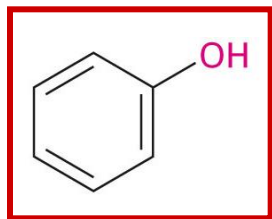
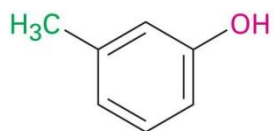


Phenol Nomenclature and Properties

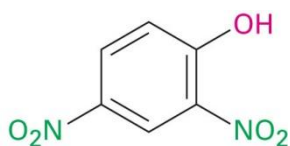


A phenol

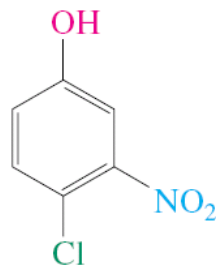
When no other functional groups of higher priority are present, phenol is used as the parent name rather than benzene.



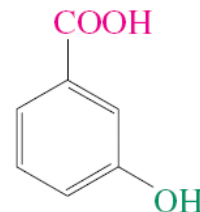
m-Methylphenol
(*m*-Cresol)



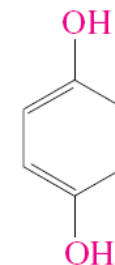
2,4-Dinitrophenol



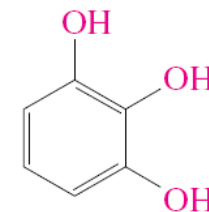
4-Chloro-3-nitrophenol



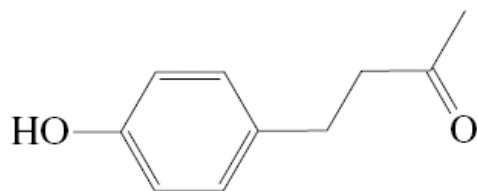
3-Hydroxybenzoic acid
(*m*-Hydroxybenzoic acid)



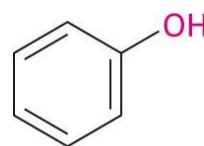
1,4-Benzenediol
(Hydroquinone)



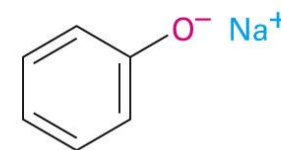
1,2,3-Benzenetriol
(Pyrogallol)



4-Hydroxyphenyl-2-butanone
(Flavor of raspberries)



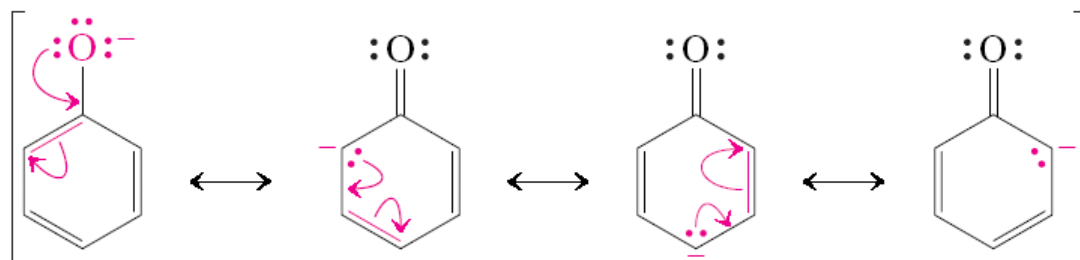
Phenol



Sodium phenoxide
(sodium phenolate)



Phenols are more acidic than alcohols, because the negative charge of phenoxide is delocalized by the phenyl ring; thus, electron-withdraw groups on the phenyl ring increase the acidity of phenols.



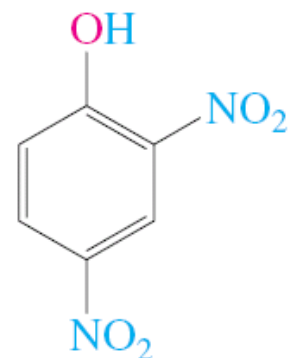
Phenoxide ion

Properties of Phenols

Compound	pK_a
$(CH_3)_3COH$	18.00
CH_3CH_2OH	16.00
H_2O	15.74
CH_3OH	15.54
CF_3CH_2OH	12.43
<i>p</i> -Aminophenol	10.46
CH_3SH	10.3
<i>p</i> -Methylphenol	10.17
Phenol	9.89
<i>p</i> -Chlorophenol	9.38
<i>p</i> -Nitrophenol	7.15

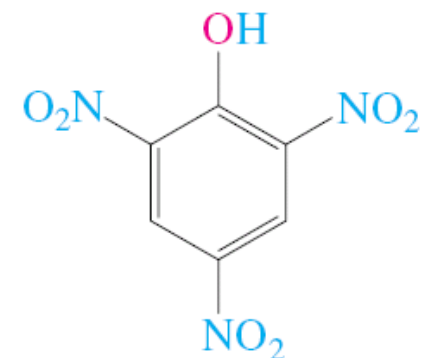
Weaker acid

Stronger acid



2,4-Dinitrophenol

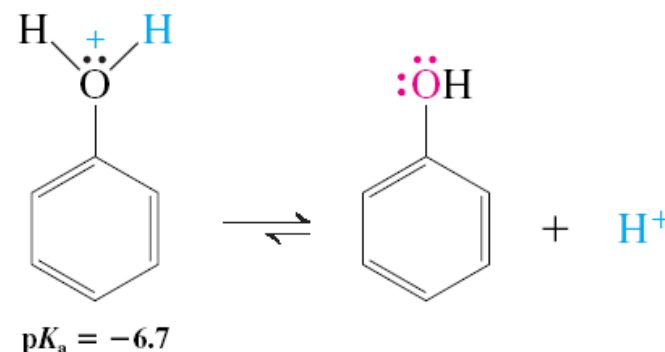
$$pK_a = 4.09$$



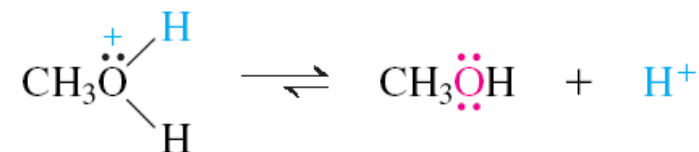
2,4,6-Trinitrophenol
(Picric acid)

$$pK_a = 0.25$$

Phenol is also weakly basic:

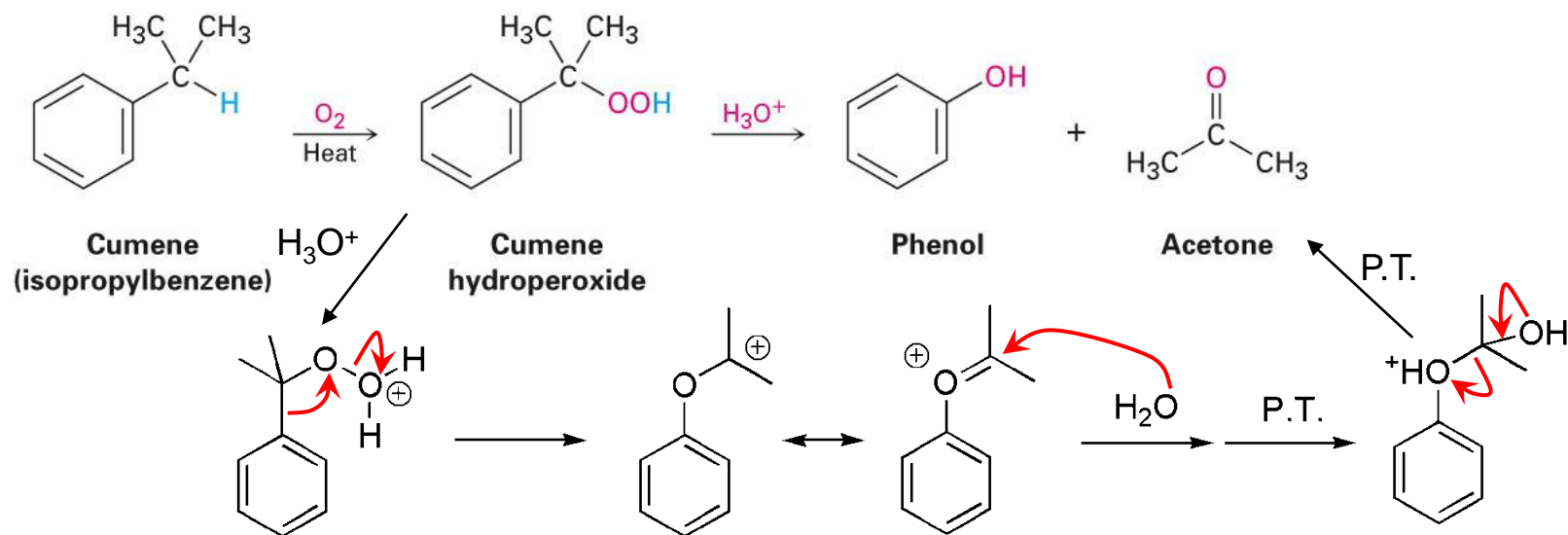


$$pK_a = -6.7$$



$$pK_a = -2.2$$

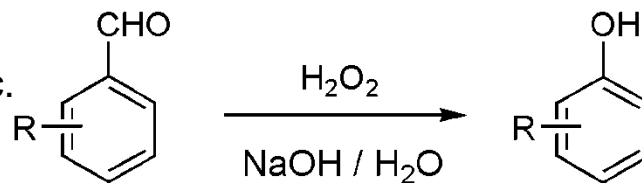
Preparations of Phenols



(Industrial method for production of phenol and acetone)

