CHEM 108

FUNDAMENTALS OF ORGANIC CHEMISTRY

FOR B.Sc. PROGRAMS OF SCIENTIFIC COLLEGES

PRE-REQUISITES COURSE; CHEM 101

CREDIT HOURS; 4 (3+1)

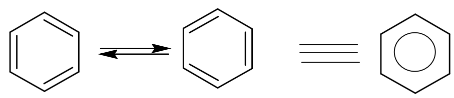
Chemistry Department, College of Science, King Saud University

CHAPTER 3

AROMATIC HYDROCARBONS

Aromatic Hydrocarbons

- **Originally called aromatic due to fragrant odors, although this definition seems inaccurate as many products posses distinctly non-fragrant smells!**
- **Currently a compound is said to be aromatic if it has *benzene-like in its properties*.**



- **Their properties differ markedly from those of aliphatic hydrocarbons.**
  ***Aromatic hydrocarbons* undergo electrophilic substitution whereas *aliphatic hydrocarbons* undergo ionic addition to double and triple bonds and free radical substitution.**
- Benzene is the *parent hydrocarbon of aromatic compounds*, because of their special chemical properties.
- Today a compound is said to be aromatic if it is *benzene-like in its properties*.

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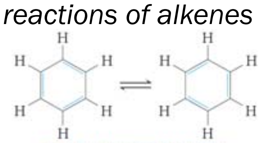
Aromatic Hydrocarbons; Structure of Benzene

- Molecular formula = C_6H_6
  The carbon-to-hydrogen ratio in benzene, suggests a highly unsaturated structure.
- *Benzene reacts mainly by substitution.*
  It does not undergo the typical addition reactions of alkenes or alkynes.
- Kekulé structure for benzene.
  - *He suggested that six carbon atoms are located at the corners of a regular hexagon, with one hydrogen atom attached to each carbon atom.*
  - *He suggested that single and double bonds alternate around the ring (conjugated system of double bonds).*
  - *Kekulé suggested that the single and double bonds exchange positions around the ring so rapidly that the typical reactions of alkenes cannot take place.*



the Kekulé structures for benzene

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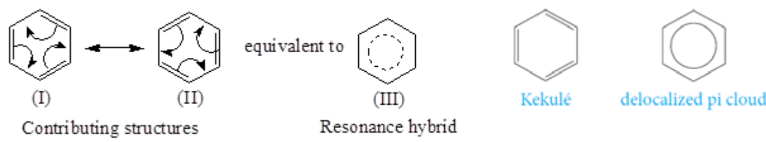
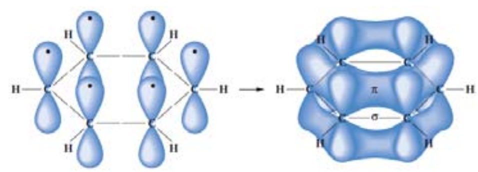
Aromatic Hydrocarbons; Structure of Benzene

- *Resonance Model for Benzene.*



- *Benzene is planar.*
- *All of the carbon–carbon bond lengths are identical*: 1.39 A°, intermediate between typical *single (1.54A°)* and *double (1.34 A°)* carbon–carbon bond lengths.
- Each carbon is therefore *sp*^{2}-hybridized.
- Bond angles of 120°.



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Aromatic Character (Aromaticity)

To be classified as aromatic, a compound must have:

❶ Cyclic structure

❷ Cyclic structure contains what looks like a continuous system of alternating double and single bonds

❸ Aromatic compounds must be planar

❹ Fulfill Hückel's rule

The number of π electrons in the compound = (4n + 2)

Where (n = 0,1, 2, 3, and so on).

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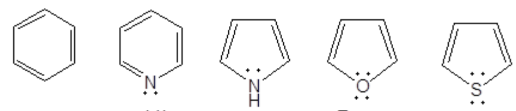
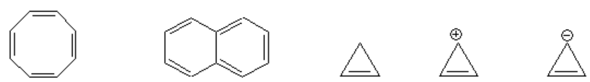
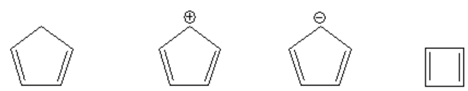
Aromatic Character (Aromaticity)

n	$4n + 2$	Structure and name of aromatic compound
1	6	 Benzene, Pyridine, Pyrrole, Furan, Thiophene

