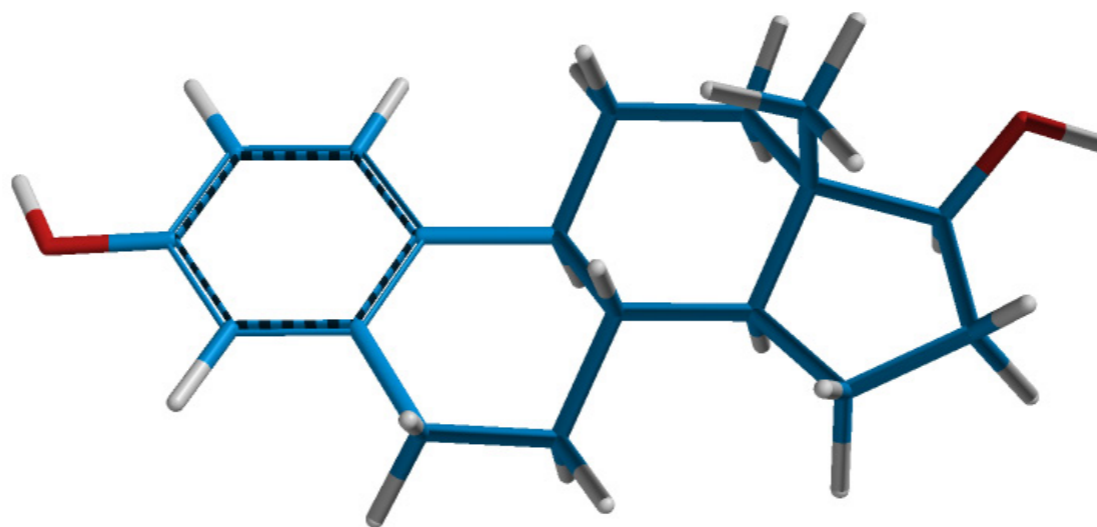


24

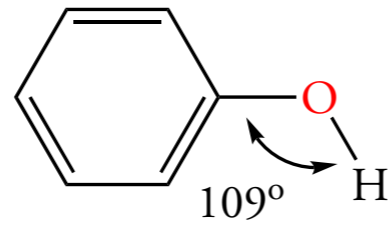
ARYL HALIDES, PHENOLS, AND ANILINES



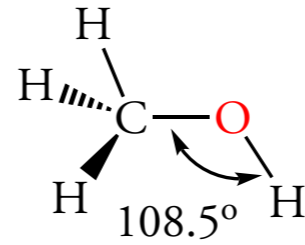
ESTRADIOL: The hydroxyl group on the left, bound to the benzene ring, is a phenol; the hydroxyl group on the right is a secondary alcohol.

24.1 PROPERTIES OF AROMATIC COMPOUNDS

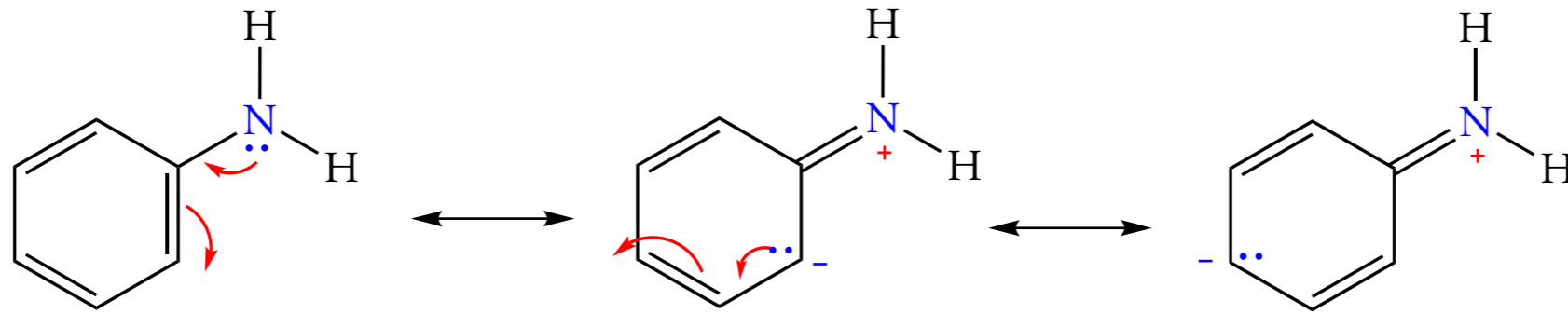
Bonding and Structure



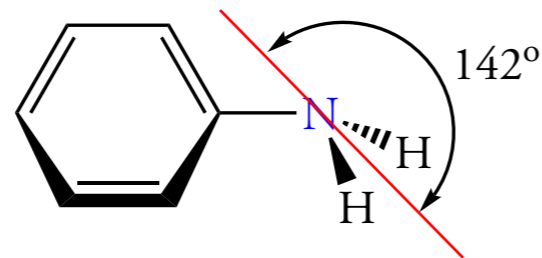
phenol



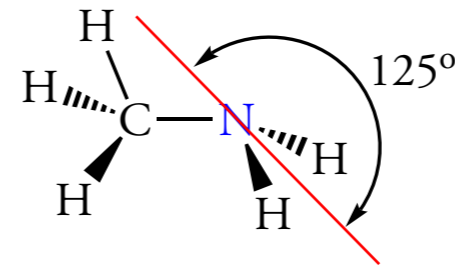
methanol



H—N—H angle bisectors



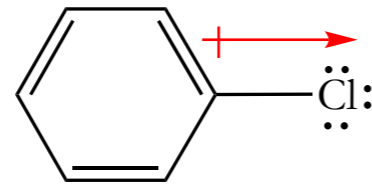
aniline



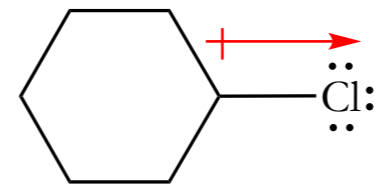
aminomethane

24.1 PROPERTIES OF AROMATIC COMPOUNDS

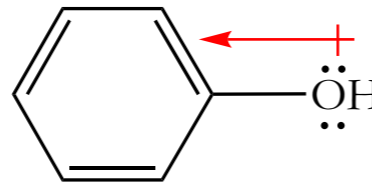
Bond Polarity



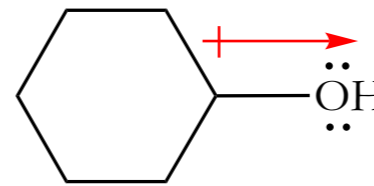
chlorobenzene
(1.7 D)



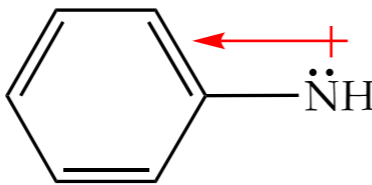
chlorocyclohexane
(2.2 D)



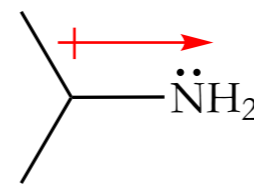
phenol
(1.5 D)



cyclohexanol
(1.7 D)



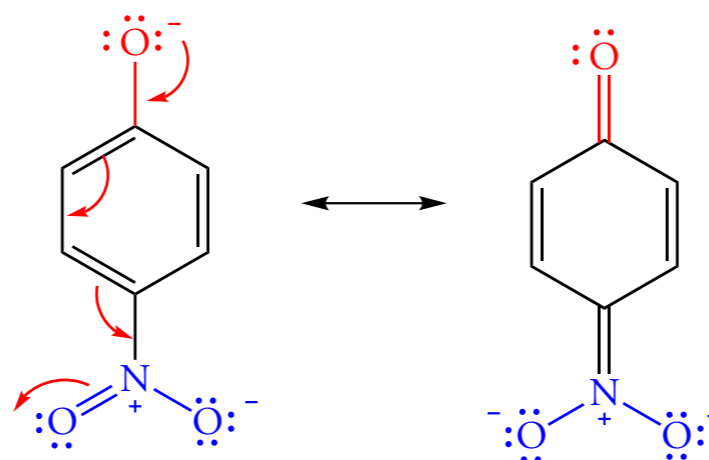
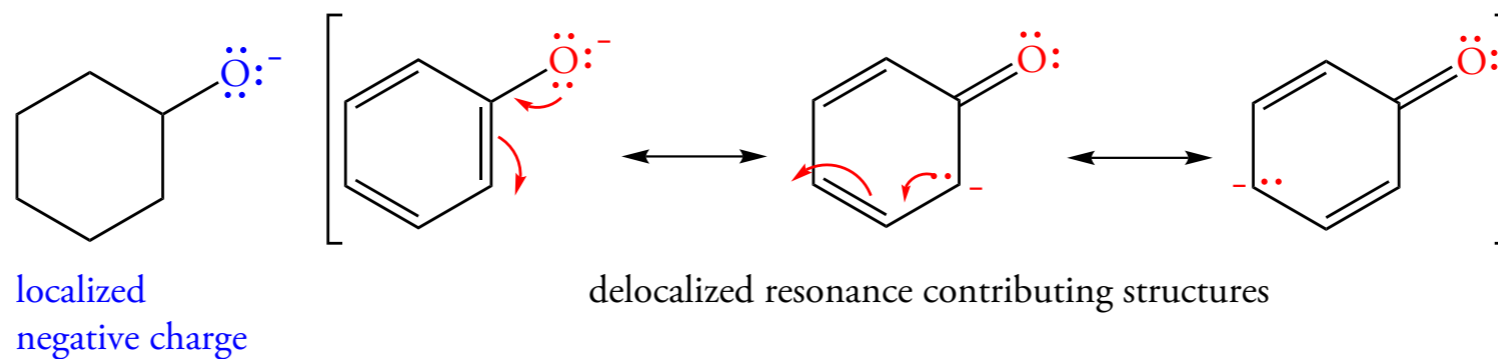
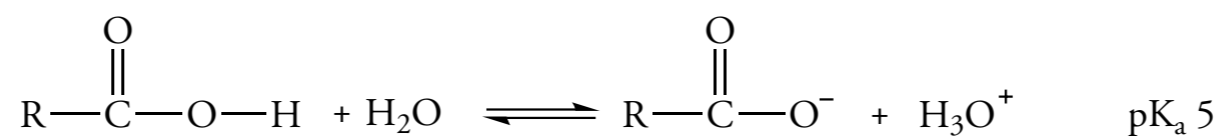
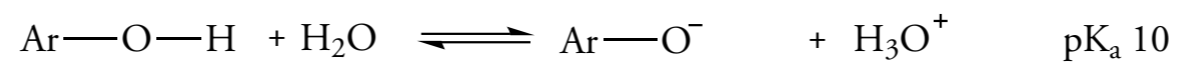
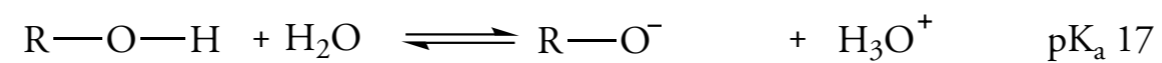
aniline
(1.3 D)



isopropylamine
(1.3 D)