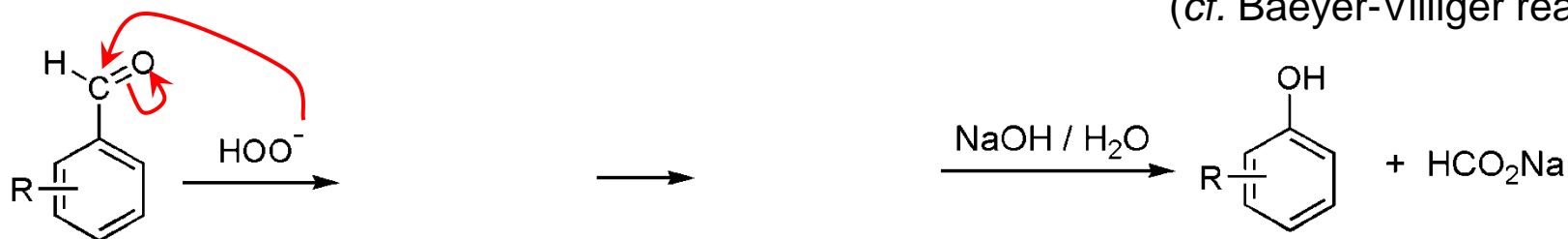
Dakin reaction

R = OH, OR, NH_2 , or NHR, alkyl, etc.
(at *o*- or *p*- position)

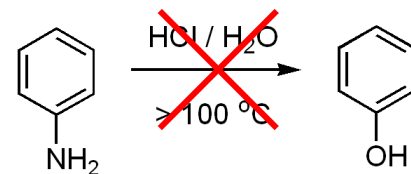
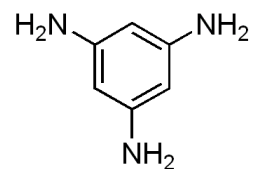
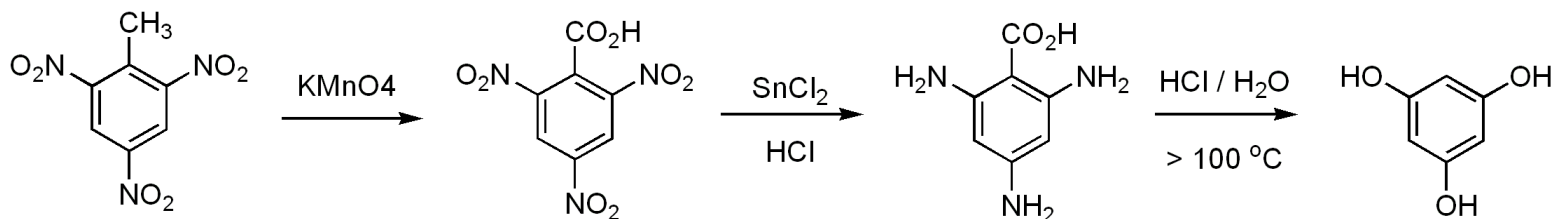
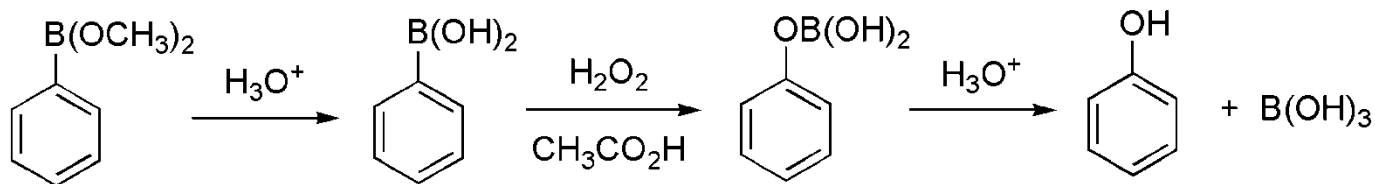
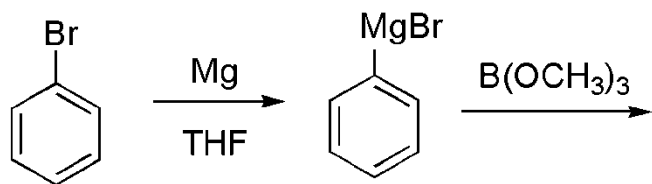
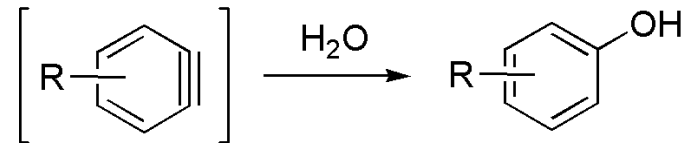
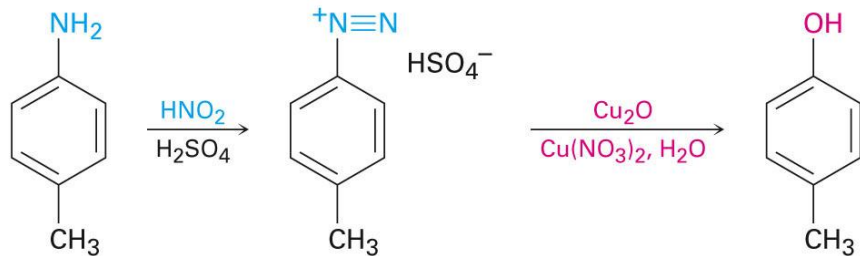


The reaction works the best for electron-rich aromatic rings.

(cf. Baeyer-Villiger reaction)

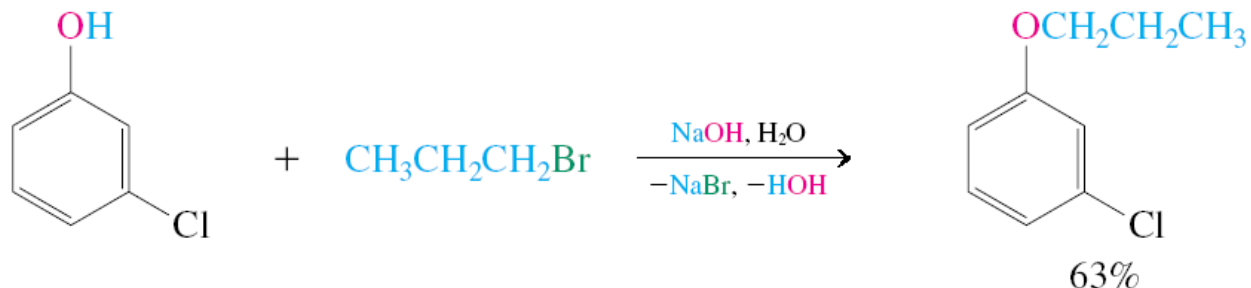


Preparations of Phenols

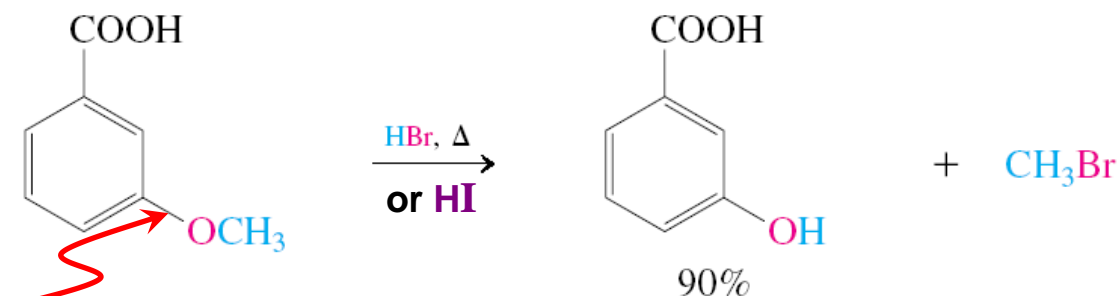


Reactions of Phenols

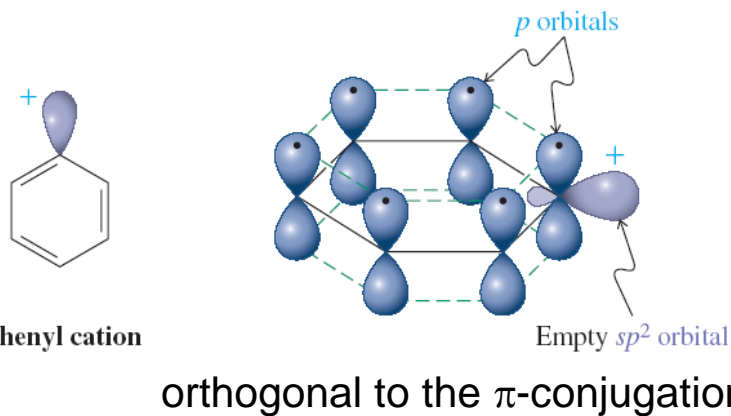
Williamson ether synthesis:



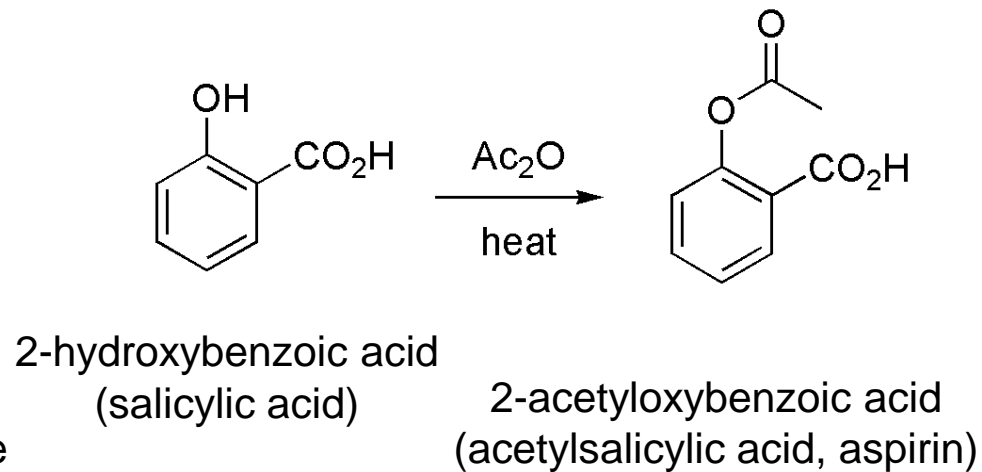
Protection-deprotection strategy for phenols:



Does not dissociate like 2° or 3° C-O bond, because phenyl cation is unstable.

