

Chemistry 110

Bettelheim, Brown, Campbell & Farrell

Eighth Edition

Introduction to General,

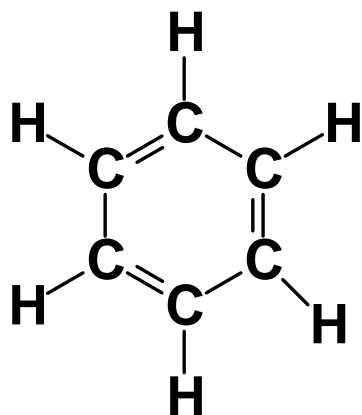
Organic and Biochemistry

Chapter 13

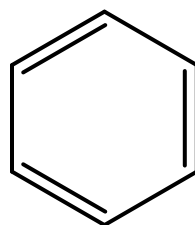
Benzene and its Derivatives

Aromatic Compounds

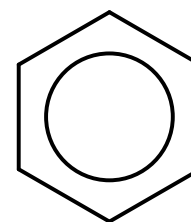
- **Aromatic compound:** a hydrocarbon that contains one or more benzene-like rings.
- **arene:** a term used to describe any given aromatic compound.
- **Ar-** , a symbol for an aromatic substituent group derived by removing an –H atom from an arene.
- **The Kekulé structure for benzene (1872):**



Kekule structure showing all atoms.



Line drawing representing a Kekule structure.



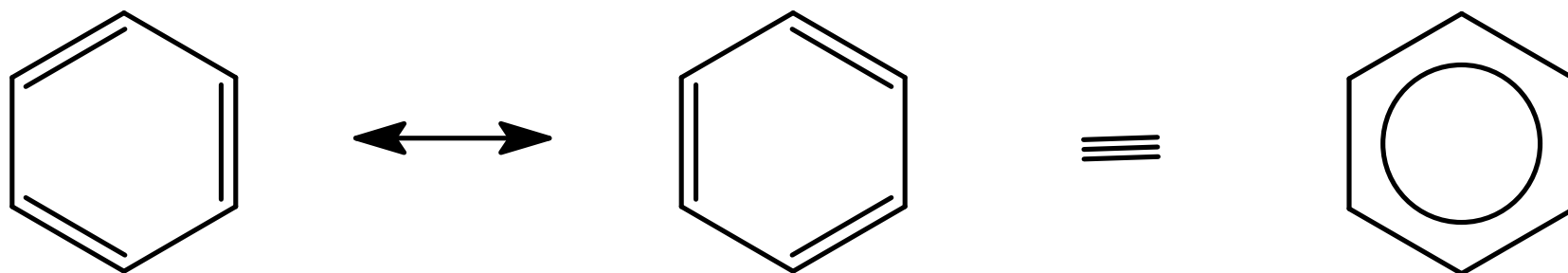
Line drawing representing the resonance hybrid.

Benzene Resonance

- **The theory of resonance, developed by Linus Pauling (1930), provided the first adequate description of the structure of benzene.**
- **According to the theory of resonance, certain molecules and ions are best described by writing two or more Lewis structures; the real molecule or ion is a resonance hybrid of these structures.**
- **Each individual Lewis structure is called a contributing structure.**
- **We show that the real molecule is a resonance hybrid of the two or more Lewis structures by using a double-headed arrow between them.**

Benzene Resonance

➤ The resonance hybrid has some of the characteristics of each Lewis contributing structure

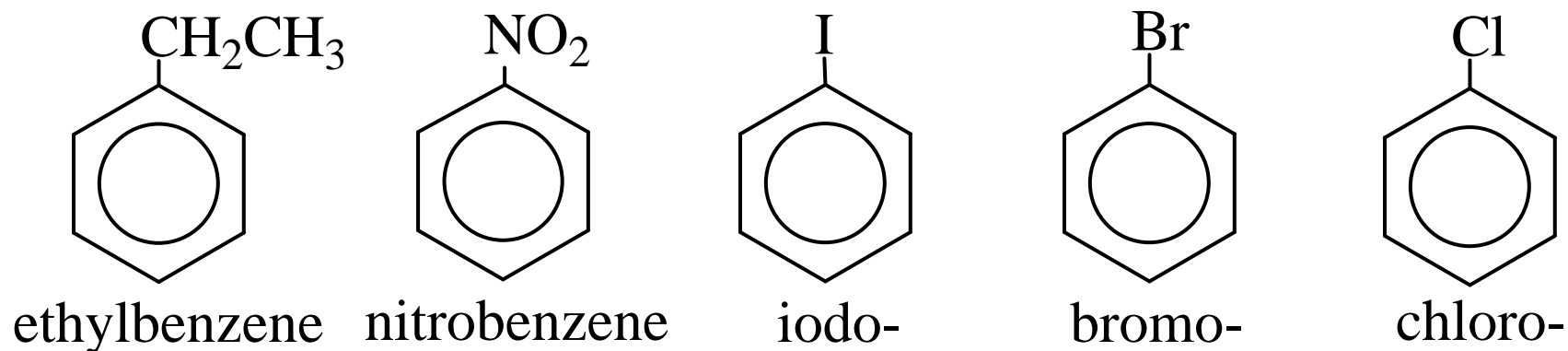


➤ The length of a carbon-carbon bond in benzene, for example, is midway between that of a carbon-carbon single bond and a double bond.