Examples



4n+2 =	8	10	2	2	4
n=	1.5	2	0	0	0.5



4n+2 =	4	4	6	4
n=	0.5	0.5	1	0.5

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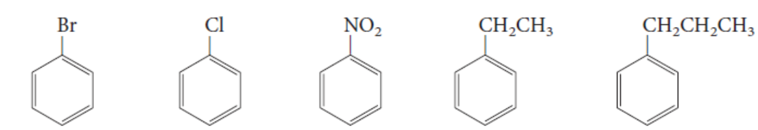
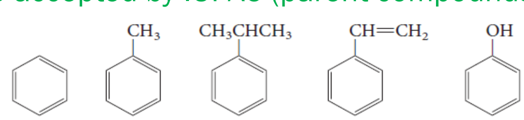
Nomenclature of Aromatic Compounds

- Monosubstituted benzenes that do not have common names accepted by IUPAC are named as derivatives of benzene.

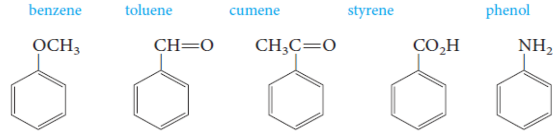


bromobenzene, chlorobenzene, nitrobenzene, ethylbenzene, propylbenzene

Common names are accepted by IUPAC (parent compounds).



benzene, toluene, cumene, styrene, phenol



anisole, benzaldehyde, acetophenone, benzoic acid, aniline

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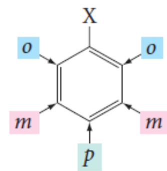
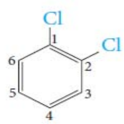
Nomenclature of Aromatic Compounds

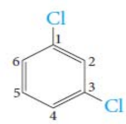
- When two substituents are present, *three isomeric structures are possible*.
  - They are designated by the prefixes; *ortho*- (*o*-), *meta*- (*m*-) and *para*- (*p*-).
  - If substituent X is attached to carbon 1; *o*- groups are on carbons 2 and 6, *m*- groups are on carbons 3 and 5, and *p*- groups are on carbon 4.



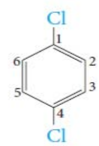
- Examples;



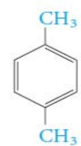
ortho-dichloro-benzene



meta-dichloro-benzene



para-dichloro-benzene



para-xylene*

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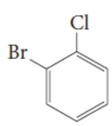
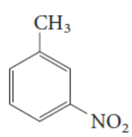
Nomenclature of Aromatic Compounds

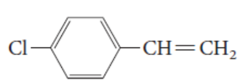
- The prefixes; *ortho*- (*o*-), *meta*- (*m*-) and *para*- (*p*-) are used when the two substituents are not identical.



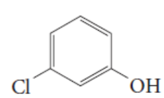
o-bromochlorobenzene (note alphabetical order)



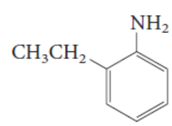
m-nitrotoluene



p-chlorostyrene

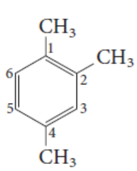


m-chlorophenol

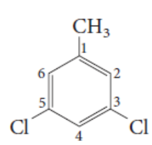


o-ethylaniline

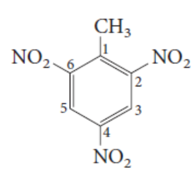
- When more than two substituents are present, their positions are designated by numbering the ring.



1,2,4-tri-methylbenzene



3,5-dichlorotoluene



2,4,6-trinitrotoluene (TNT)

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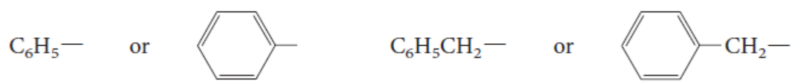
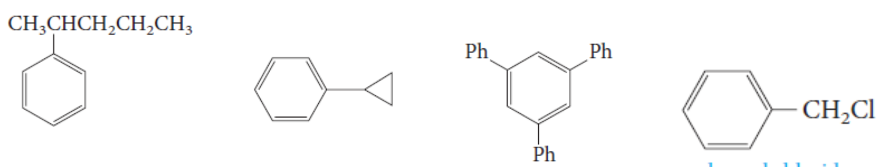
Nomenclature of Aromatic Compounds

- Two groups with special names occur frequently in aromatic compounds; the phenyl group and the benzyl group.