24.1 PROPERTIES OF AROMATIC COMPOUNDS

Phenols



24.1 PROPERTIES OF AROMATIC COMPOUNDS

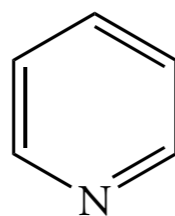
Phenols

Table 24.1
pK_a Values of Phenols

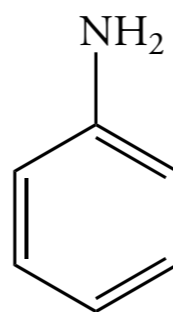
Substituent	Ortho	Meta	Para
H	10	10	10
bromo	8.42	8.87	9.26
chloro	8.48	9.02	9.38
cyano			7.95
methoxy	9.08	9.65	10.21
methyl	10.29	10.09	10.26
nitro	7.22	8.39	7.15

24.1 PROPERTIES OF AROMATIC COMPOUNDS

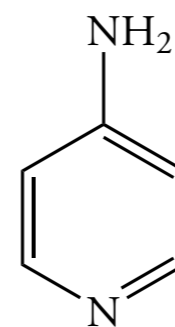
Anilines



pyridine
 $pK_b = 8.7$



aniline
 $pK_b = 9.4$

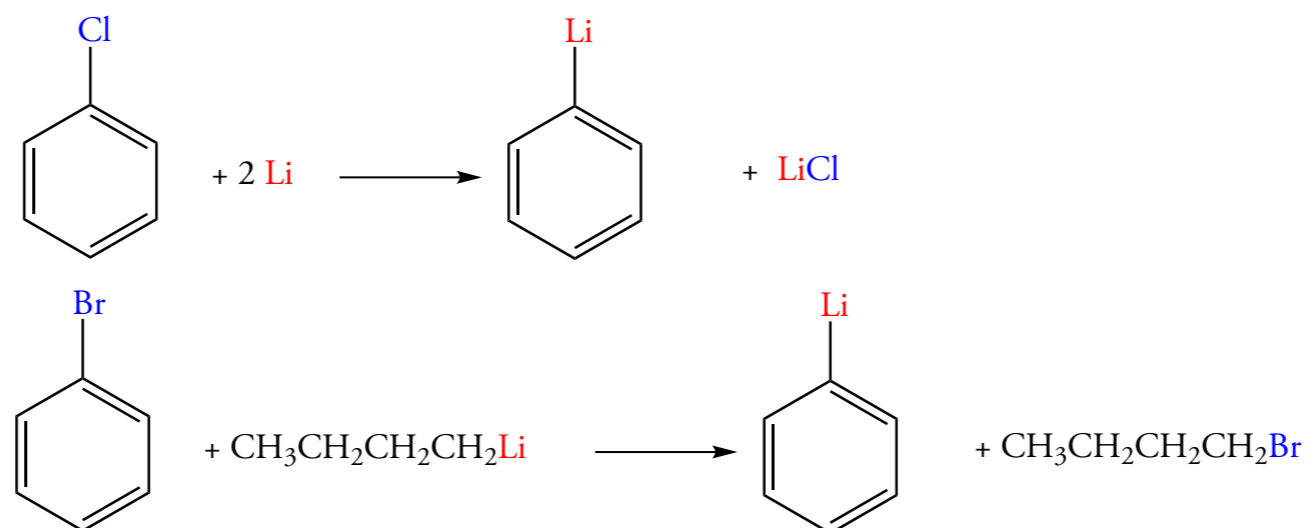
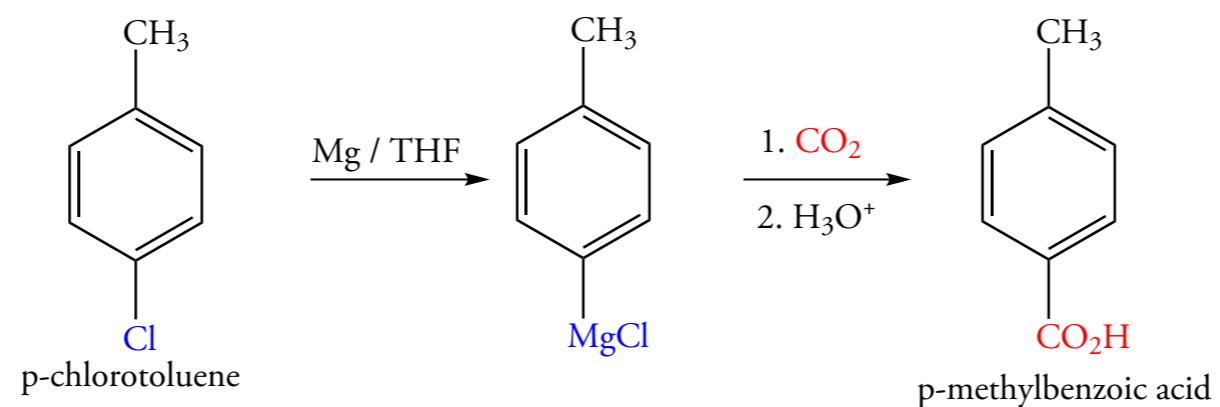
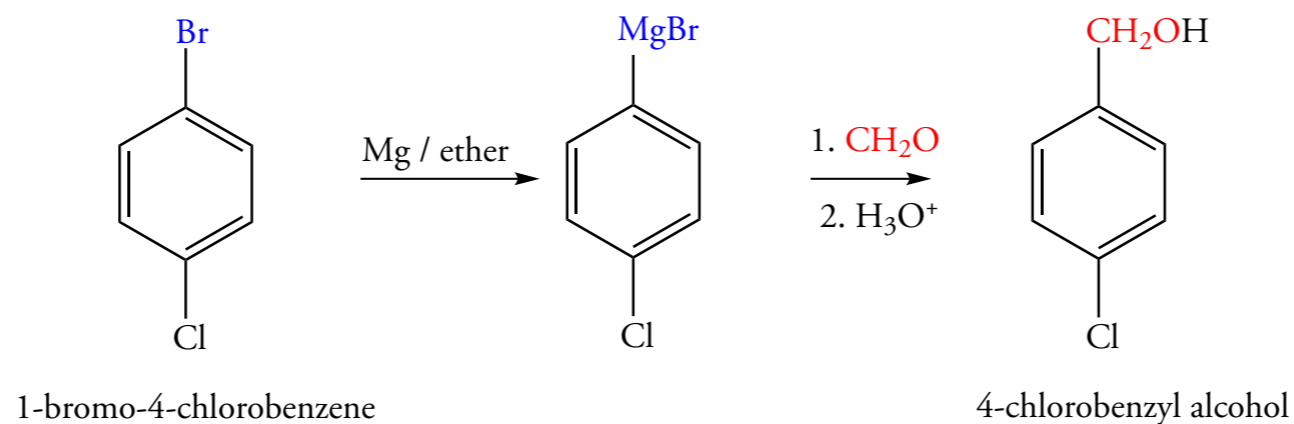
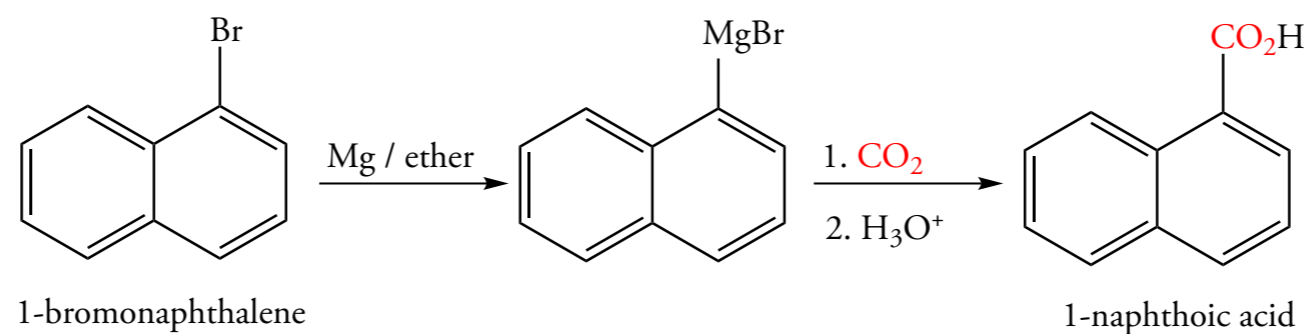


4-aminopyridine
 $pK_b = 4.9$

Table 24.2
 pK_b Values of Anilines

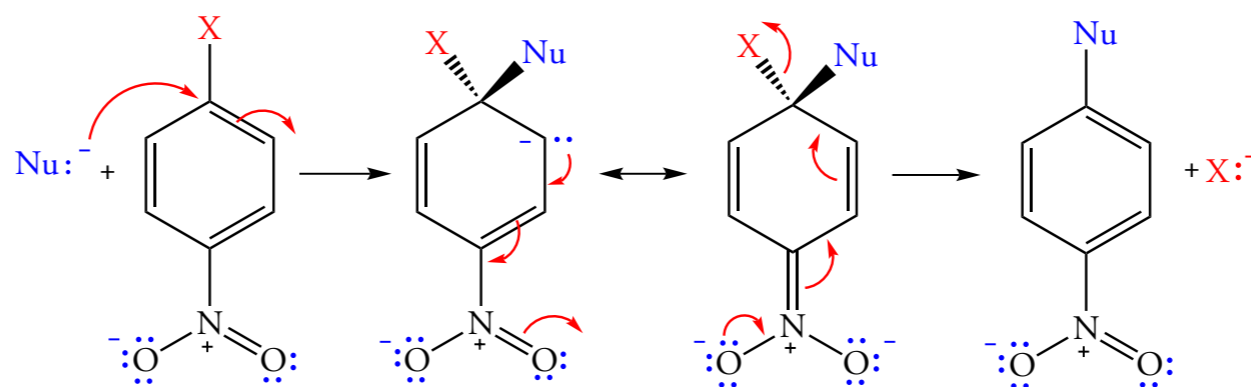
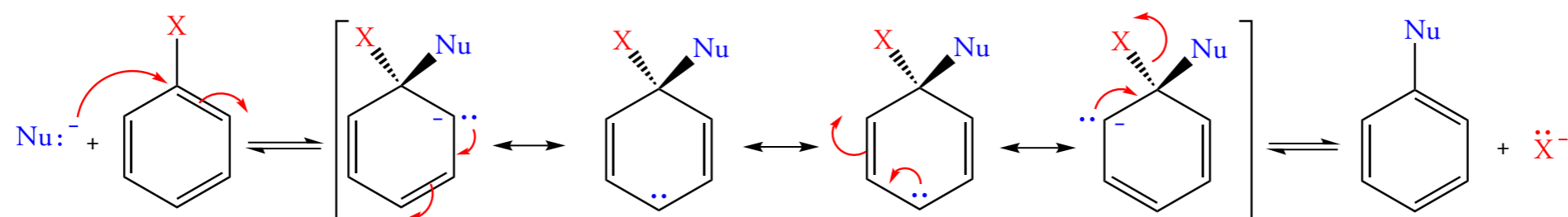
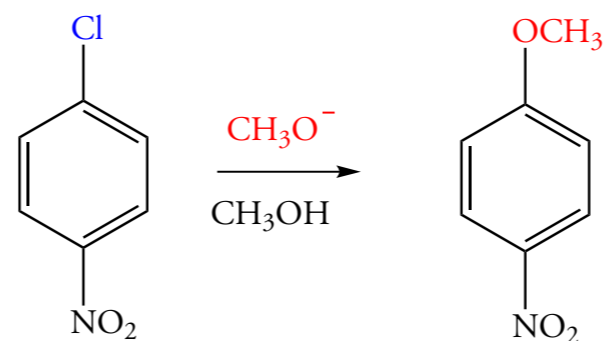
Substituent	Ortho	Meta	Para
H	9.40	9.40	9.40
bromo	11.47	10.42	10.14
chloro	11.35	10.48	10.02
cyano	13.05	11.25	12.26
methoxy	9.48	9.77	8.66
methyl	9.56	9.28	8.90
nitro	14.26	11.53	13.00
trifluoromethyl		10.80	11.25

24.3 CONVERTING ARYL HALIDES TO GRIGNARD REAGENTS AND ORGANOLITHIUM REAGENTS



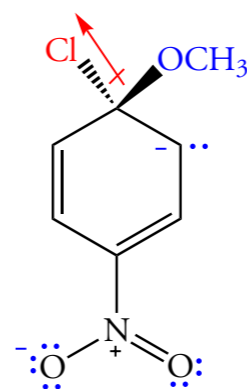
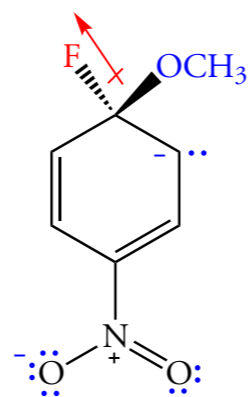
24.4 NUCLEOPHILIC AROMATIC SUBSTITUTION

Addition-Elimination



Fluorine is very effective in withdrawing electrons.