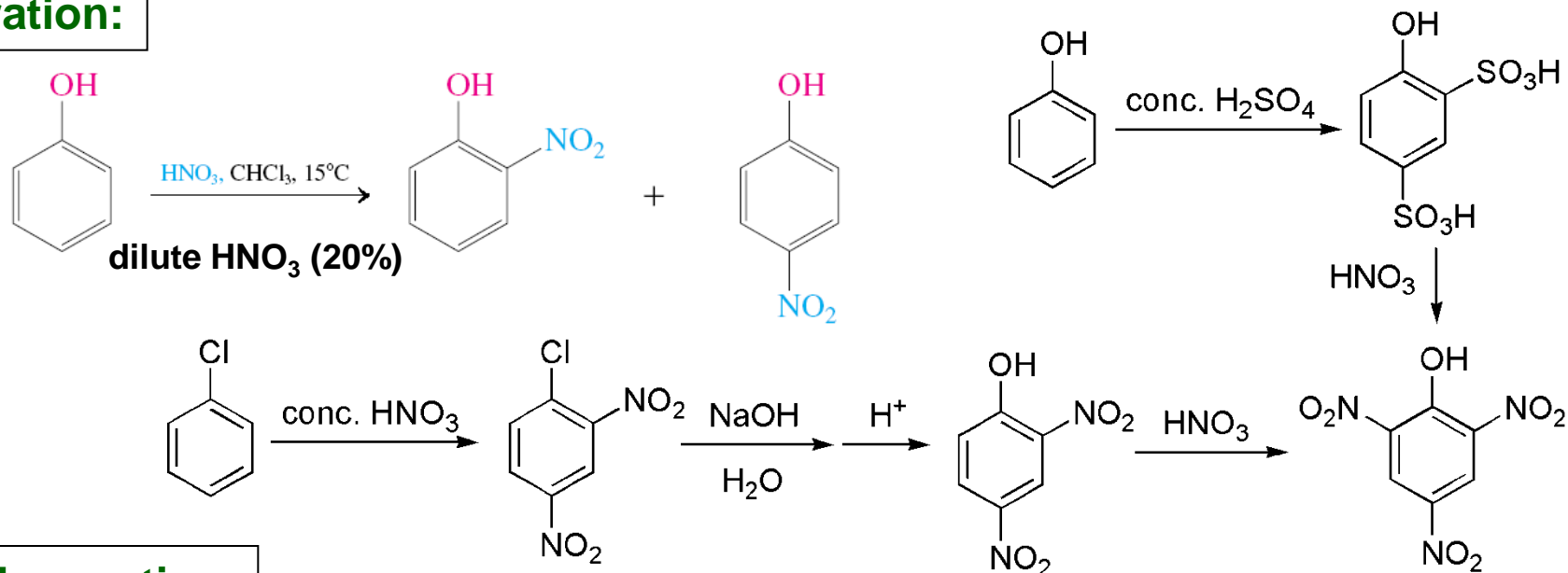


Aspirin: a phenyl alkanolate drug

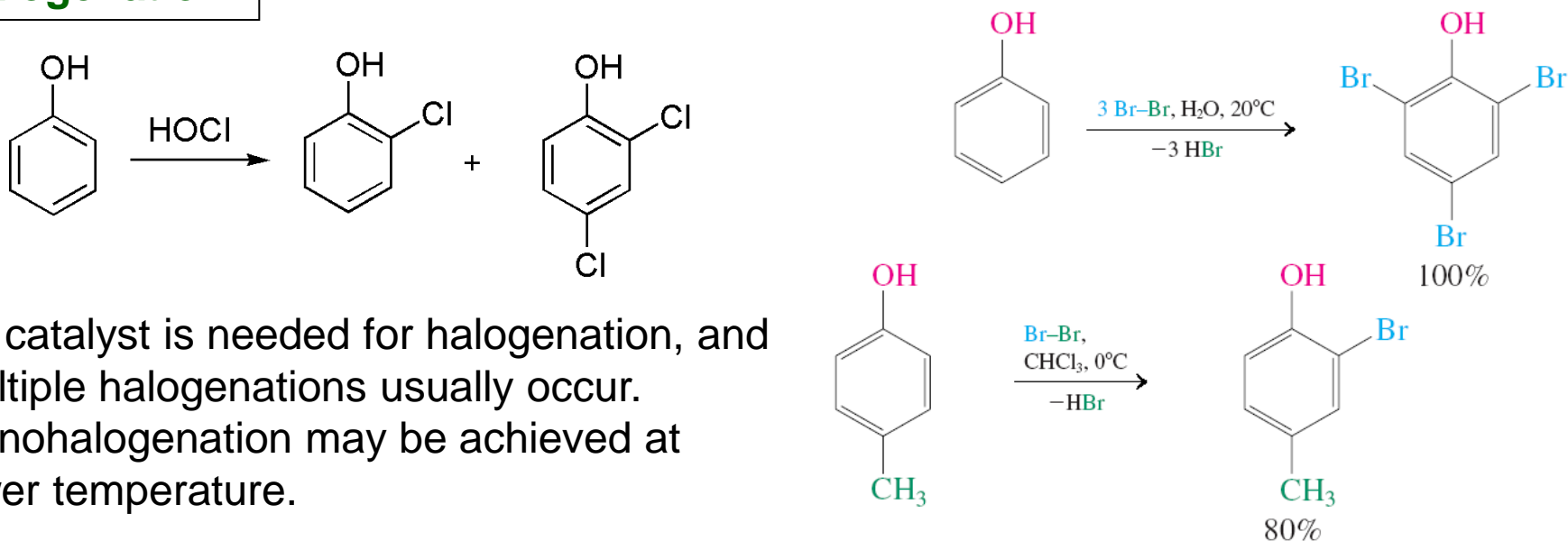


Electrophilic Substitutions of Phenols

Nitration:



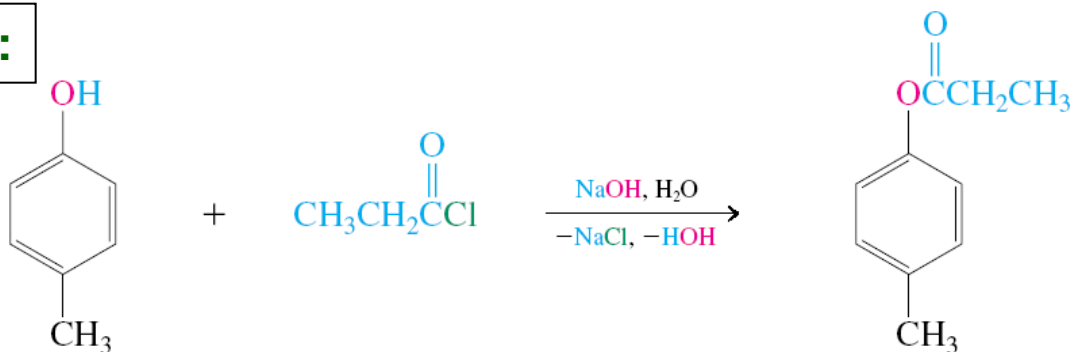
Halogenation:



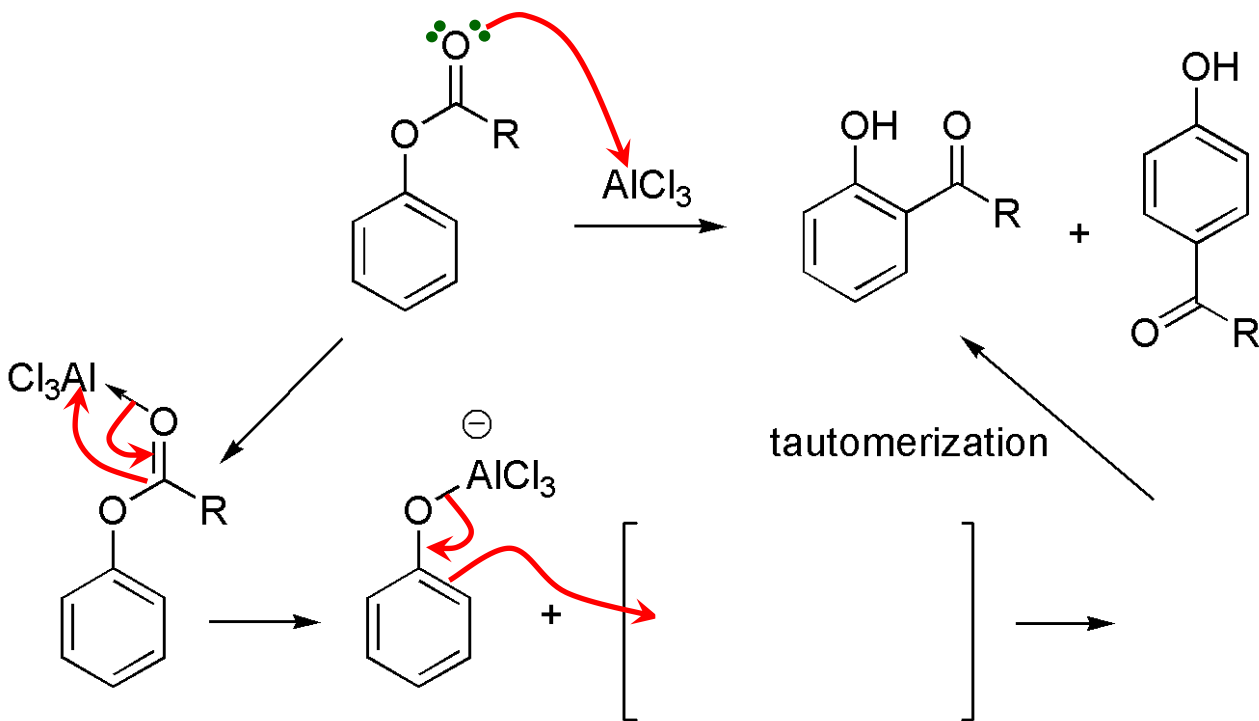
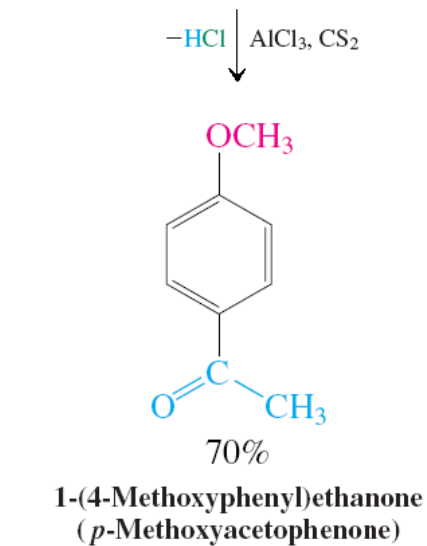
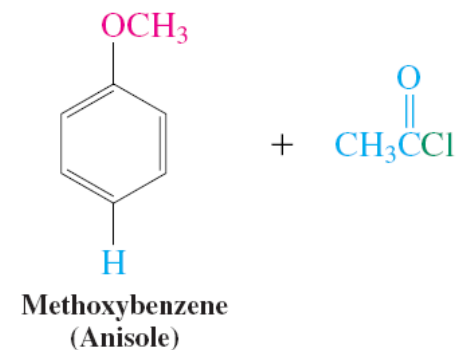
No catalyst is needed for halogenation, and multiple halogenations usually occur. Monohalogenation may be achieved at lower temperature.