phenyl group benzyl group

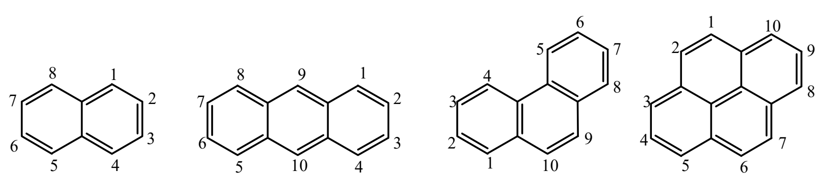
- Examples;



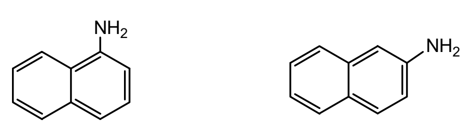
2-phenylpentane (or 2-pentylbenzene) phenylcyclopropane (or cyclopropylbenzene) 1,3,5-triphenylbenzene benzyl chloride

Nomenclature of Aromatic Compounds

- Polynuclear aromatic hydrocarbons containing two, three & four rings are :



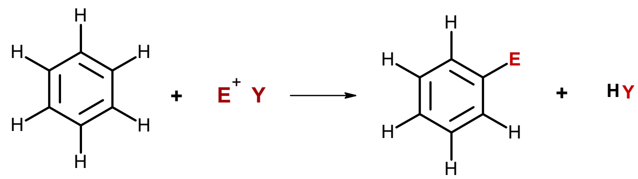
Naphthalene Anthracene Phenancrene Pyrene



IUPAC name:	1-Aminonaphthalene	2-Aminonaphthalene
Common name:	a-Naphthaylamine (a weak carcinogen)	B-Naphthaylamine (a strong carcinogen)

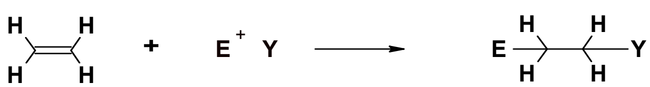
Electrophilic Aromatic Substitution Reactions

- In this reaction, an electrophile E $^{+}$ replaces a hydrogen atom, from the aromatic ring system.



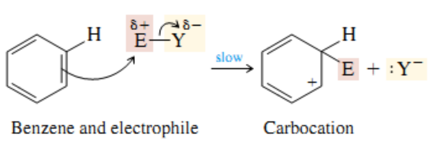
Arene — Electrophilic reagent — Product of electrophilic aromatic substitution

- This reaction is in contrast to electrophilic addition to the double bonds of alkene

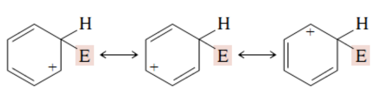


Alkene — Electrophilic reagent — Product of electrophilic addition

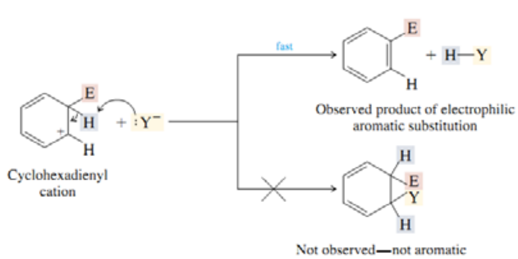
Electrophilic Aromatic Substitution Reactions



The electrophile E^{+} approaches the cloud of the aromatic ring and forms a bond to carbon, creating a +ve charge in the ring



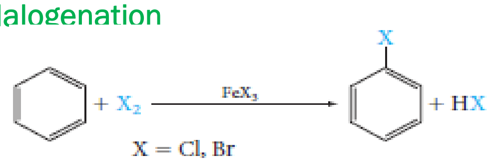
The removal of the proton by the nucleophile Y $^{-}$, which leads to the restoration of the aromatic ring



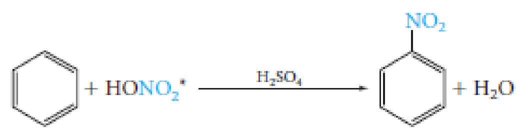
The net overall result is the substitution of the group E^{+} for a proton H^{+}.