➤ The most important difference is that the benzene unsaturation does not add molecules, only ring substituents may be commonly changed by reaction.

Naming of Benzene Derivatives

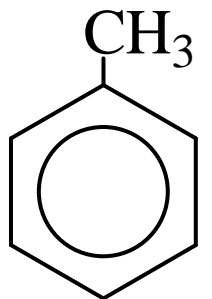
- **The phenyl group (C_6H_5- or Ph-):** the substituent group derived by removing one H from benzene.
- **monosubstituted alkylbenzenes are named as derivatives of benzene; for example:**



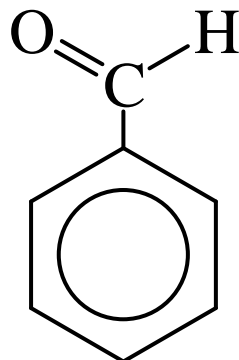
- **the IUPAC system also retains certain common names for several of the simpler monosubstituted alkylbenzenes e.g.: toluene , styrene.**

Naming of Benzene Derivatives

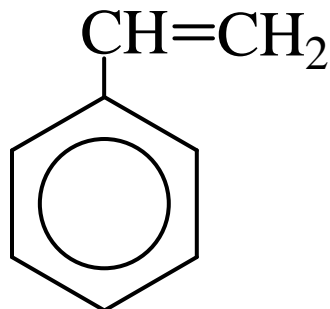
➤ the common names for these monosubstituted benzenes are also retained.



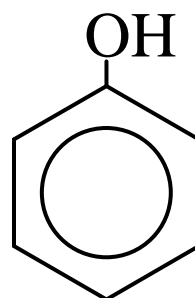
toluene



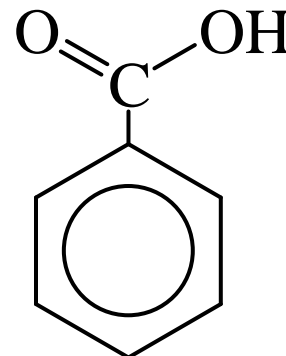
benzaldehyde



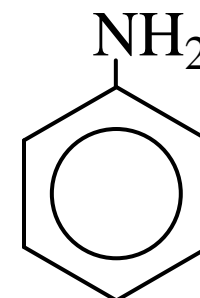
styrene



phenol



benzoic acid



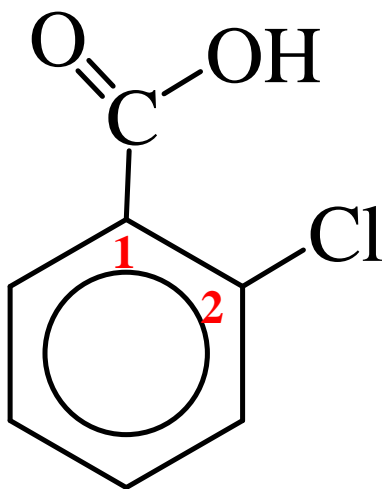
aniline

➤ When additional substituents are added to these compounds, they are named as derivatives of these compounds, locator numbers start with the substituent imparting the special name.

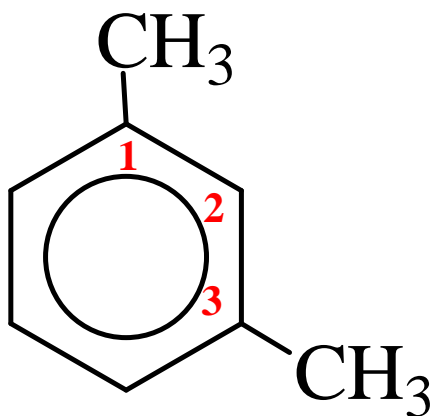
Naming of Benzene Derivatives

When two substituents occur on a benzene ring, three isomers are possible; they may be located by

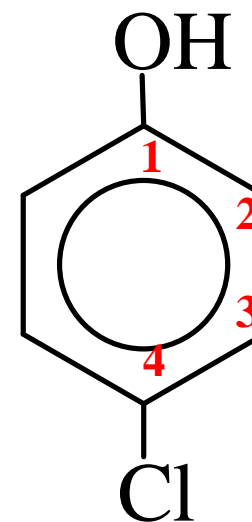
- numbering the atoms of the ring or
- using the locators ortho (o), meta (m), and para (p)