Chlorine is less effective in withdrawing electrons.



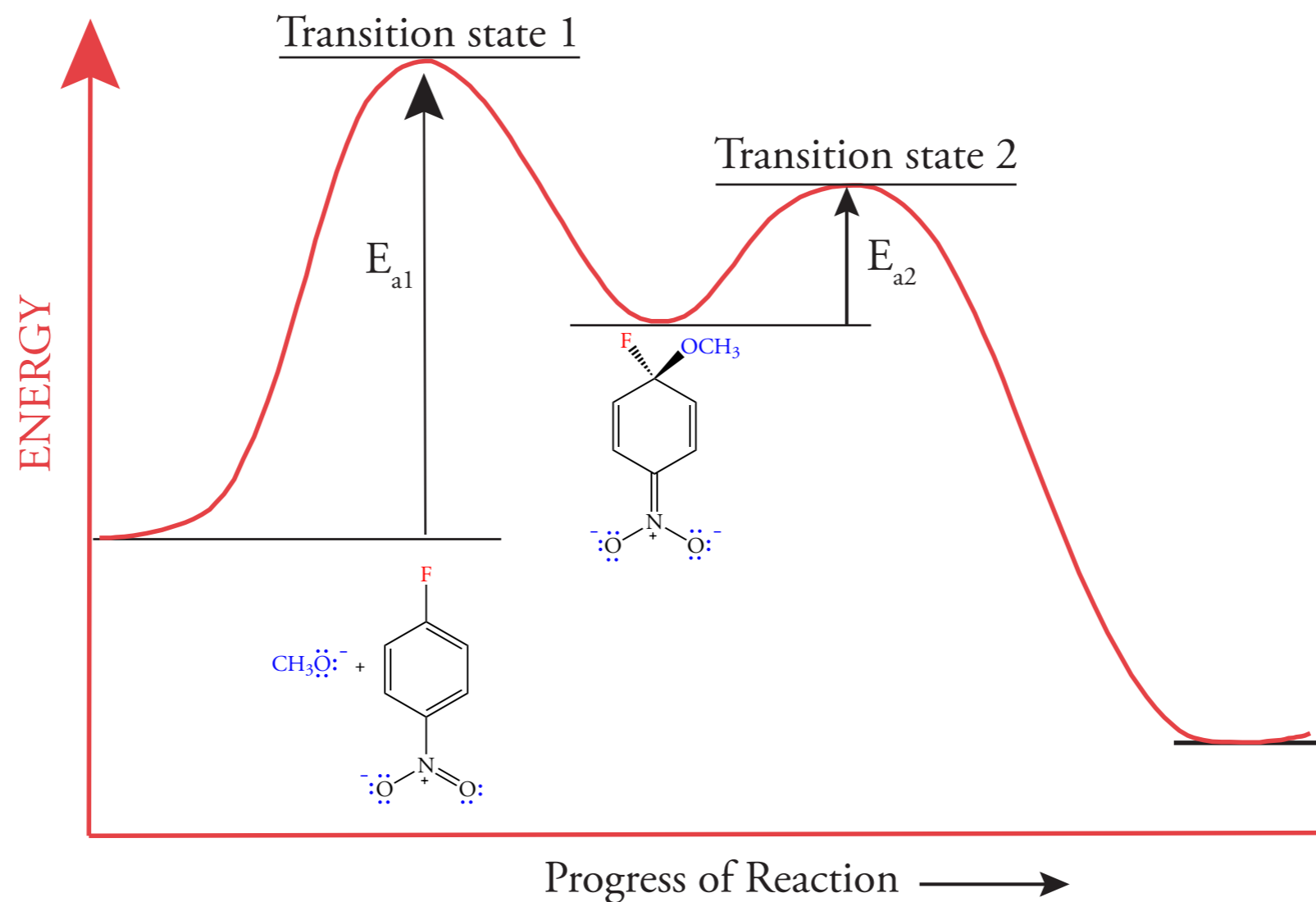
Stabilized cyclohexadienyl anion

24.4 NUCLEOPHILIC AROMATIC SUBSTITUTION

Addition-Elimination

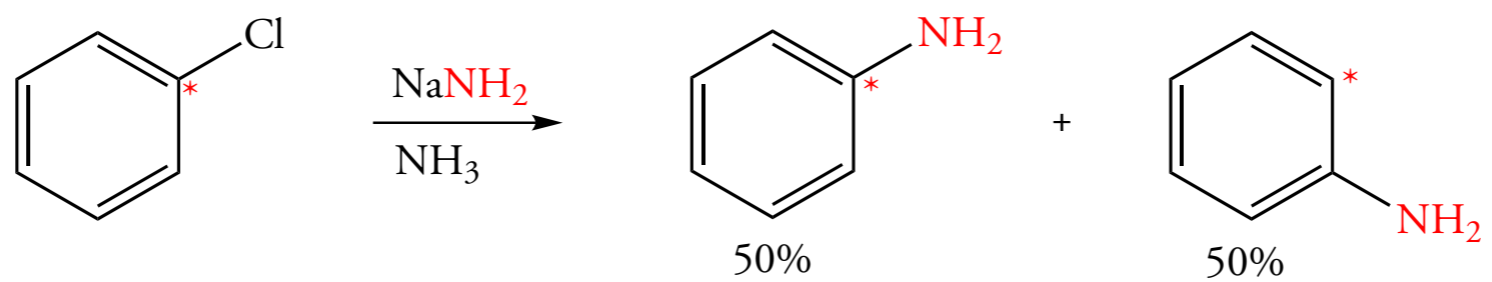
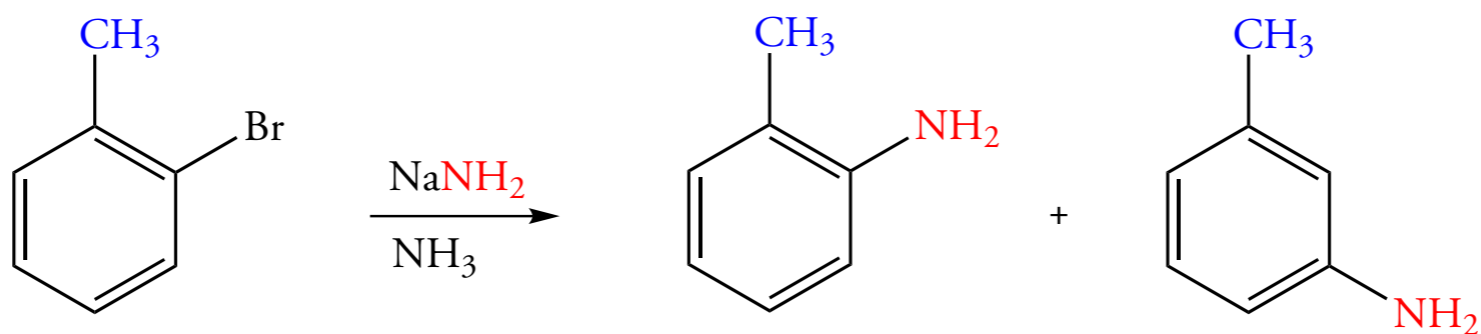
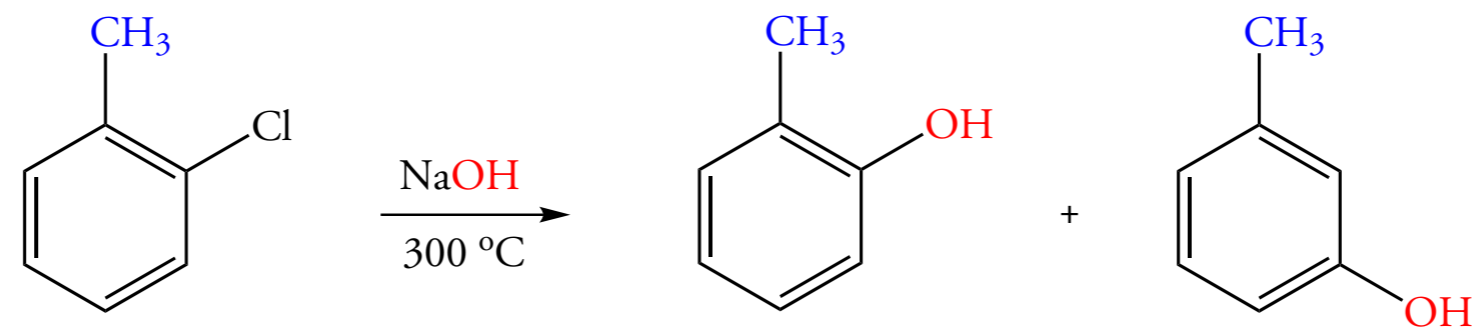
Figure 24.1 Addition Elimination Reaction

The rate-determining step is the addition of the nucleophile to give a tetrahedral intermediate that then reacts in a faster second step to eliminate the leaving group.



