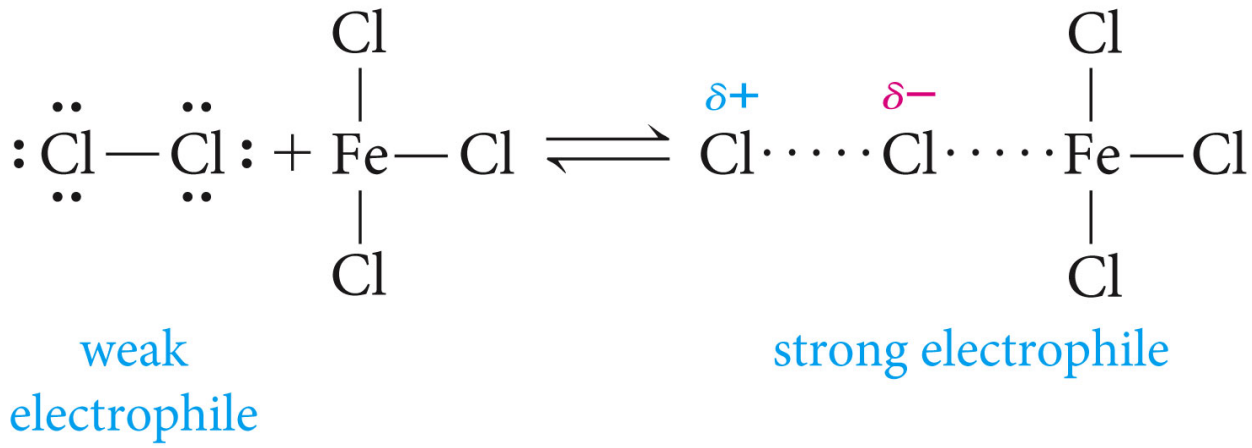
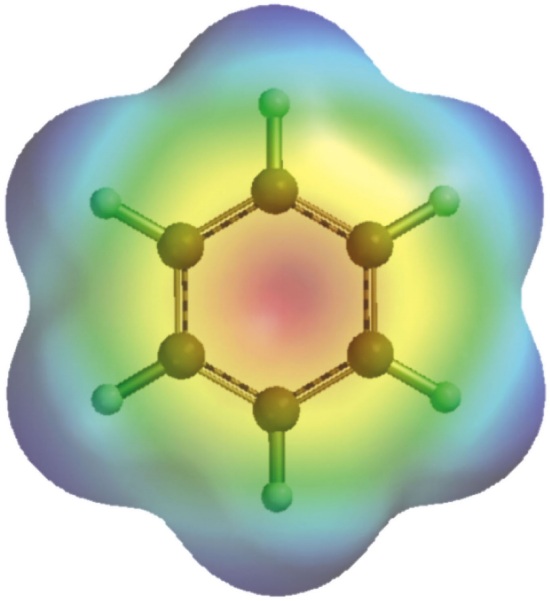
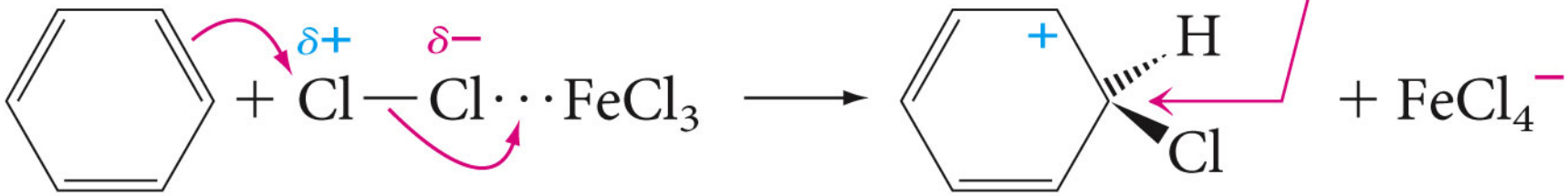
The Mechanisms of Electrophilic Substitutions

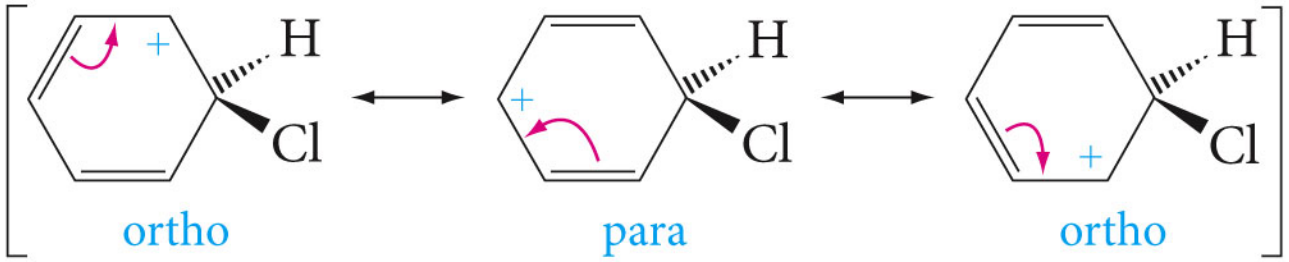




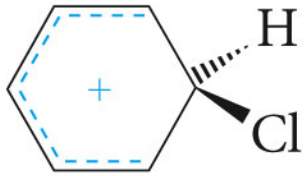
This carbon is sp^3-hybridized; it is bonded to *four* other atoms, and has no double bond to it.



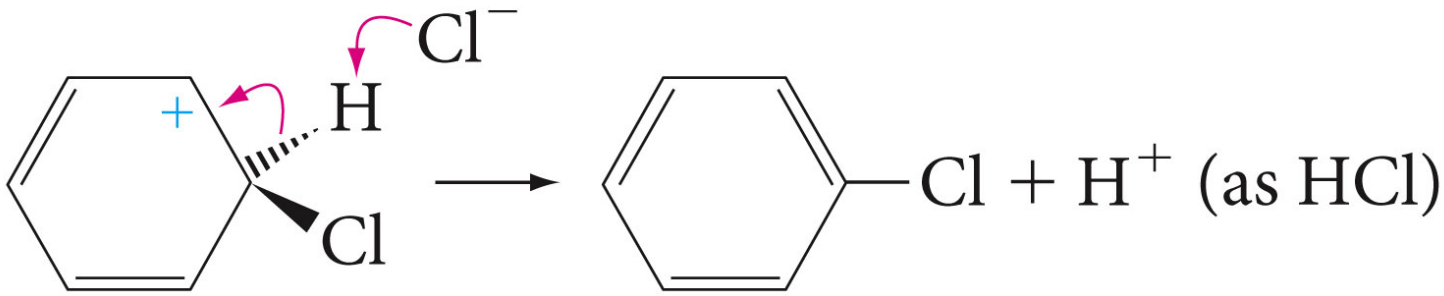
a benzenonium ion
(a carbocation)