2-chlorobenzoic acid
o-chlorobenzoic acid



1,3-dimethylbenzene
m-xylene

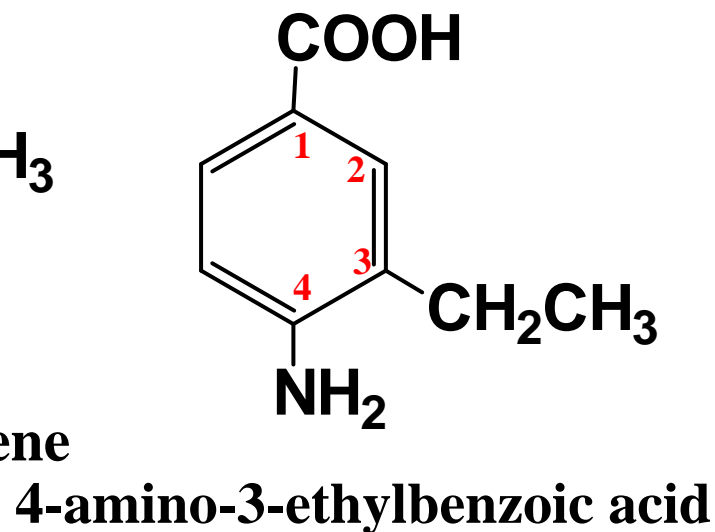
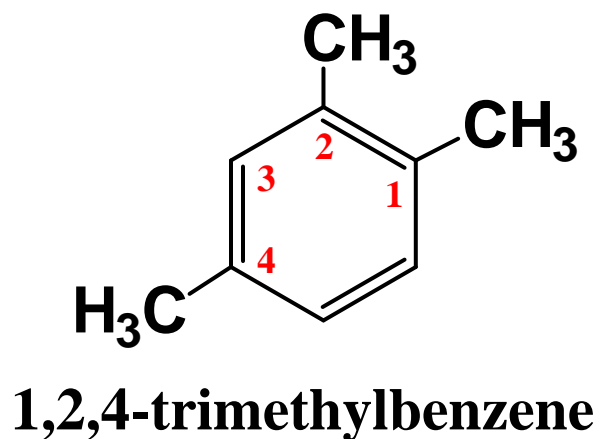
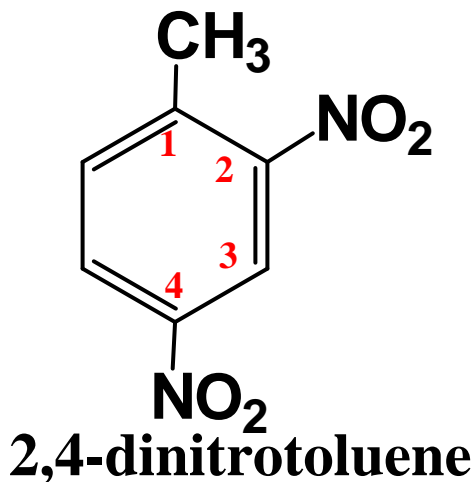


4-chlorophenol
p-chlorophenol

Naming of Benzene Derivatives

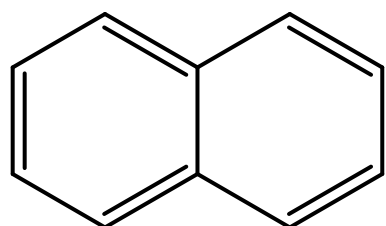
For three or more substituents:

- **If one of the substituents imparts a special name, name the molecule as a derivative of that parent, numbering from that substituent.**
- **If none of the substituents imparts a special name, number the substituents to give the smallest set of numbers, and list them in alphabetical order before the ending "benzene"**

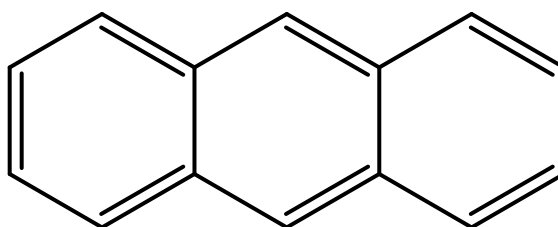


Polynuclear Aromatic Hydrocarbons

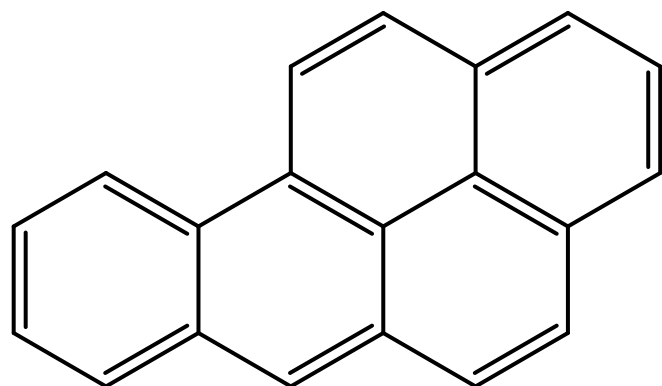
An aromatic hydrocarbon that contains two or more benzene rings, with each pair of rings sharing two adjacent carbon atoms, such as:



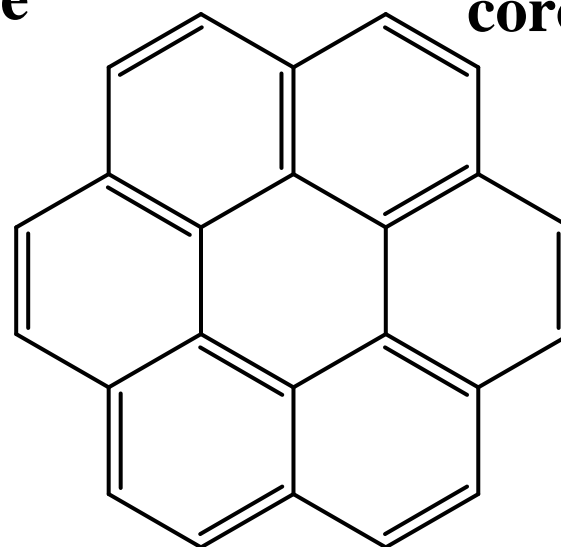
naphthalene



anthracene



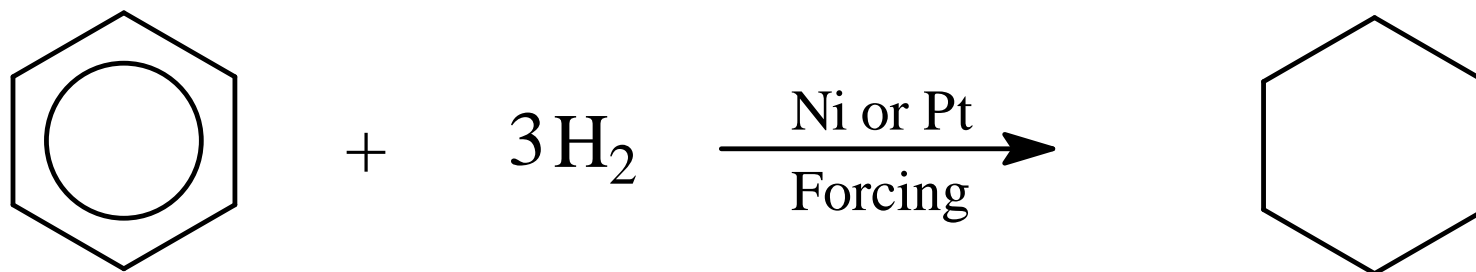
benzo[a]pyrene



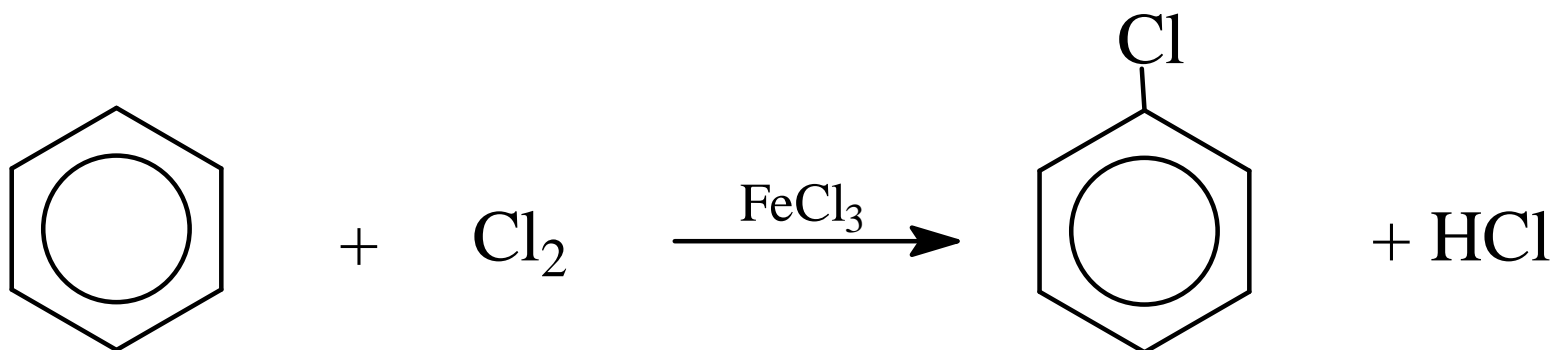
