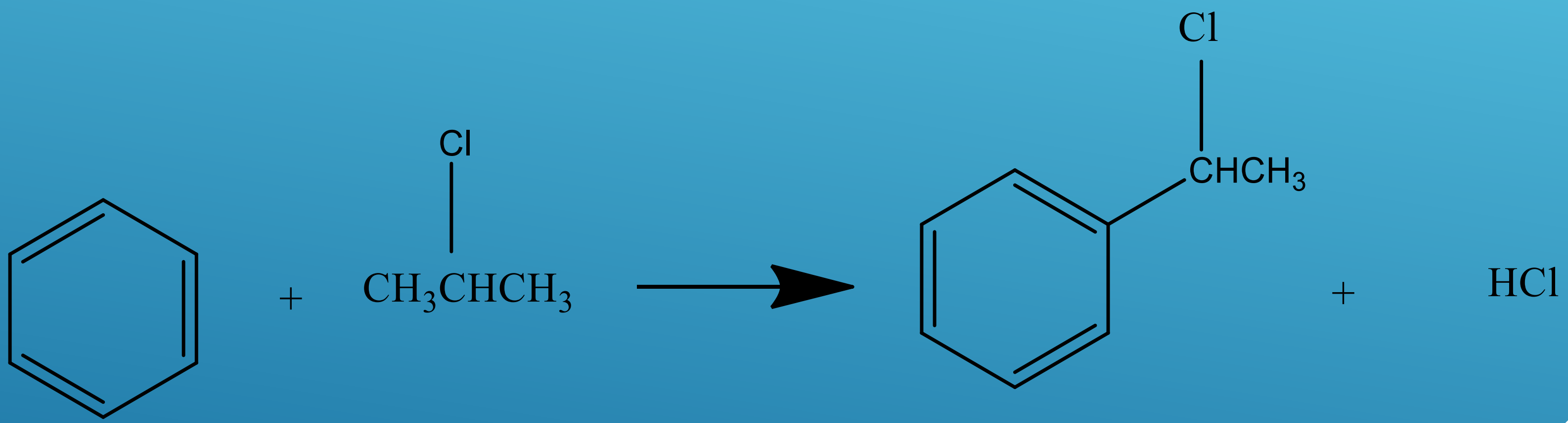
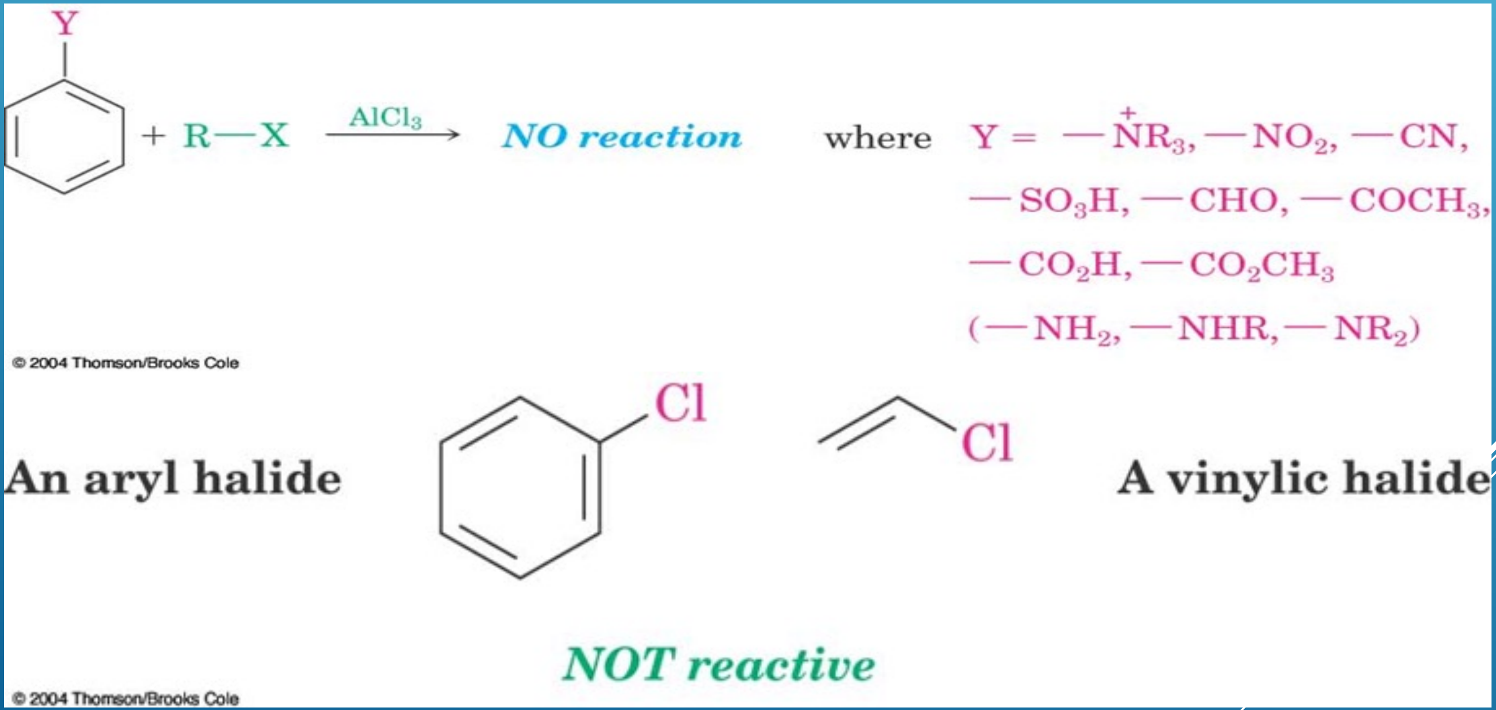
ALKYLATION OF BENZENE- FRIEDAL-CRAFTS REACTION.

- Benzene reacts with alkyl halide in the presence of $AlCl_3$ catalyst to form alkyl benzene.
- Example: Benzene reacts with 2-chloropropane in the presence of $AlCl_3$ catalyst to yield isopropyl benzene (also called as cumene).



