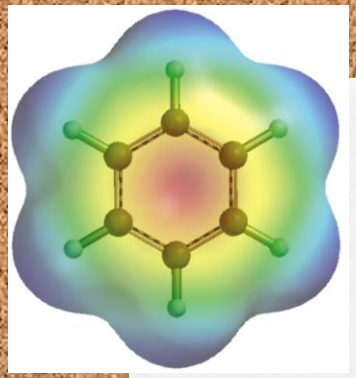
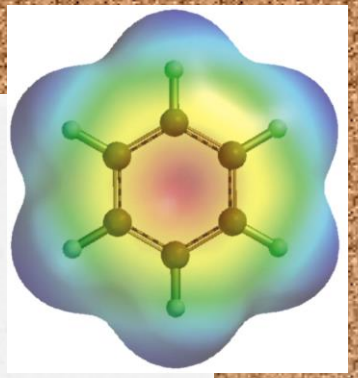
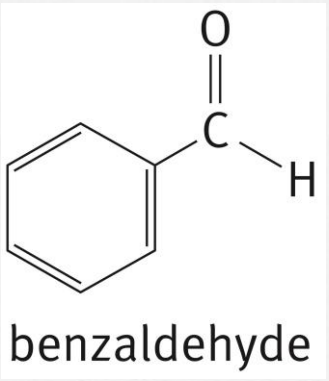


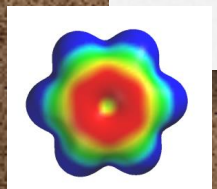


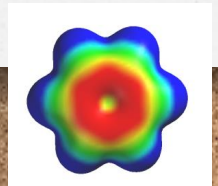
Chapter 4: Aromatic Compounds

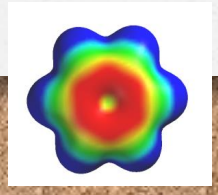


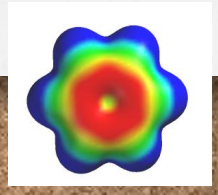
benzaldehyde

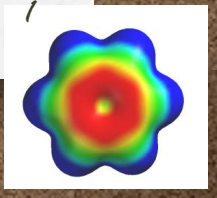
Bitter almonds are the source of the aromatic compound benzaldehyde











Some Facts About Benzene

1-Reacts mainly by substitution:

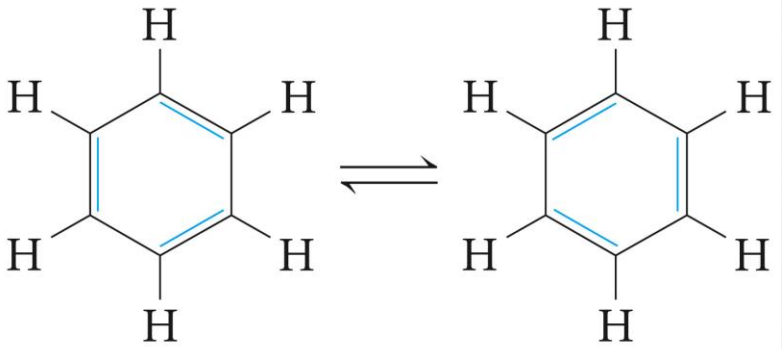
$$C_6H_6 + Br_2 \xrightarrow[\text{catalyst}]{FeBr_3} C_6H_5Br + HBr$$

benzene → bromobenzene

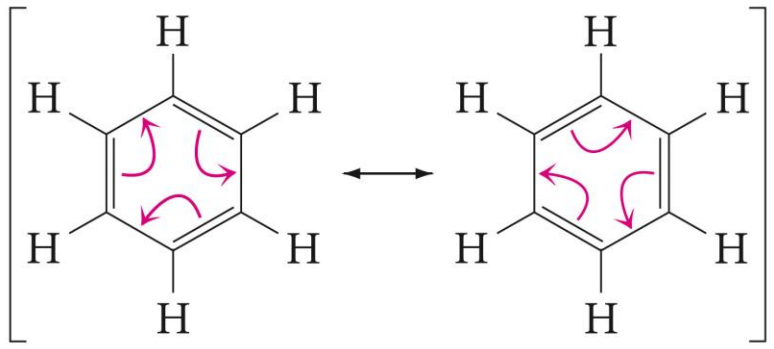
$$C_6H_6 + Cl_2 \xrightarrow[\text{catalyst}]{FeCl_3} C_6H_5Cl + HCl$$

benzene → chlorobenzene

2-Resonance hybrid structures of Benzene:

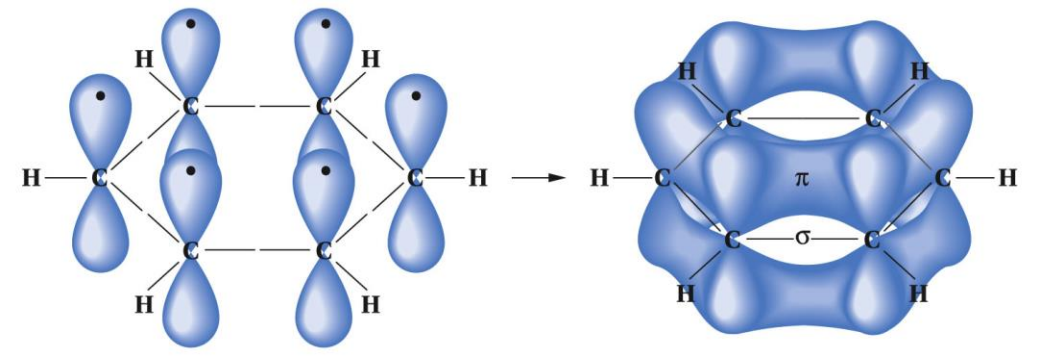


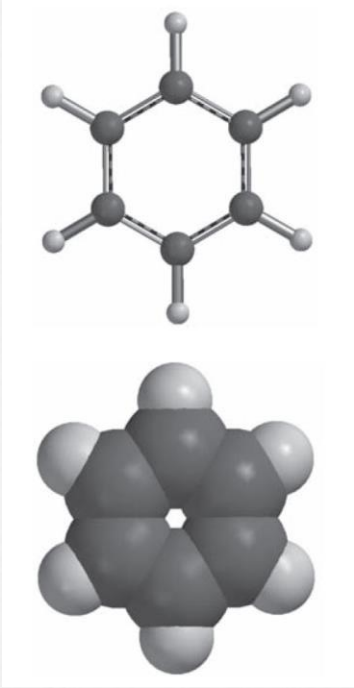
the Kekulé structures for benzene



Benzene is a resonance hybrid of these two contributing structures.

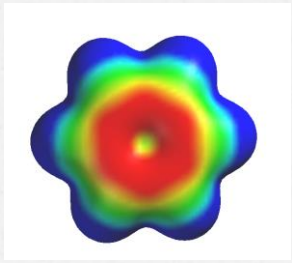
3-The Orbital Model for Benzene:





Symmetrical Hexagon

4-Symbols for Benzene:



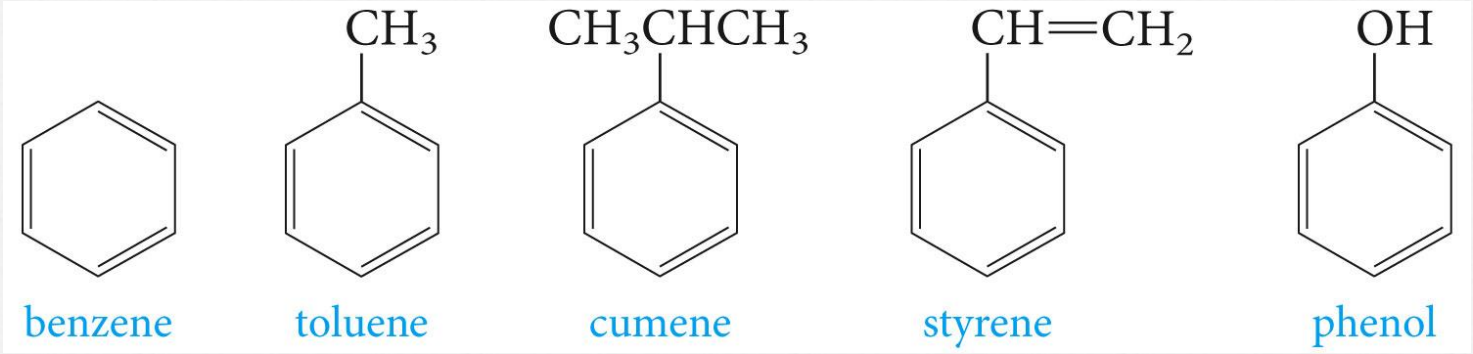
5-Benzene has stabilization resonance energy:

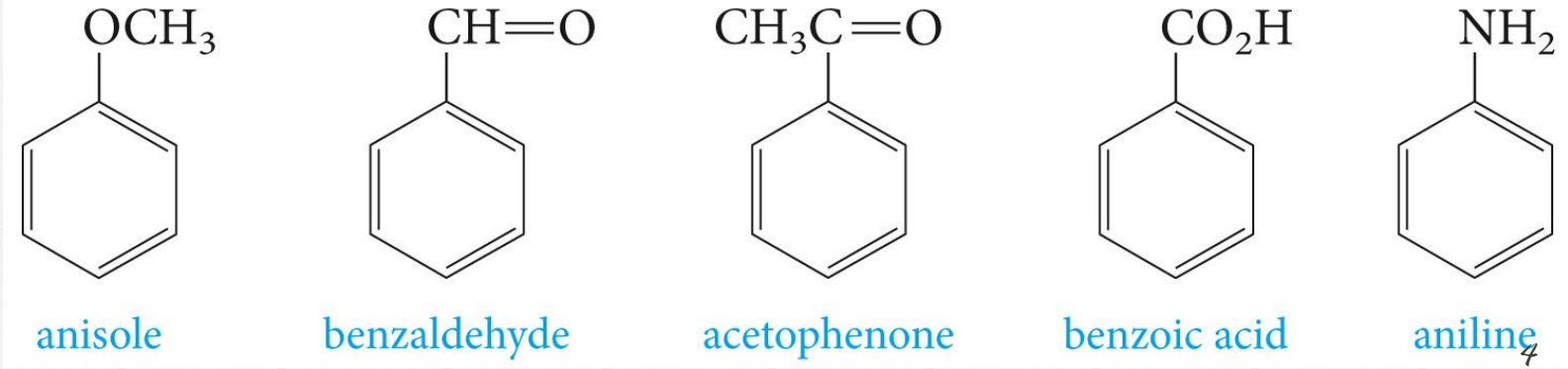
(R.E)benzene = 36 K cal/mol

Nomenclature of Aromatic Compounds

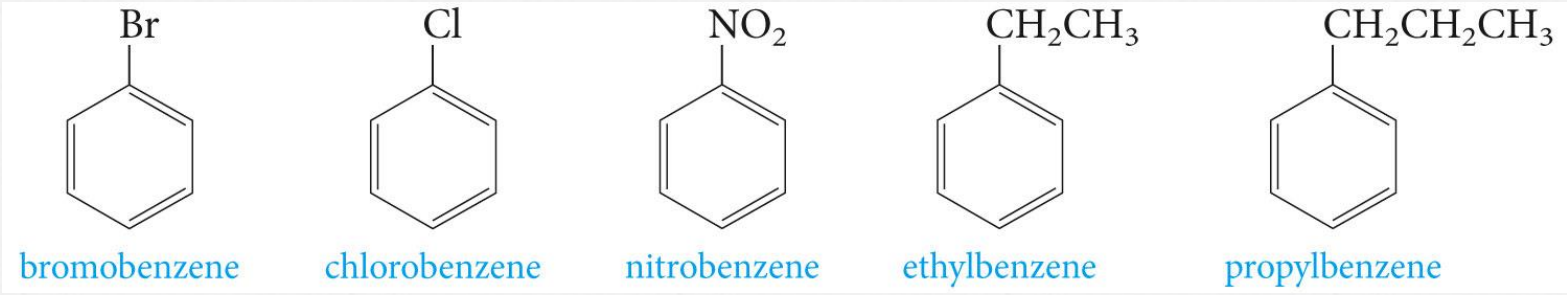
1-Monosubstituted benzenes

A-Monosubstituted benzenes with common names:



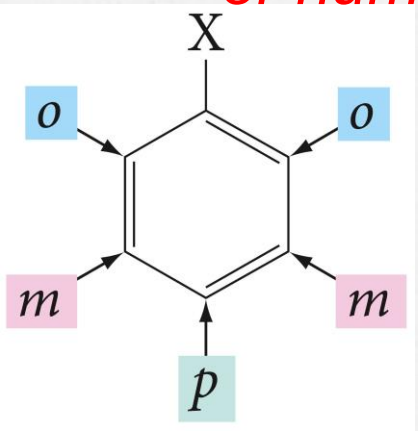


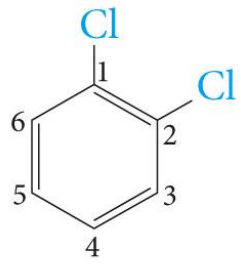
B-Monosubstituted benzenes that do not have common names



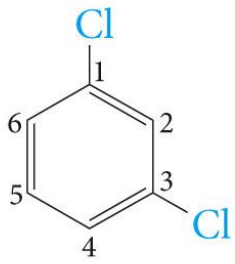
2- Disubstitued Benzene:

use prefixes *ortho-* (o-), *meta-* (*m*-), and *para-* (*p*-), *or numbers*

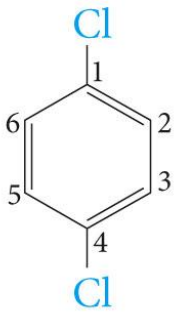




ortho-dichloro-benzene



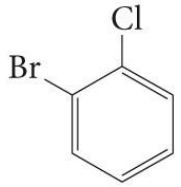
meta-dichloro-benzene



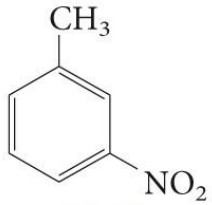
para-dichloro-benzene

para-xylene**

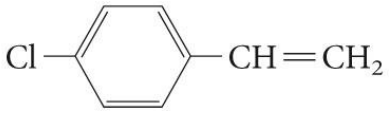
para-chlorobenzene-sulfonic acid



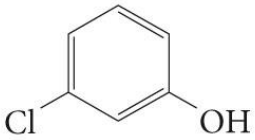
o-bromochlorobenzene
(note alphabetical order)



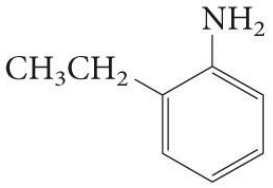
m-nitrotoluene



p-chlorostyrene



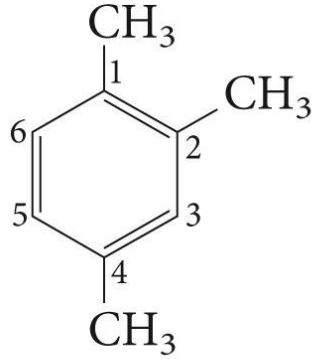
m-chlorophenol



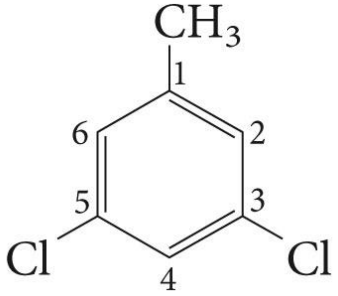
o-ethylaniline

3- Polysubstituted Benzene:

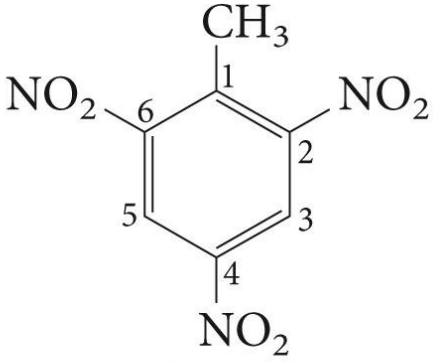
Their positions are designated by numbering the ring.