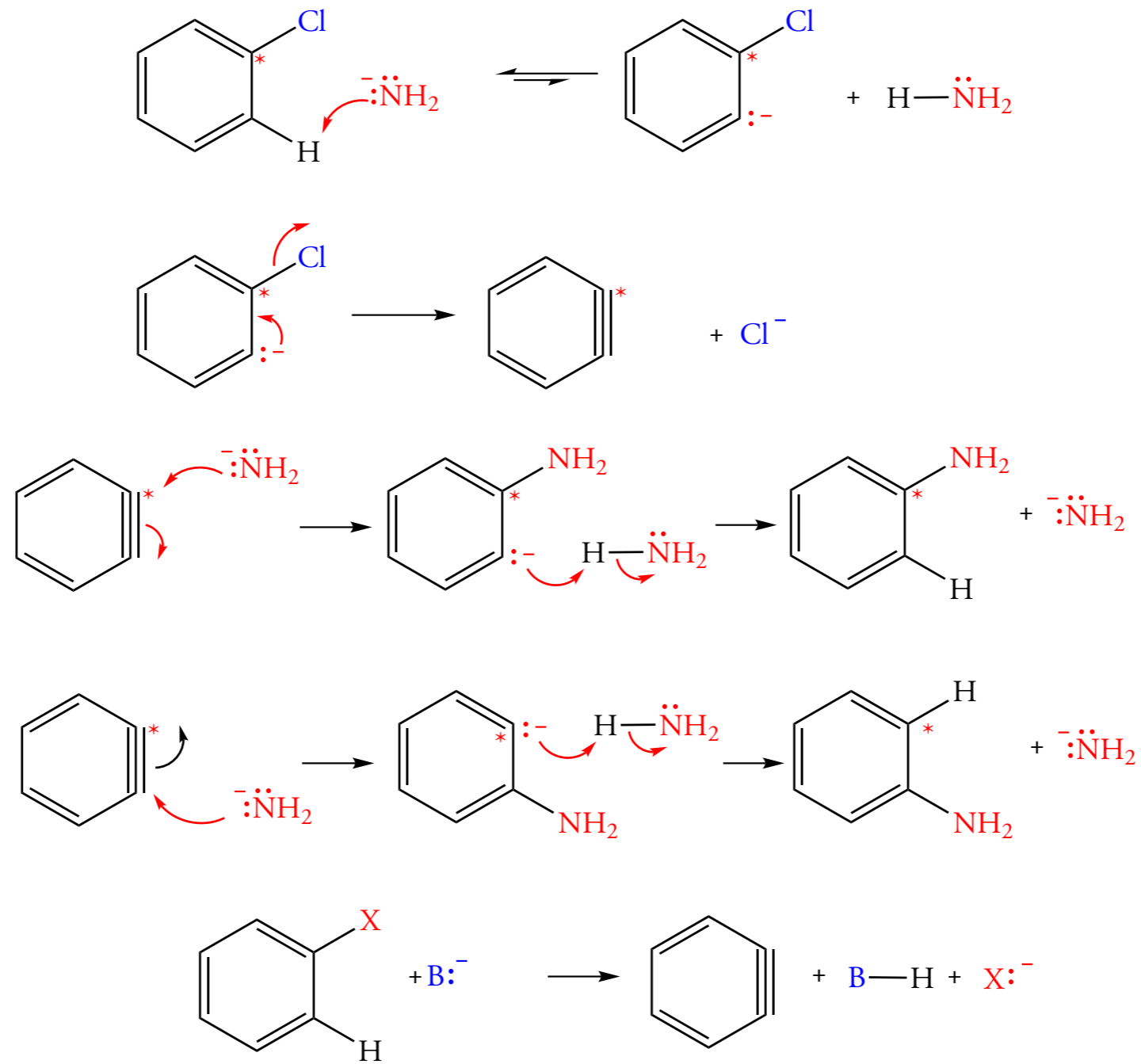
24.4 NUCLEOPHILIC AROMATIC SUBSTITUTION

Elimination-Addition



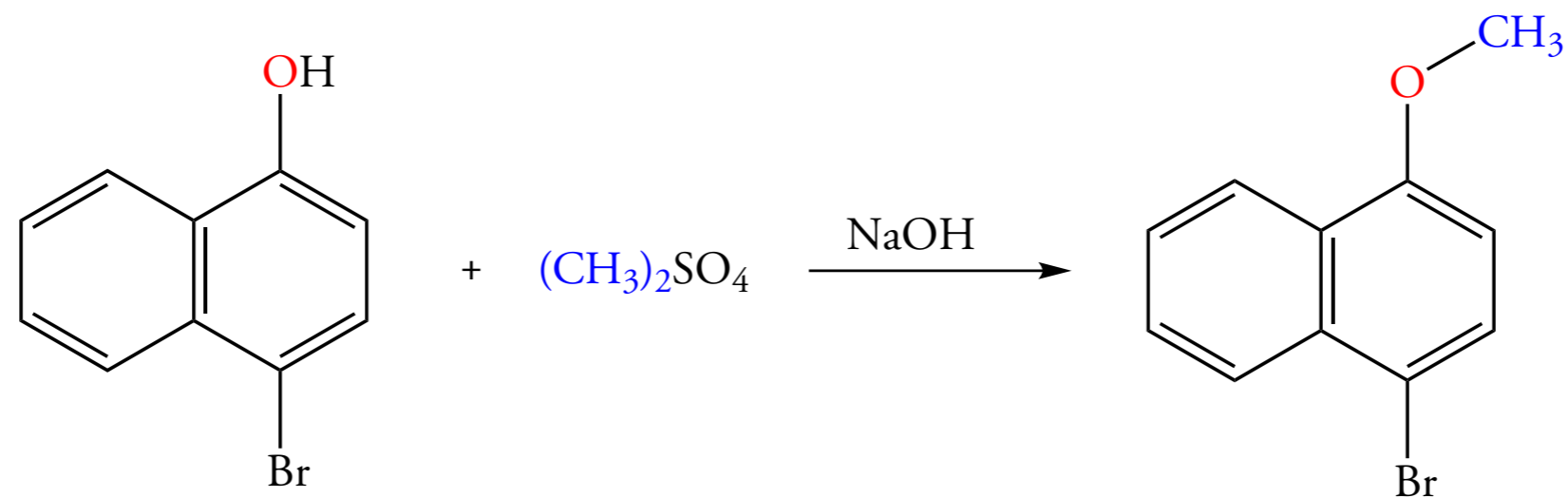
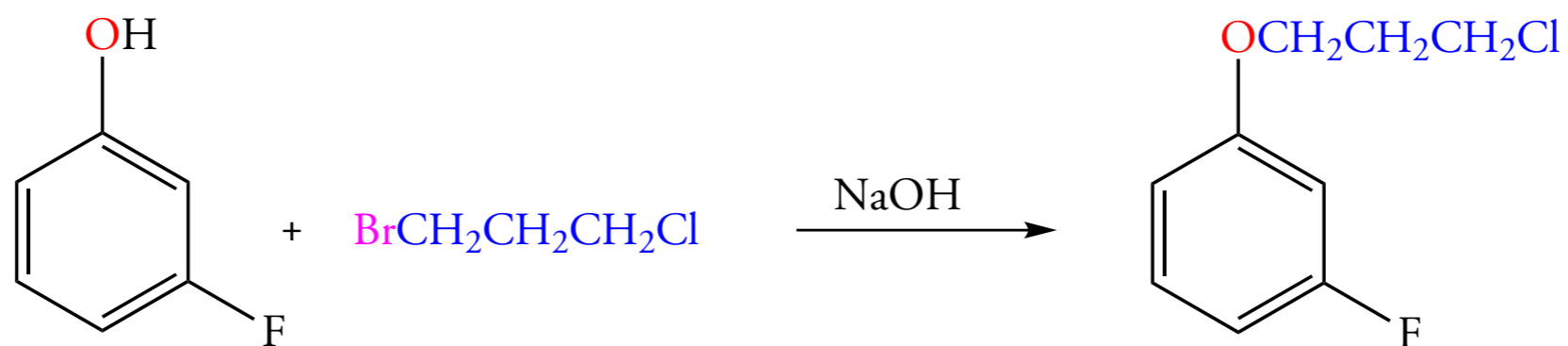
24.4 NUCLEOPHILIC AROMATIC SUBSTITUTION

Elimination-Addition



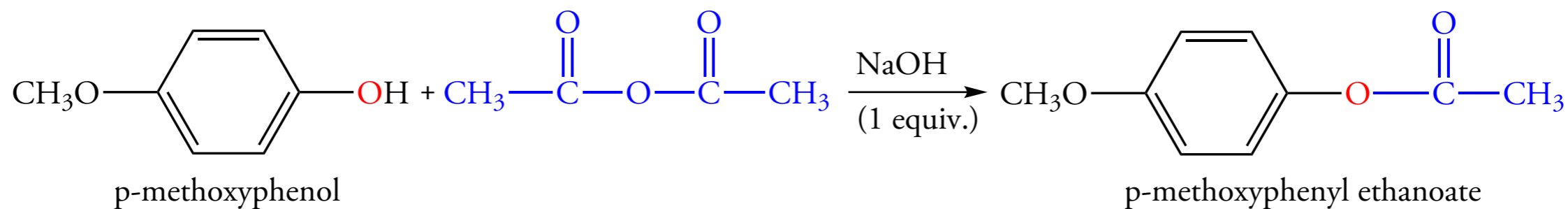
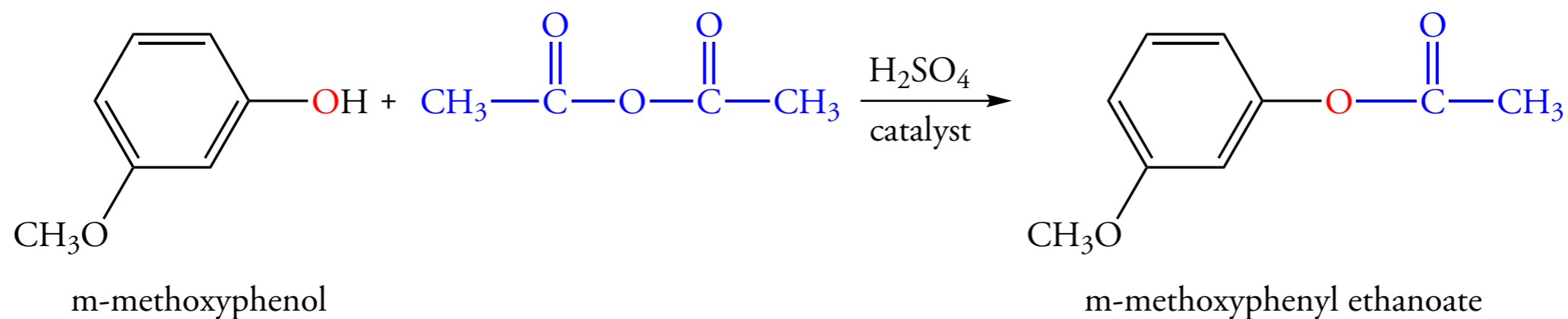
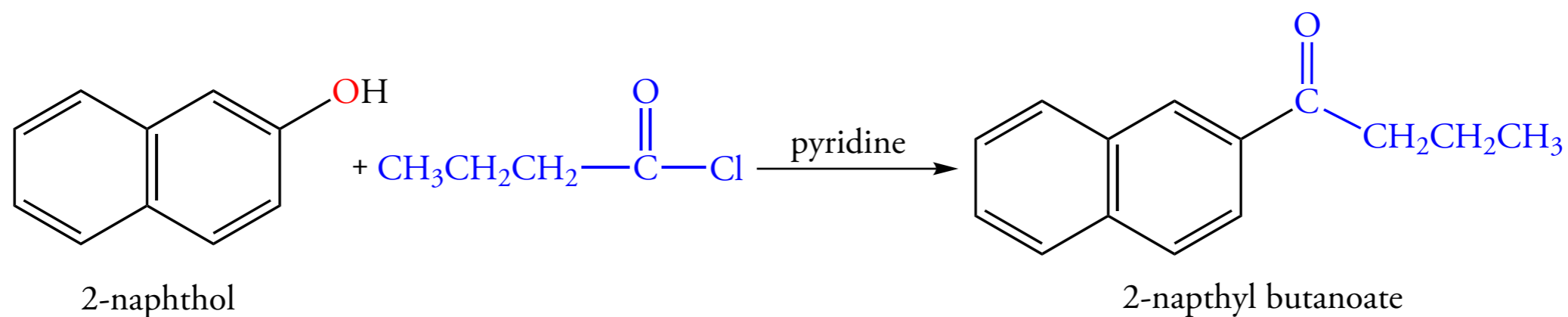
24.5 AN OVERVIEW OF PHENOL REACTIONS

