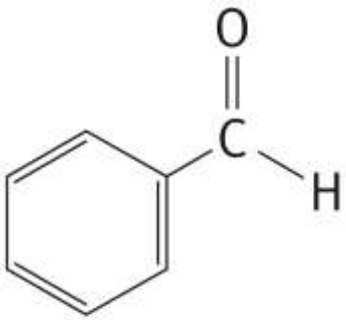
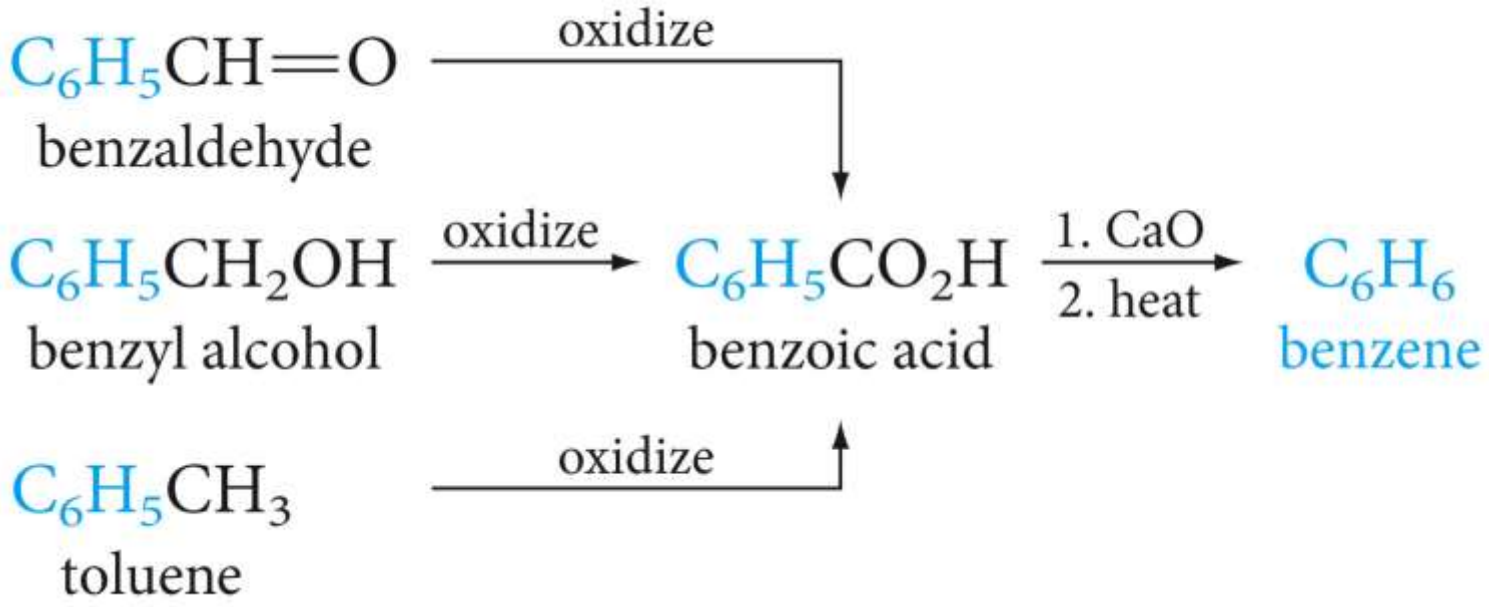
Chapter 4: Aromatic Compounds



benzaldehyde

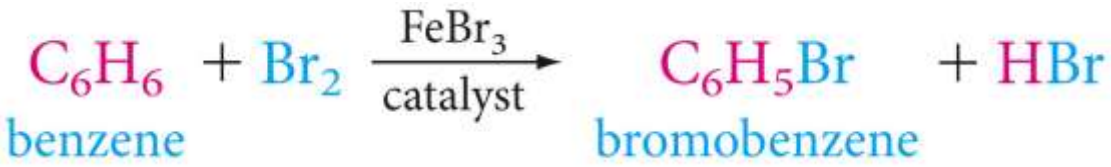
Bitter almonds are the source of the aromatic compound benzaldehyde

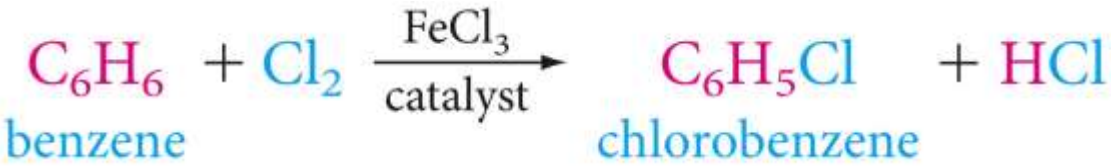
Sources of Benzene



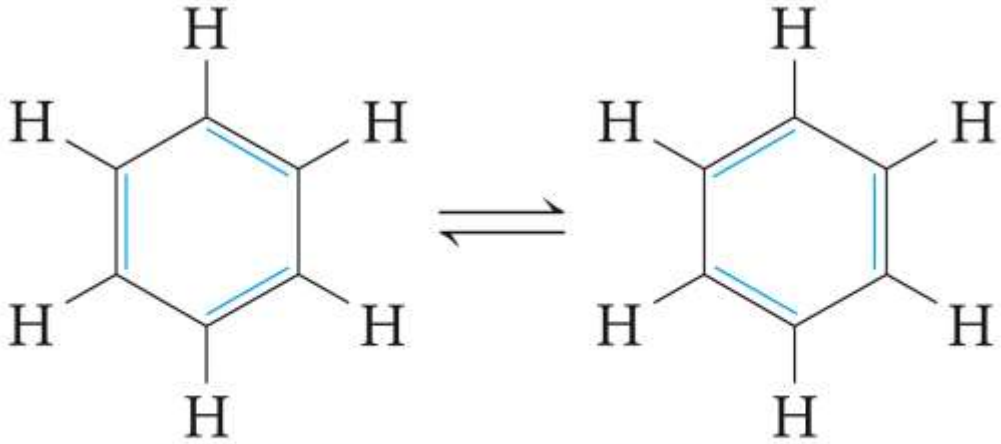
Some Facts About Benzene

Reacts mainly by substitution

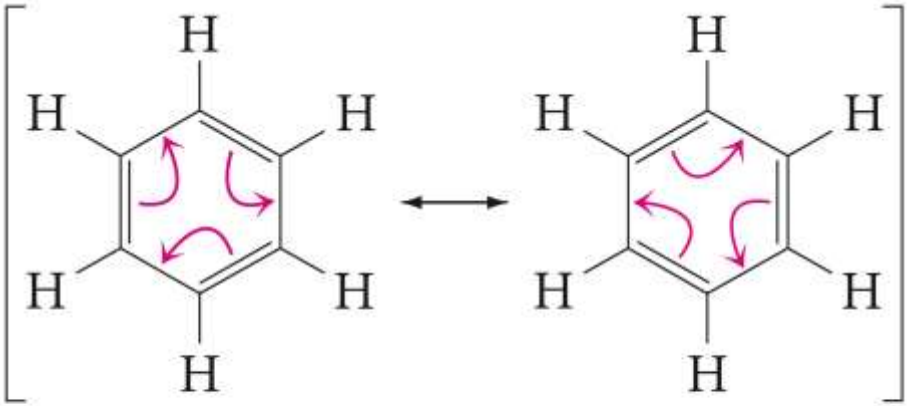




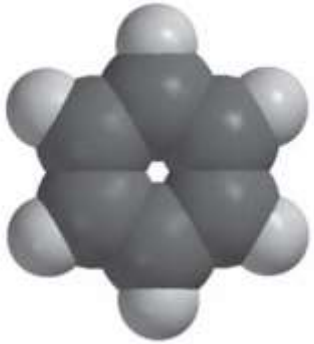
Friedrich August Kekule'



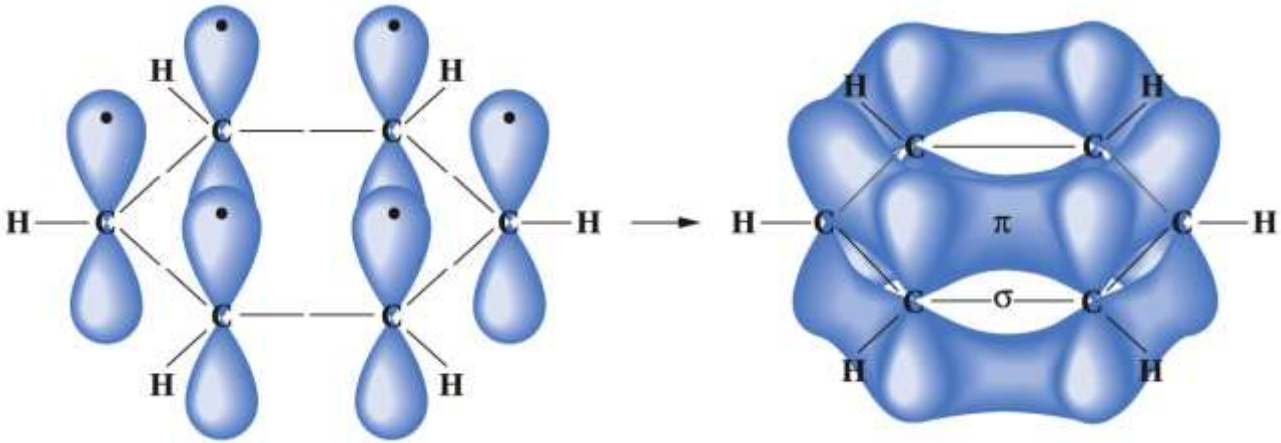
the Kekulé structures for benzene



Benzene is a resonance hybrid of these two contributing structures.



The Orbital Model for Benzene



Symbols for Benzene

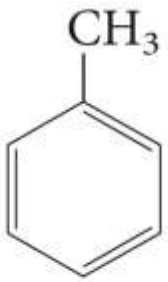
Kekulé

delocalized pi cloud

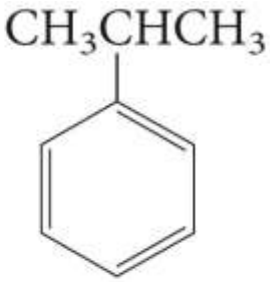
Nomenclature of Aromatic Compounds

Monosubstituted benzenes with common names

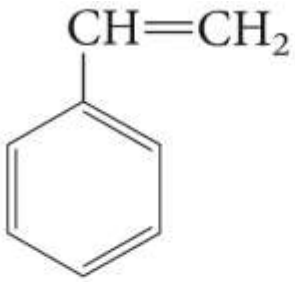
benzene



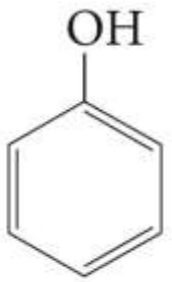
toluene



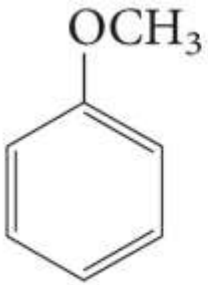
cumene



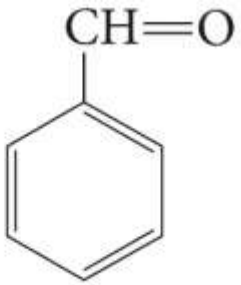
styrene



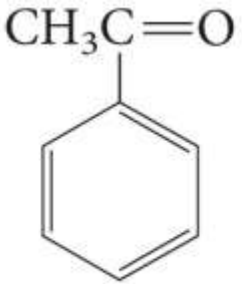
phenol



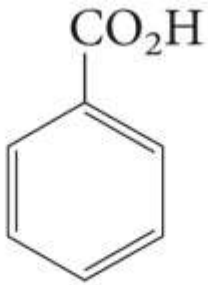
anisole



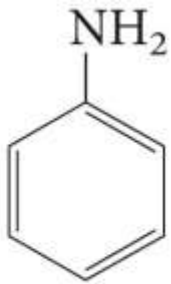
benzaldehyde



acetophenone

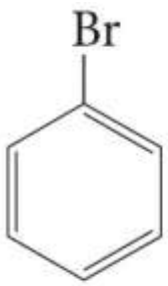


benzoic acid

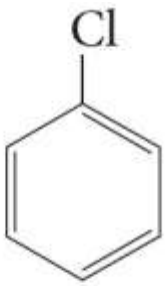


aniline

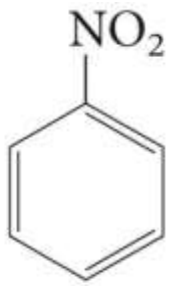
Monosubstituted benzenes that do not have common names



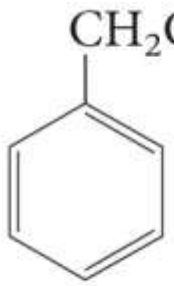
bromobenzene



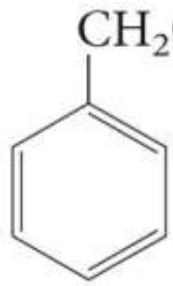
chlorobenzene



nitrobenzene

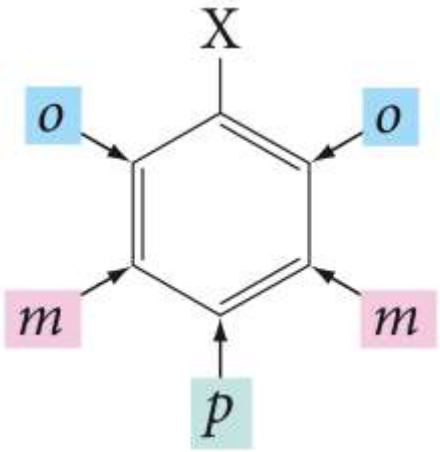


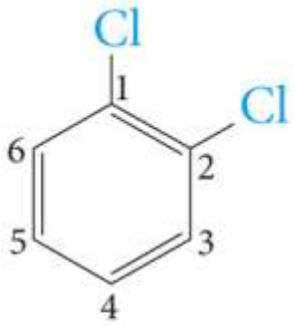
ethylbenzene



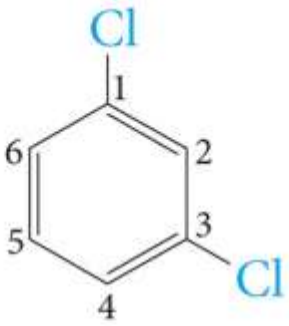
propylbenzene

When two substituents are present, we use prefixes *ortho*-, *meta*-, and *para*-, usually abbreviated as o-, m-, and p-, respectively.

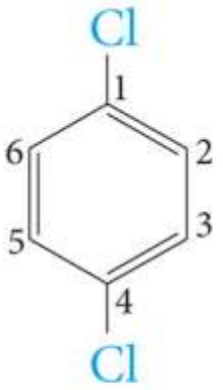




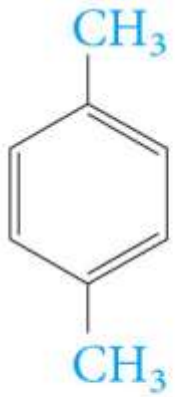
ortho-dichloro-benzene



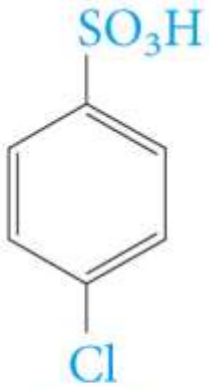
meta-dichloro-benzene



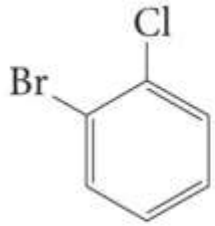
para-dichloro-benzene



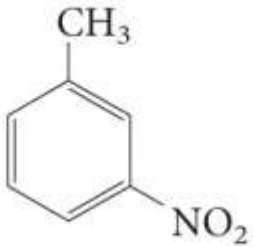
para-xylene**



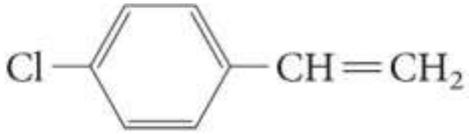
para-chlorobenzene-sulfonic acid



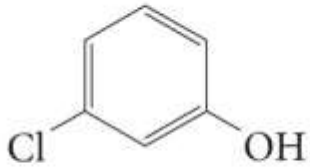
o-bromochlorobenzene
(note alphabetical order)



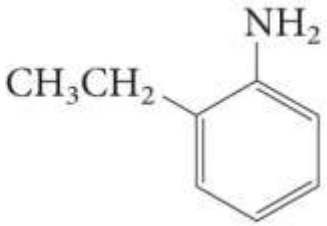
m-nitrotoluene



p-chlorostyrene

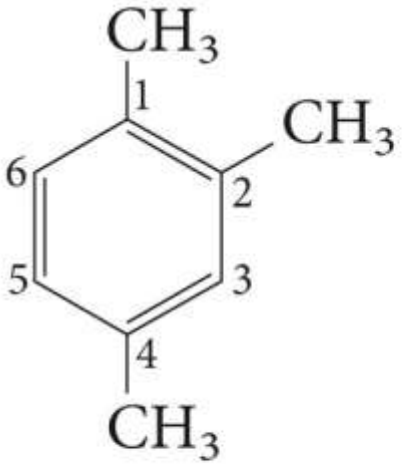


m-chlorophenol

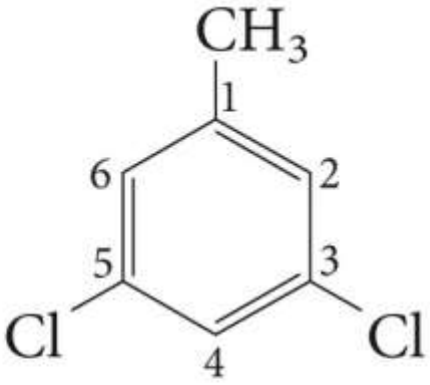


o-ethylaniline

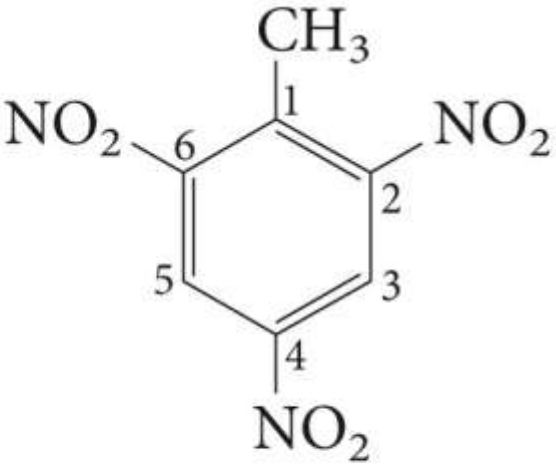
For more than two substituents, their positions are designated by numbering the ring.



1,2,4-tri-methylbenzene

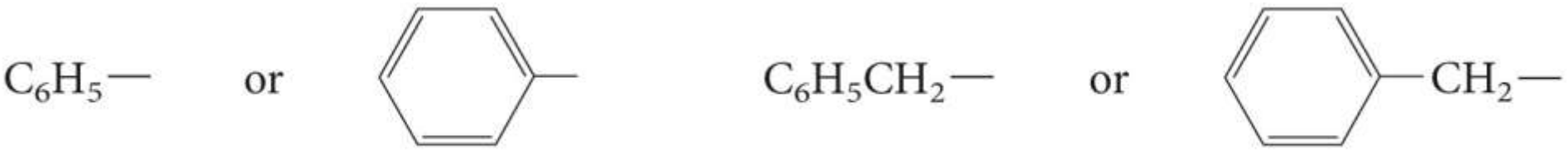


3,5-dichlorotoluene



2,4,6-trinitrotoluene (TNT)

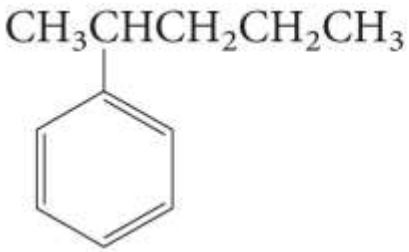
Aromatic hydrocarbons, as a class called Arenes (Ar) the aryl groups are therefore aromatic substituents.



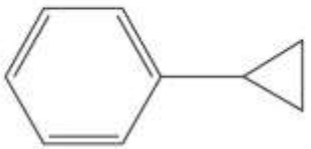
phenyl group

benzyl group

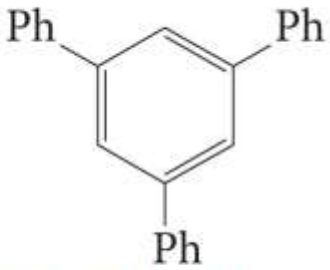
The symbol Ph is sometimes used as an abbreviation for phenyl group



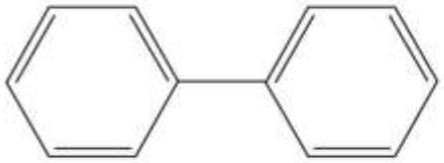
2-phenylpentane
(or 2-pentylbenzene)



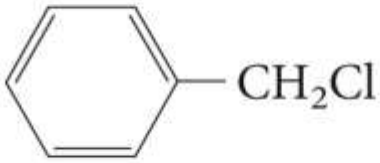
phenylcyclopropane
(or cyclopropylbenzene)



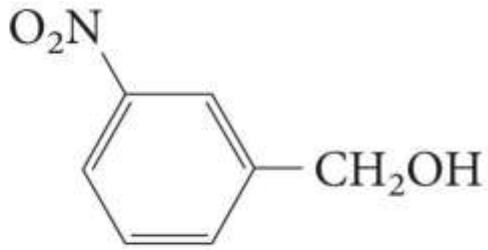
1,3,5-triphenylbenzene



biphenyl

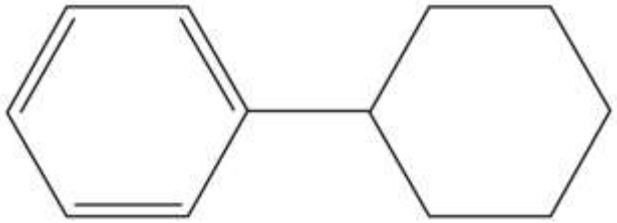


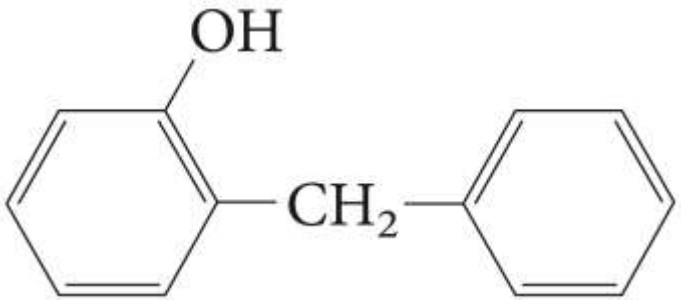
benzyl chloride



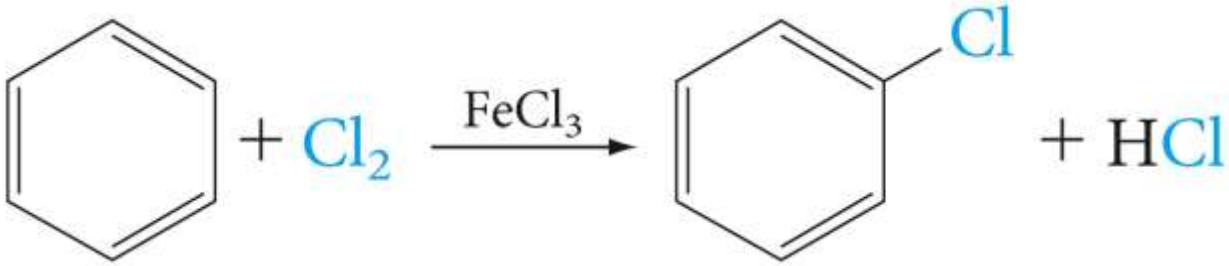
m-nitrobenzyl alcohol

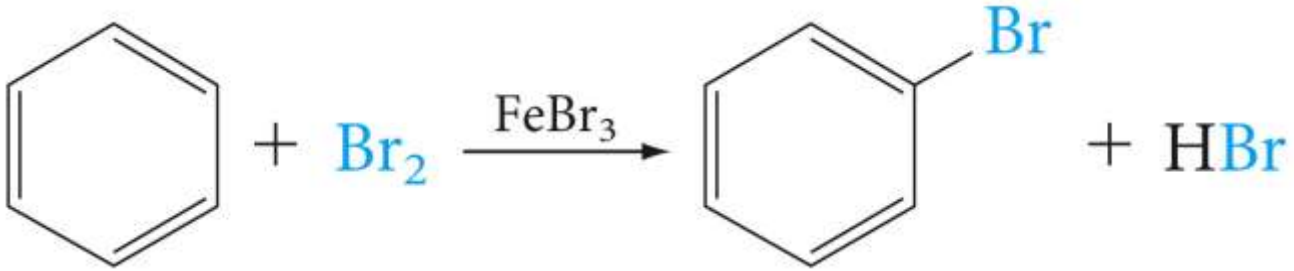
Name the following structures

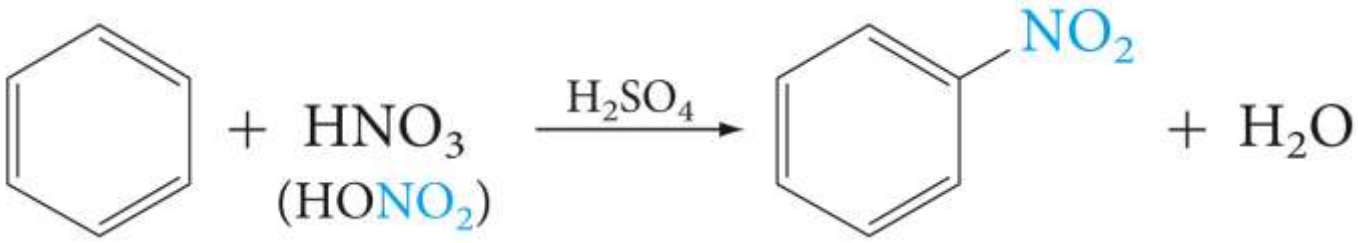


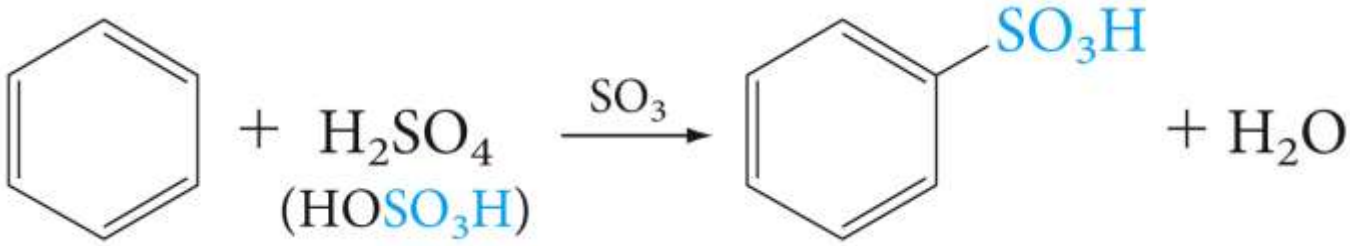


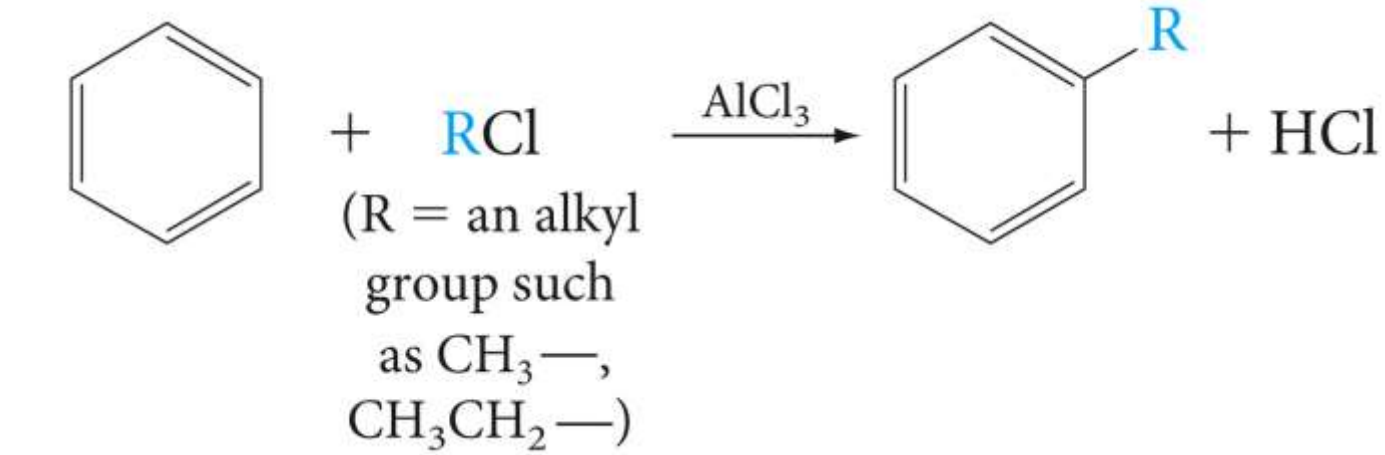
Electrophilic Aromatic Substitution

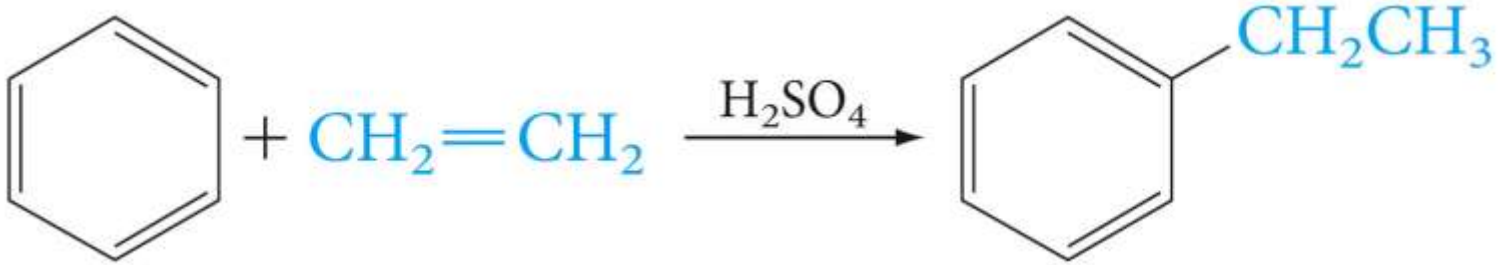


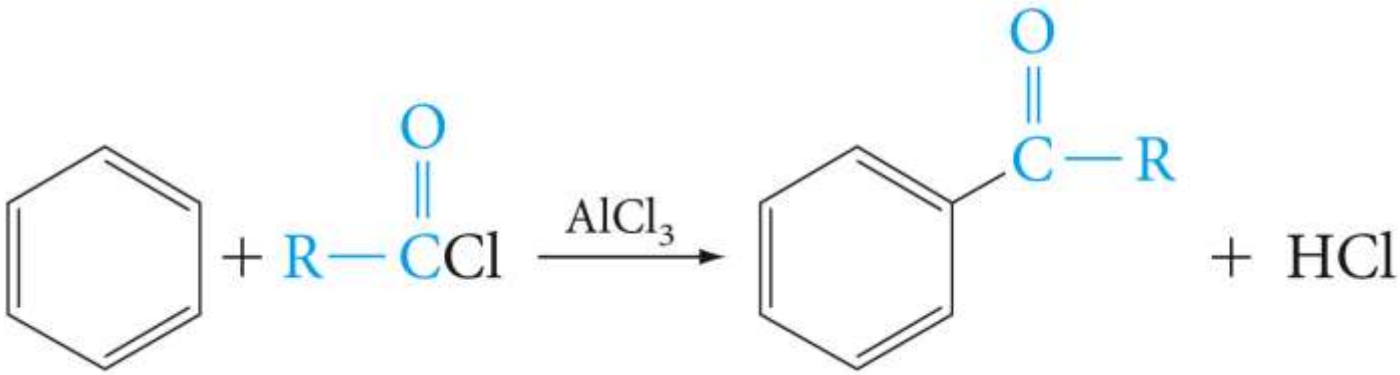



+ HNO3
(HONO2)
H2SO4
NO2
+ H2O

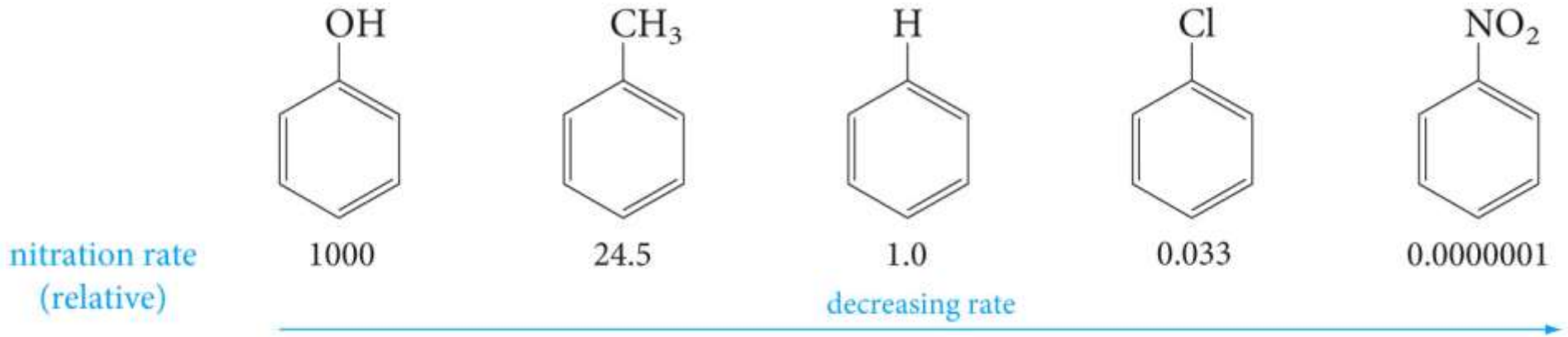

+ H2SO4
(HOSO3H)
SO3
SO3H
+ H2O

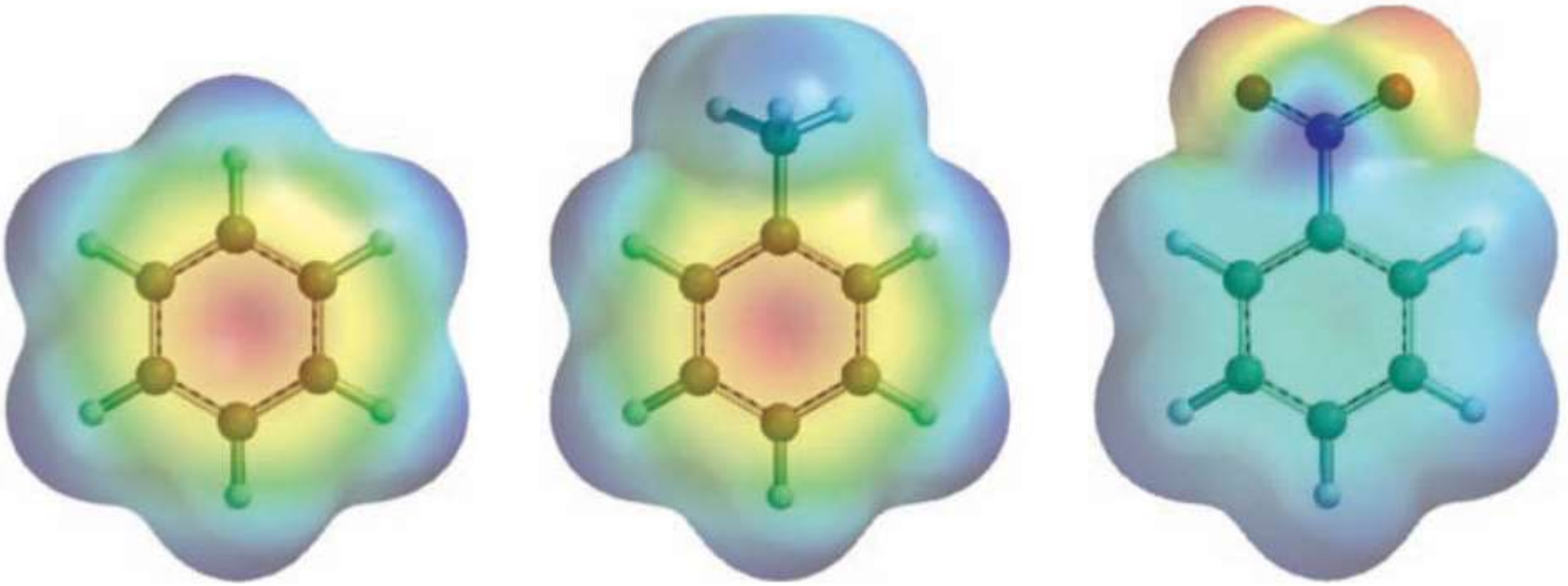

+ RCl
(R = an alkyl group such as CH3—, CH3CH2—)
AlCl3
R
+ HCl


+ CH2=CH2
H2SO4
CH2CH3

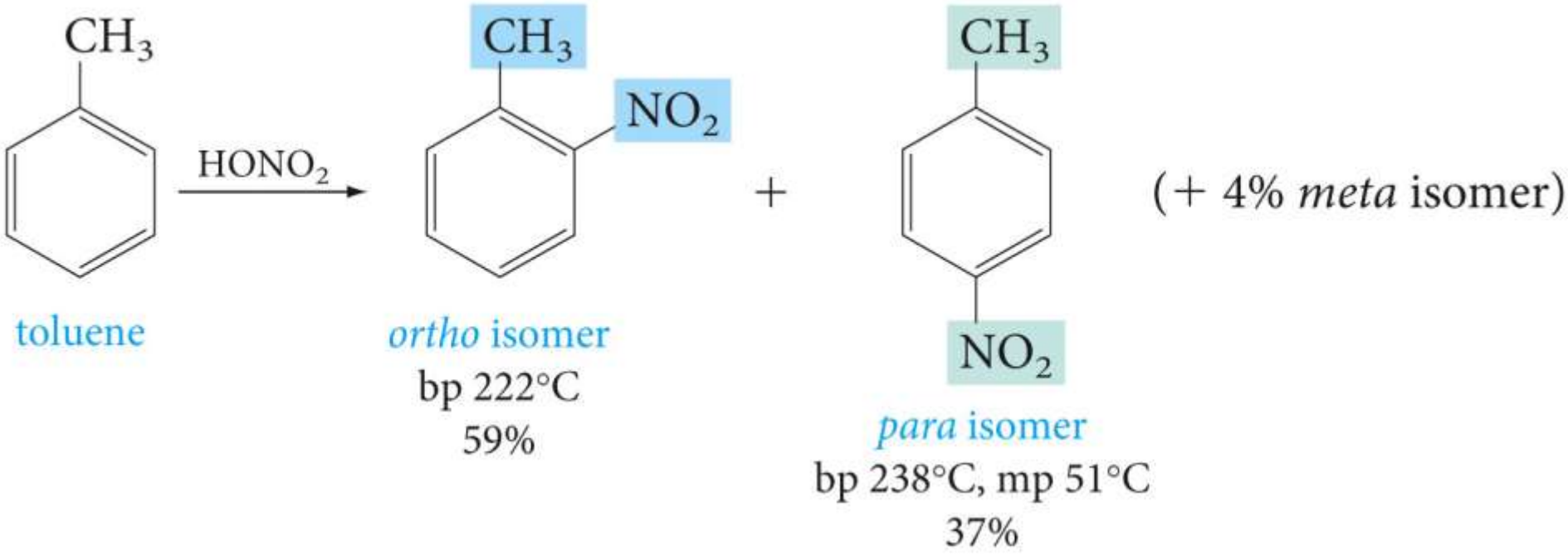

O
R—C
Cl
AlCl3
O
C—R
+ HCl

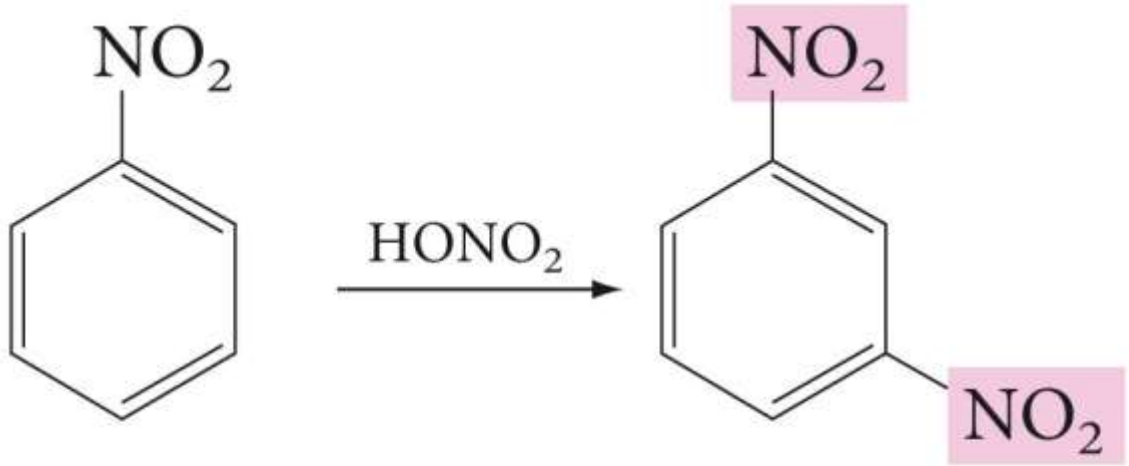
Ring-Activating and ring-Deactivating Substituents





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





nitrobenzene

meta isomer

mp 89°C

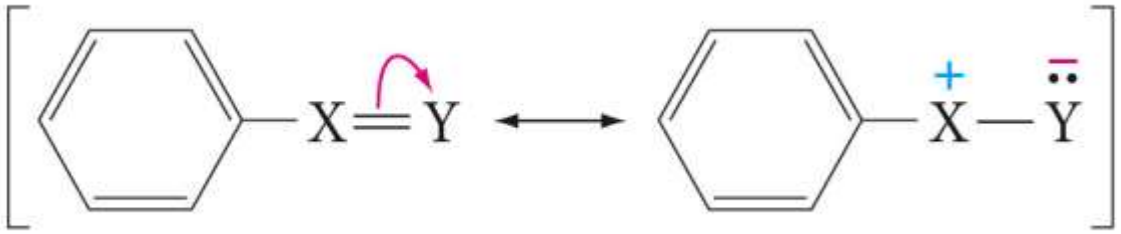
93%

(+ 7% *ortho* isomer)

Table 4.1 Directing and Activating Effects of Common Functional Groups (Groups are Listed in Decreasing Order of Activation)

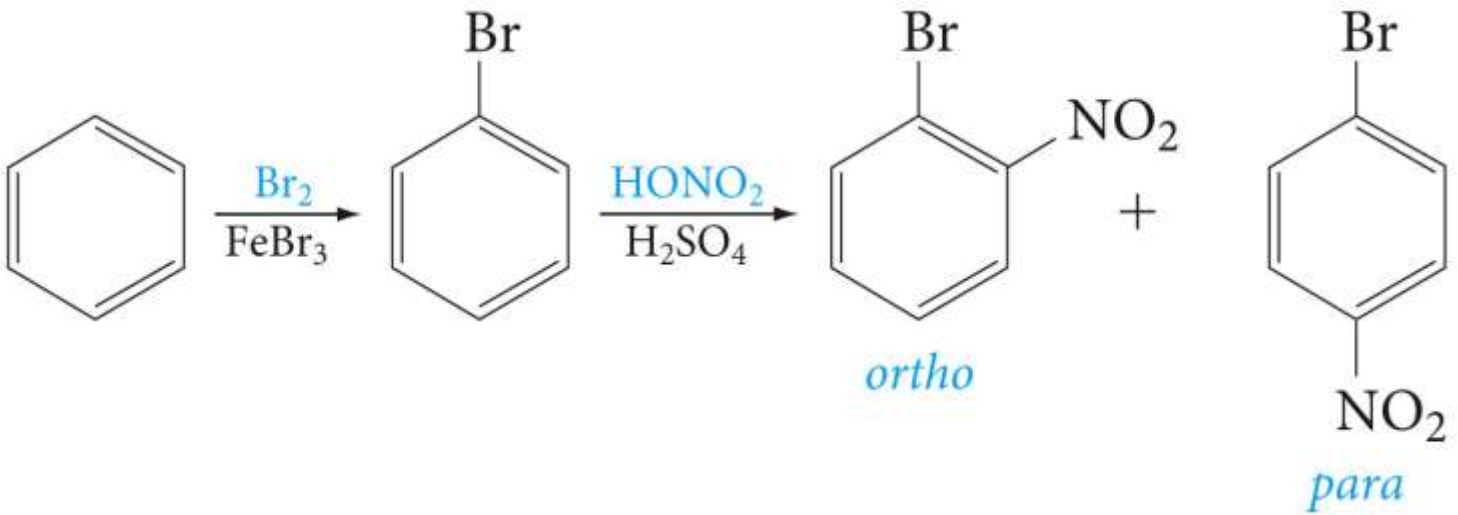
	Substituent group	Name of group	
Ortho,Para-Directing	$-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$	amino	Activating
	$-\ddot{O}H$, $-\ddot{O}CH_3$, $-\ddot{O}R$	hydroxy, alkoxy	
	$-\ddot{N}HC(=O)-R$	acylamino	
	$-CH_3$, $-CH_2CH_3$, $-R$	alkyl	
	$-\ddot{F}:$, $-\ddot{Cl}:$, $-\ddot{Br}:$, $-\ddot{I}:$	halo	Deactivating
Meta-Directing	$-C(=O)-R$ $-C(=O)-\ddot{O}H$	acyl, carboxy	
	$-C(=O)-\ddot{N}H_2$ $-C(=O)-\ddot{O}R$	carboxamido, carboalkoxy	
	$-S(=O)(=O)-\ddot{O}H$	sulfonic acid	
	$-C\equiv N:$	cyano	
	$-N^{+}(=O)-\ddot{O}:^{-}$	nitro	

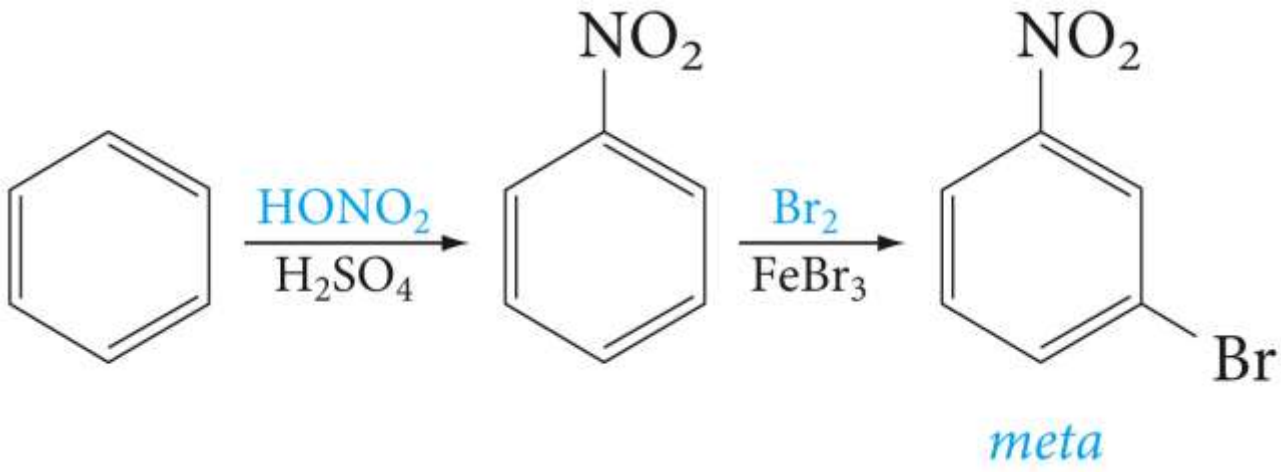
$-\ddot{F}:$ $-\ddot{O}H$ $-\ddot{N}H_2$



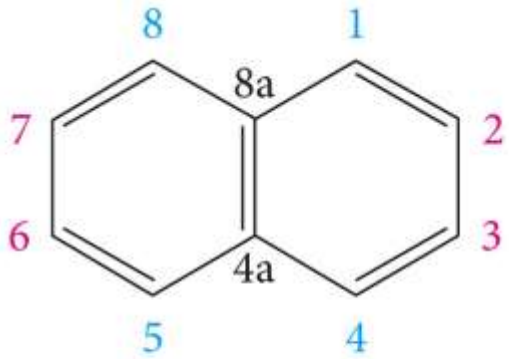
Y is an electron-withdrawing atom such as oxygen or nitrogen; atom X carries a positive charge in one of the resonance contributors.

Importance of Directing Effects in Synthesis



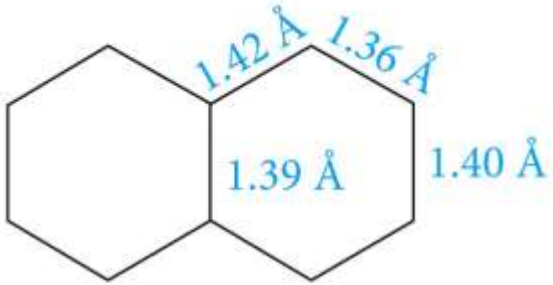

NO2
HONO2
H2SO4
NO2
Br2
FeBr3
Br
meta

Polycyclic Aromatic Hydrocarbons

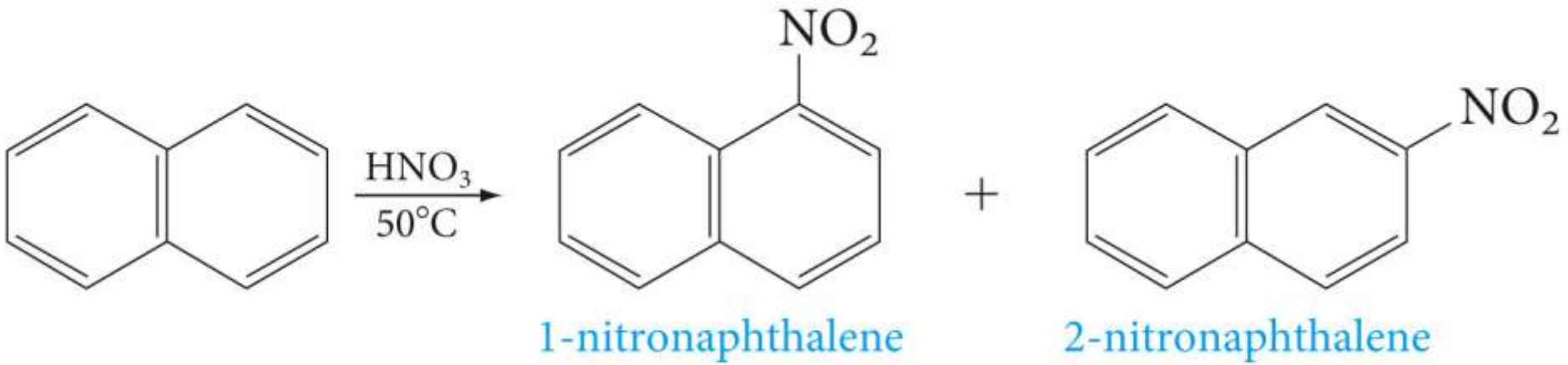


naphthalene

mp 80°C



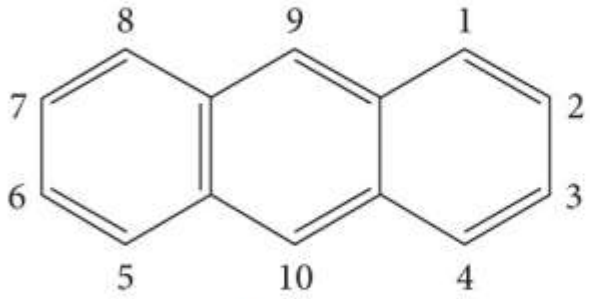
bond lengths in naphthalene



1-nitronaphthalene + 2-nitronaphthalene

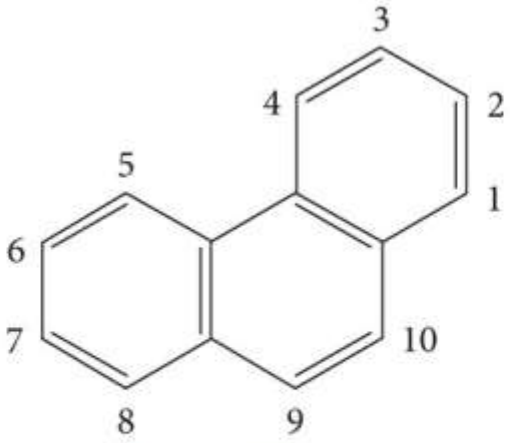
(ratio 10:1)