Reactions of Phenols

Acylation:

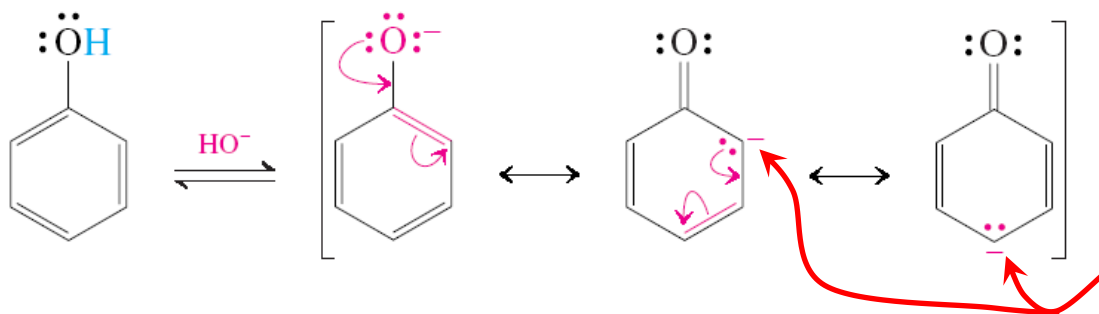
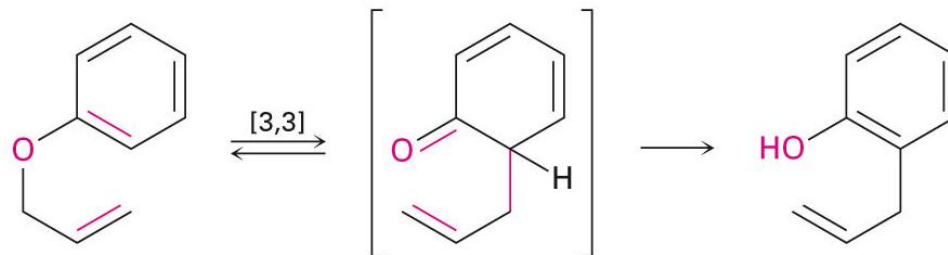


Fries rearrangement:

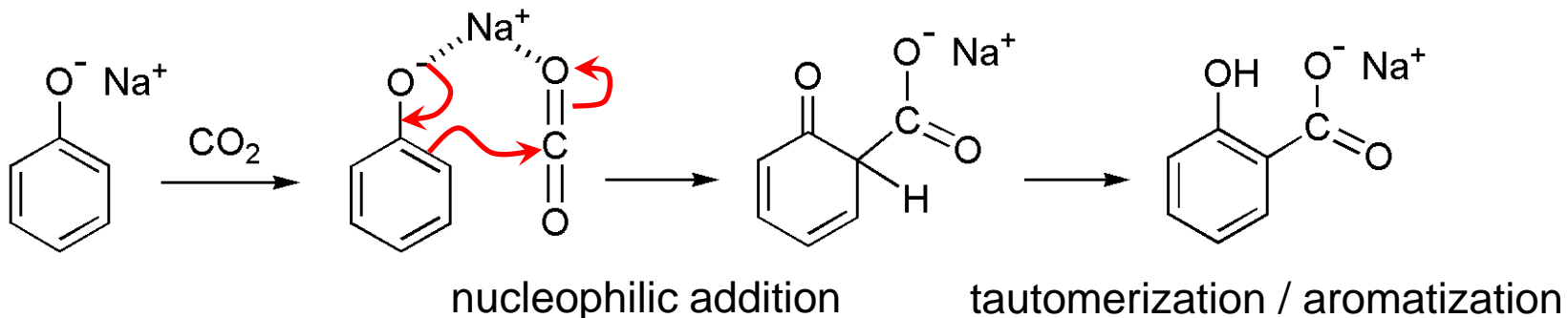
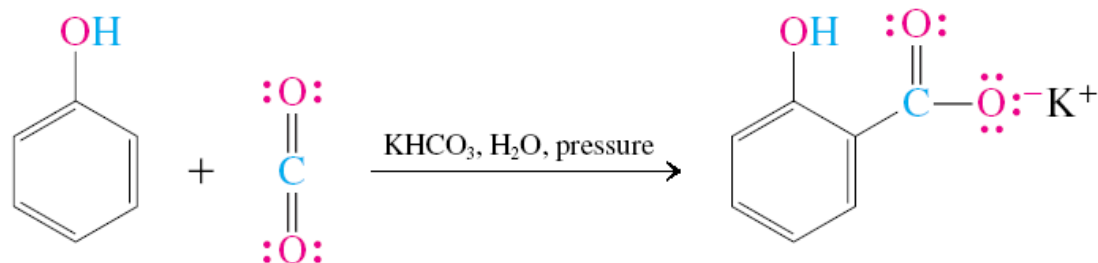


Reactions of Phenols

Claisen rearrangement

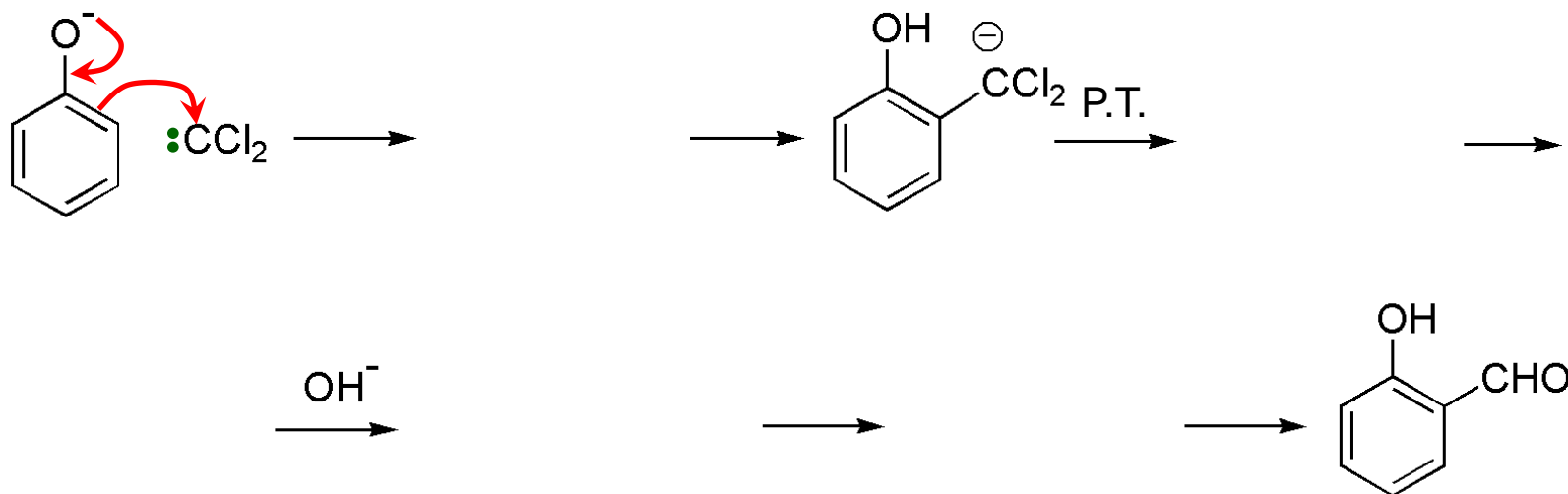
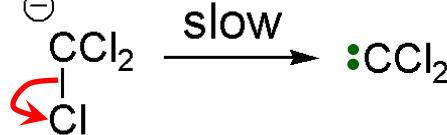
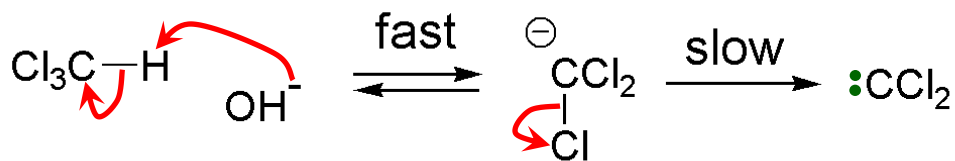
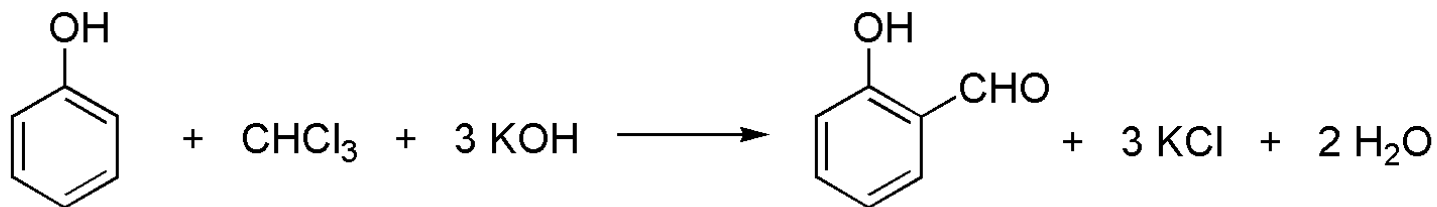