Ether Synthesis



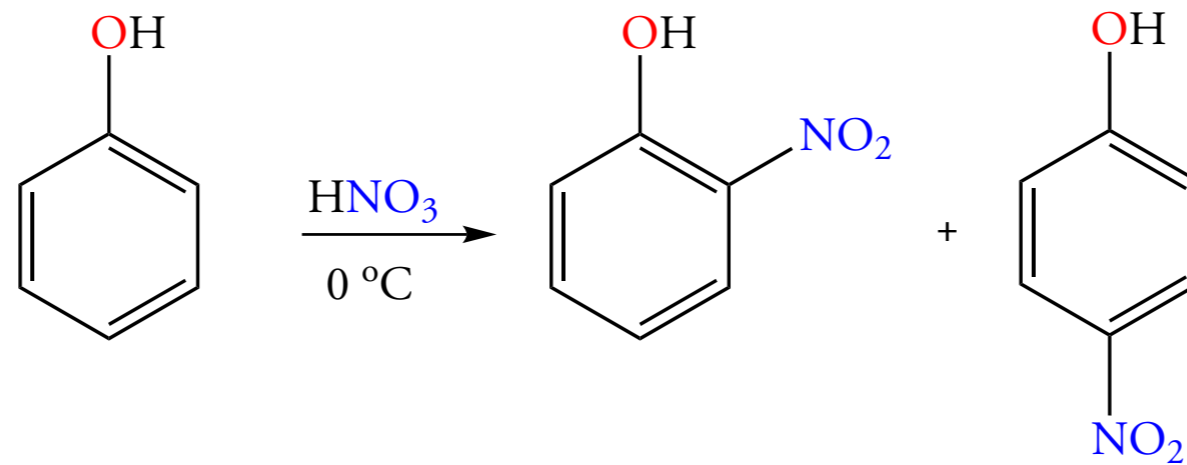
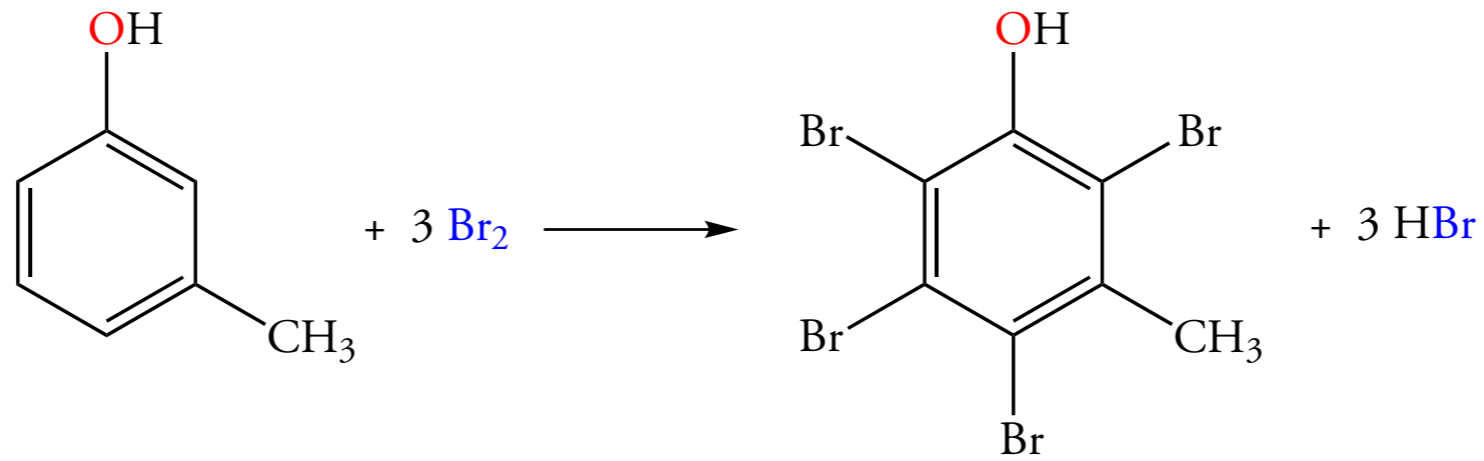
24.5 AN OVERVIEW OF PHENOL REACTIONS

Ester Synthesis

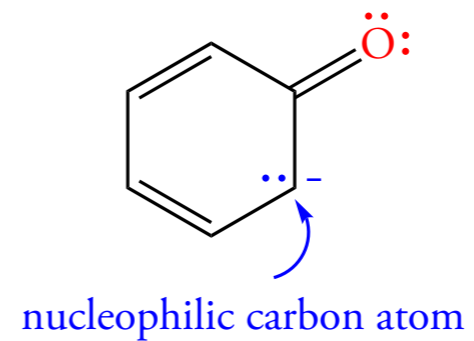
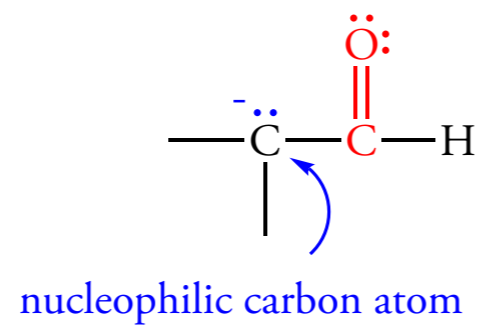
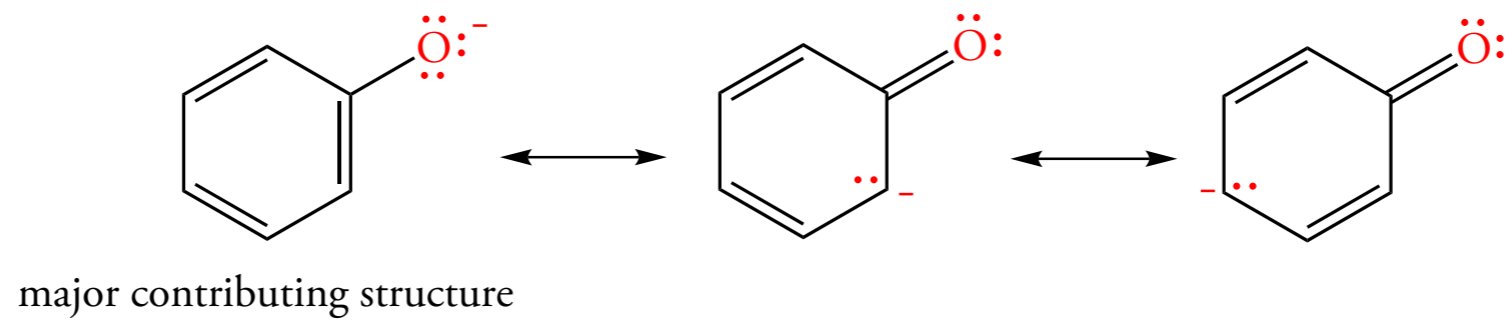
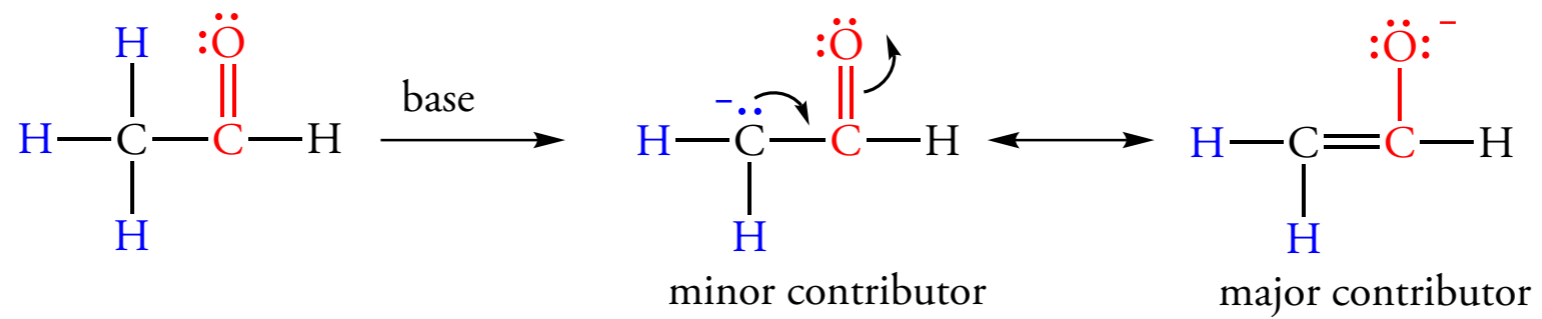