1,2,4-tri-
methylbenzene

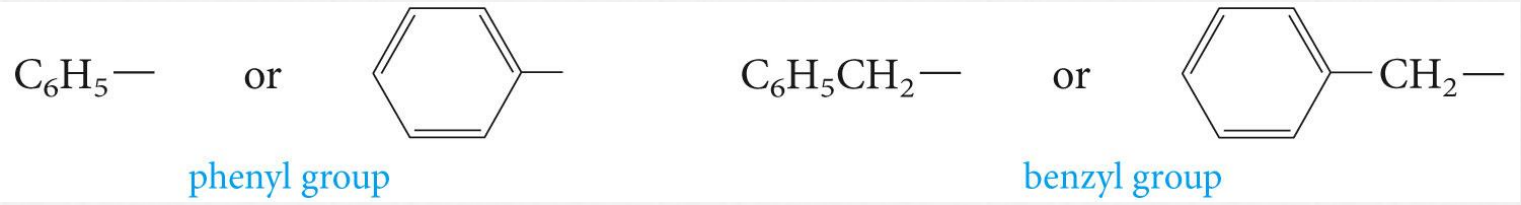


3,5-dichlorotoluene

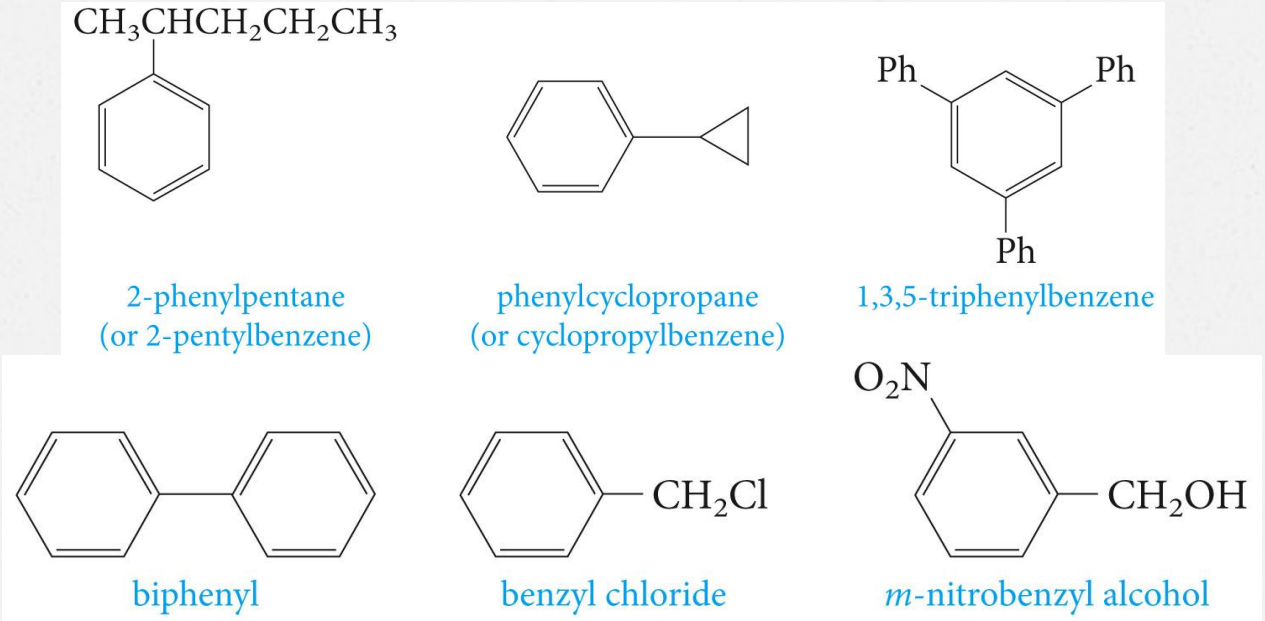


2,4,6-trinitrotoluene
(TNT)

Aromatic hydrocarbons, as a class called Arenes (Ar) the aryl groups are therefore aromatic substituents.

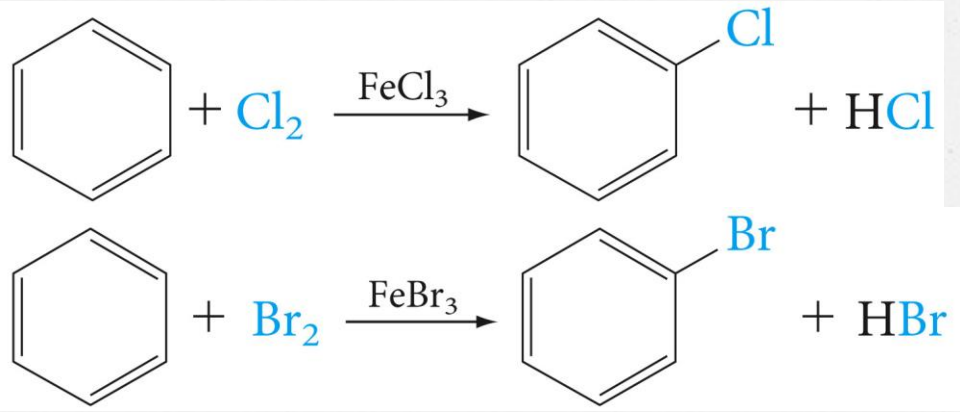


The symbol Ph is sometimes used as an abbreviation for phenyl group

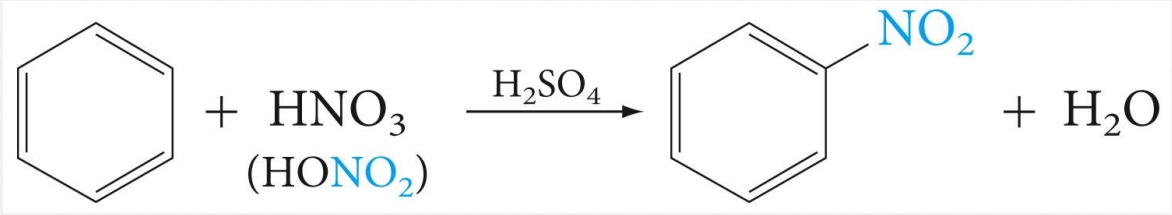


Electrophilic Aromatic Substitution

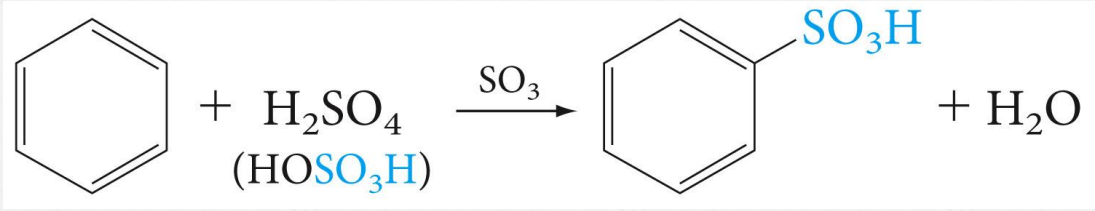
1-Halogenation: Chlorination and Bromination