Electrophilic Aromatic Substitution Reactions

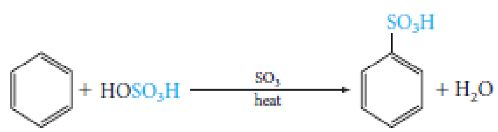
1) Halogenation



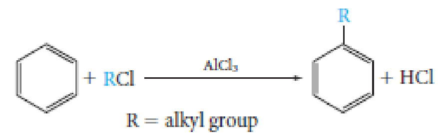
2) Nitration



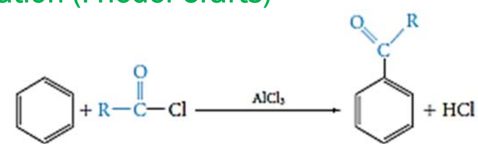
3) Sulfonation



4) Alkylation (Friedel-Crafts)



5) Acylation (Friedel-Crafts)



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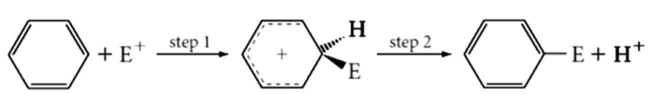
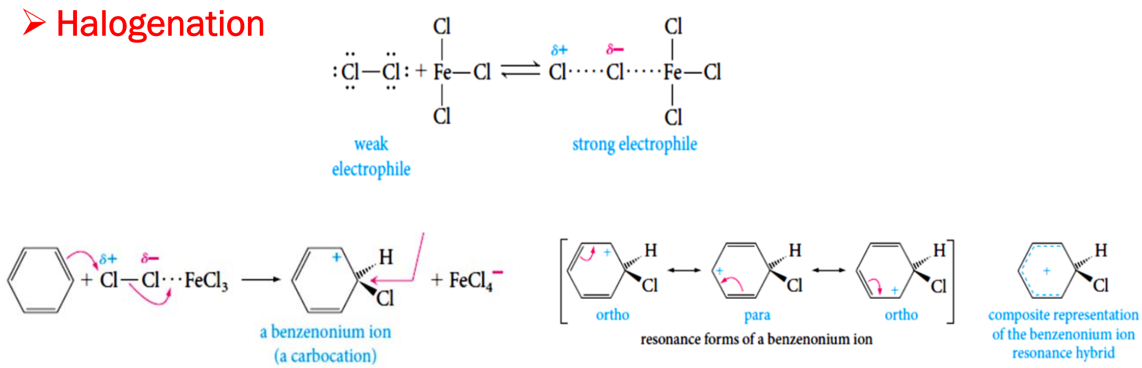
Electrophilic Aromatic Substitution Reactions

The Mechanism of Electrophilic Aromatic Substitution

We can generalize this two-step mechanism for all the electrophilic aromatic substitutions.



➢ Halogenation



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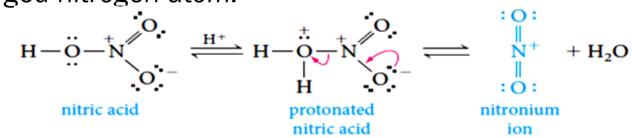
Electrophilic Aromatic Substitution Reactions

The Mechanism of Electrophilic Aromatic Substitution

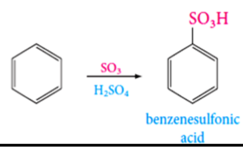
➢ Nitration

In aromatic nitration reactions, the sulfuric acid catalyst protonates the nitric acid, which then loses water to generate the nitronium ion (NO_2^+), which contains a positively charged nitrogen atom.



➢ Sulfonation

We use either concentrated or fuming sulfuric acid, and the electrophile may be sulfur trioxide, SO_3, or protonated sulfur trioxide, $^+SO_3H$.

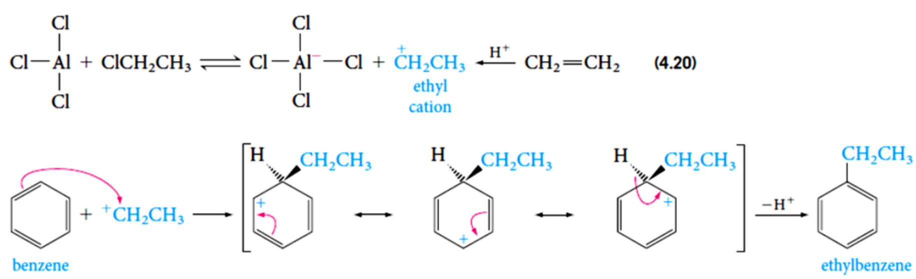


Electrophilic Aromatic Substitution Reactions

The Mechanism of Electrophilic Aromatic Substitution

➢ Friedel–Crafts Alkylation

The electrophile is a carbocation, which can be formed either by removing a halide ion from an alkyl halide with a Lewis acid catalyst (for example, $AlCl_3$).