24.5 AN OVERVIEW OF PHENOL REACTIONS

Electrophilic Substitution

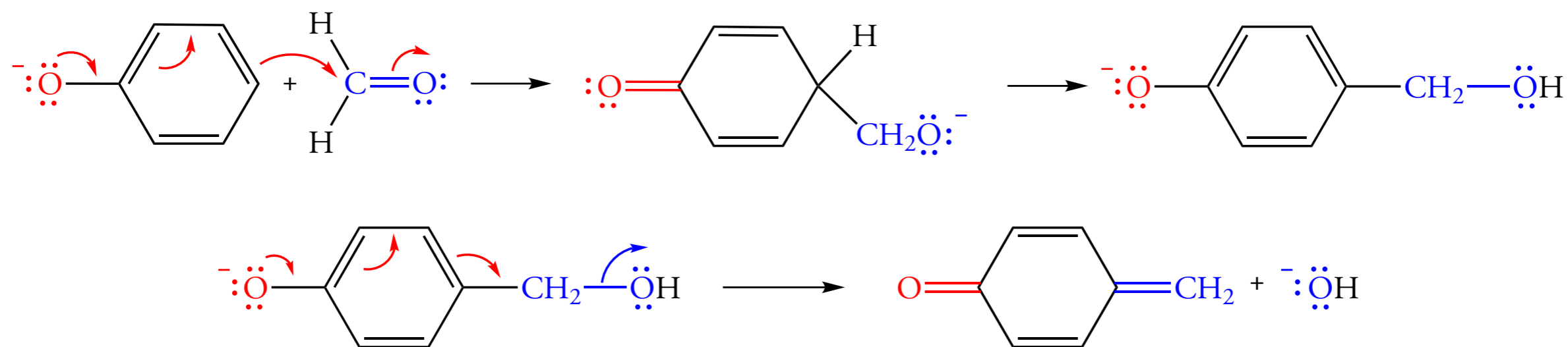


24.6 REACTIONS OF PHENOXIDE IONS



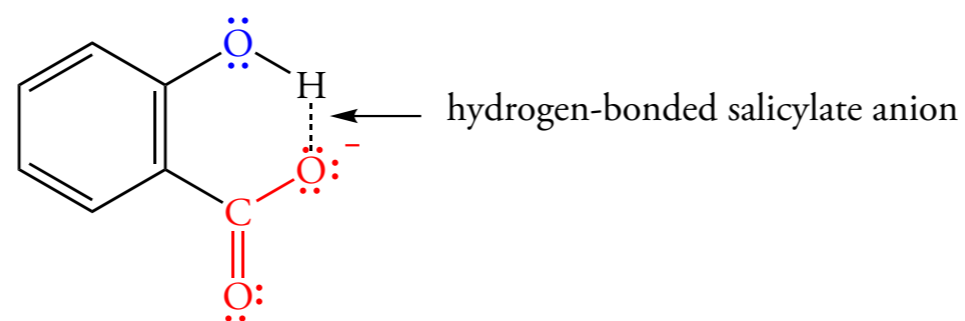
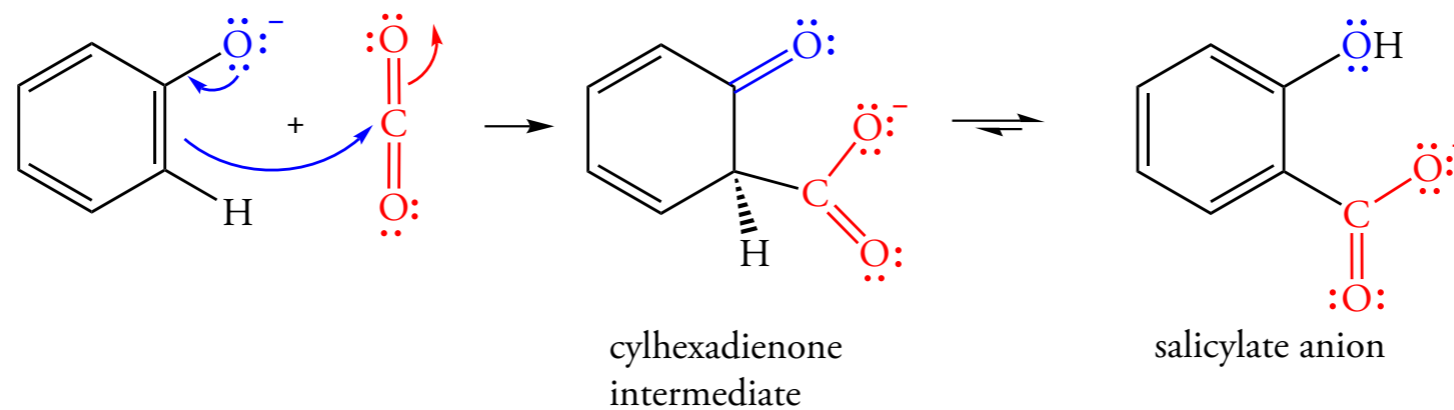
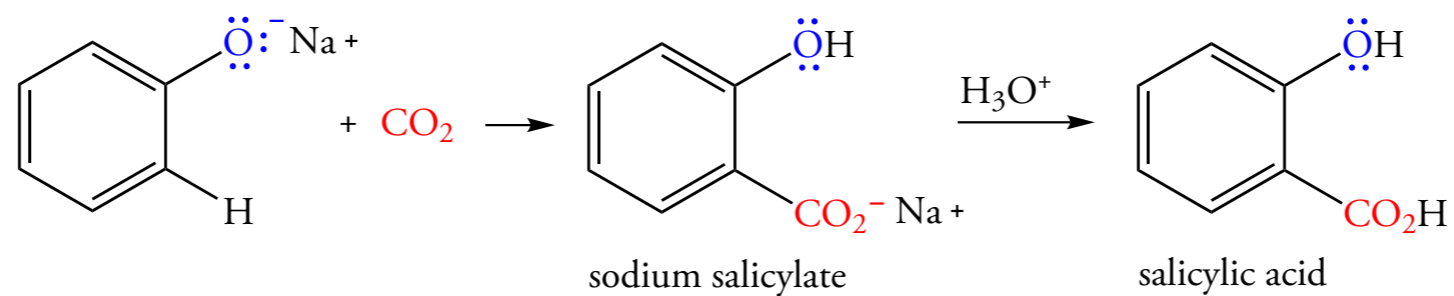
24.6 REACTIONS OF PHENOXIDE IONS

Addition to Formaldehyde

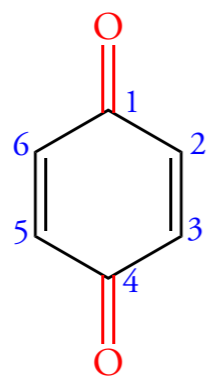


24.6 REACTIONS OF PHENOXIDE IONS

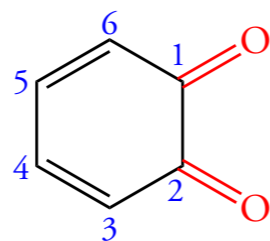
The Kolbe Synthesis



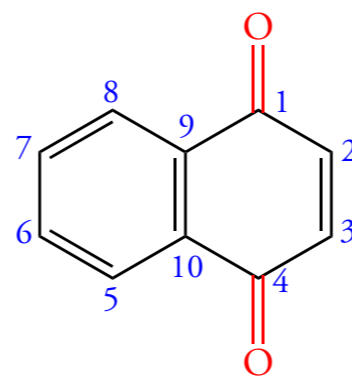
24.7 QUINONES



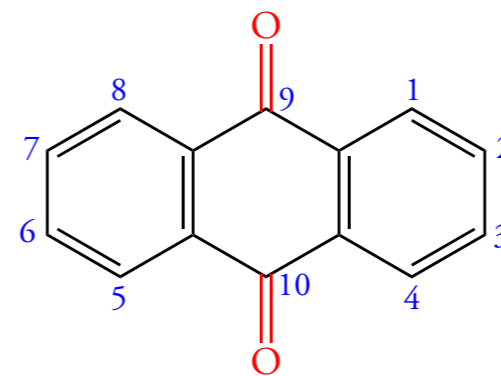
p-benzoquinone



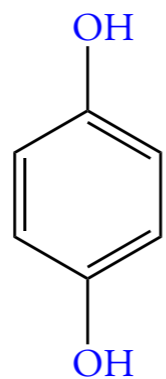
o-benzoquinone



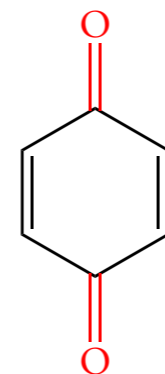
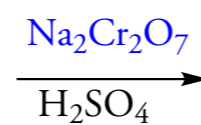
1,4-naphthaquinone



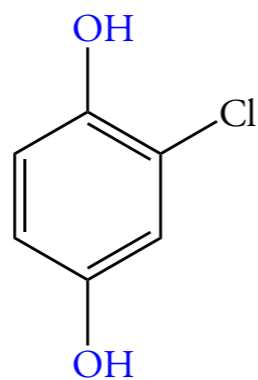
9,10-phenanthraquinone



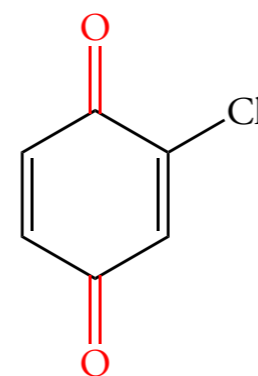
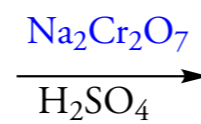
hydroquinone



p-benzoquinone
(quinone)

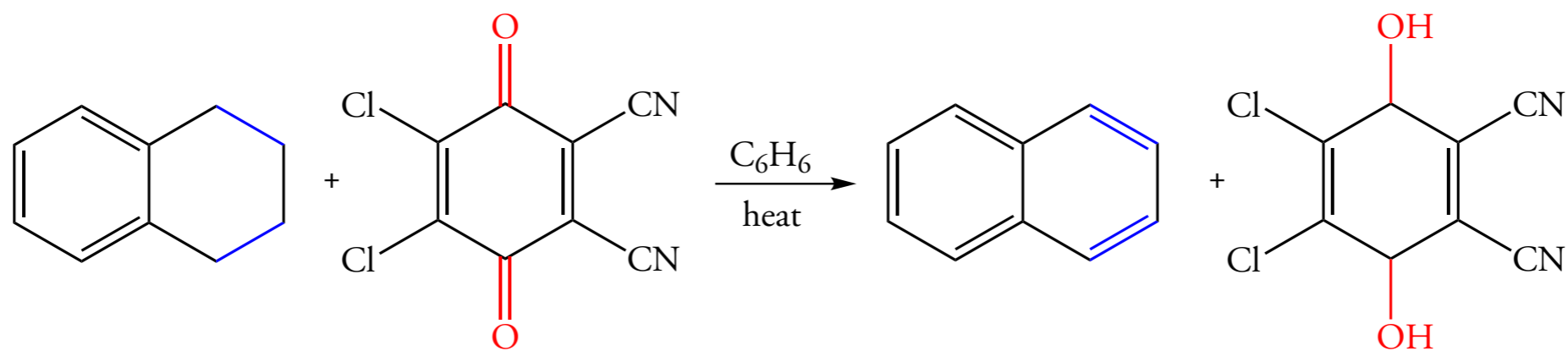
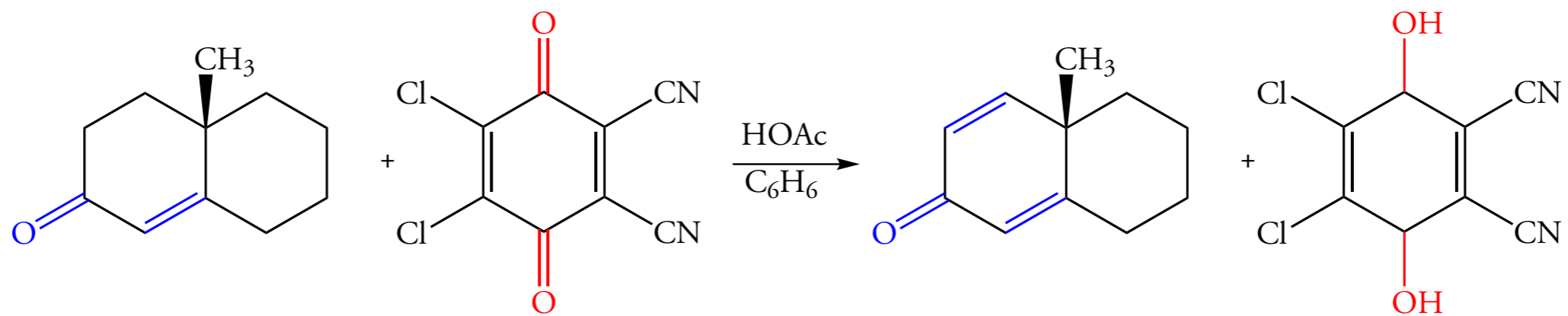


hydroquinone



2-chloro-1,4-benzoquinone

24.7 QUINONES



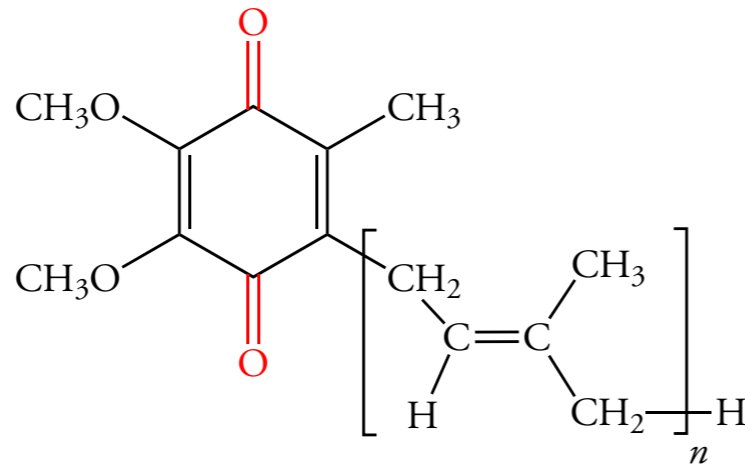
24.7 QUINONES

Table 24.3
Reduction Potentials of Quinones

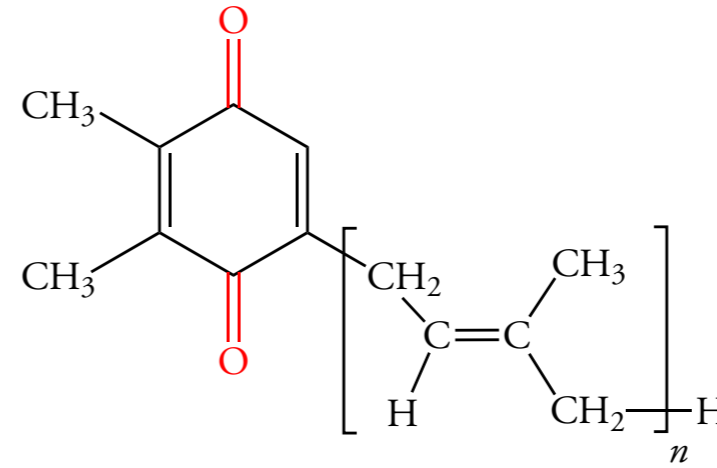
Quinone	Reduction Potential E° (volts)
1,4-benzoquinone	0.699
2-methyl-1,4-benzoquinone	0.645
2-hydroxyl-1,4-benzoquinone	0.590
2-bromo-1,4-benzoquinone	0.715
2-chloro-1,4-benzoquinone	0.713
1,4-naphthaquinone	0.47
1,2-naphthaquinone	0.56
9,10-anthraquinone	0.13
9,10-phenanthraquinone	0.44