LIMITATIONS OF THE FRIEDAL-CRAFTS ALKYLATION

- Only alkyl halides can be used (F, Cl, I, Br).
- Aryl halides and vinylic halides do not react (their carbocations are too hard to form).
- Will not work with rings containing an amino group substituent or a strongly electron-withdrawing group.



where $Y = -\overset{+}{N}R_3, -NO_2, -CN, -SO_3H, -CHO, -COCH_3, -CO_2H, -CO_2CH_3$ $(-NH_2, -NHR, -NR_2)$

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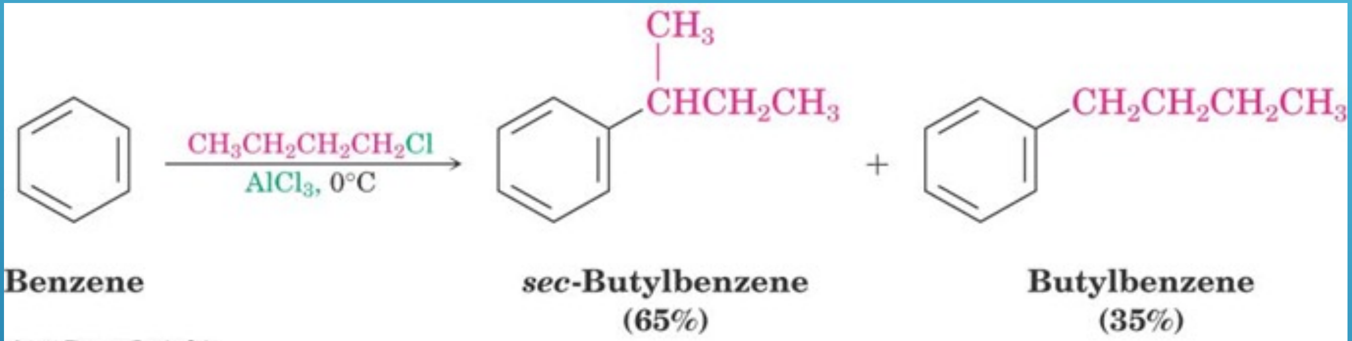
CARBOCATION REARRANGEMENTS DURING ALKYLATION

- Similar to those that occur during electrophilic additions to alkenes.
- Can involve H or alkyl shifts.



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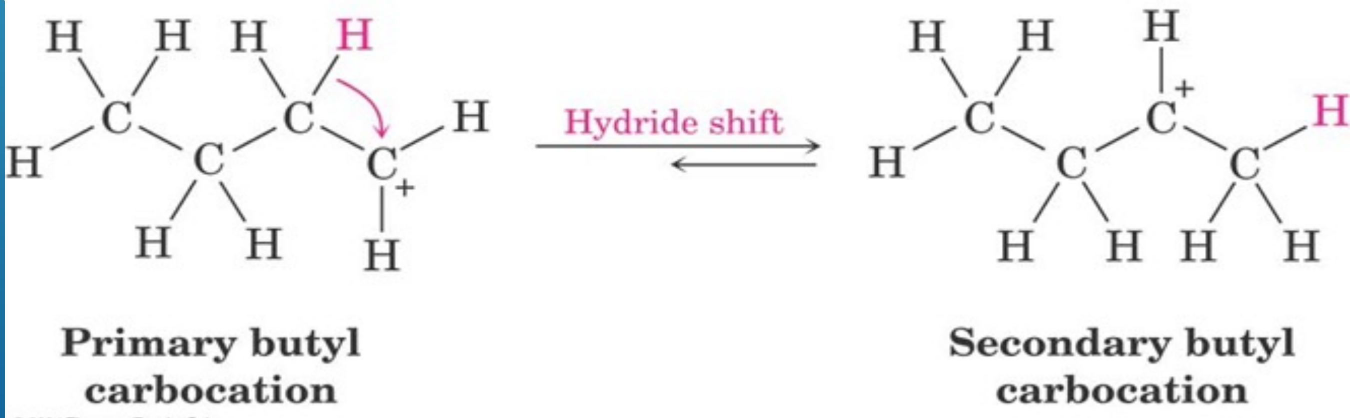

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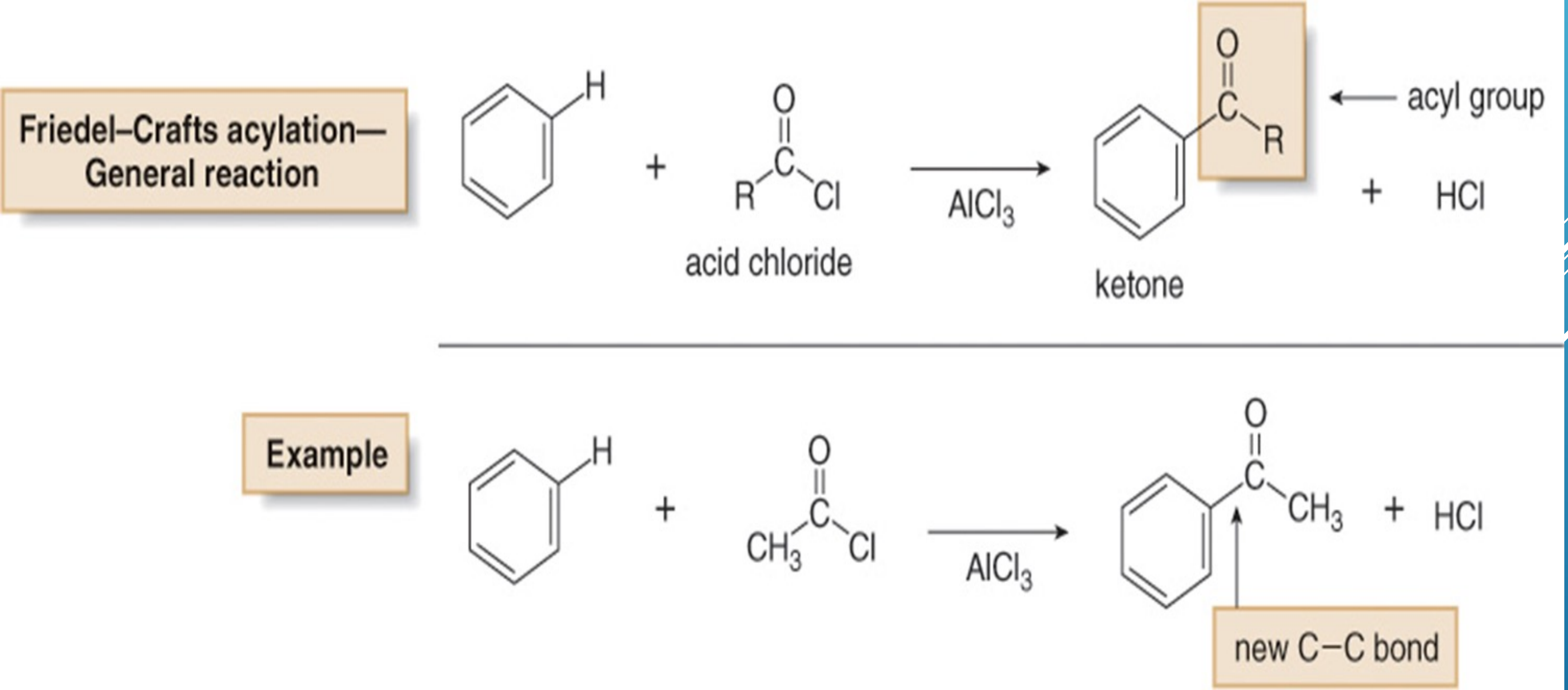
ACYLATION OF BENZENE: FRIEDAL-CRAFT'S ACYLATION REACTION