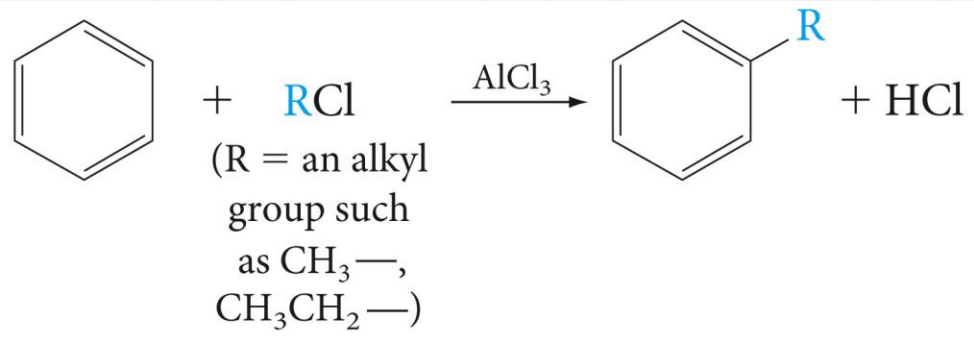
2-Nitration:

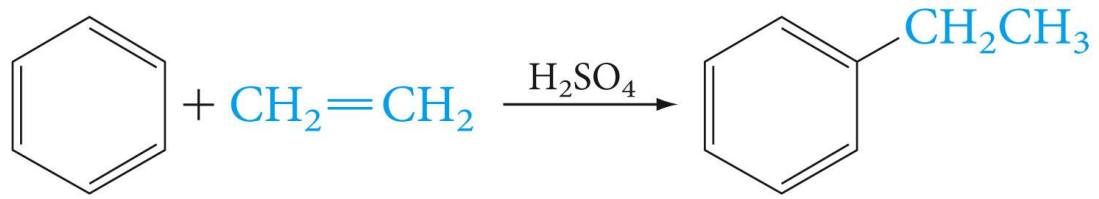


3-Sulfonation:

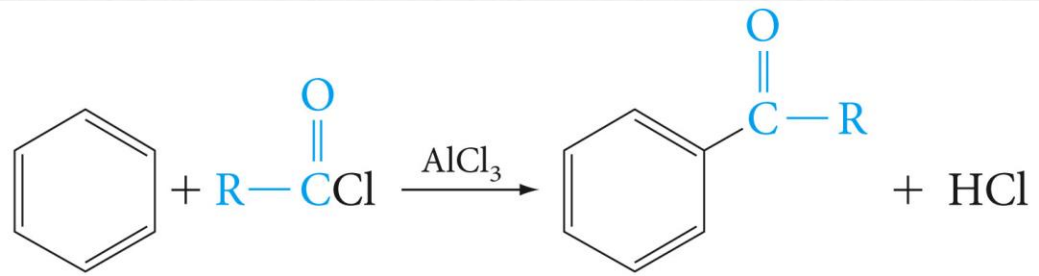


4-Friedel – Craft`s Alkylation:

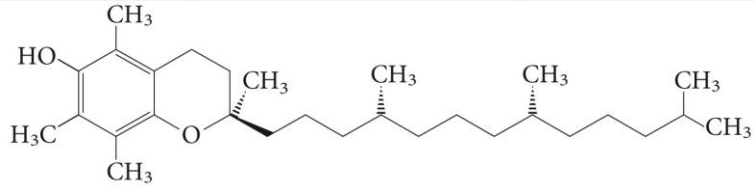


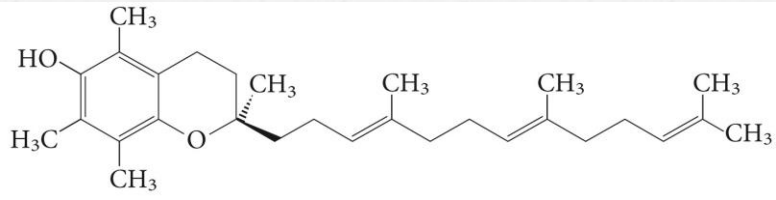


5-Friedel – Craft`s Acylation:

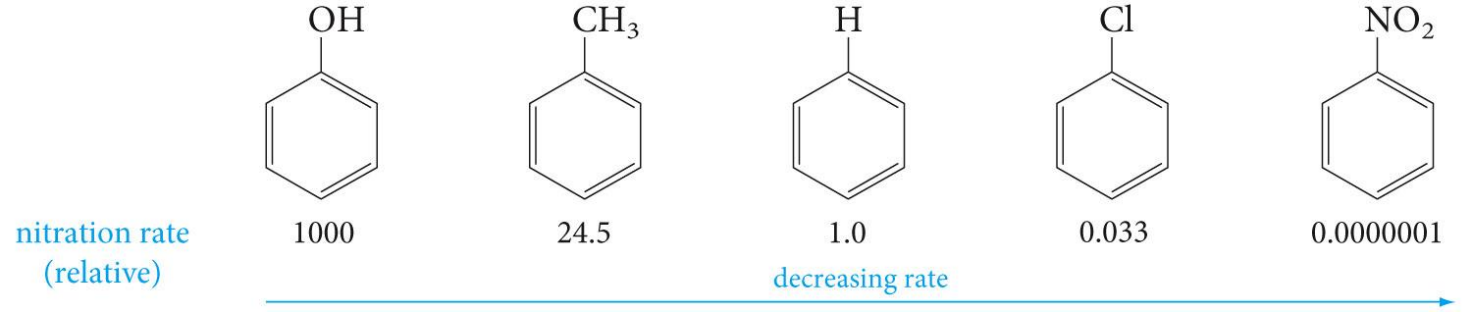


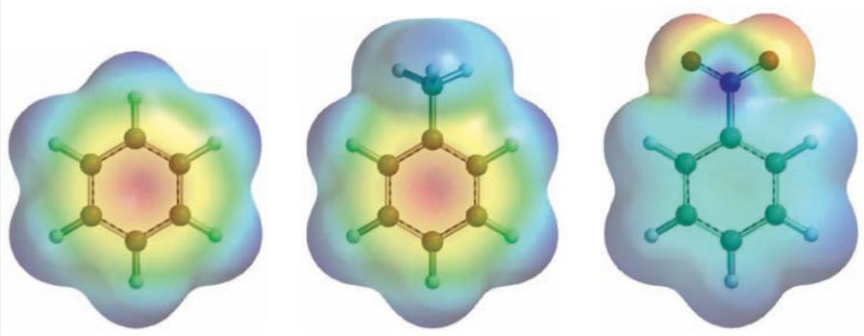
Vitamin E- (TCP and TCT)





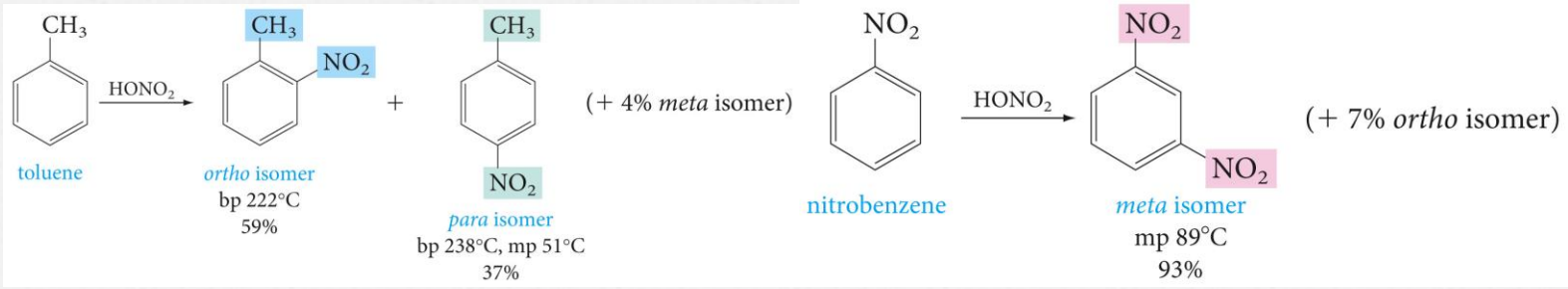
Ring-Activating and ring-Deactivating Substituents