24.7 QUINONES

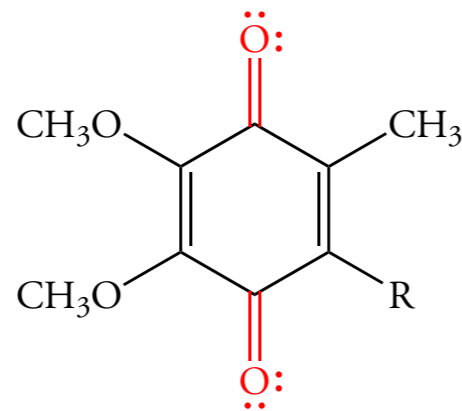
Coenzyme Q: The Ubiquitous Quinone



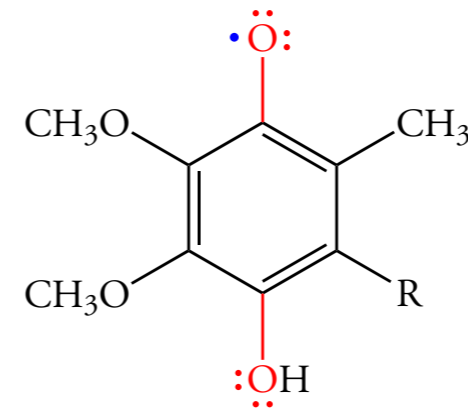
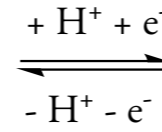
ubiquinone (CoQ)



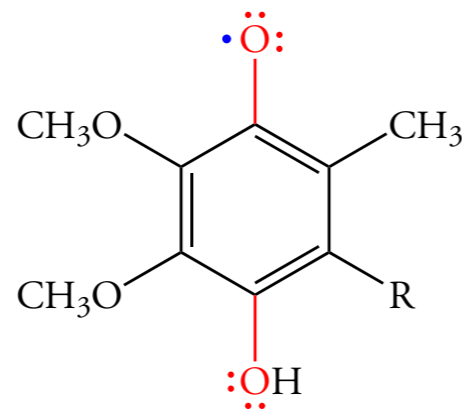
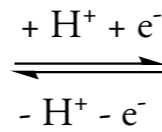
plastoquinone



ubiquinone (CoQ)



semiquinone
(extensively delocalized free radical)

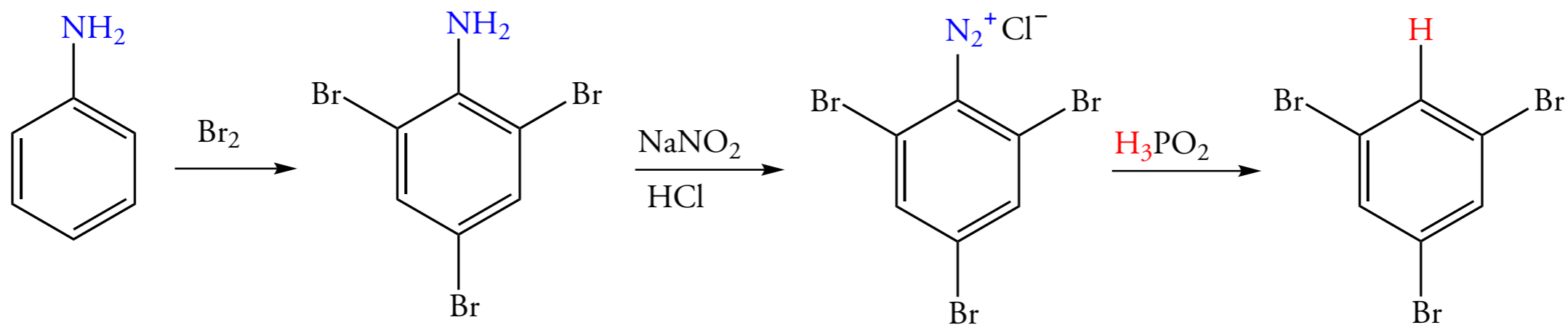
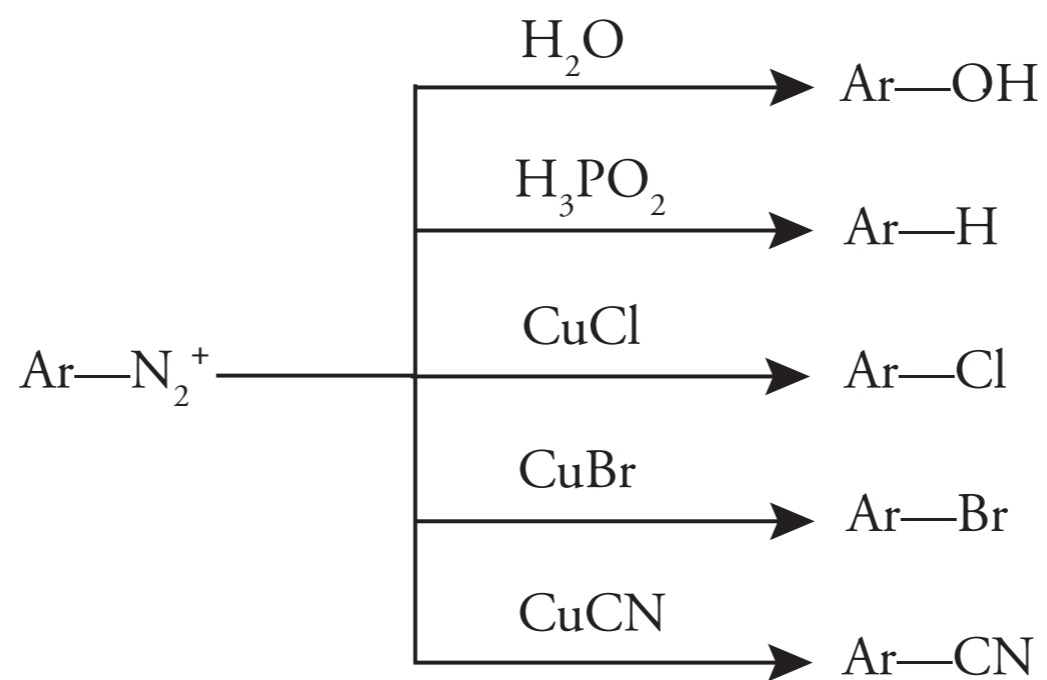


ubiquinol (QH₂)

24.8 SUBSTITUTION REACTIONS OF ARYLDIAZONIUM SALTS

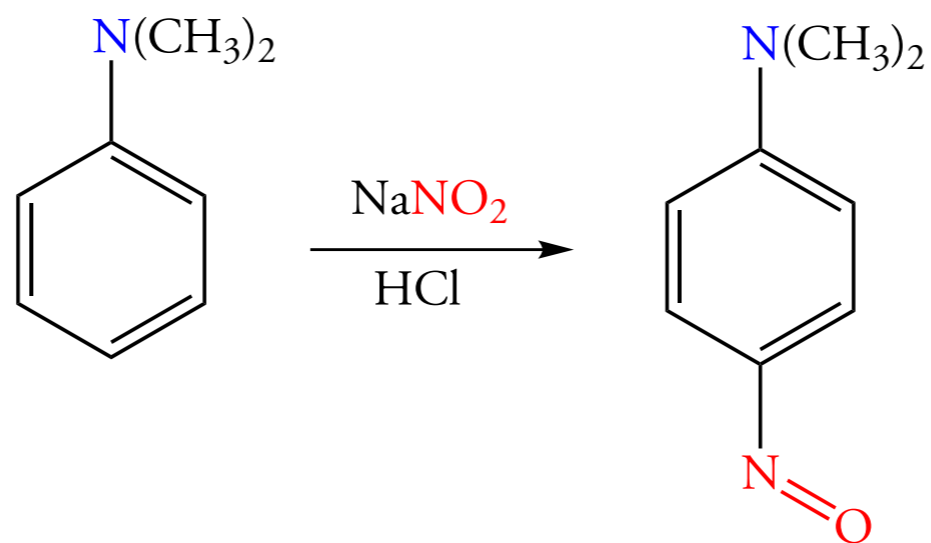
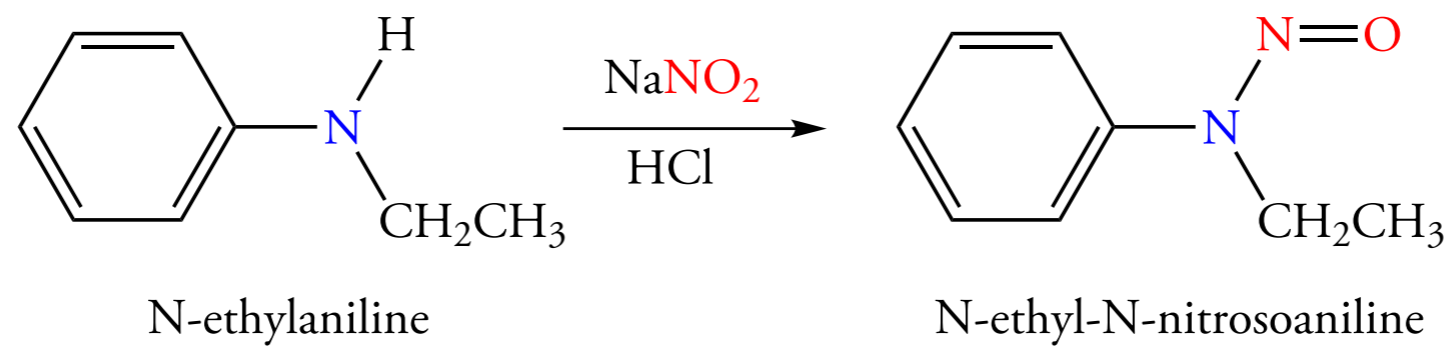
Reactions of Aryldiazonium Ions