- In Friedal-Crafts acylation, a benzene ring is treated with an acid chloride (RCOCl) and $AlCl_3$ to form a ketone.
- Because the new group bonded to the benzene ring is called an acyl group, the transfer of an acyl group from one atom to another is an acylation.

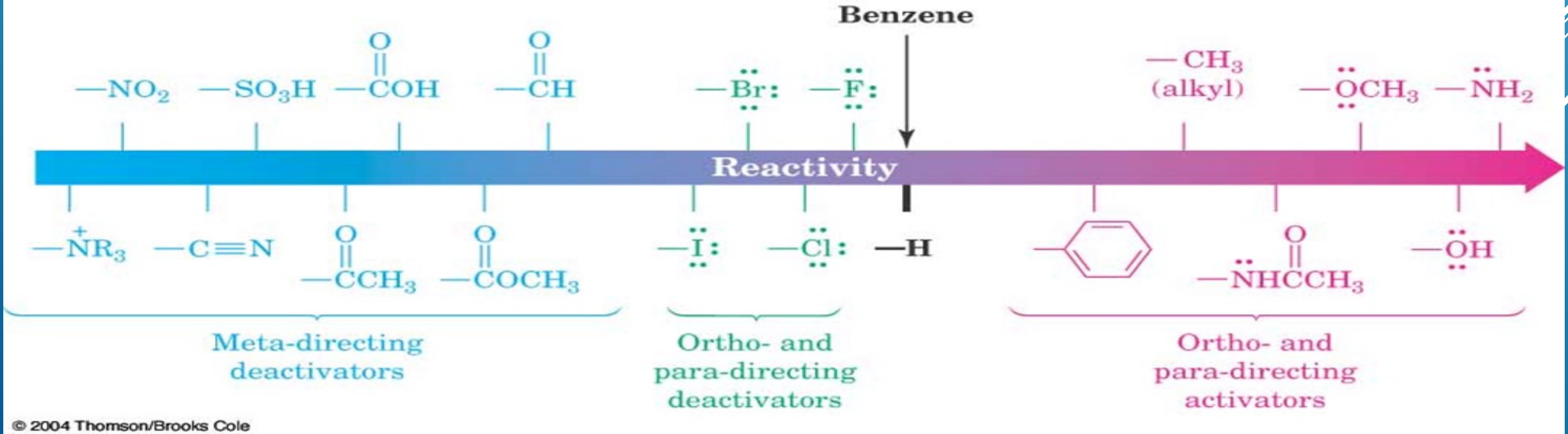


SUBSTITUENT EFFECTS IN ELECTROPHILIC SUBSTITUTION REACTIONS

- Substituents can cause a compound to be (much) more or (much) less reactive than benzene.
- Substituents affect the orientation of the reaction – the positional relationship is controlled.

Substituents can be classified into 3 groups based on the site of reaction and reactivity:

- *ortho*- and *para*-directing activators.
- *ortho*- and *para*-directing deactivators.
- *meta*-directing deactivators.