coronene

Reactions of Benzene

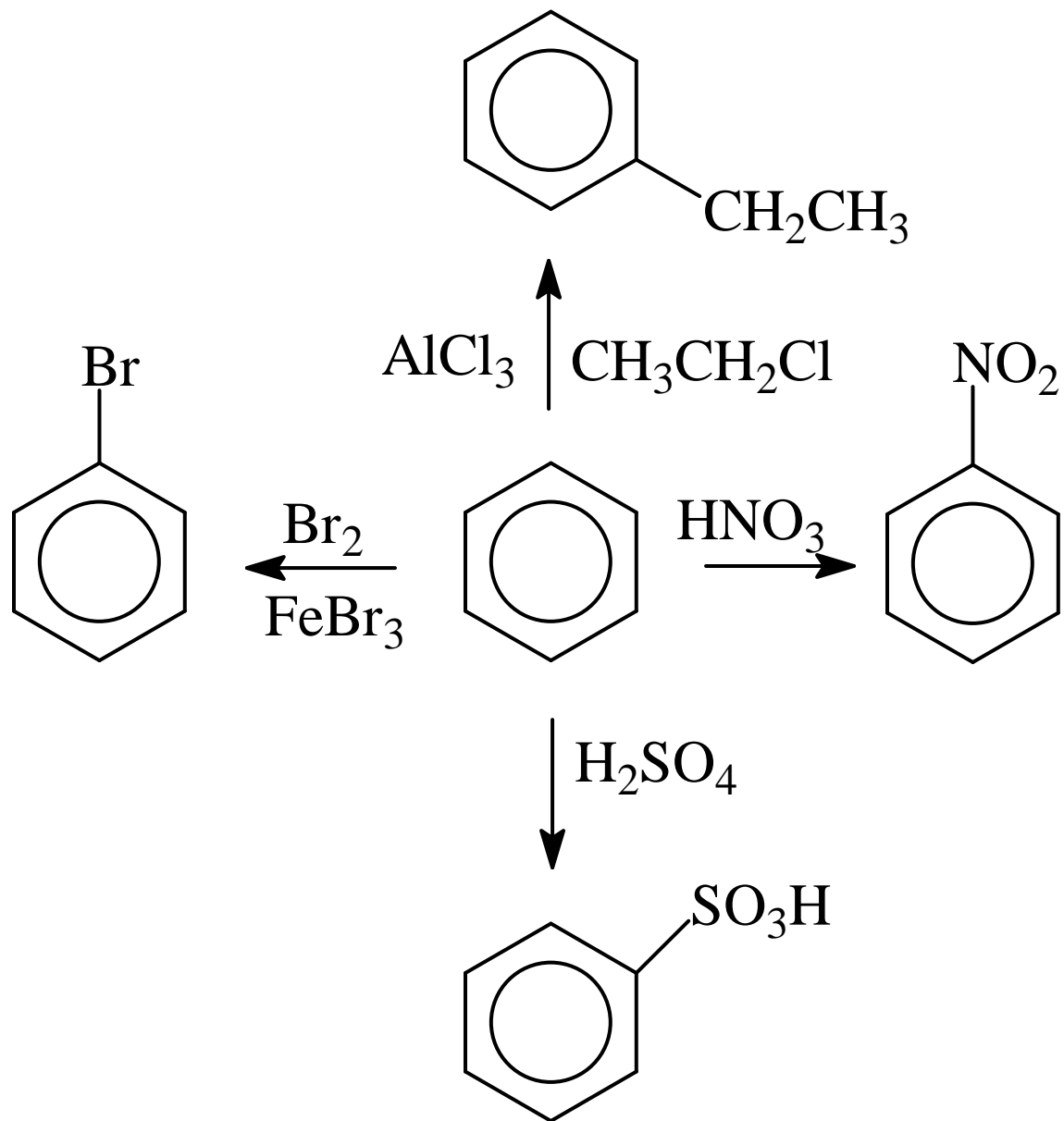
Benzene Undergoes Addition Only Under Forcing Conditions