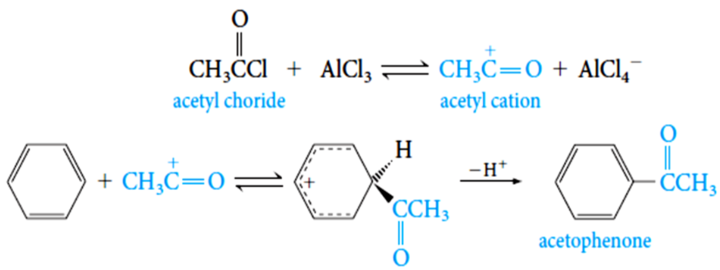


Electrophilic Aromatic Substitution Reactions

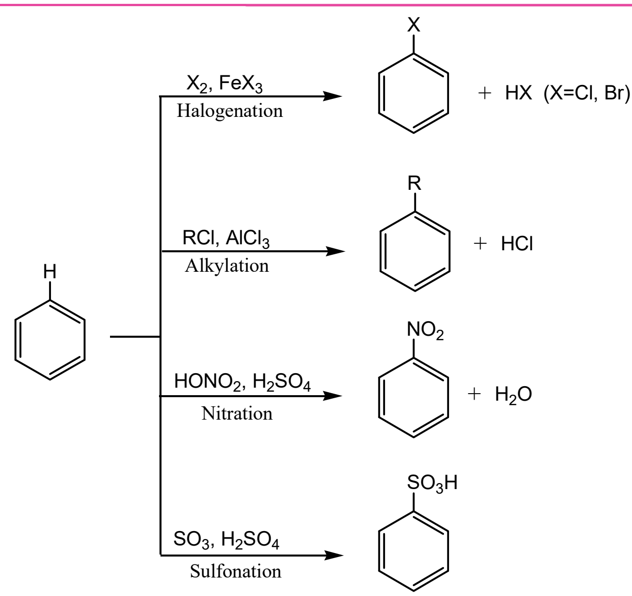
The Mechanism of Electrophilic Aromatic Substitution

➢ Friedel–Crafts Acylation

The electrophile is an acyl cation generated from an acid derivative, usually an acyl halide. The reaction provides a useful general route to aromatic ketones.

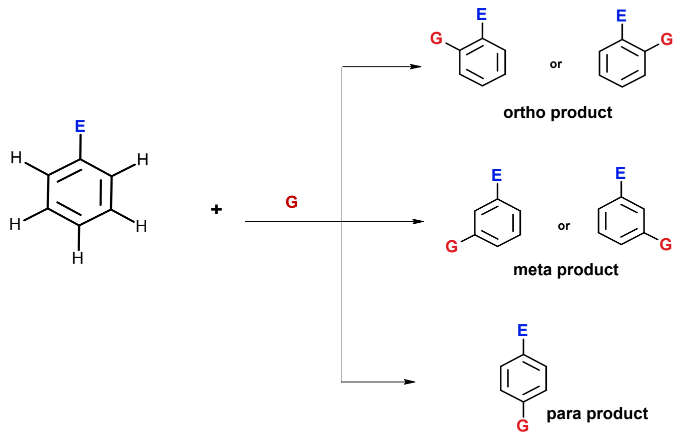


Electrophilic Aromatic Substitution Reactions



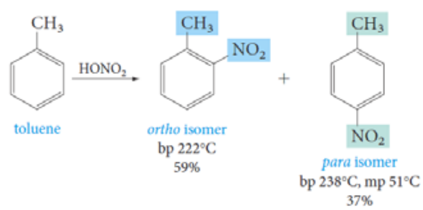
Disubstituted Benzenes: Orientation

Introduction of a second group, G, into a monosubstituted benzene, $C_6H_5 - E$

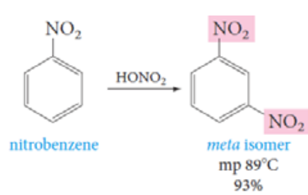


Disubstituted Benzenes: Orientation

- Substituents already present on an aromatic ring determine the position taken by a new substituent.
- Example; nitration of toluene gives mainly a mixture of *o*- and *p*-nitrotoluene.