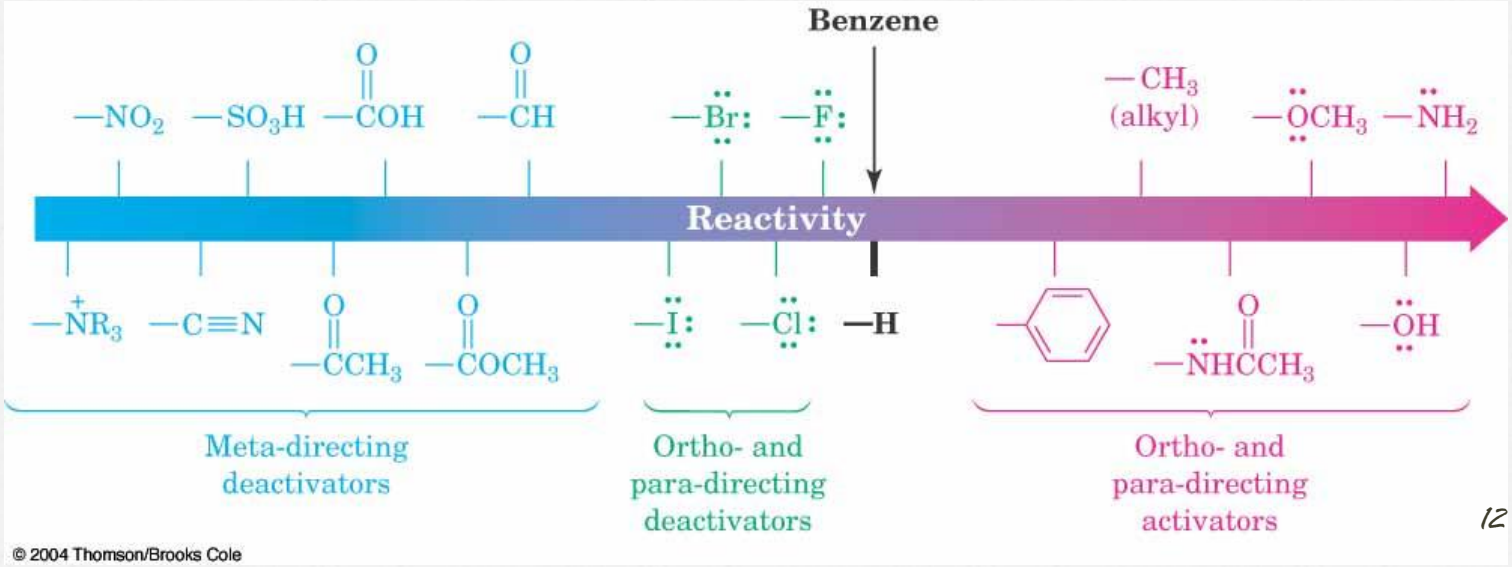


Benzene Activating Substituents Deactivating Substituents

Ortho, *Para*-Directing and *Meta*-Directing Groups

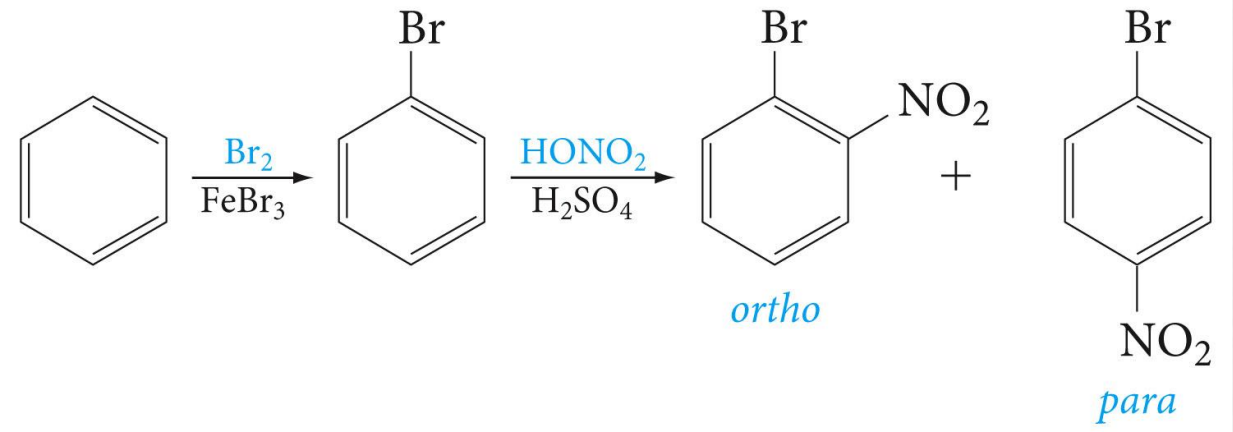


Reactivity and Orientation of substituents on Benzene

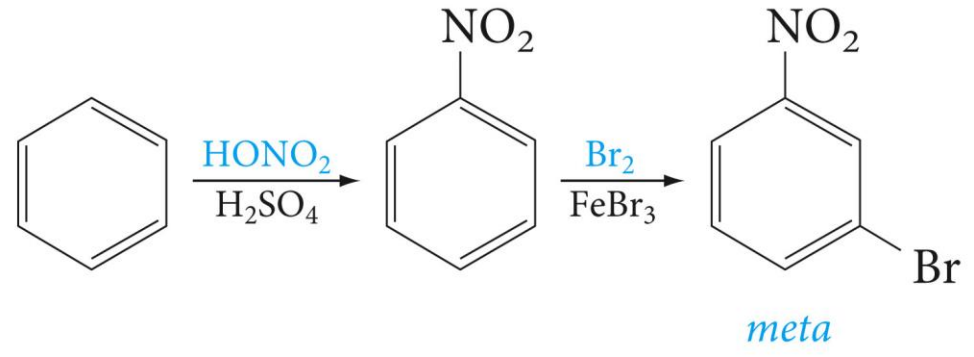


Importance of Directing Effects in Synthesis

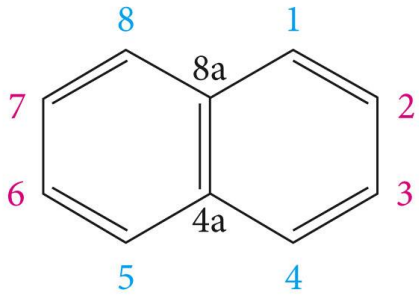
Synthesis of o- and p-Bromonitrobenzene



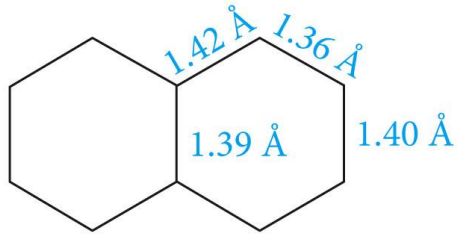
Synthesis of m-Bromonitrobenzene



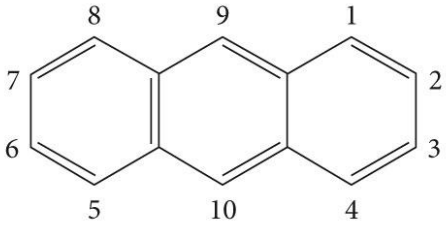
Fused Polycyclic Aromatic Hydrocarbons



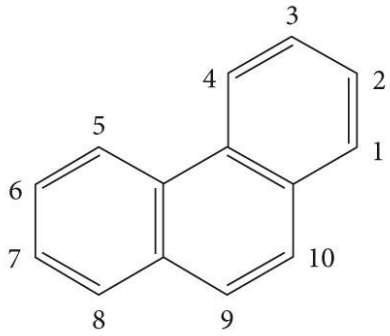
naphthalene
mp 80°C



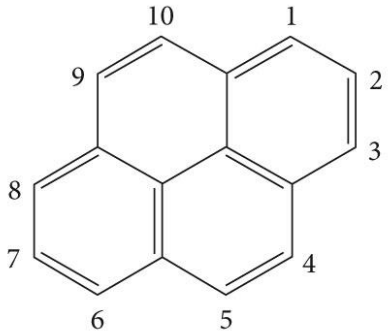
bond lengths in naphthalene



anthracene
mp 217°C



phenanthrene
mp 98°C

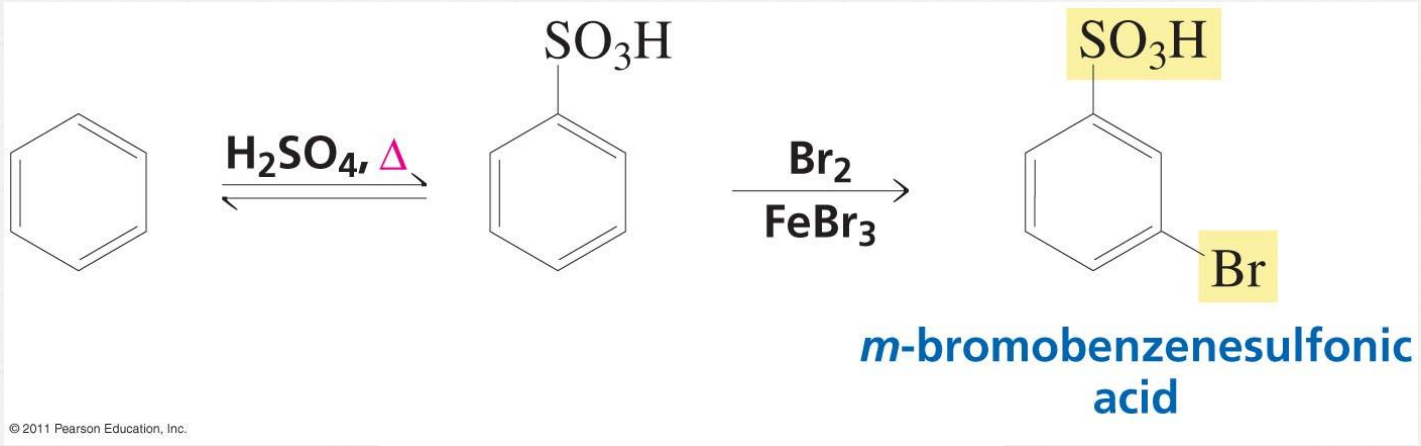


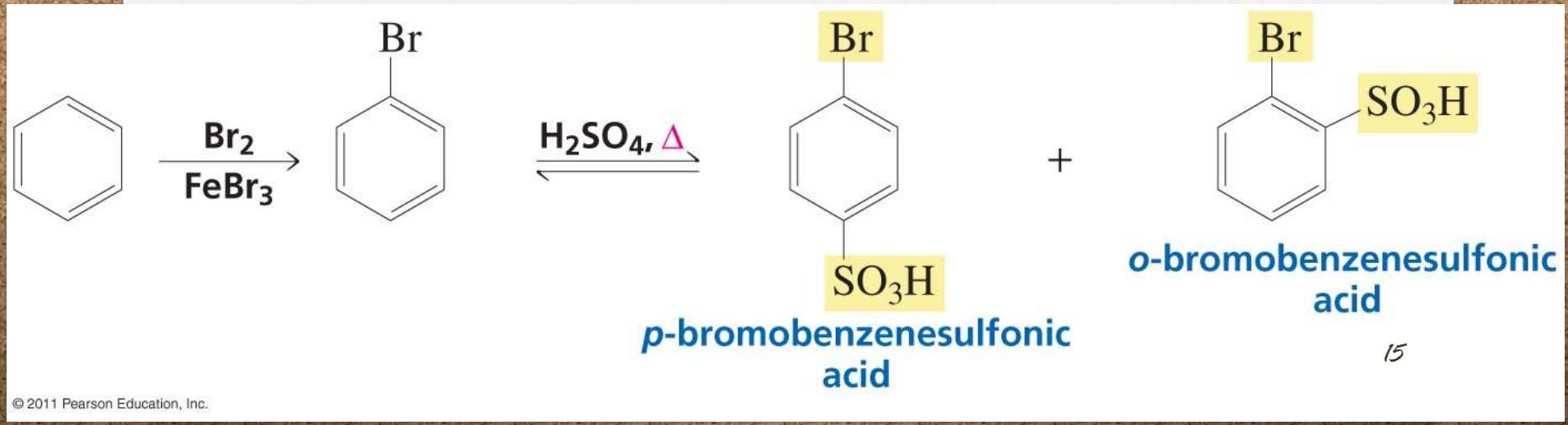
pyrene
mp 156°C

Fused polycyclic aromatic hydrocarbons are Carcinogenic compounds

Q,,, Devise a synthesis for each of the following, starting with benzene:

a. *m-bromobenzenesulfonic acid* *b. p-bromobenzenesulfonic acid*





practice

4.20 Write structural formulas for the following compounds:

a. *p*-chlorostyrene
b. 2,3,5-trifluoroaniline
c. *o*-chlorophenol
d. allylbenzene
e. *p*-isopropylphenol
f. *p*-dimethylbenzene

4.37 Predict whether the following substituents on the benzene ring are likely to be *ortho,para* directing or *meta* directing and whether they are likely to be ring activating or ring deactivating:

a. $-\overset{+}{N}H(CH_3)_2$
b. $-C(=O)-OCH_3$
c. $-SCH_3$
d. $-N=O$
e. $-C\equiv N$
f. $-Br$
g. $-OCH(CH_3)_2$

4.43 For the compounds named below,

(1) draw the structure of each compound.
(2) using benzene or toluene as the only aromatic starting material, devise a synthesis of each compound.

a. *p*-bromotoluene
b. *p*-nitroethylbenzene
c. *p*-bromonitrobenzene
d. *p*-isopropylbenzenesulfonic acid
e. *tert*-butylcyclohexane

THE END OF CHAPTER 4

Aromatic Compounds

BEST WISHES & GOOD LUCK