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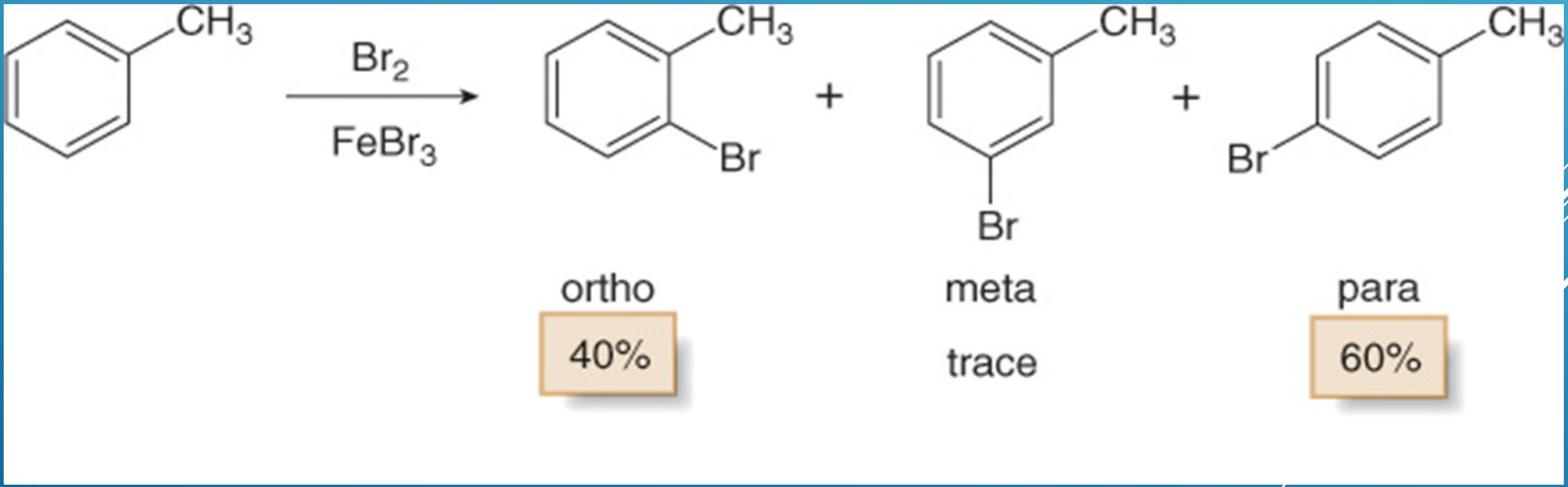
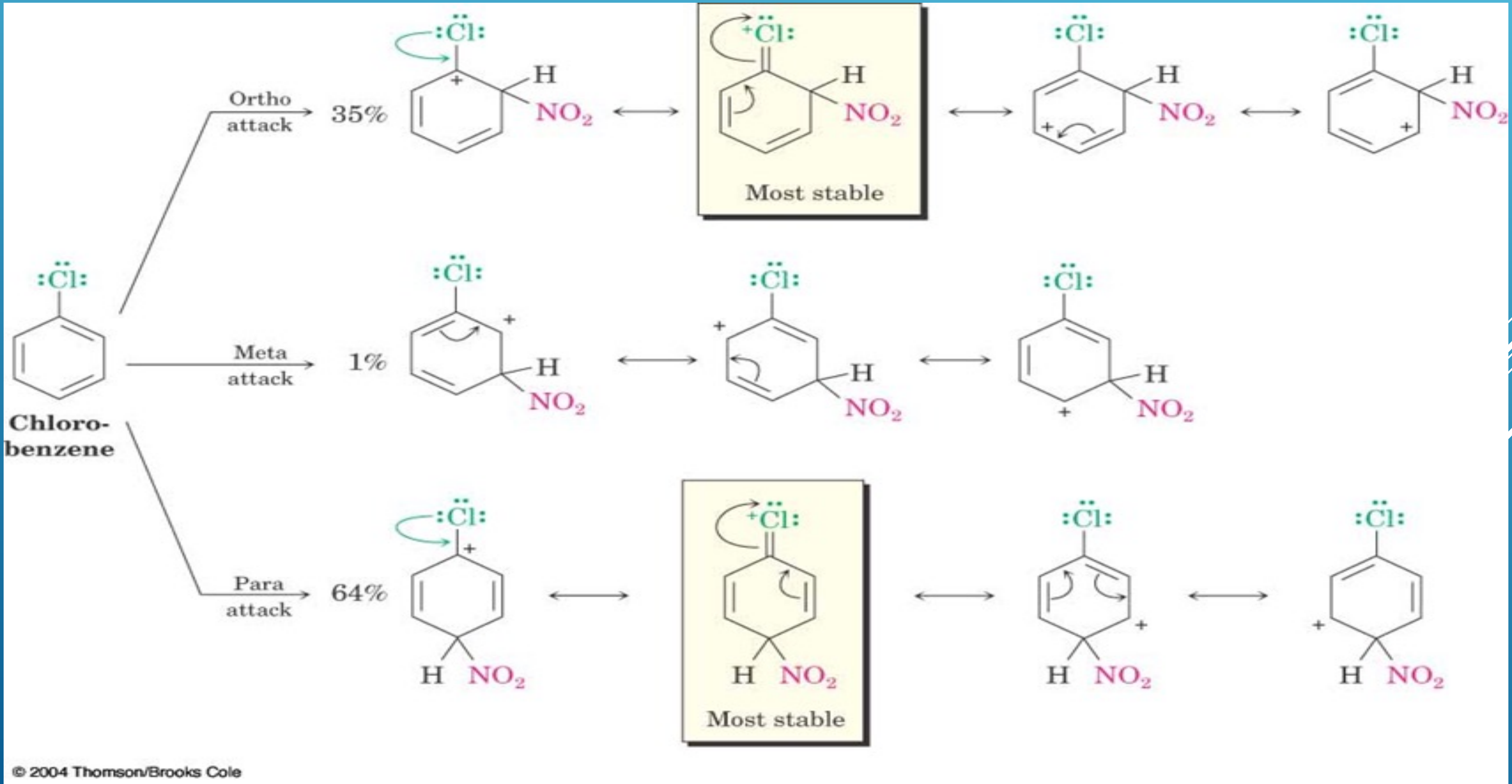
ORTHO-PARA DIRECTING ACTIVATORS

- Toluene reacts faster than benzene in all substitution reactions.
- The electron-donating CH_3 group activates the benzene ring to electrophilic attack.
- *Ortho* and *para* products predominates.
- The $-CH_3$,-OH groups are *ortho*, *para* directing groups, and they react faster than benzene.



ORTHO-PARA DIRECTING DEACTIVATORS

- Halogens present on a ring direct the electrophile, to *ortho* or *para* positions, and they react slower than benzene.
- Resonance effect is only at the *ortho* and *para* positions, stabilizing carbocation intermediate.



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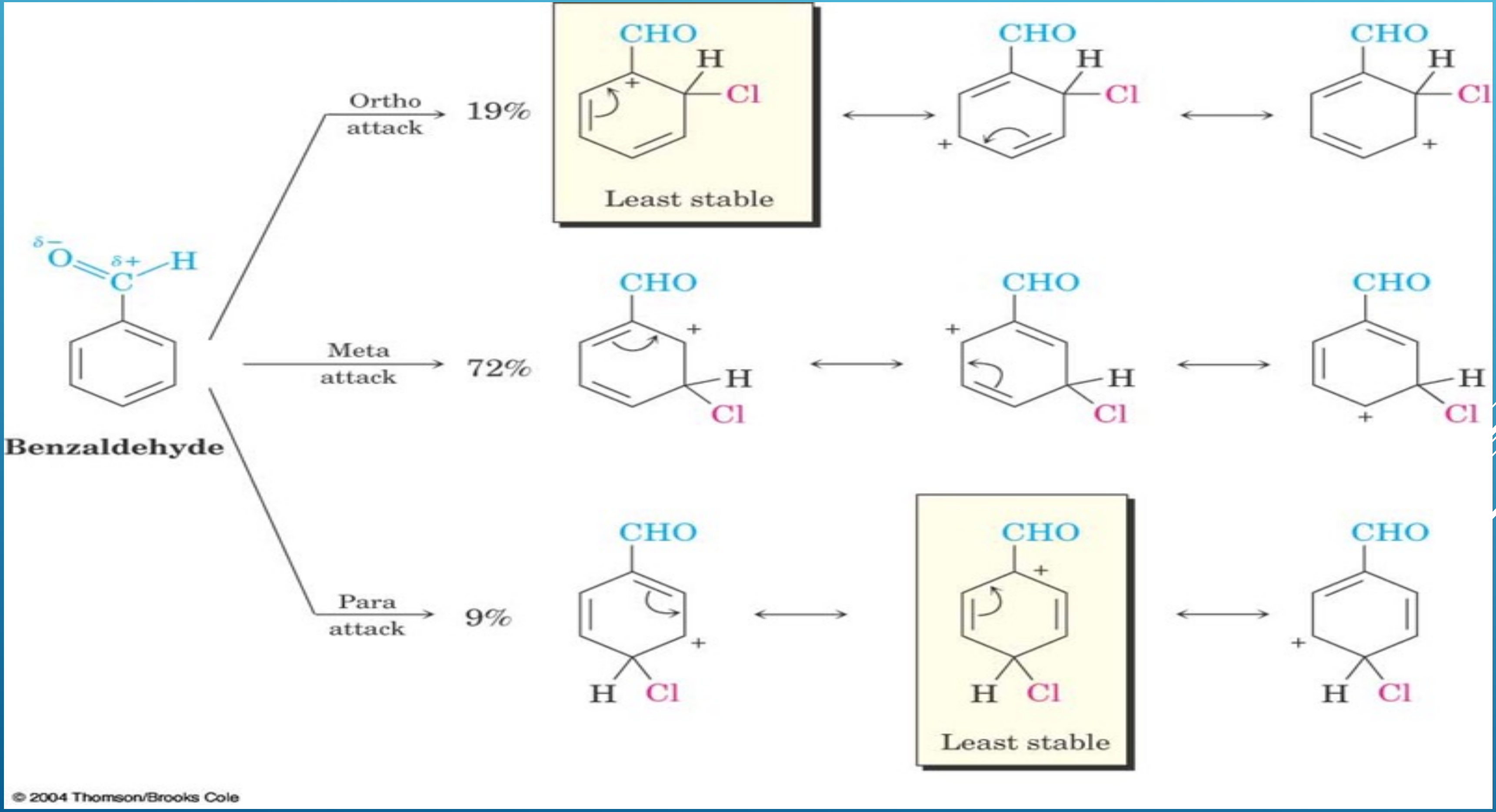
META DIRECTORS DEACTIVATORS