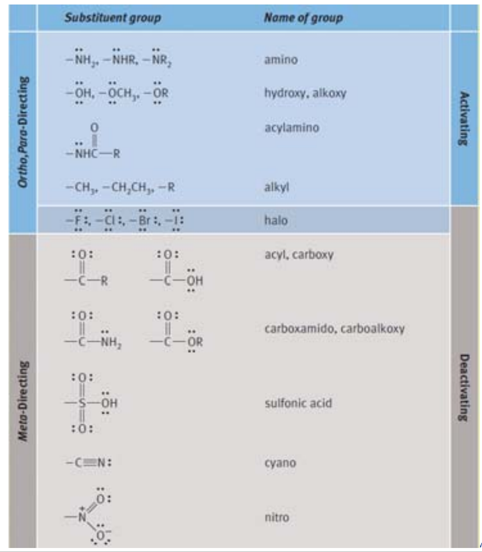
- On the other hand, nitration of nitrobenzene under similar conditions gives mainly the *meta* isomer.



Disubstituted Benzenes: Orientation& Reactivity

Directing and Activating Effects of Common Functional Groups

- *Substituents that release electrons to the ring will activate the ring toward electrophilic substitution.*
- *Substituents that withdraw electrons from the ring will deactivate the ring toward electrophilic substitution.*

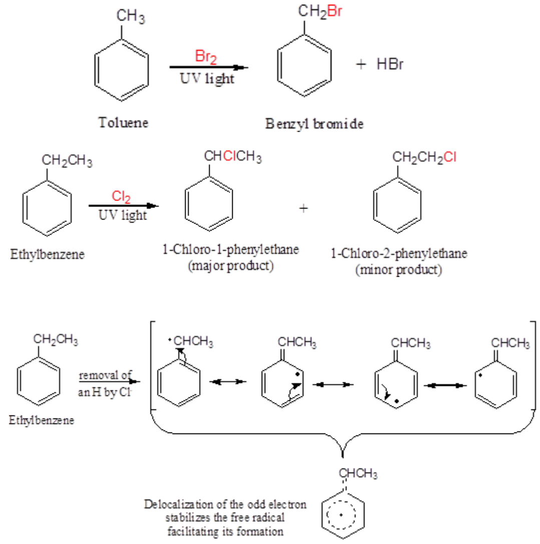


Disubstituted Benzenes: Orientation& Reactivity

Substituent	Effect on reactivity
o,p- director	
-NH_2, -NHR, -NR_2 , -OH,	Very strongly activating
-NHCOR , OR	Strongly activating
-C_6H_5, -CH_3, -R (Alkyl), CH_2=CHR	Moderately activating
H	Standard for comparison
-F, -Cl, -Br, -I	Deactivating
m- director	
-SO_3H, -COOH, -COOR	Strongly deactivating
, -CHO, -COR, -CN	
-NO_2, -CF_3	Very strongly deactivating

Side-Chain Reactions of Benzene-Derivatives

1. Halogenation of an Alkyl Side Chain



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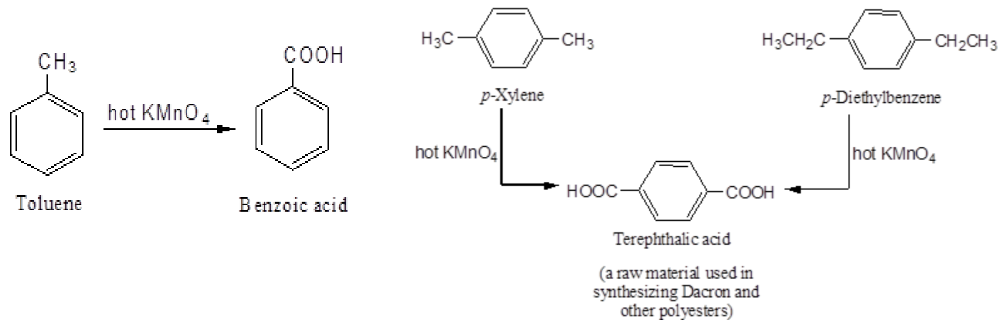
Side-Chain Reactions of Benzene-Derivatives

2. Oxidation of an Alkyl Side Chain

- Conversion into a carboxyl group, -COOH, by treatment with hot potassium permanganate.
- Regardless the length of the alkyl chain, the product is always the same.



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