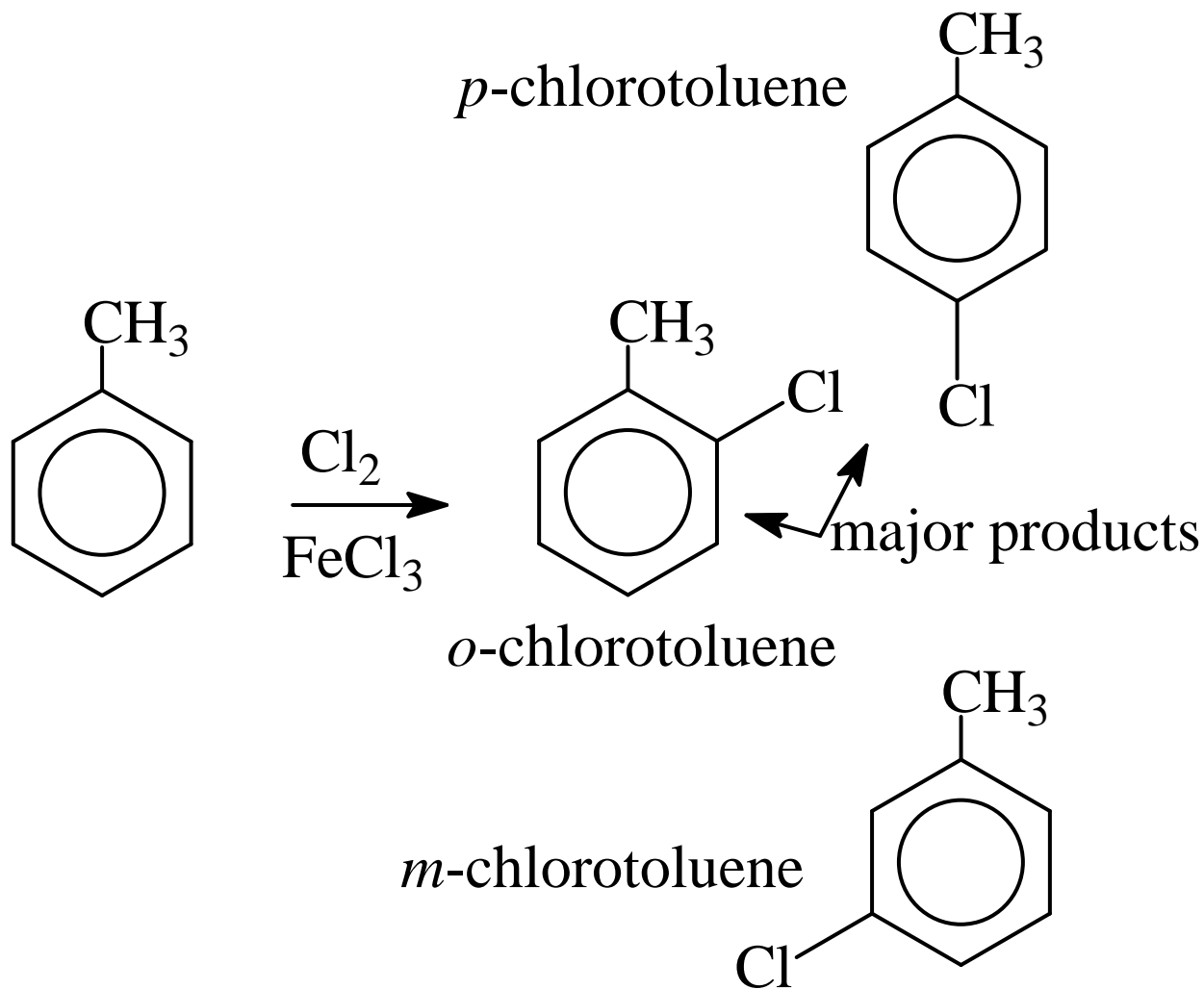
It Mostly Undergoes Substitution



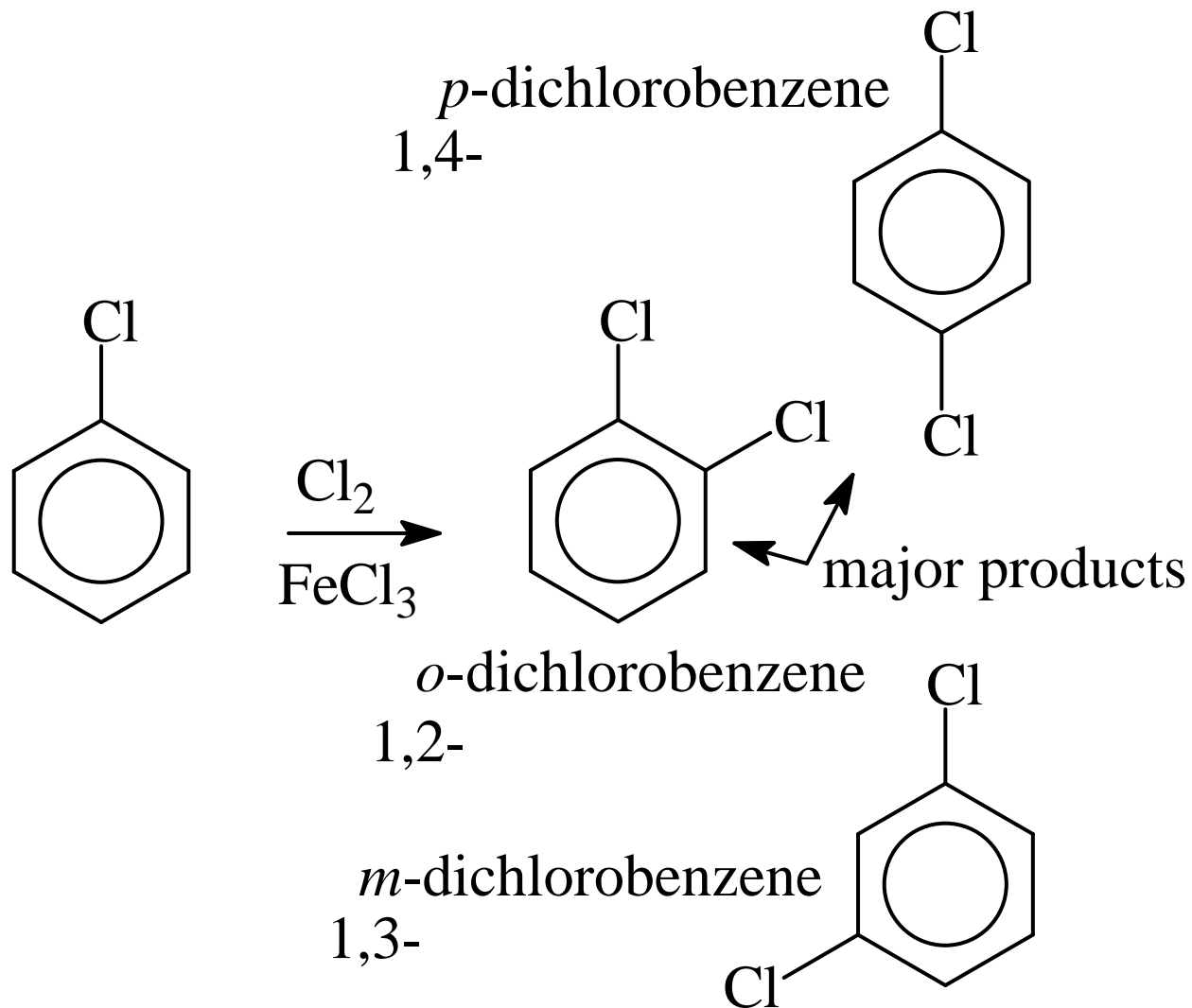
Other Substitution Reactions of Benzene



Substitution on Toluene

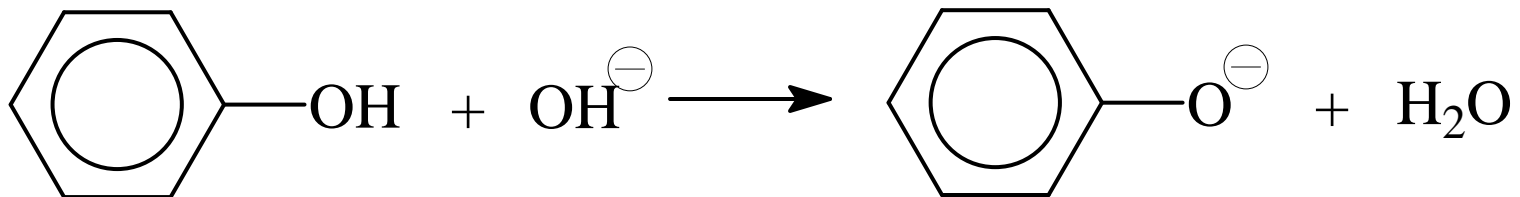


Substitution on Chlorobenzene



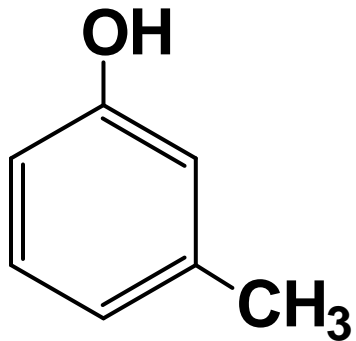
PHENOLS

- Phenols – The *hydroxy* group must be bonded directly to the benzene ring.
- Phenols are weakly acidic and ionize in basic solution forming water soluble phenoxide anions.

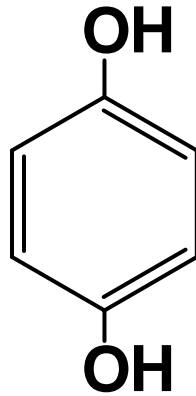


- Phenols are easily oxidized, the ring itself is attacked and phenols become dark on exposure to air.
- The antioxidant properties found in phenols are useful in food preservatives and in biological repair mechanisms.