- Carbonyl (C=O), -CN groups are *meta* directing groups.
- These groups direct an electrophile to *m*-position, but they react slower than benzene.



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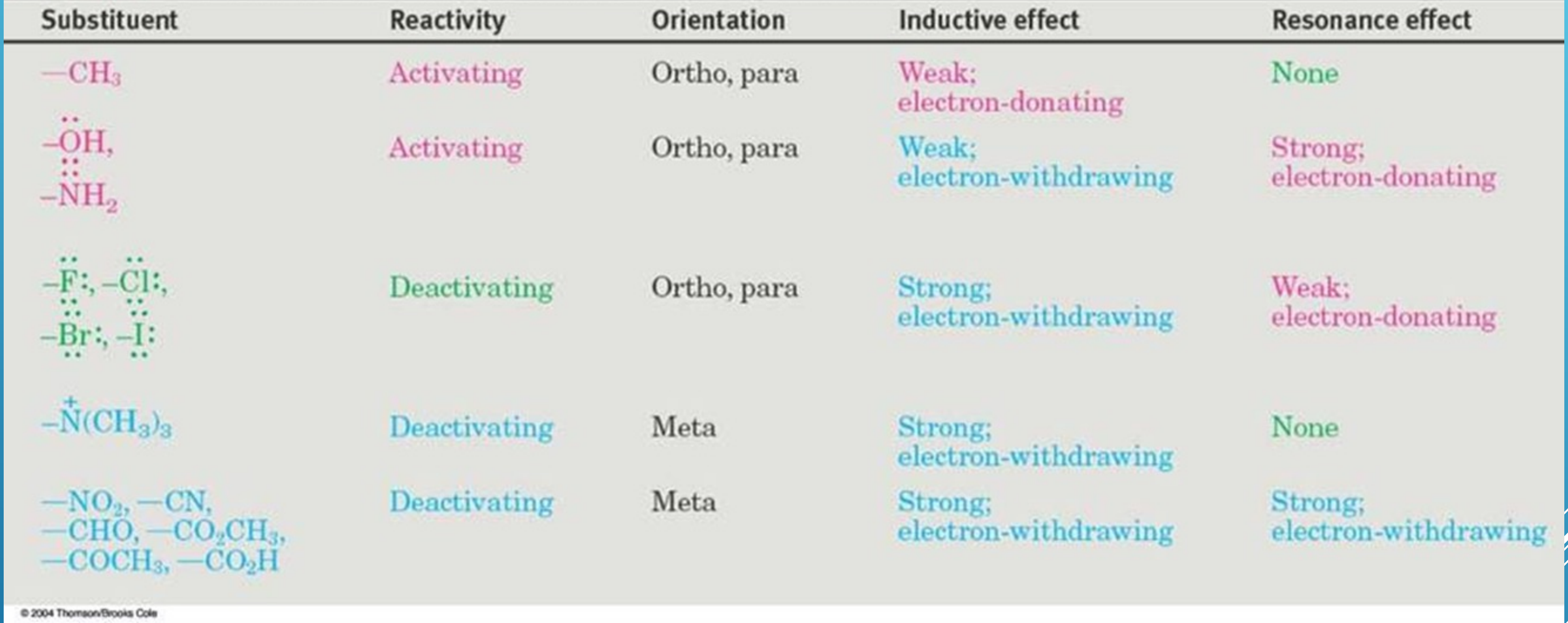
EFFECT OF SUBSTITUENTS IN AROMATIC SUBSTITUTION



Substituent	Reactivity	Orientation	Inductive effect	Resonance effect
$-CH_3$	Activating	Ortho, para	Weak; electron-donating	None
$-\ddot{O}H$, $-\ddot{N}H_2$	Activating	Ortho, para	Weak; electron-withdrawing	Strong; electron-donating
$-\ddot{F}:$, $-\ddot{Cl}:$, $-\ddot{Br}:$, $-\ddot{I}:$	Deactivating	Ortho, para	Strong; electron-withdrawing	Weak; electron-donating
$-\overset{+}{N}(CH_3)_3$	Deactivating	Meta	Strong; electron-withdrawing	None
$-NO_2$, $-CN$, $-CHO$, $-CO_2CH_3$, $-COCH_3$, $-CO_2H$	Deactivating	Meta	Strong; electron-withdrawing	Strong; electron-withdrawing

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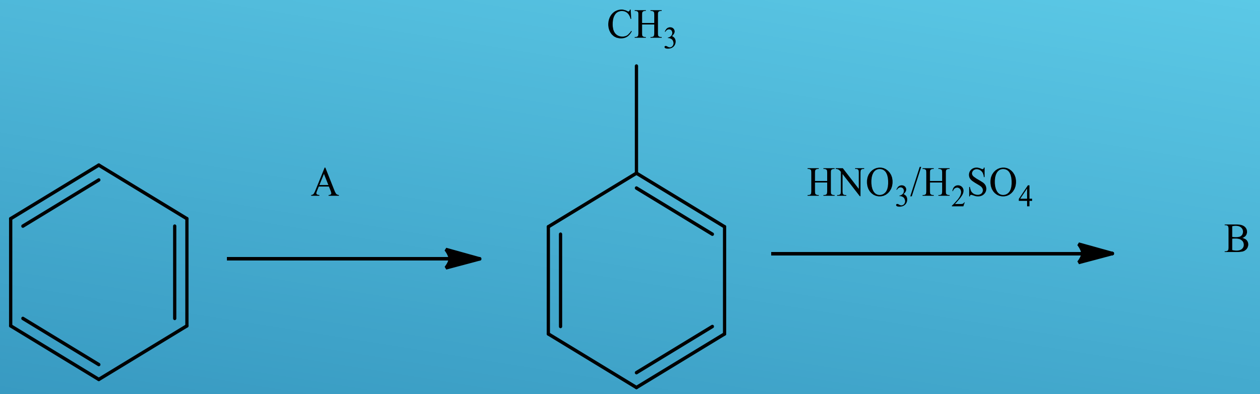
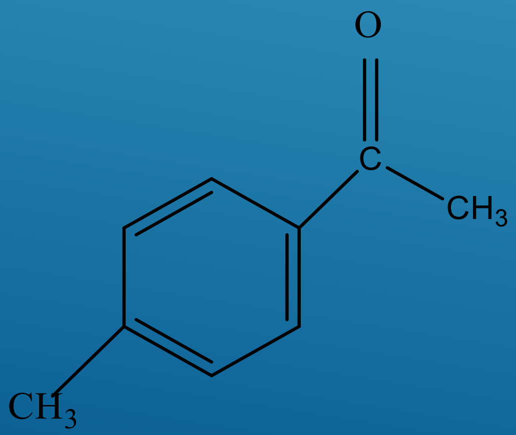
ORGANIC SYNTHESIS

1.

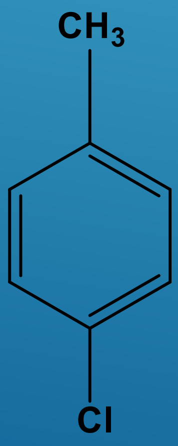


2. Starting from benzene, how would you synthesize the following substances?

A.



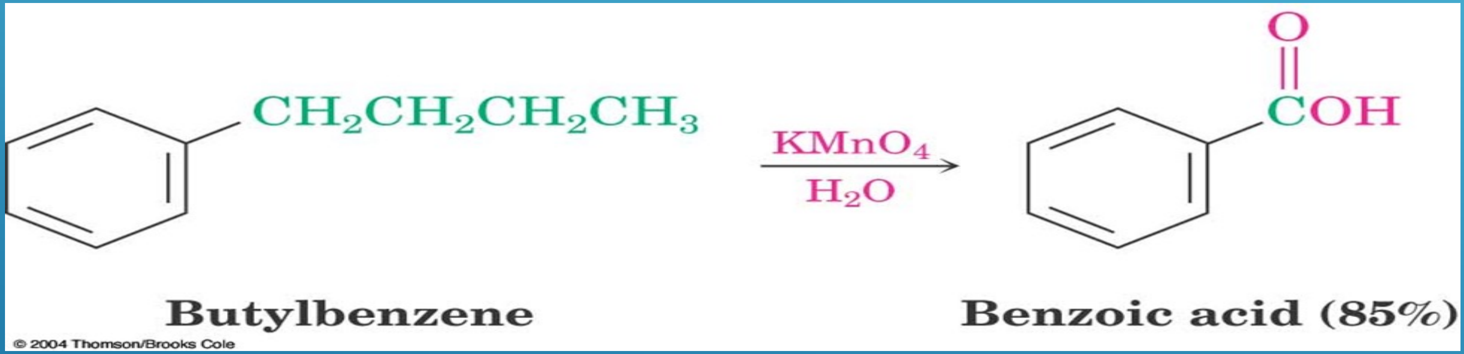
B.



OXIDATION AND REDUCTION OF AROMATIC COMPOUNDS

- Alkyl side chains can be oxidized to -CO_2H by strong reagents such as $KMnO_4$ and $Na_2Cr_2O_7$ if they have a C-H next to the ring.
- Converts an alkyl benzene into a benzoic acid,

$$\text{Ar-R} \longrightarrow \text{Ar-CO}_2\text{H}.$$



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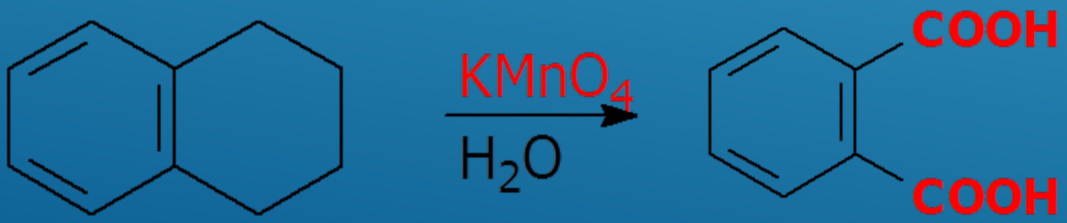
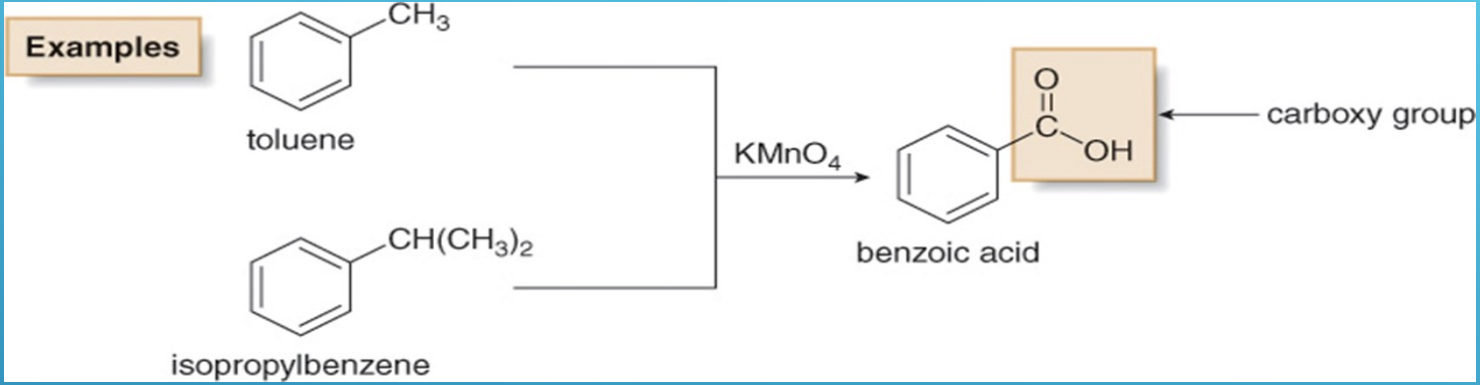