Kolbe-Schmitt reaction



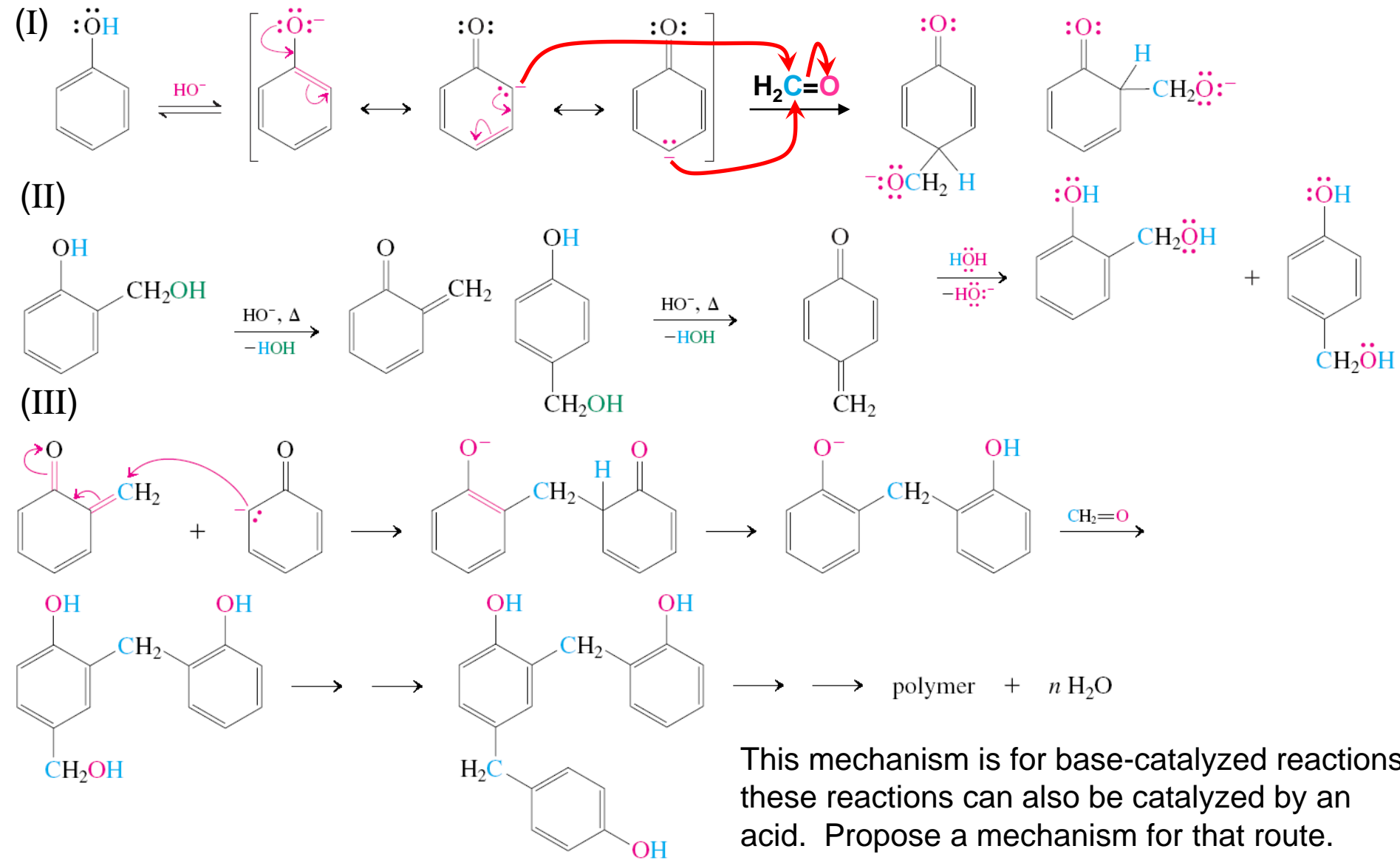
Reactions of Phenols

Reimer-Tiemann reaction:

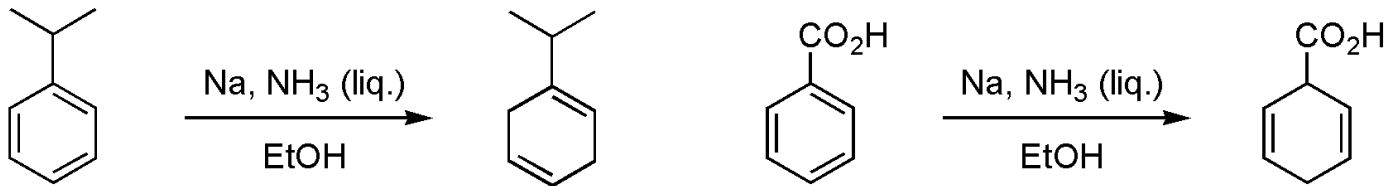


Hydroxymethylation of Phenol

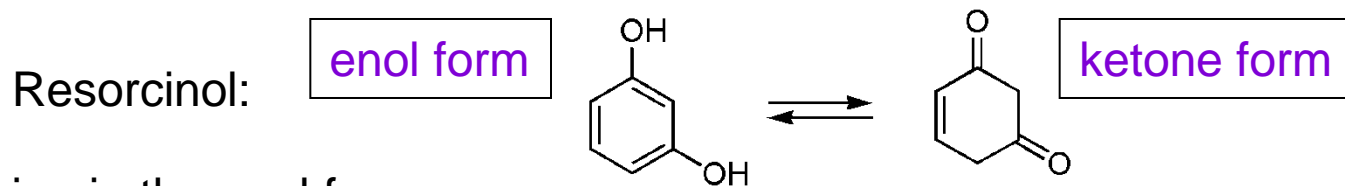
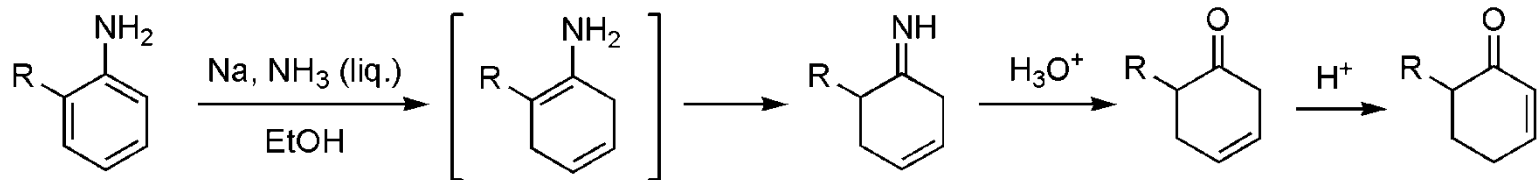
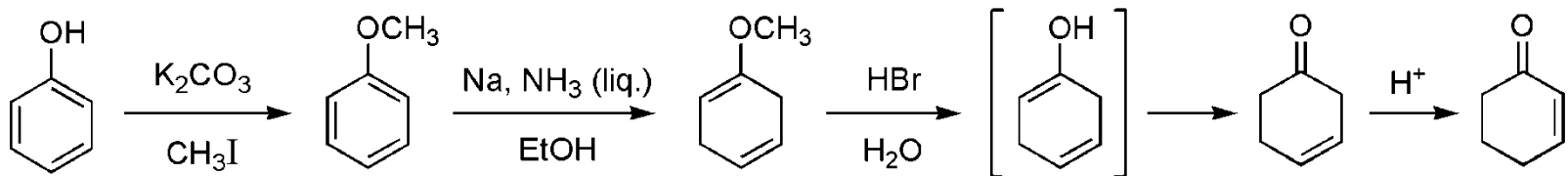
Synthesis of phenolic resin (Bakelite, a phenol-formaldehyde copolymer) :



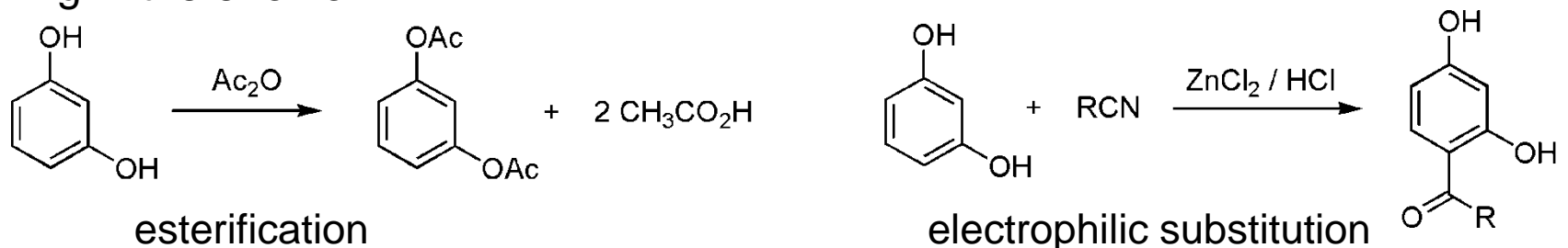
Birch Reduction and Resorcinol



Phenols do not undergo Birch reduction, but phenyl ethers can be reduced via Birch reduction.