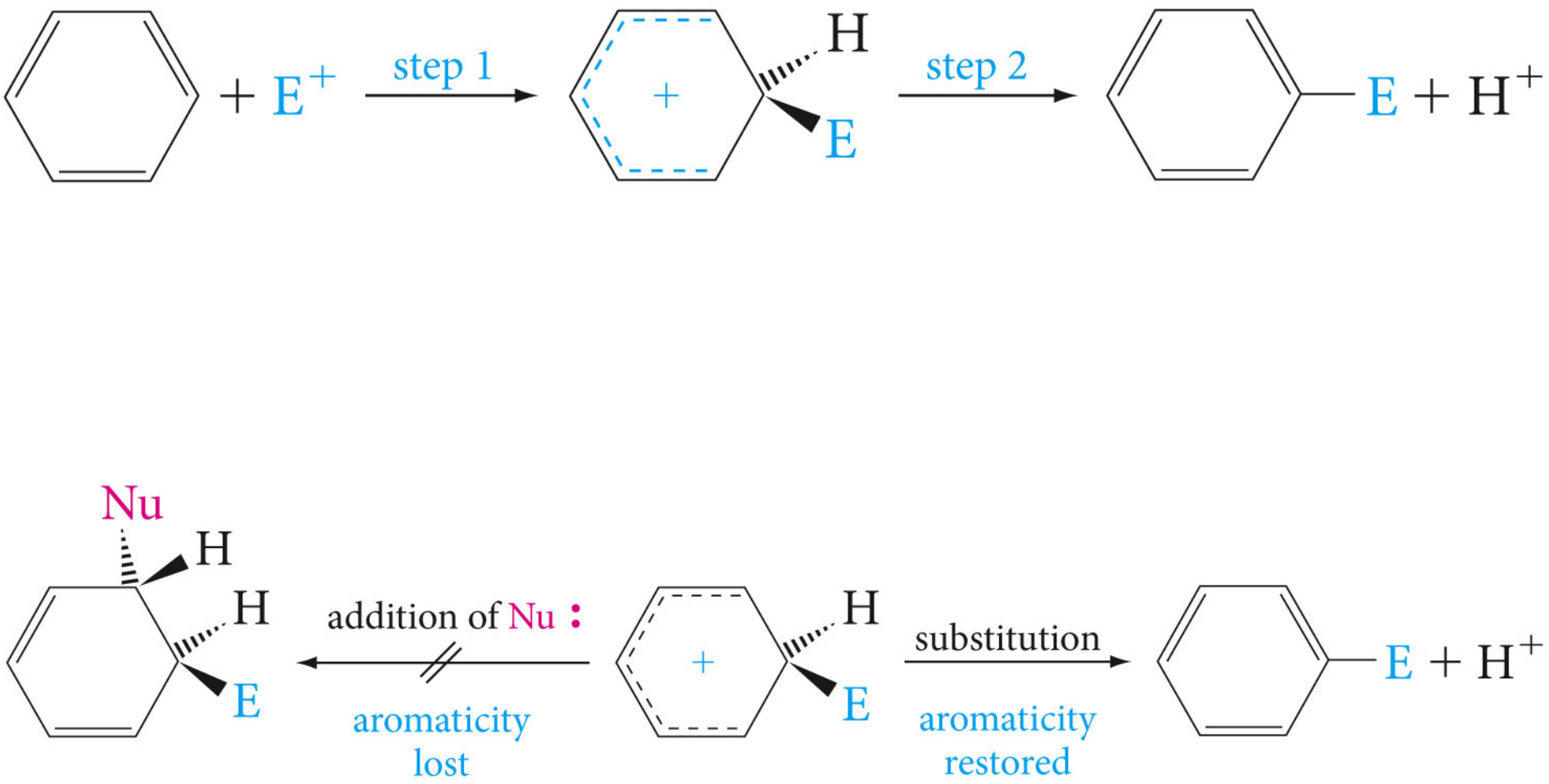


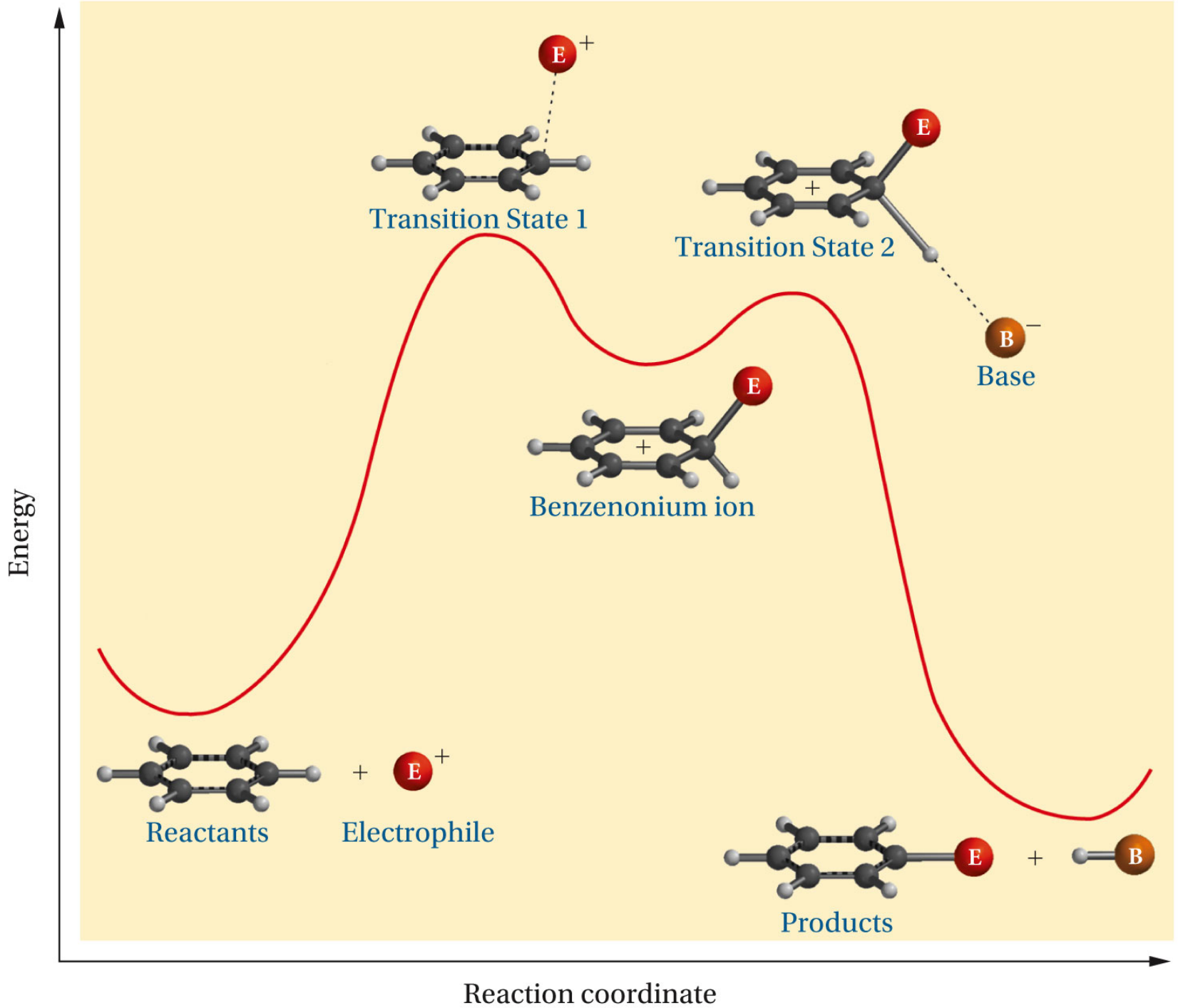
resonance forms of a benzenonium ion



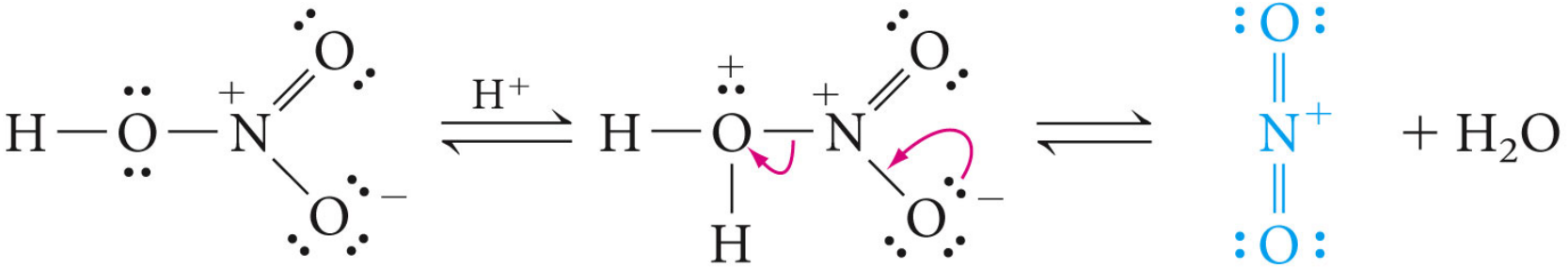
composite representation of the benzenonium ion resonance hybrid




+ E+
step 1
H
+
E
step 2
E + H+
Nu
H
H
E
addition of Nu :
aromaticity
lost
H
+
E
substitution
aromaticity
restored
E + H+


Energy
Reaction coordinate
E
+
Transition State 1
E
+
Transition State 2
B
−
Base
E
+
Benzenonium ion
Reactants
+
E
+
Electrophile
E
+
B
Products

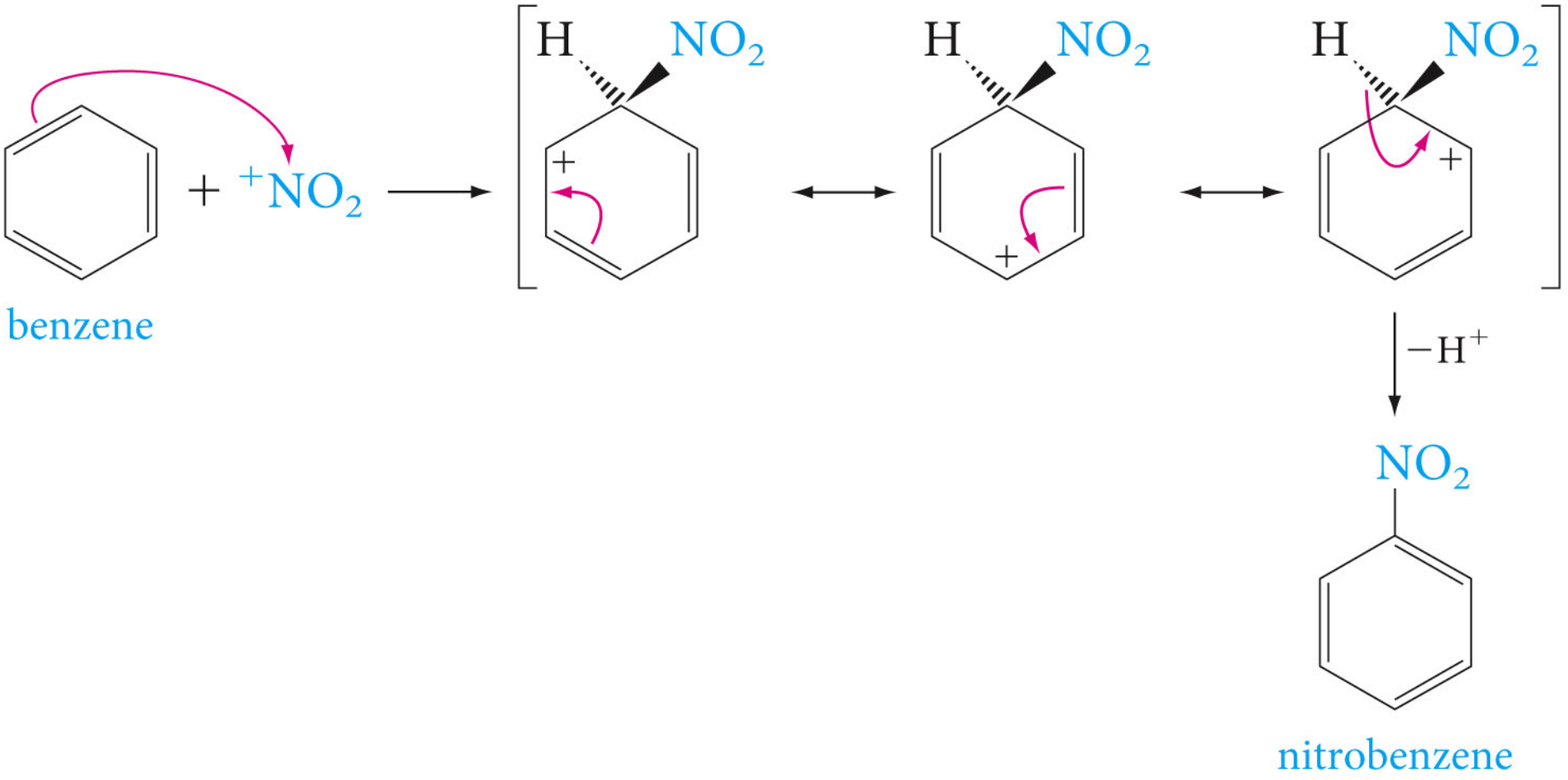
Nitration



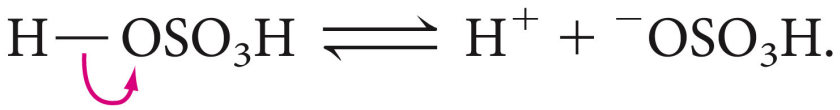
nitric acid

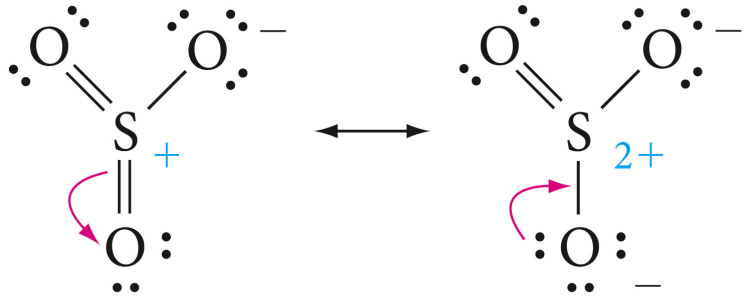
protonated nitric acid

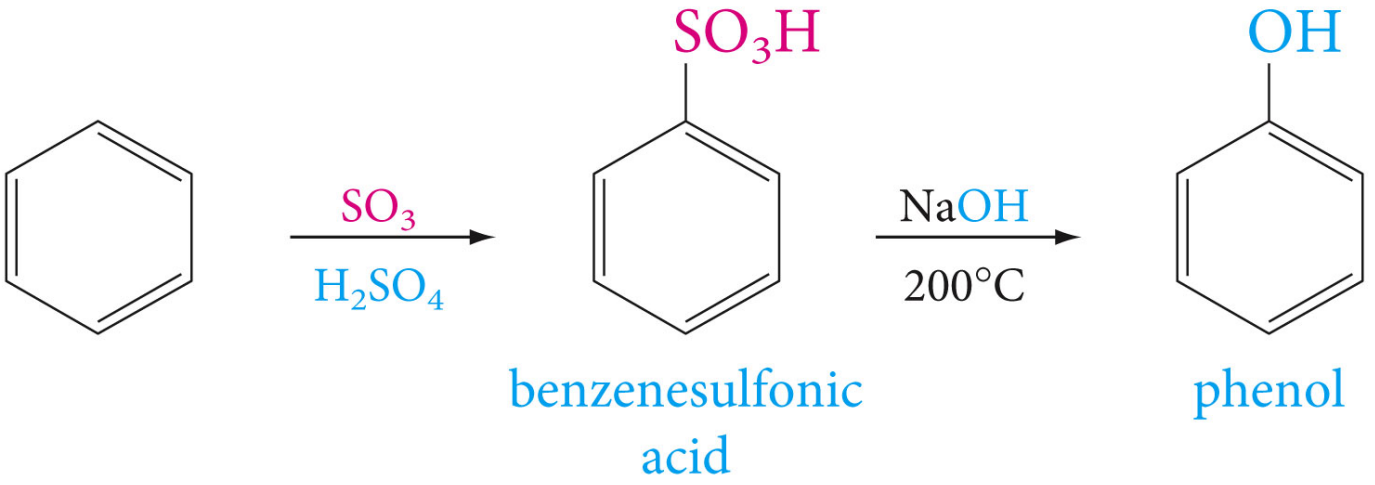
nitronium ion


benzene
+ +NO2
H
NO2
+
H
NO2
+
H
NO2
+
−H+
NO2
nitrobenzene

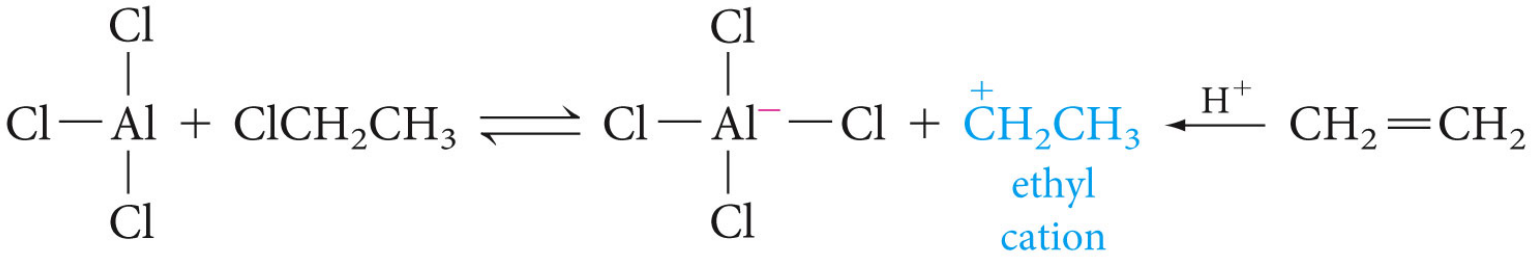
sulfonation

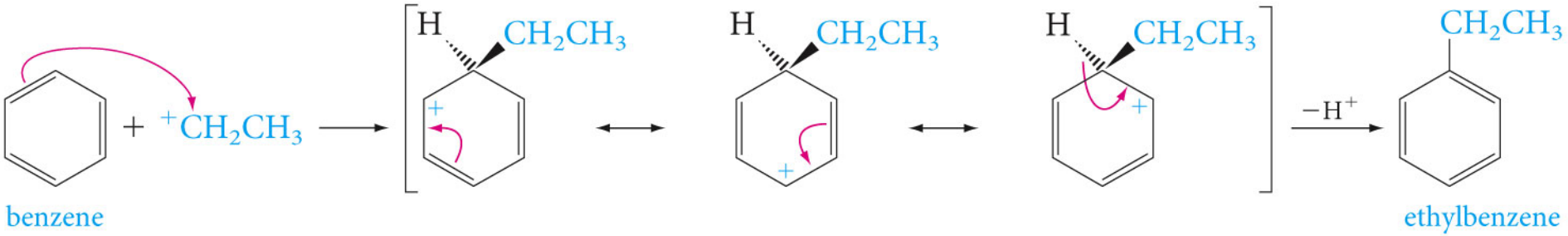


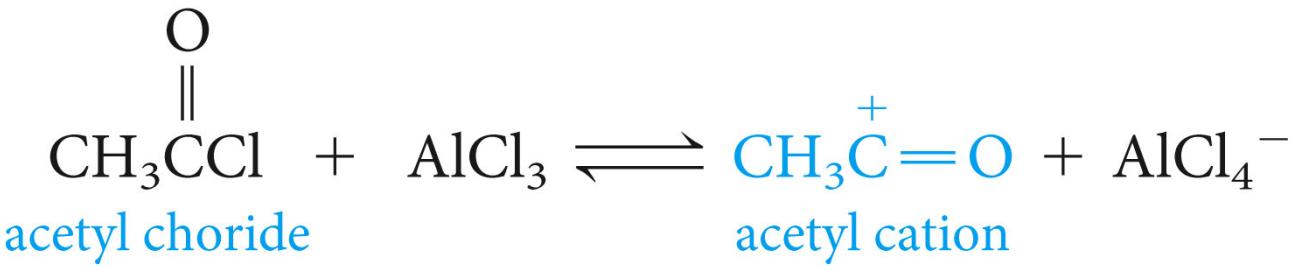


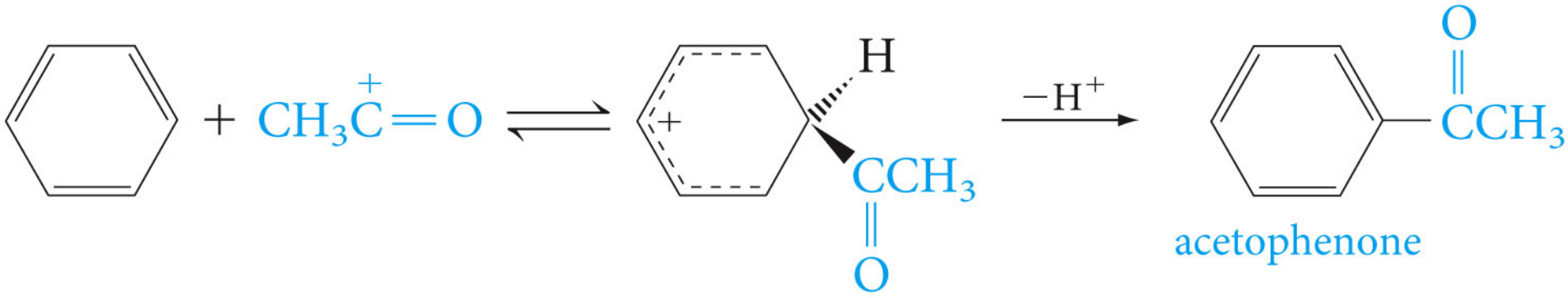


Alkylation and Acylation (Friedel-Crafts reaction)

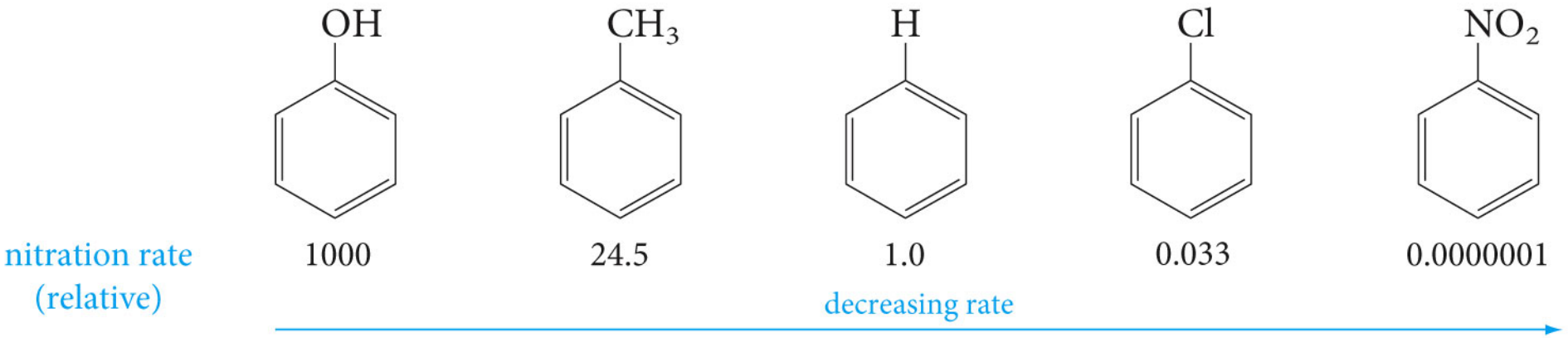


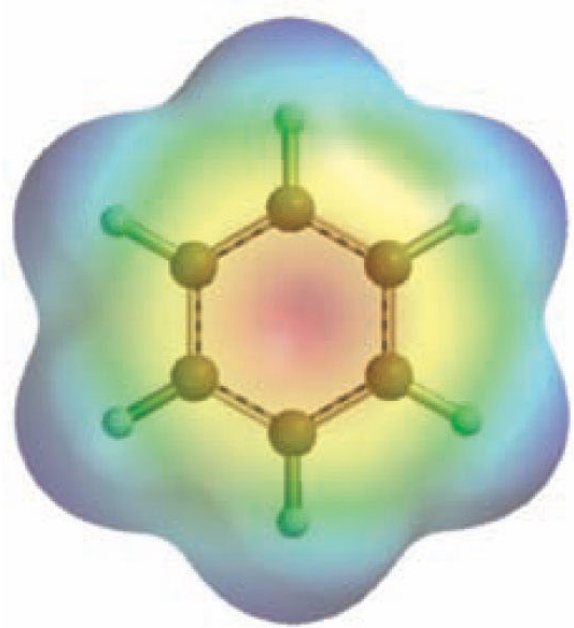


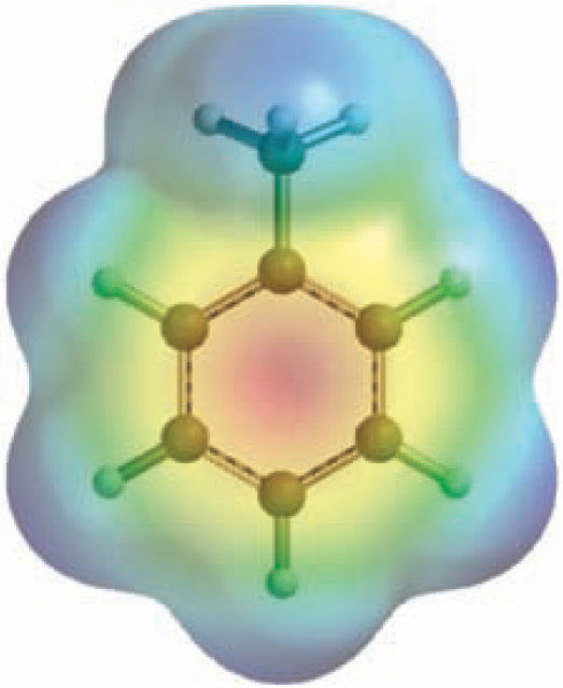

O
CH3CCl
AlCl3
CH3C=O
AlCl4−
acetyl choride
acetyl cation

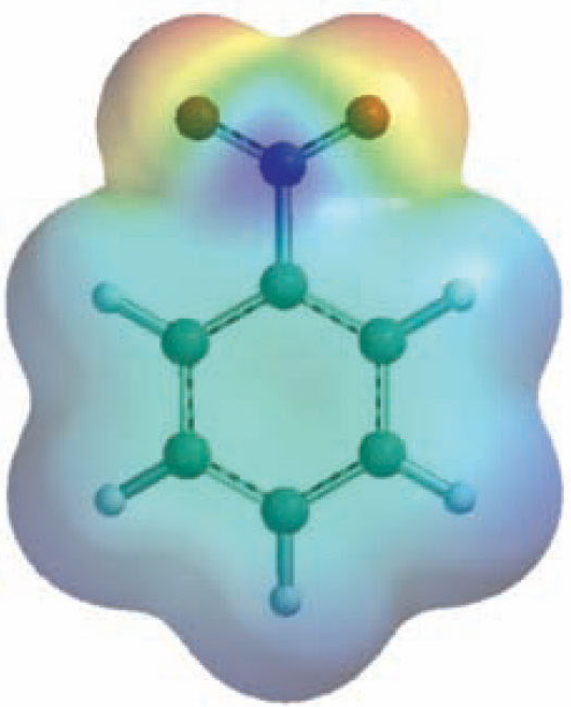

CH3C=O
H
CCH3
O
−H+
O
CCH3
acetophenone

Ring-Activating and ring-Deactivating Substituents

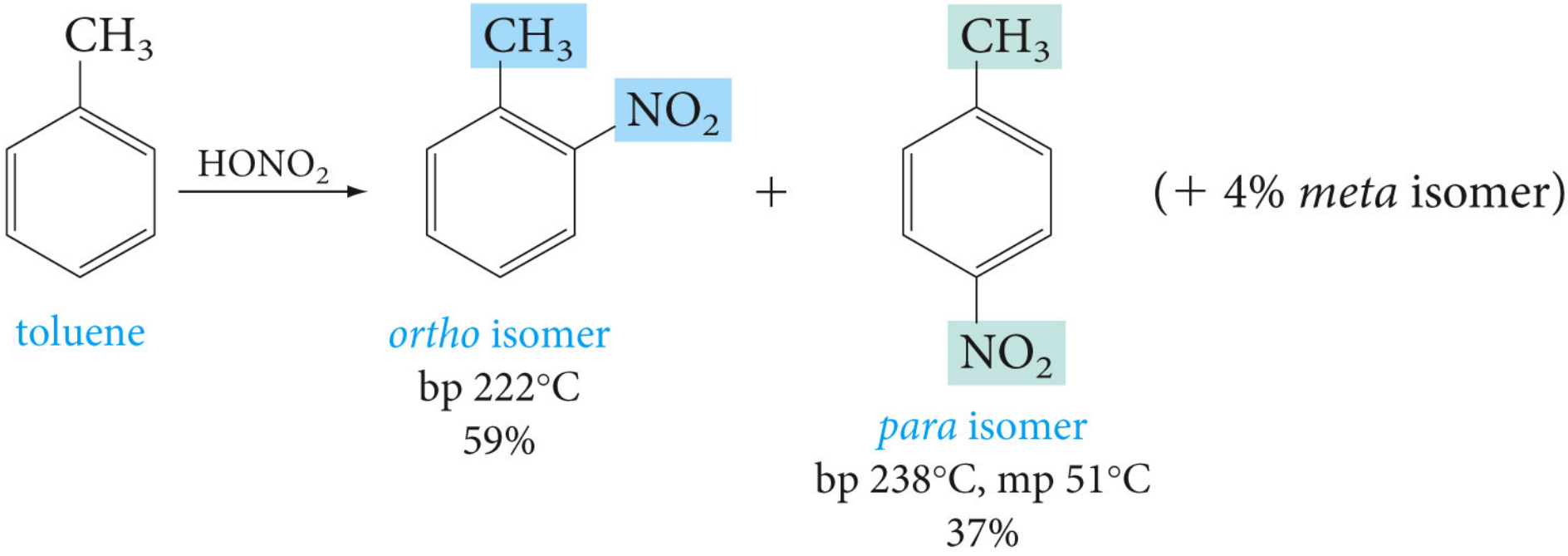


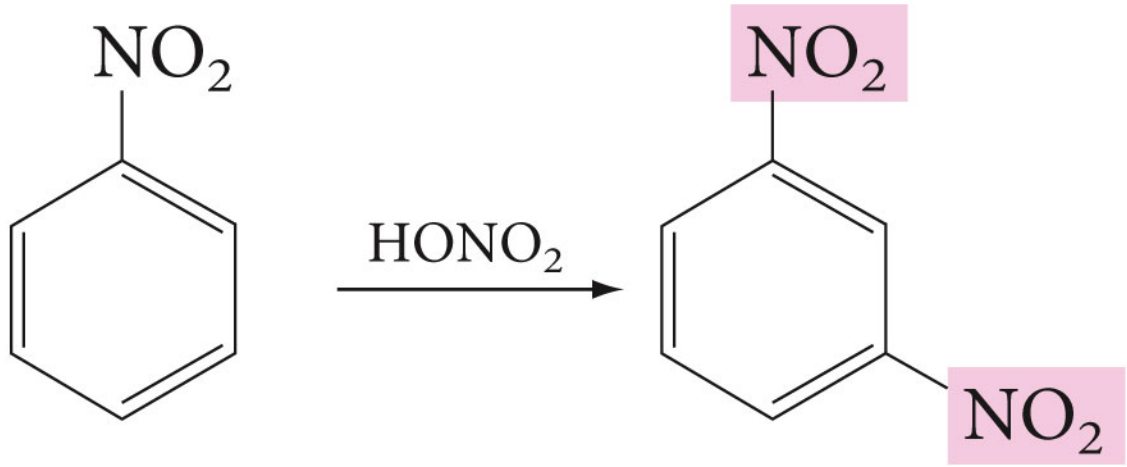






Ortho, *Para*-Directing and *Meta*-Directing Groups





nitrobenzene

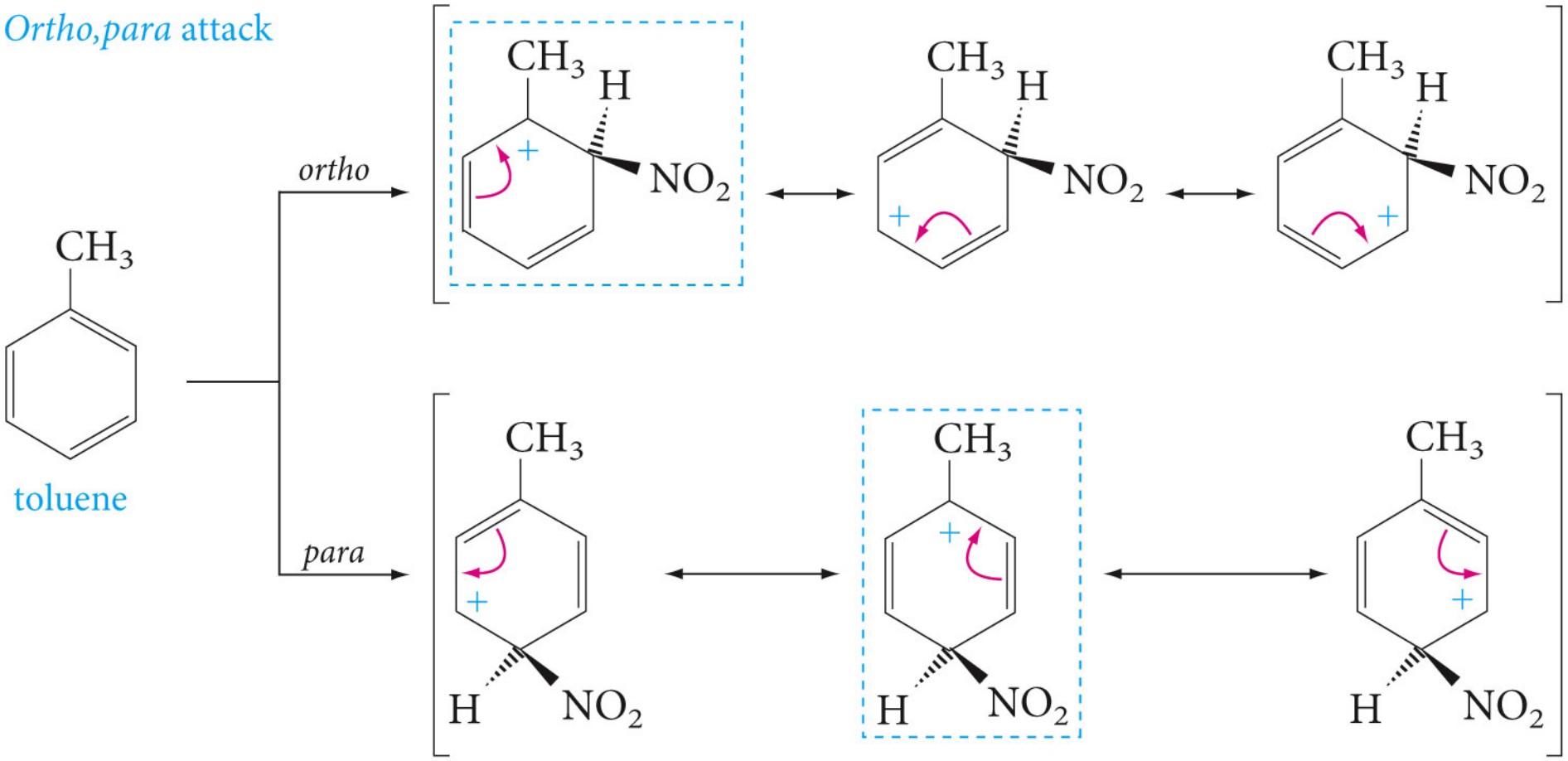
meta isomer

mp 89°C

93%

(+ 7% *ortho* isomer)

Ortho, *Para*-Directing Groups



Meta attack

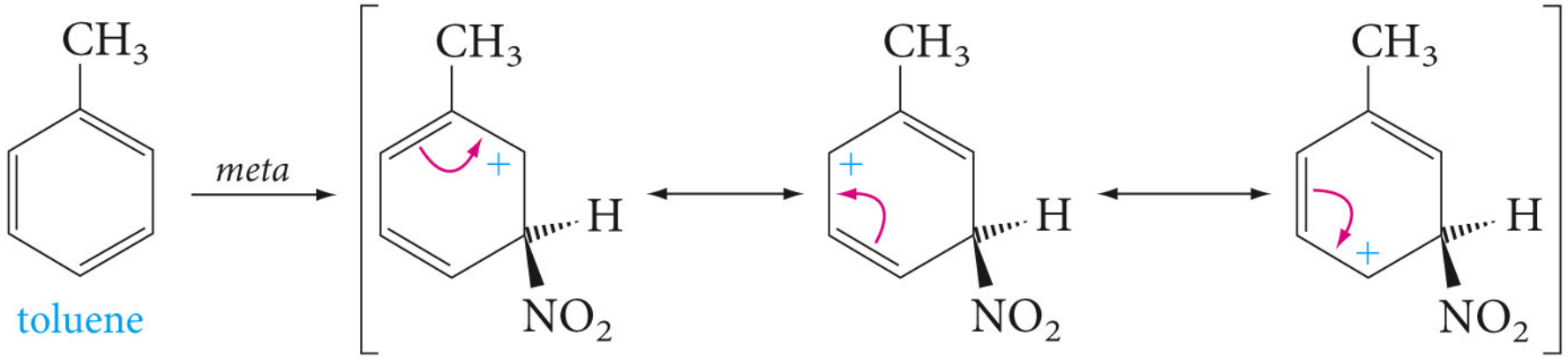
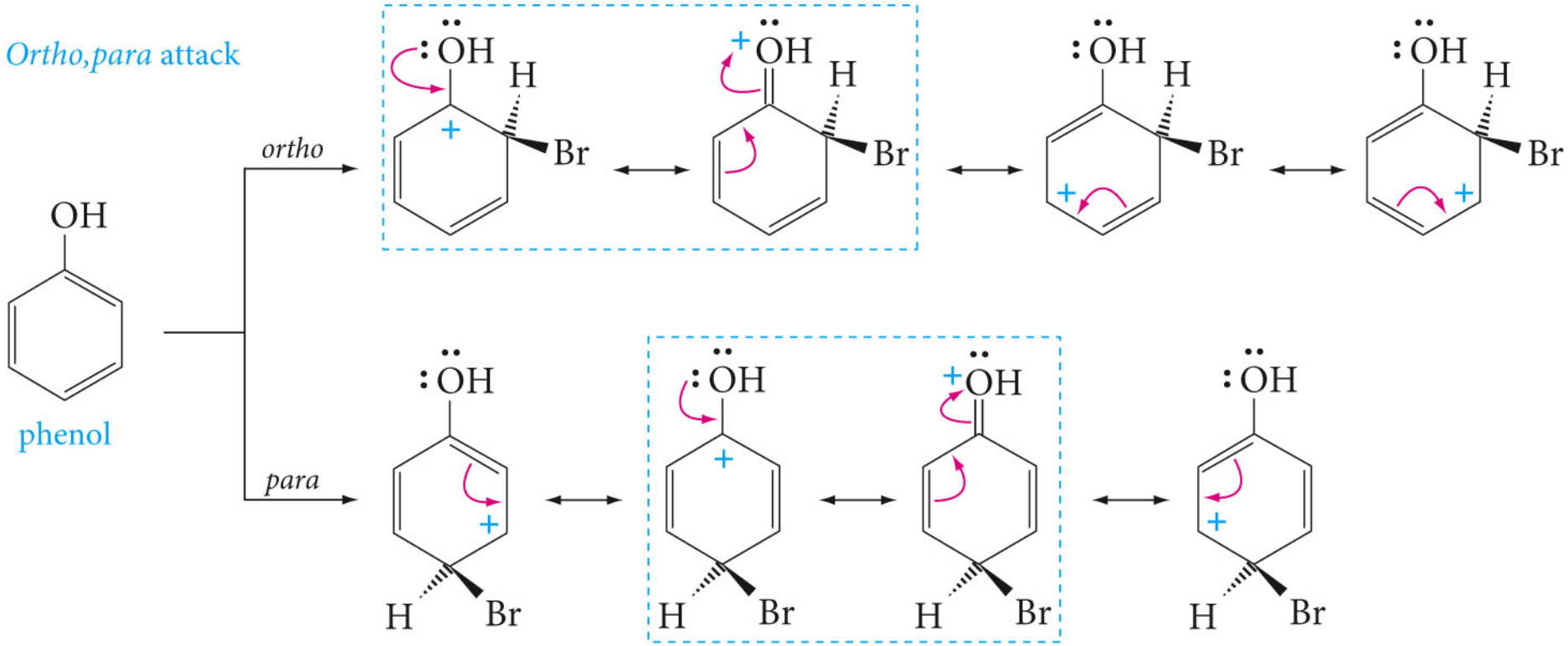


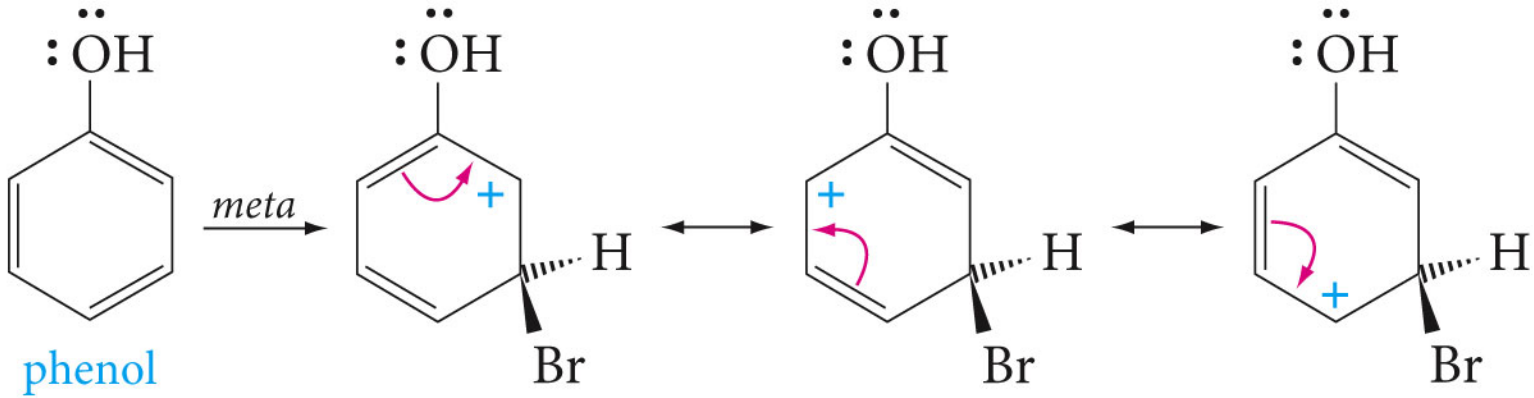
Table 4.1 Directing and Activating Effects of Common Functional Groups (Groups are Listed in Decreasing Order of Activation)

	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	$-C(=O)-R$ $-C(=O)-OH$	acyl, carboxy	
	$-C(=O)-NH_2$ $-C(=O)-OR$	carboxamido, carboalkoxy	
	$-S(=O)(=O)-OH$	sulfonic acid	
	$-C\equiv N:$	cyano	
	$-N^{+}(=O)-O^{-}$	nitro	

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

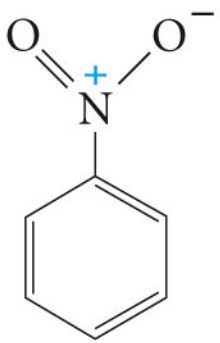

Ortho,para attack
OH
phenol
ortho
para
:OH
H
Br
+

Meta attack

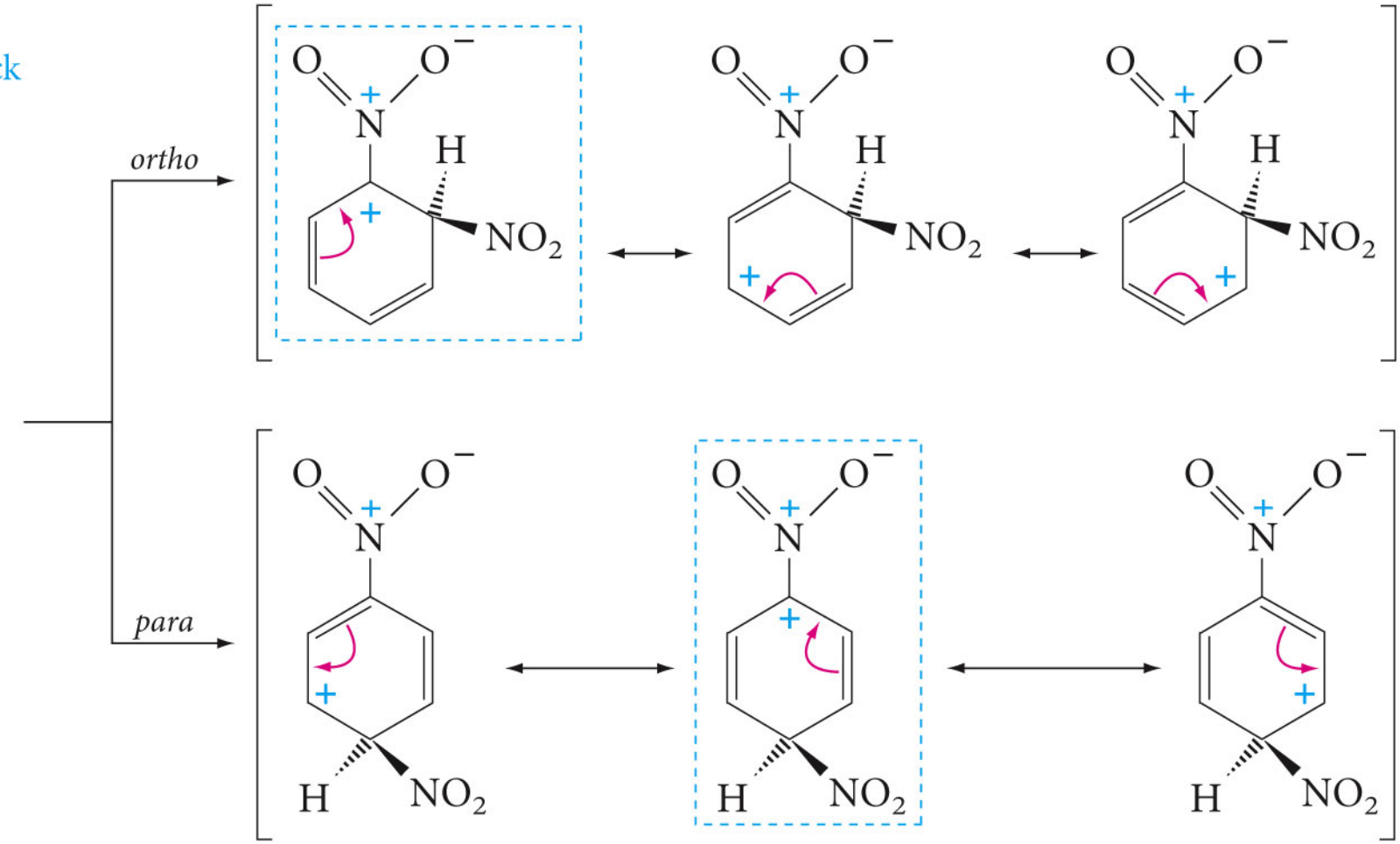


phenol

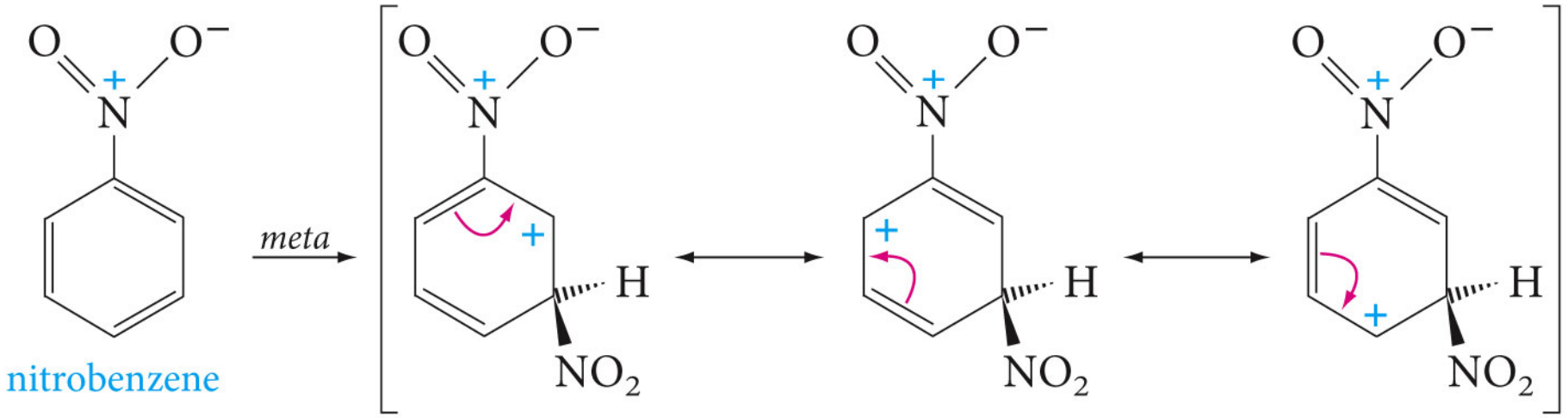
Ortho,para attack



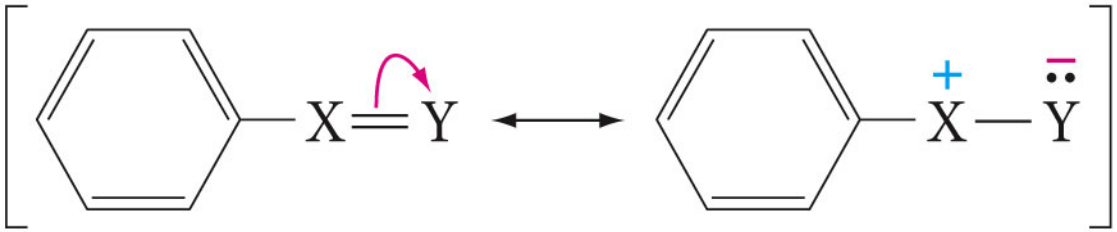
nitrobenzene



Meta attack

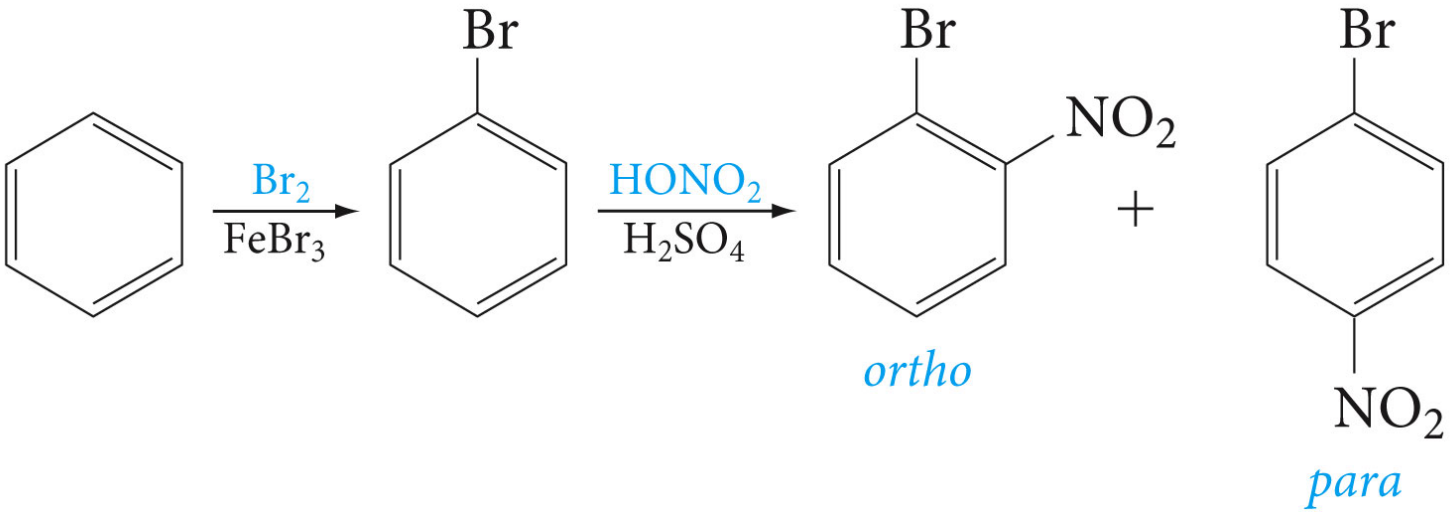


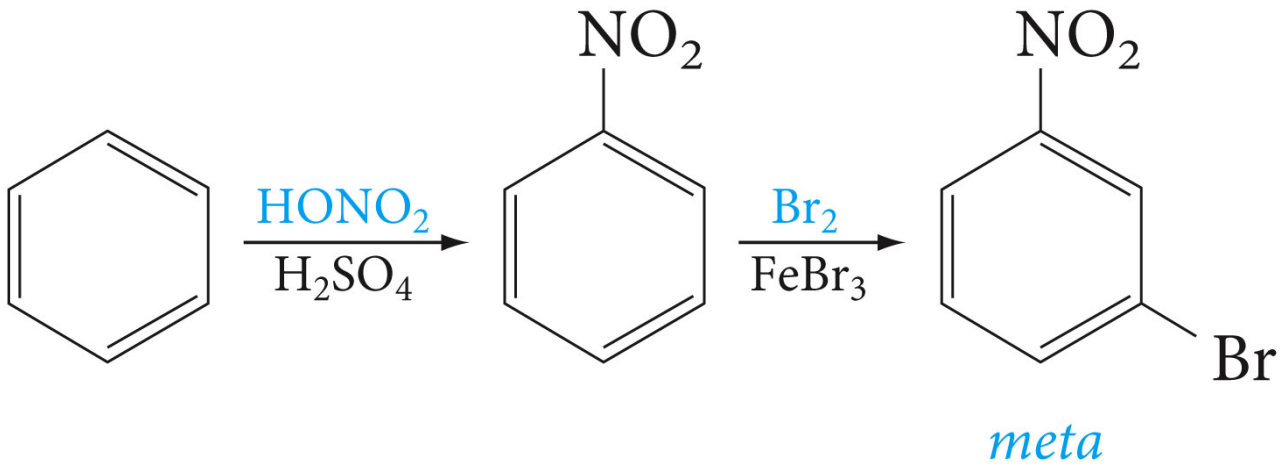
nitrobenzene



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