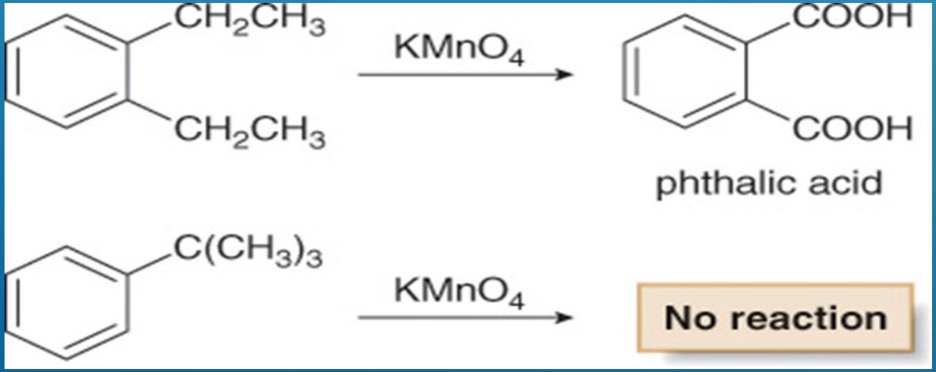
OXIDATION OF AROMATIC COMPOUNDS

Arenes containing at least one benzylic C—H bond are oxidized with $KMnO_4$ to benzoic acid.



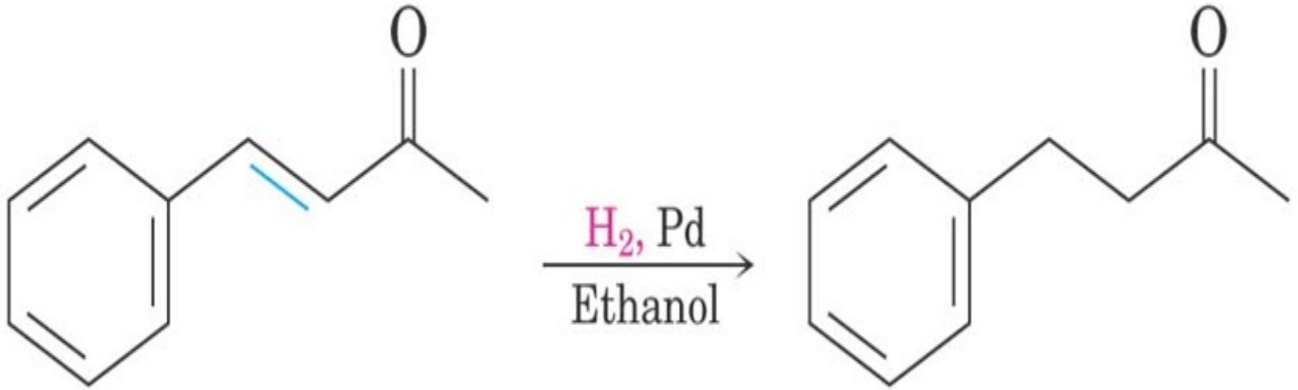
Substrates with more than one alkyl group are oxidized to dicarboxylic acids.

Compounds without a benzylic hydrogen are inert to oxidation.



REDUCTION OF AROMATIC COMPOUNDS

- Aromatic rings are inert to catalytic hydrogenation under conditions that reduce alkene double bonds.
- Can selectively reduce an alkene double bond in the presence of an aromatic ring.
- Reduction of an aromatic ring requires more powerful reducing conditions (high pressure or rhodium catalysts).



4-Phenyl-3-buten-2-one

4-Phenyl-2-butanone (100%)

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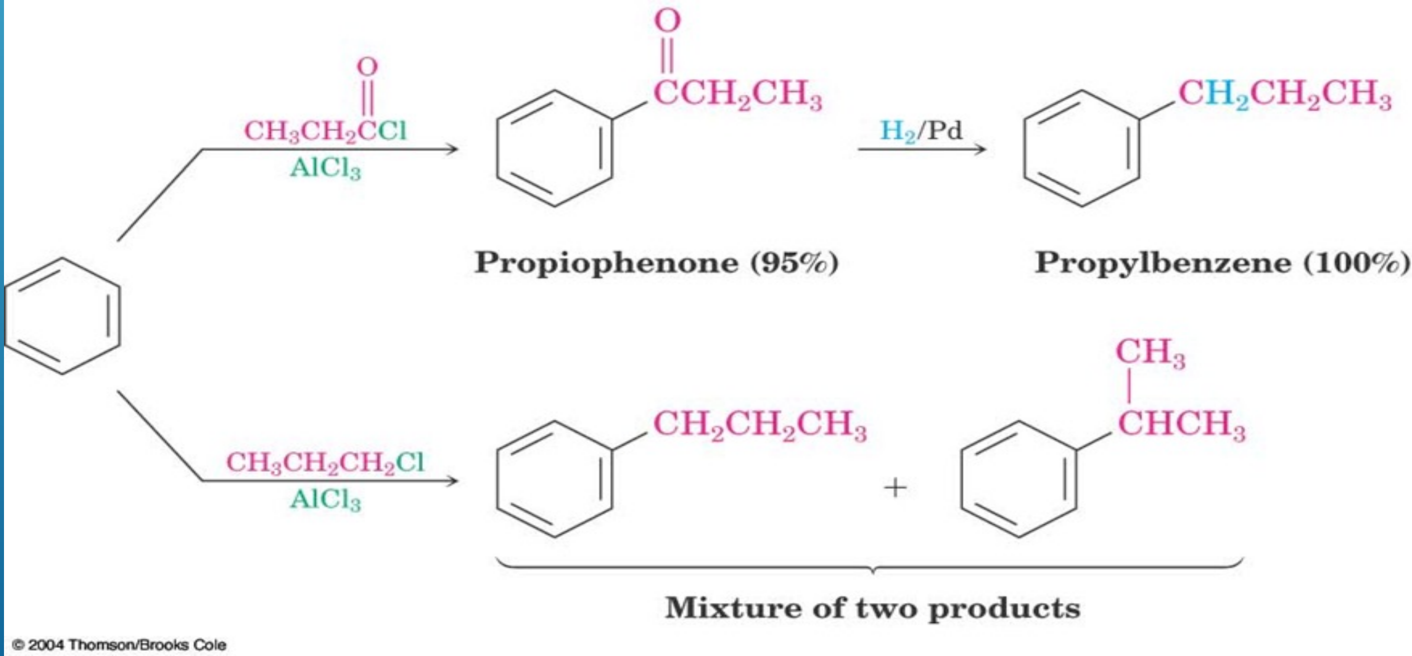
REDUCTION OF ARYL ALKYL BENZENES