Fused polycyclic hydrocarbons



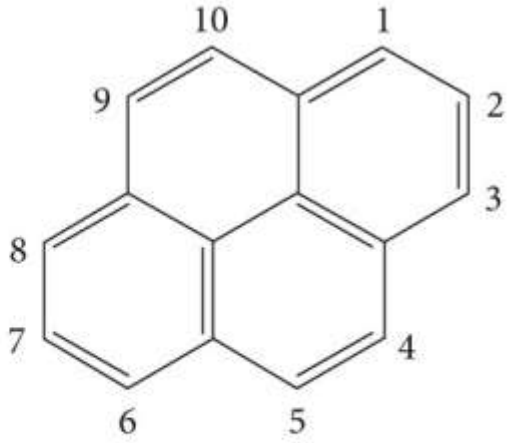
anthracene

mp 217°C



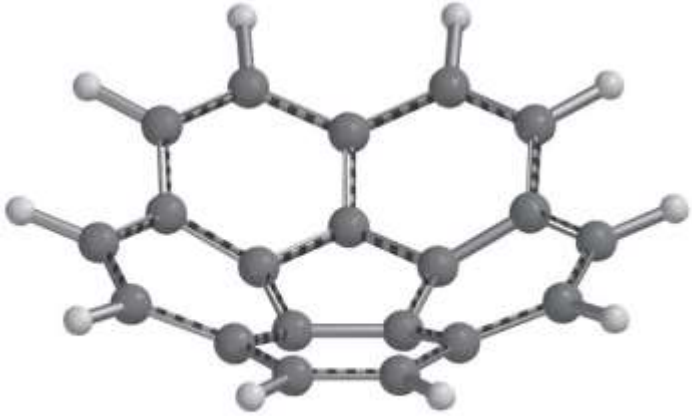
phenanthrene

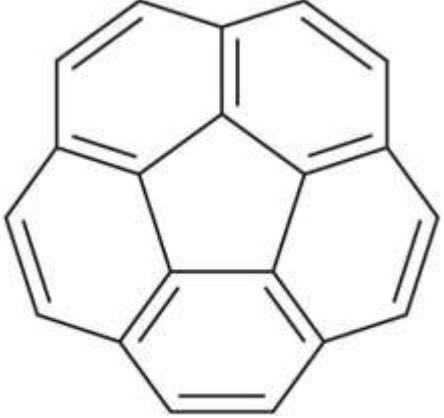
mp 98°C



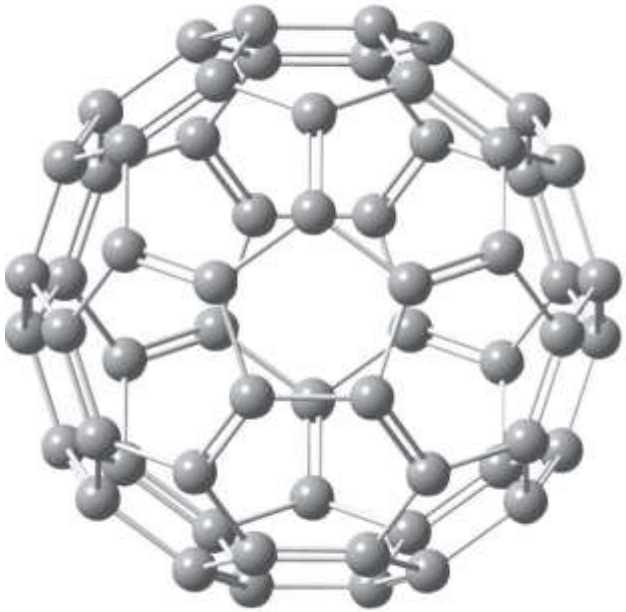
pyrene

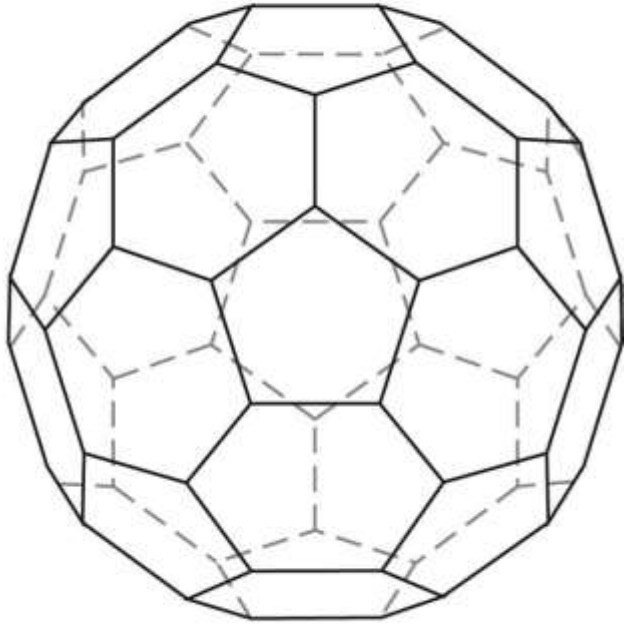
mp 156°C



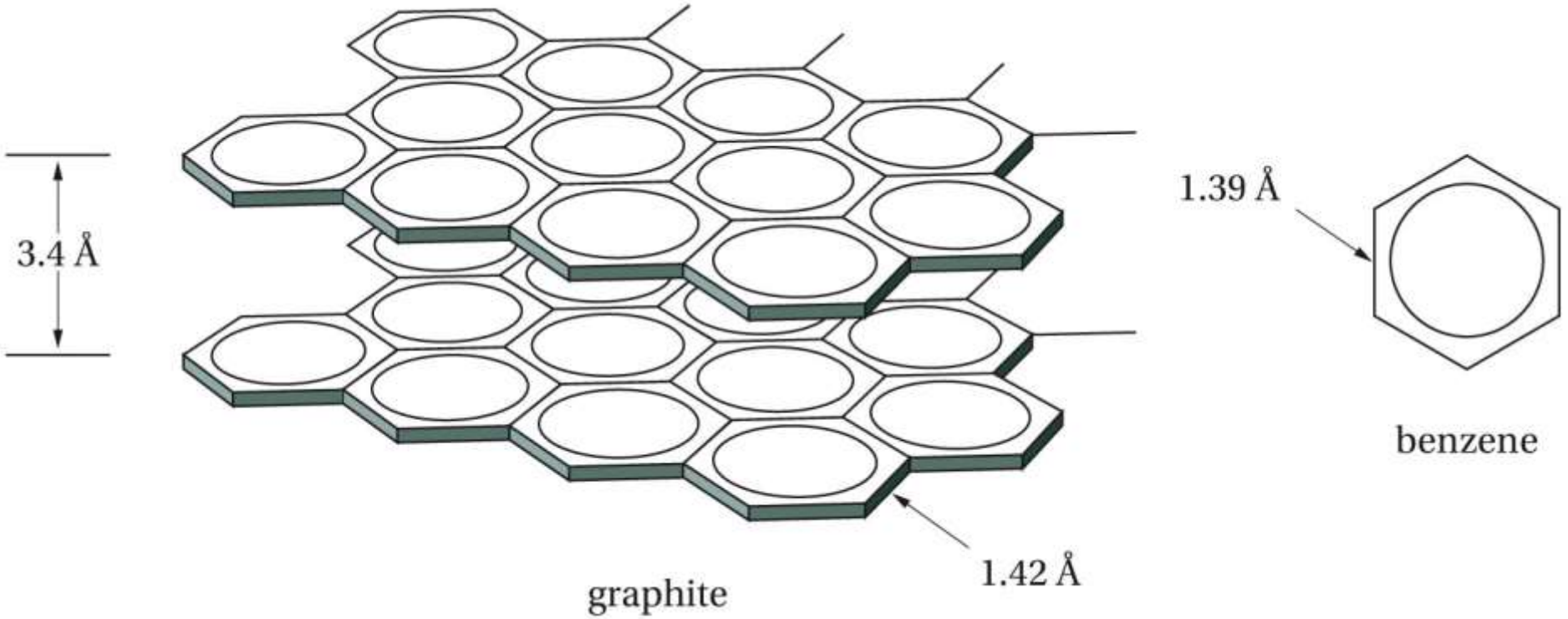


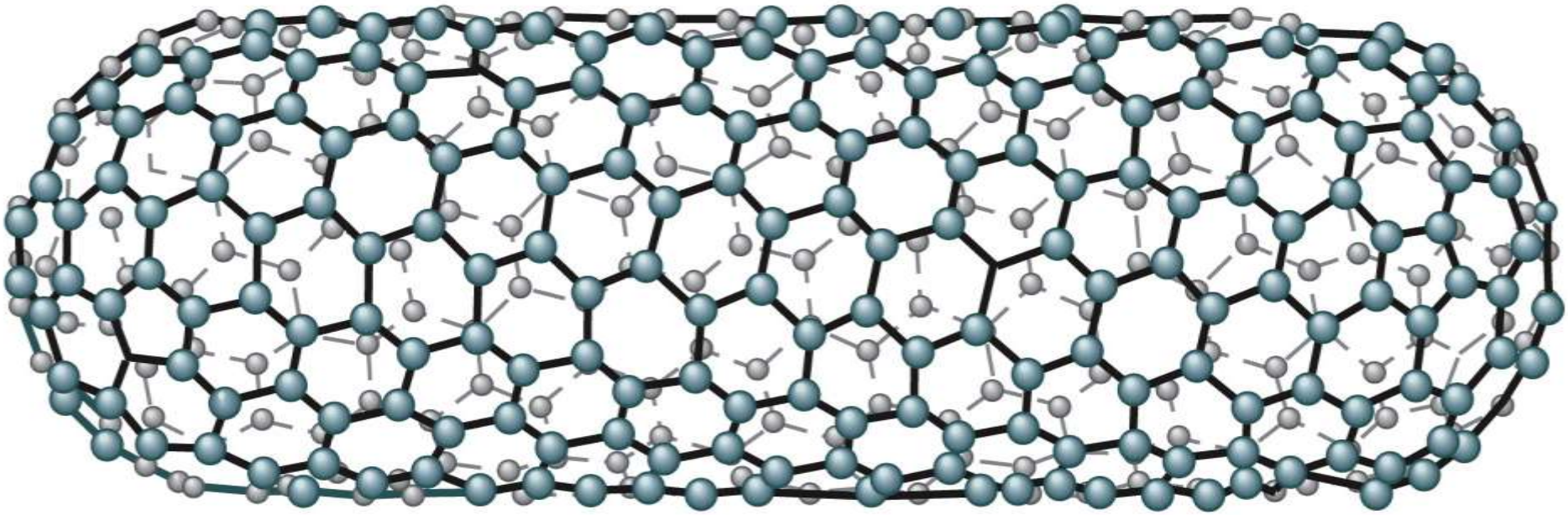
corannulene





C_{60} (the pi bonds are not shown)


3.4 Å
1.42 Å
graphite
1.39 Å
benzene



Carbon nanotube[1]