Figure 24.3 Summary of Syntheses Using Aryldiazonium Ion Reactions

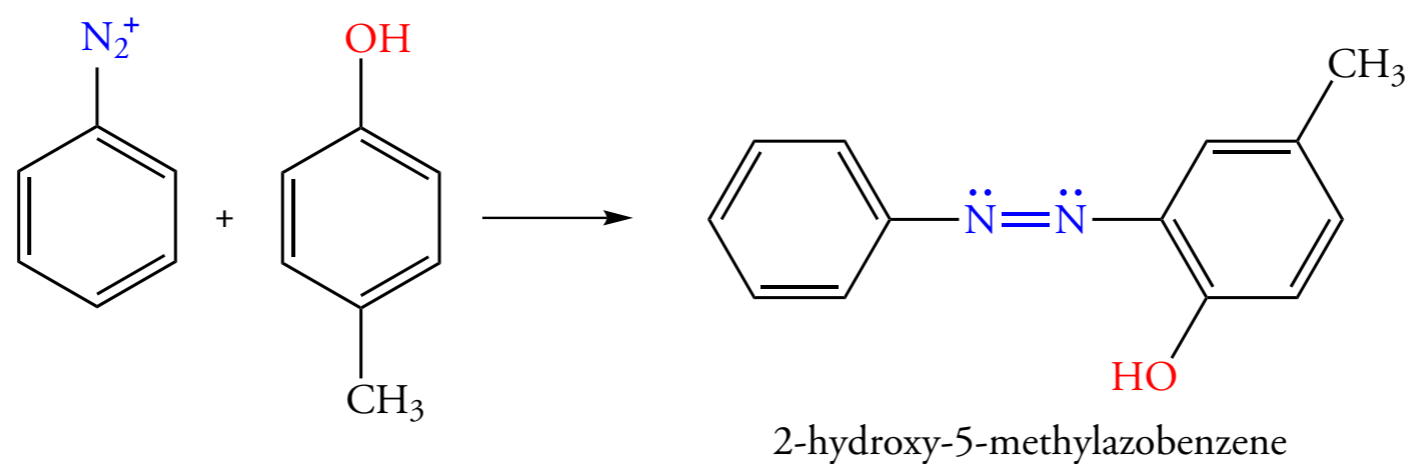
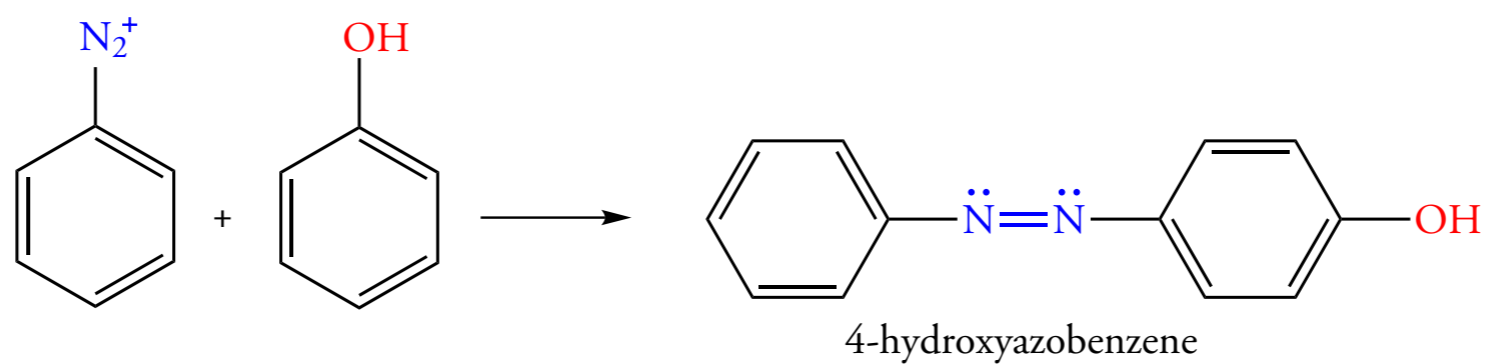
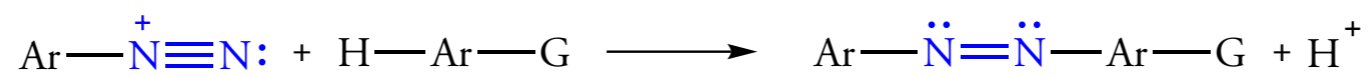
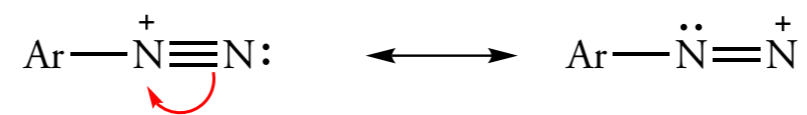


24.8 SUBSTITUTION REACTIONS OF ARYLDIAZONIUM SALTS

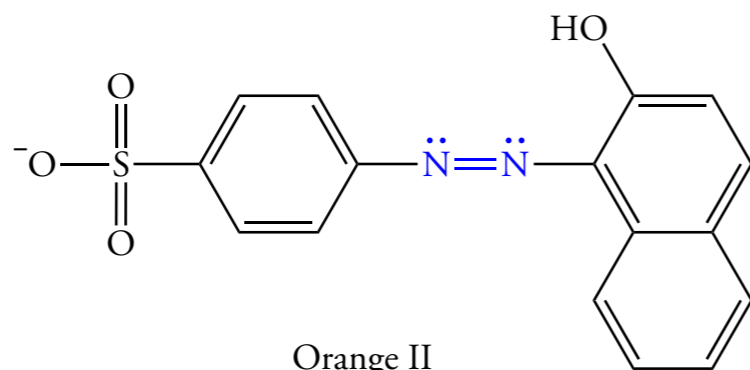
Nitrosation of Arylamines



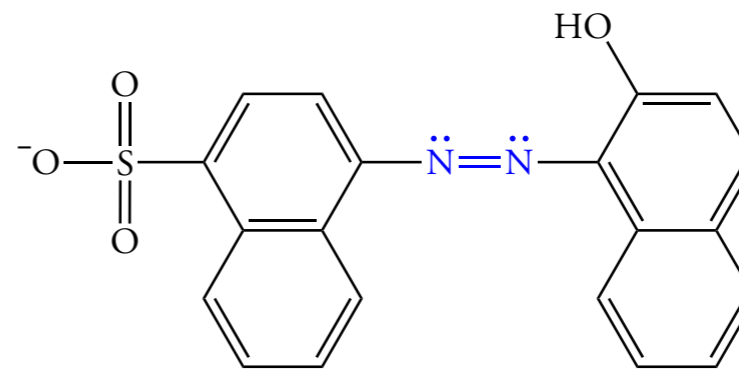
24.9 AZO COMPOUNDS



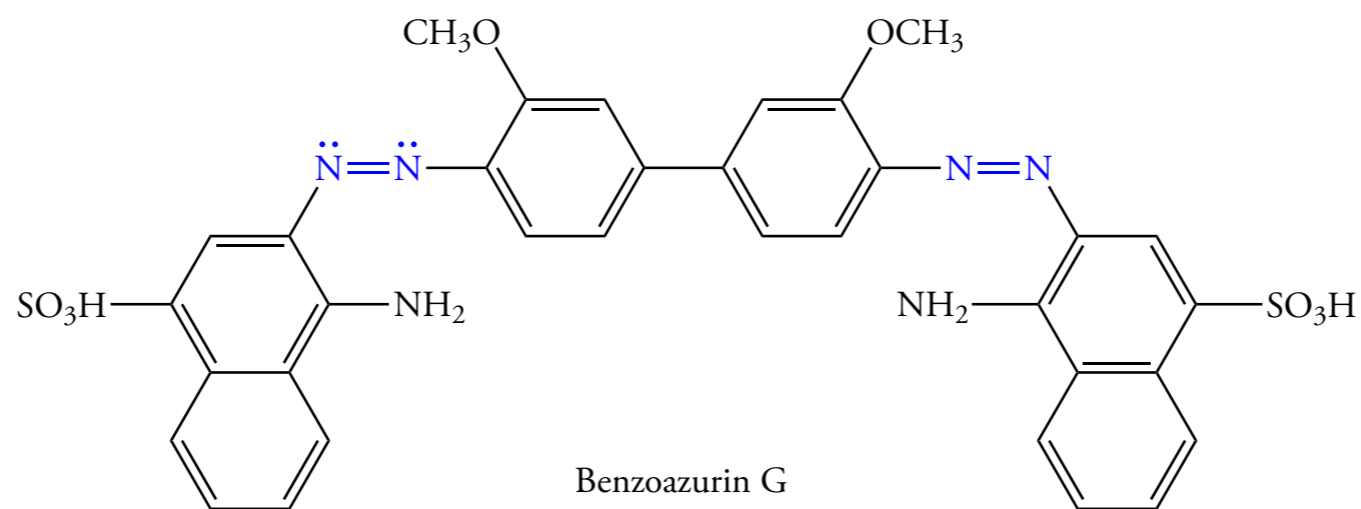
24.9 AZO COMPOUNDS



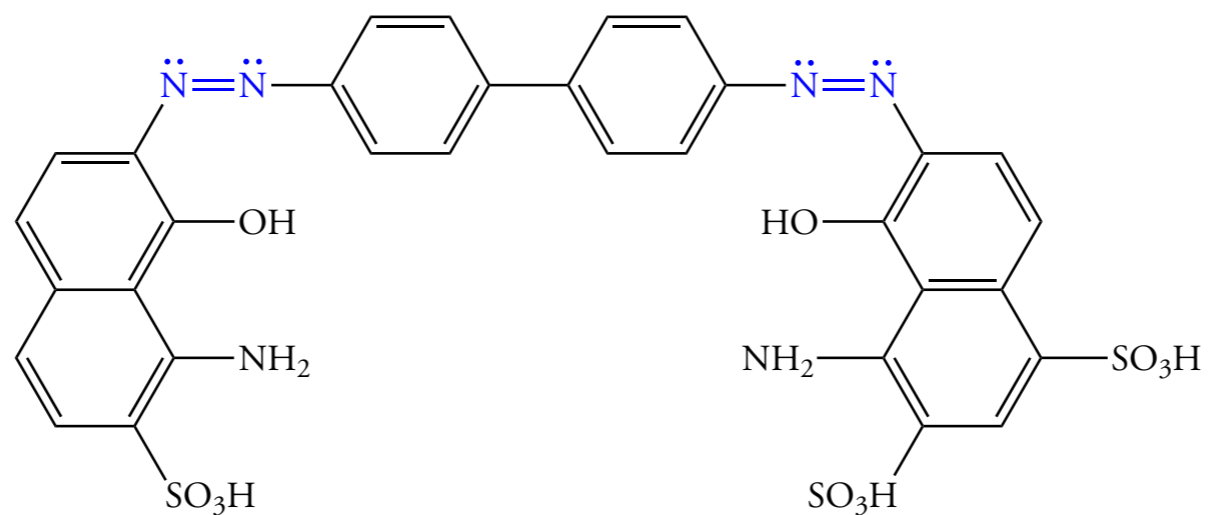
Orange II
 $\lambda_{\max} = 484 \text{ nm}$



Fast Red A
 $\lambda_{\max} = 505 \text{ nm}$



Benzoazurin G
 $\lambda_{\max} = 509 \text{ nm}$



Sky blue 6B
 $\lambda_{\max} = 627 \text{ nm}$