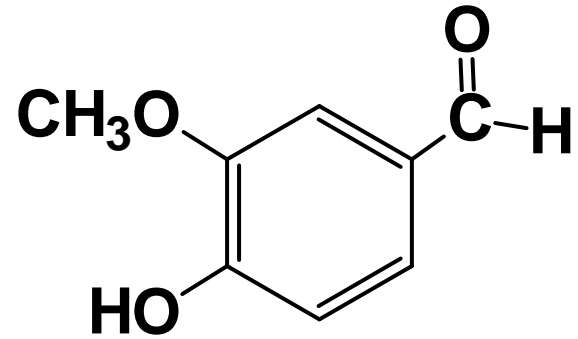
Some Common Phenols



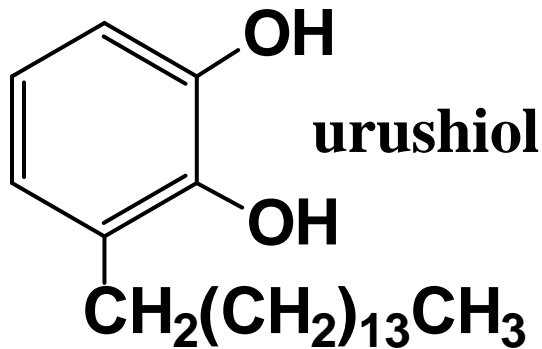
m-cresol
3-methylphenol



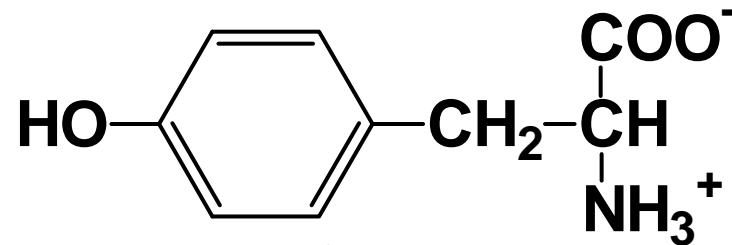
hydroquinone
1,4-benzenediol



vanillin
4-hydroxy-3-methoxy-
benzaldehyde

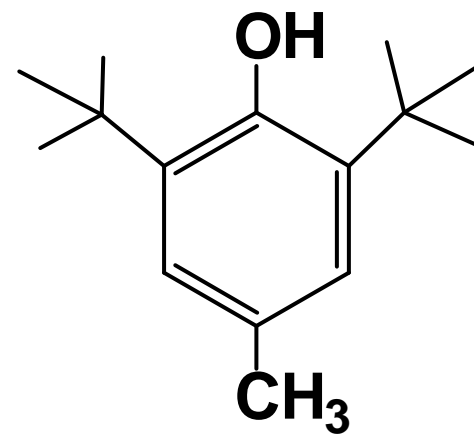
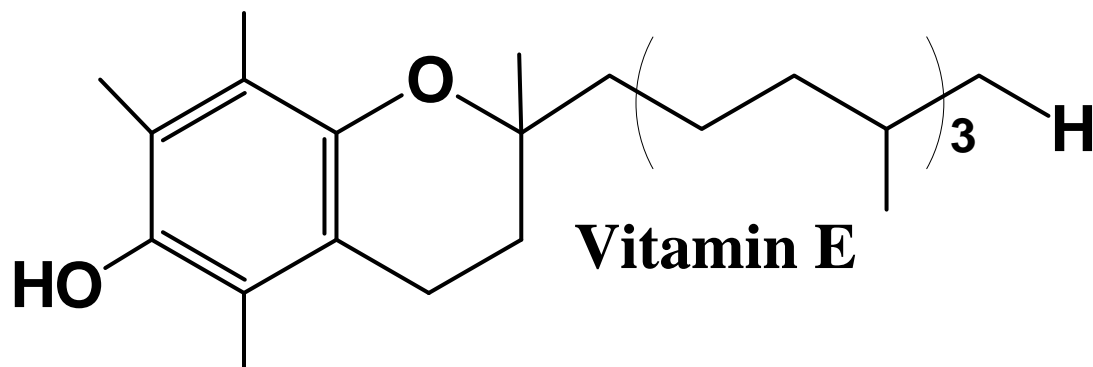


urushiol



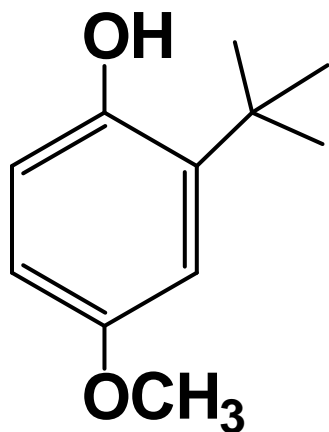
tyrosine

Some Common Antioxidant Phenols



2,6-di-*tert*-butyl-4-methylphenol

Butylatedhydroxytoluene (BHT)



2-*tert*-butyl-4-methoxyphenol

Butylatedhydroxyanisole (BHA)