- Aromatic ring activates neighboring carbonyl group toward reduction.
- Ketone is converted into an alkyl benzene by catalytic hydrogenation over Pd catalyst.



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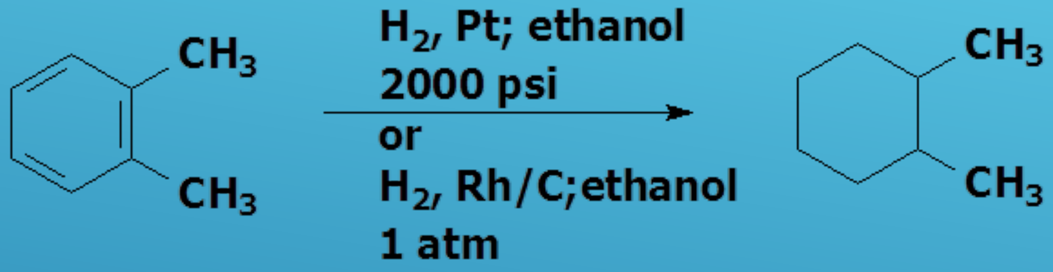
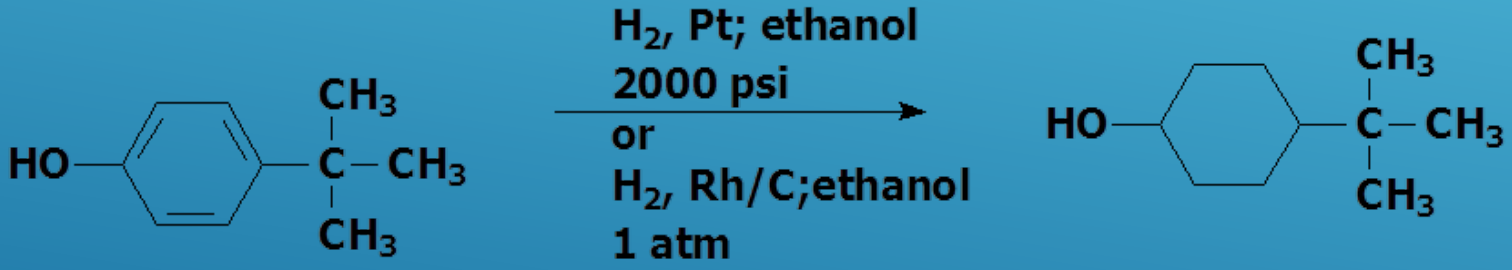
REDUCTION OF AROMATIC COMPOUNDS





ORGANIC SYNTHESIS

1. Starting with toluene, show how to synthesize the following compounds?

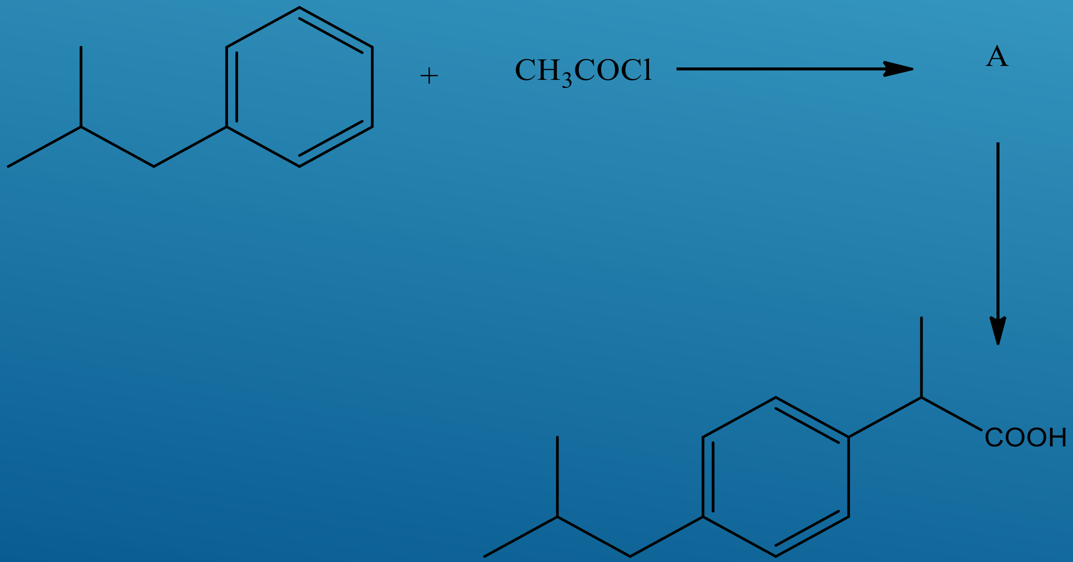
a) *o*-Bromotoluene

b) *m*-Nitrobenzenesulfonic acid

2. Starting with benzene, show how to synthesize the following compounds?

a). *o*-Nitrobenzoic acid b). *p*-*tert*-Butylbenzoic acid

3. Identify the product A in the given reaction.



ORGANIC SYNTHESIS

1. Synthesize *m*-chloronitrobenzene starting from benzene.

2. Synthesize *p*-bromobenzoic acid.