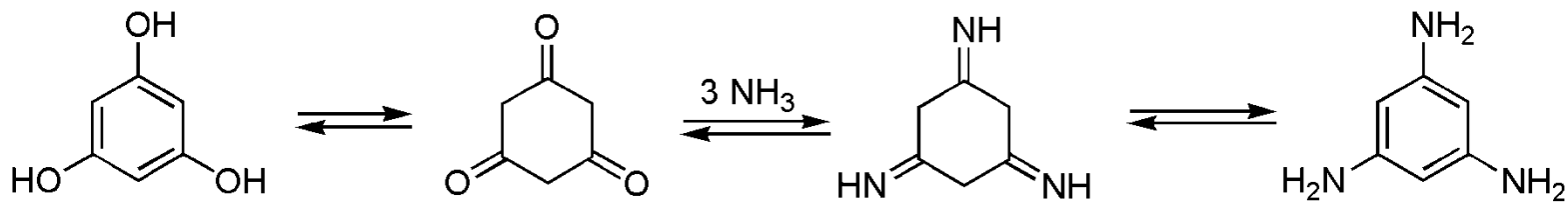
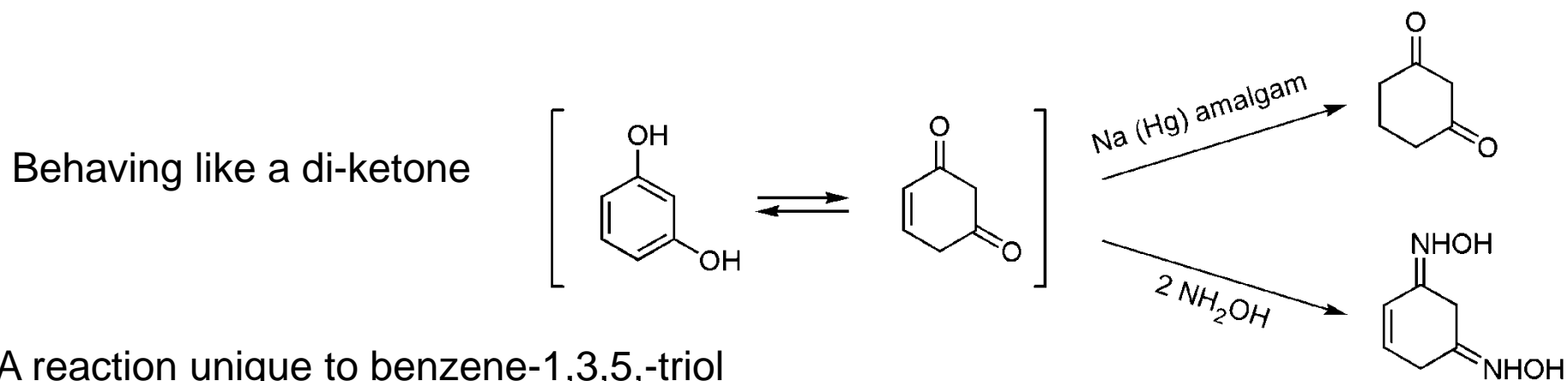


Behaving in the enol form:

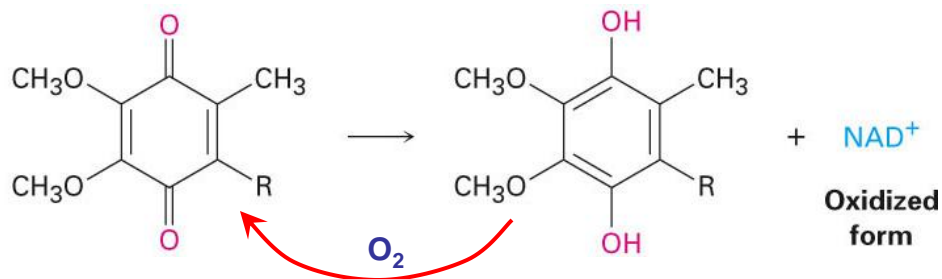
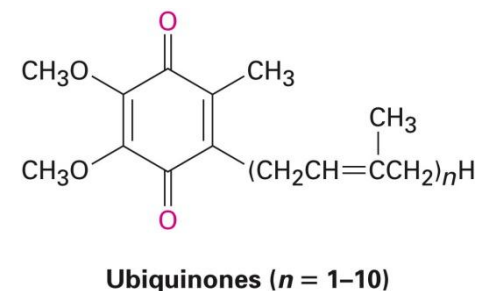
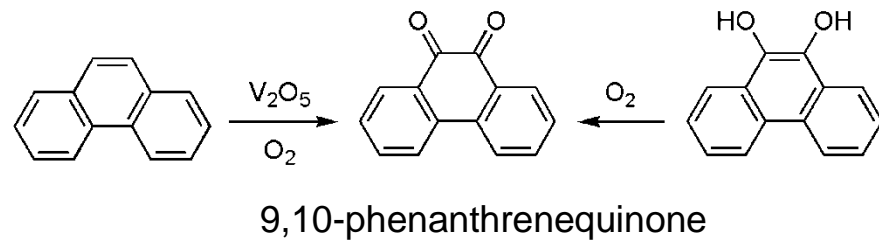
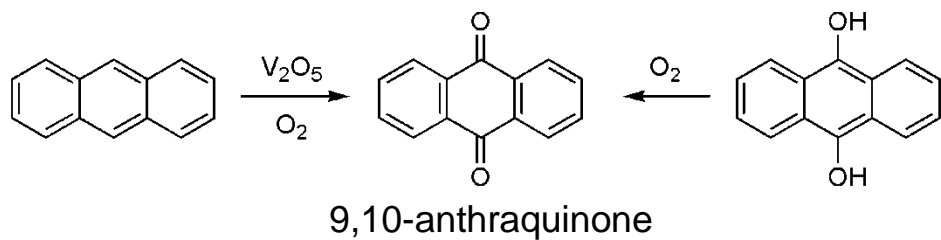
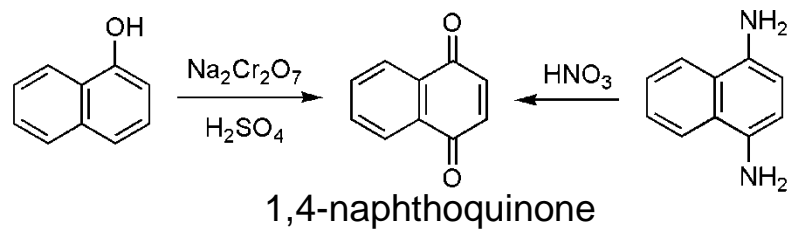
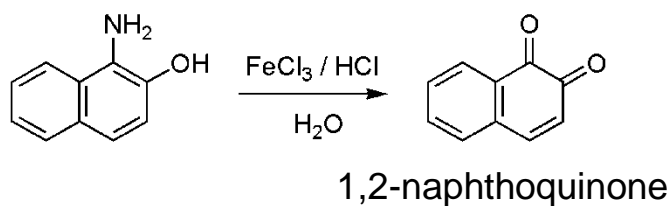
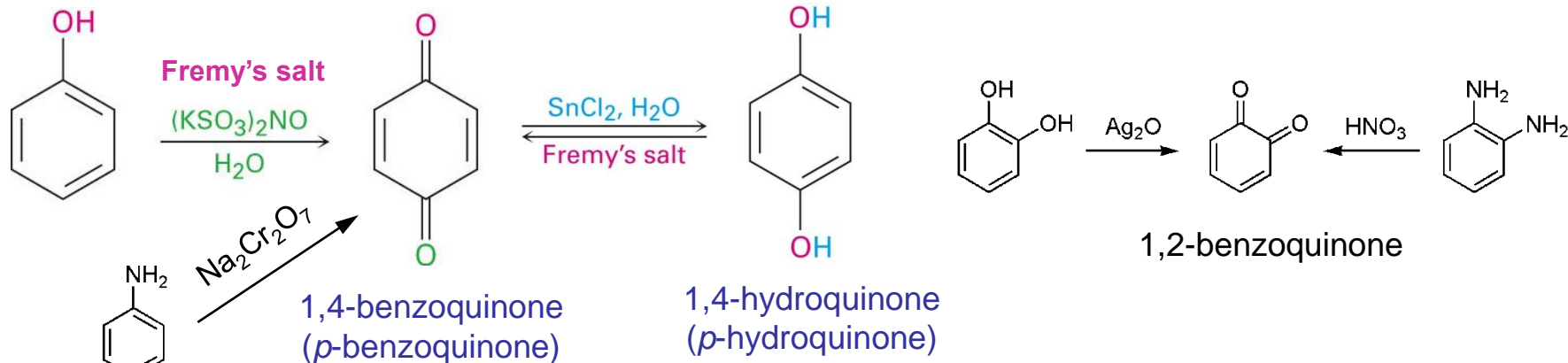


Reactions of Polyphenols

Mechanism of Houben-Hoesch reaction:

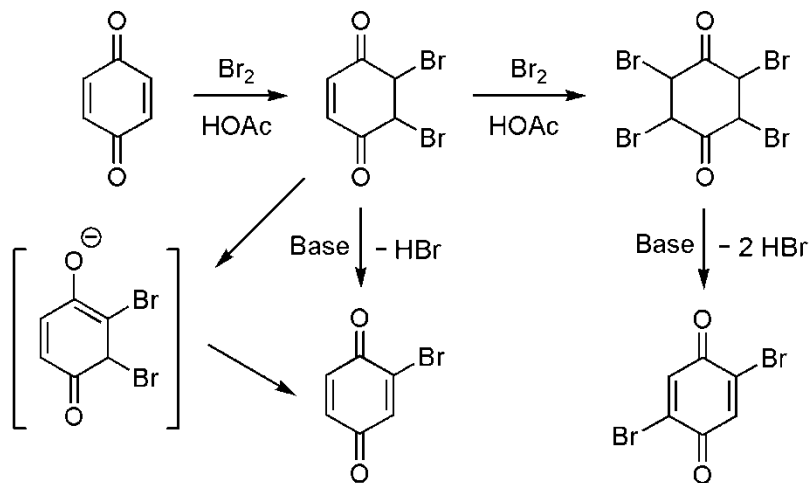


Oxidation of Phenols -- Quinones

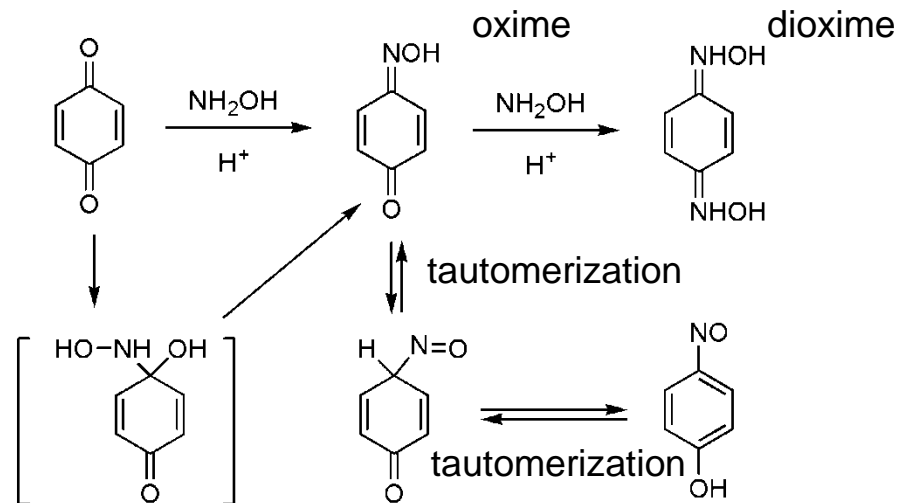


Reactions of Quinones

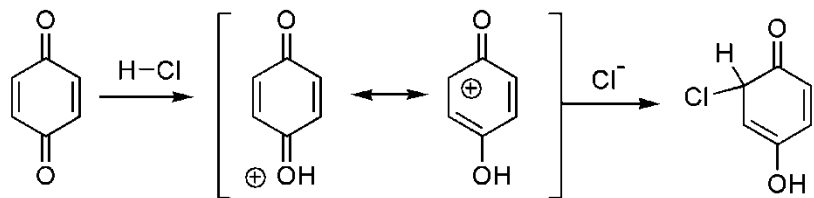
Electrophilic addition:



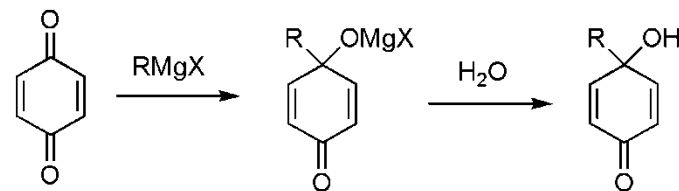
Nucleophilic addition: 1,2-addition of amine derivatives



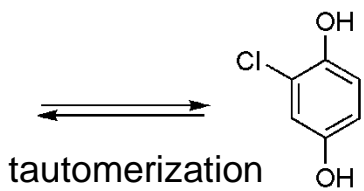
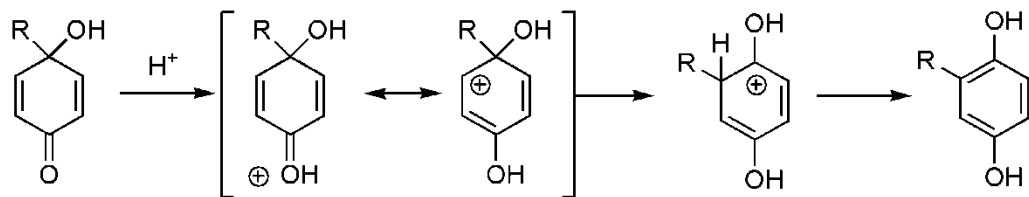
1,4-addition of HCl:



1,2-addition of Grignard reagents:

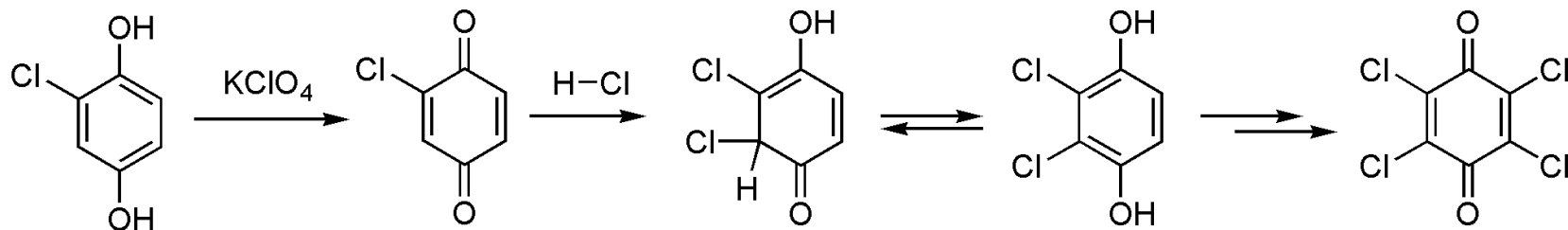


under acidic conditions:

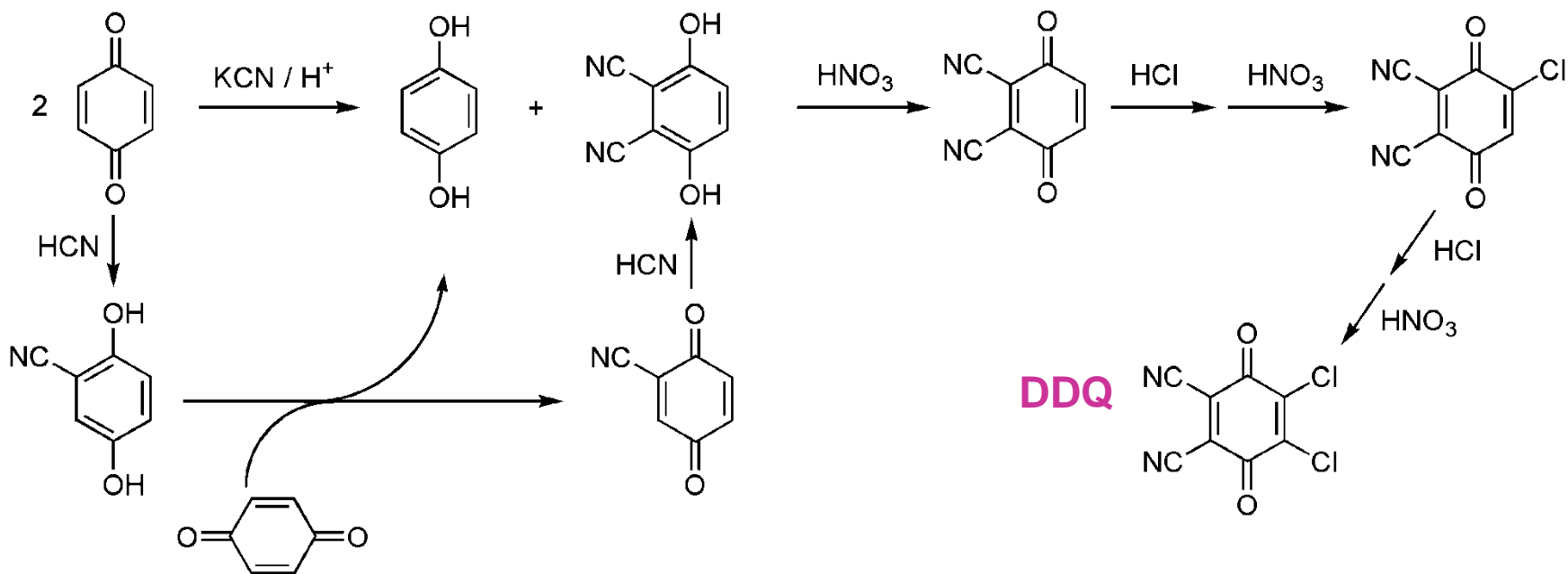


Reactions of Quinones

1,4-addition of HCl:



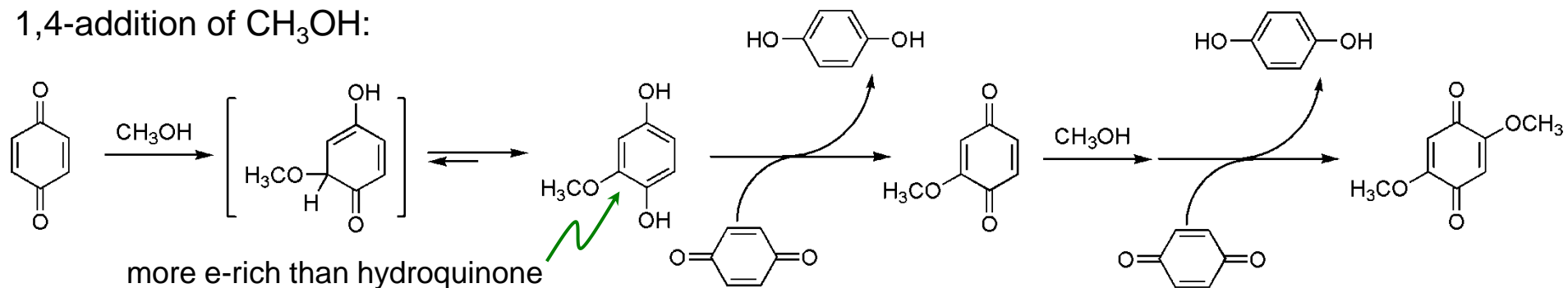
1,4-addition of HCN:



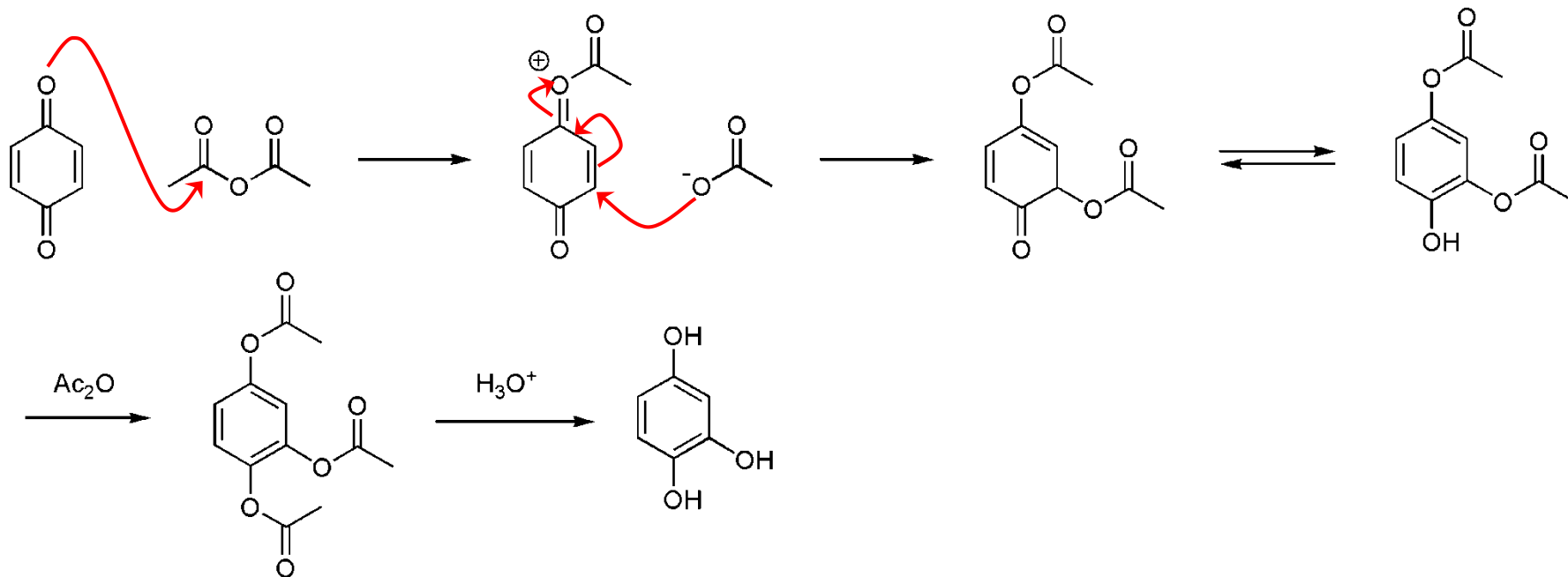
TCQ and DDQ are useful oxidative reagents for dehydrogenation.

Reactions of Quinones

1,4-addition of CH_3OH :

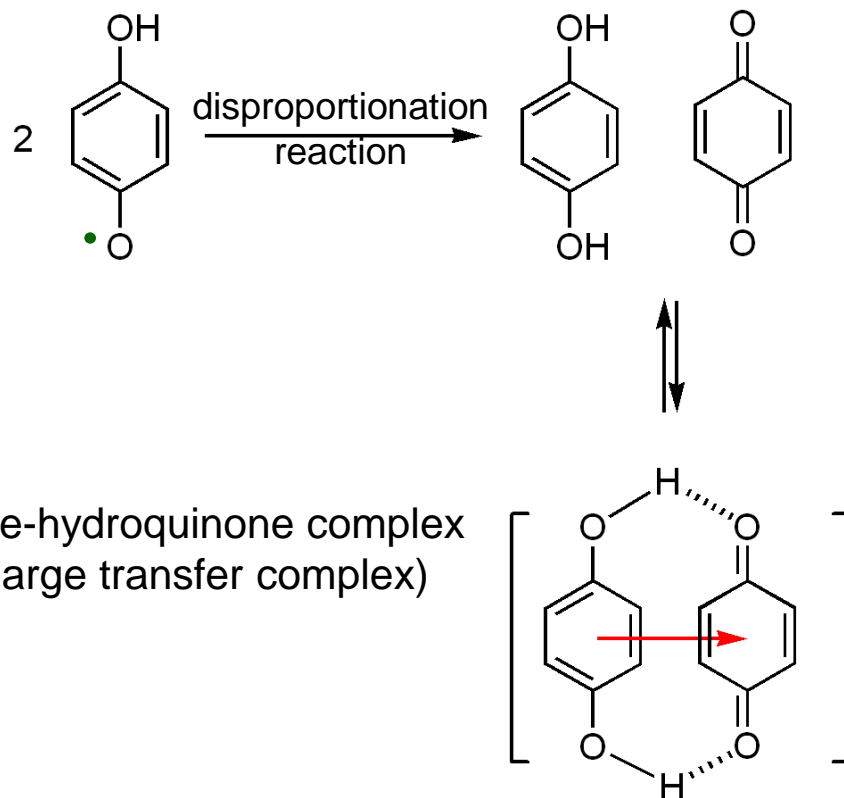
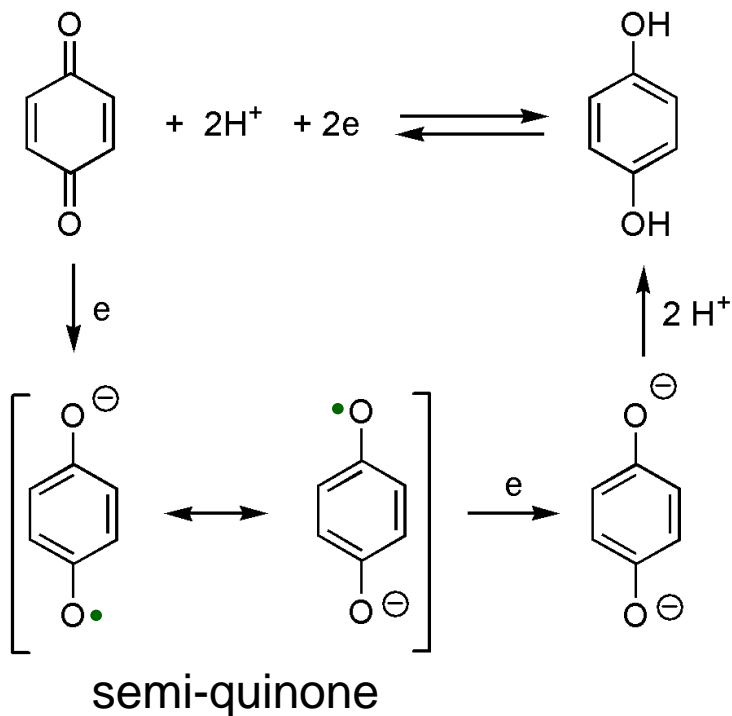


Reaction with acetic anhydride:

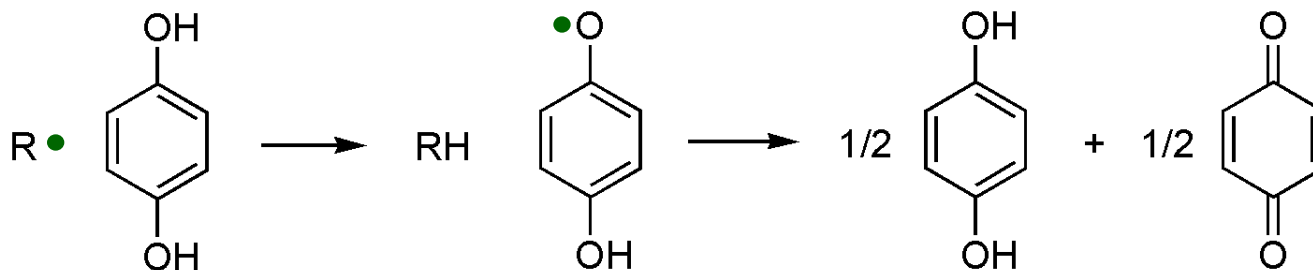


Redox Properties of Quinones and Hydroquinones

A reversible electrochemical redox process:

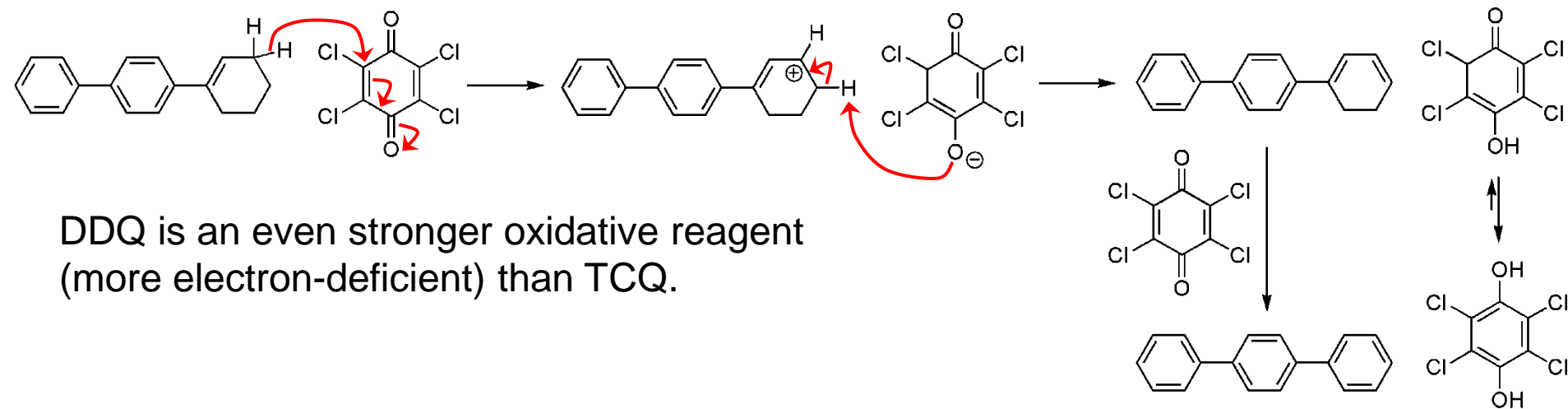


Hydroquinone is a good anti-oxidant and radical inhibitor (which inhibits radical chain reactions).



Redox Properties of Quinones and Hydroquinones

Electron-deficient quinones are good dehydrogenative oxidant.



Reacting as dienophiles:

