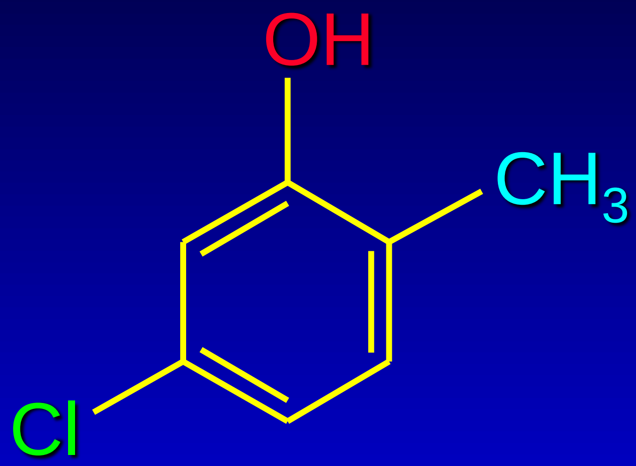
Phenols

Assistant Lecturer:- Jalal Hasan Mohammed

Nomenclature



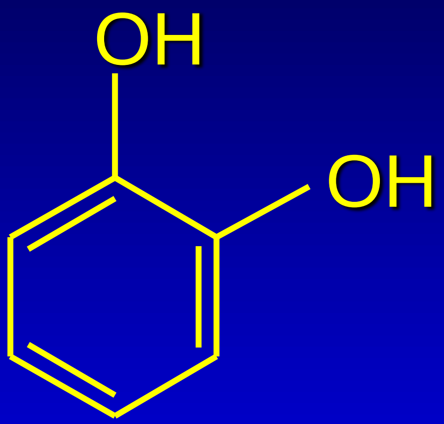
5-Chloro-2-methylphenol

named on basis of phenol as parent

substituents listed in alphabetical order

lowest numerical sequence: first point of difference rule

Nomenclature

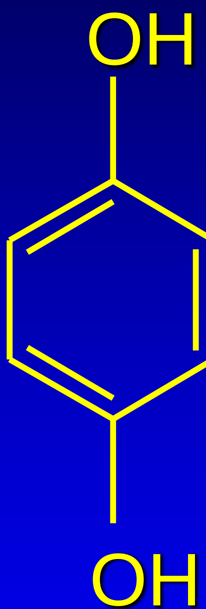


1,2-Benzenediol

(common name: pyrocatechol)

1,3-Benzenediol

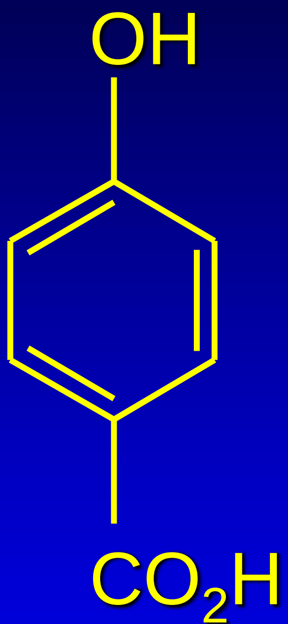
(common name: resorcinol)



1,4-Benzenediol

(common name: hydroquinone)

Nomenclature

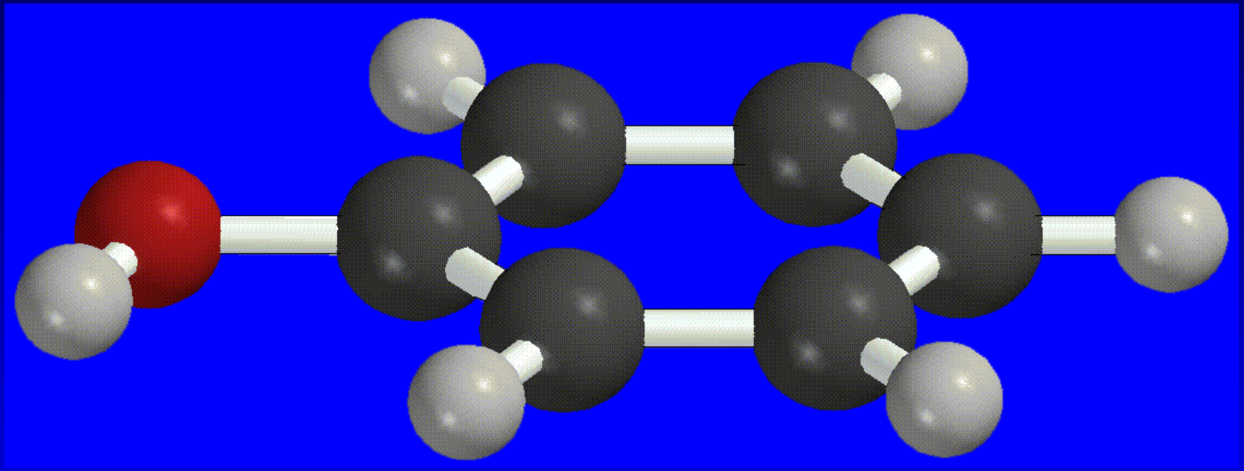


p-Hydroxybenzoic acid

name on basis of benzoic acid as parent

higher oxidation states of carbon outrank hydroxyl group

Structure of Phenol



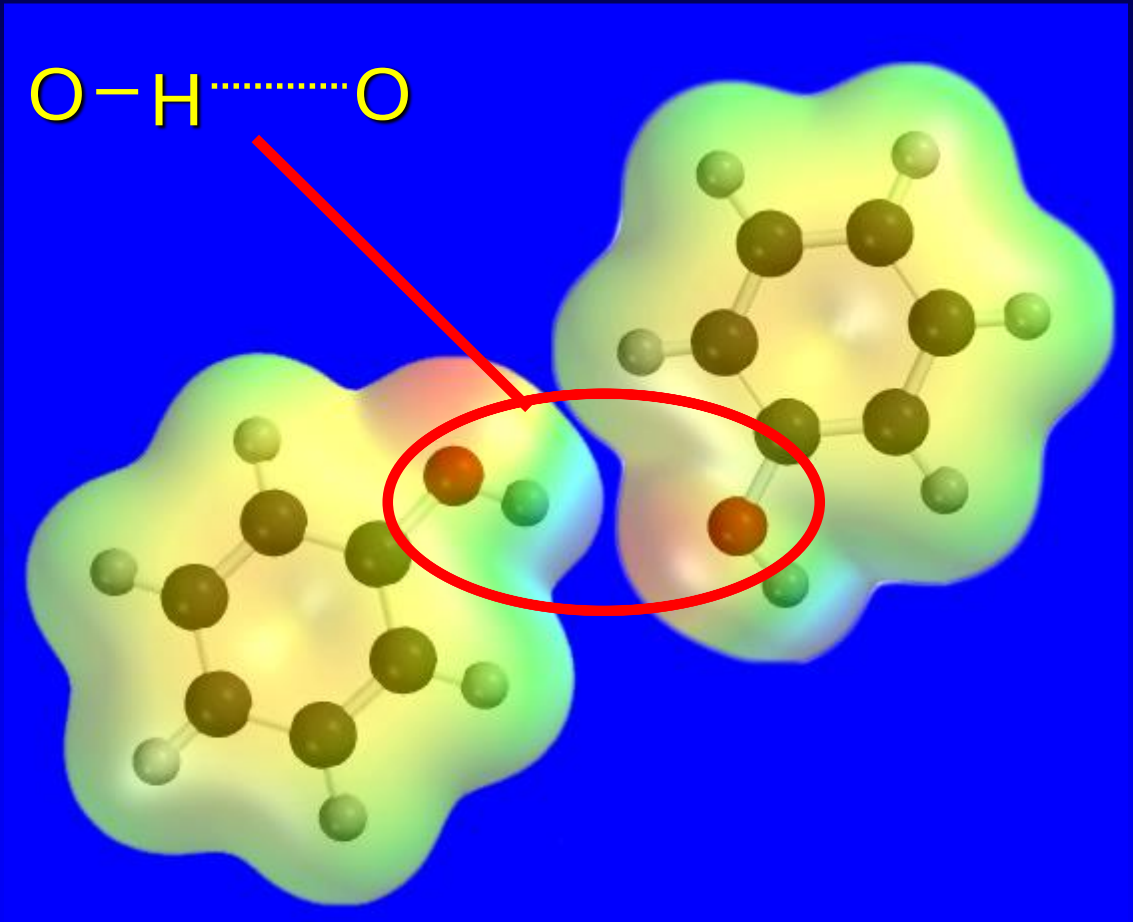
phenol is planar

C—O bond distance is 136 pm, which is slightly shorter than that of CH_3OH (142 pm)

Physical Properties

The OH group of phenols allows hydrogen bonding to other phenol molecules and to water.

Hydrogen Bonding in Phenols



Physical Properties (Table 24.1)

Compared to compounds of similar size and molecular weight, hydrogen bonding in phenol raises its melting point, boiling point, and solubility in water.

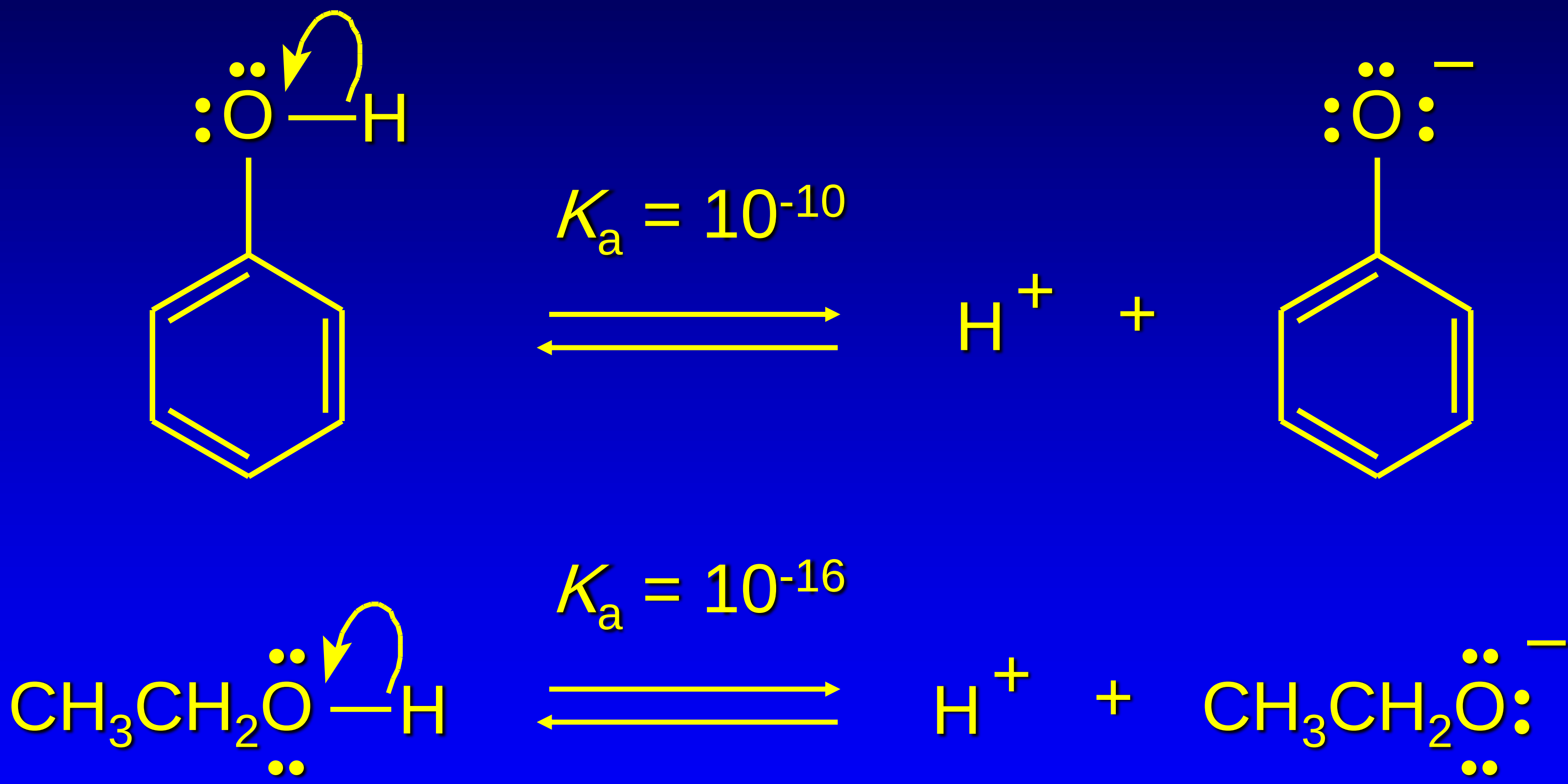
Physical Properties (Table 24.1)

	$C_6H_5CH_3$	C_6H_5OH	C_6H_5F
Molecular weight	92	94	96
Melting point (°C)	–95	43	–41
Boiling point (°C,1 atm)	111	132	85
Solubility in H_2O (g/100 mL,25°C)	0.05	8.2	0.2

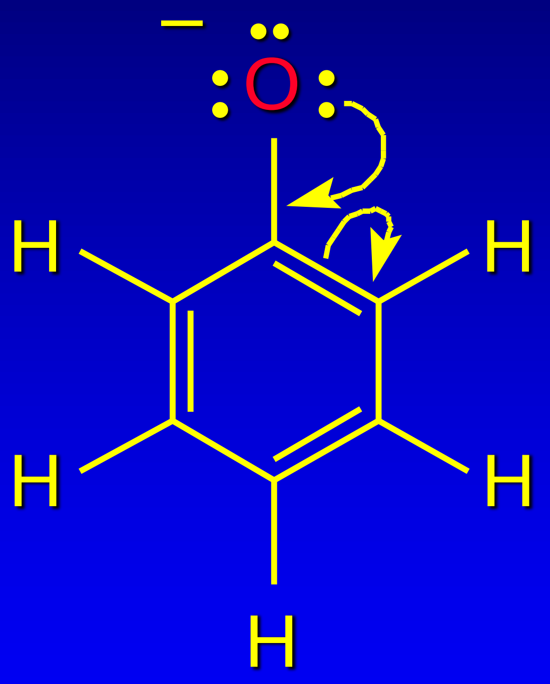
Acidity of Phenols

most characteristic property of phenols is their acidity

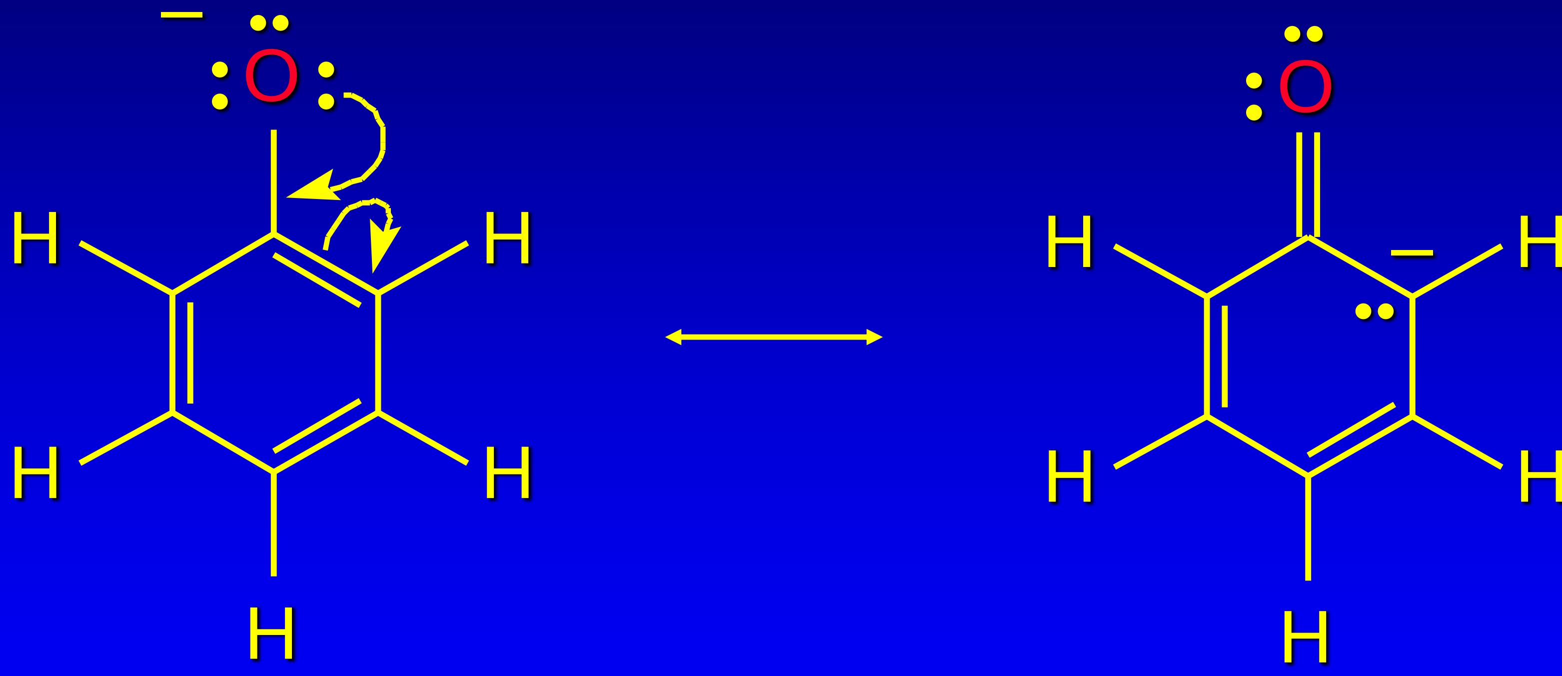
Compare



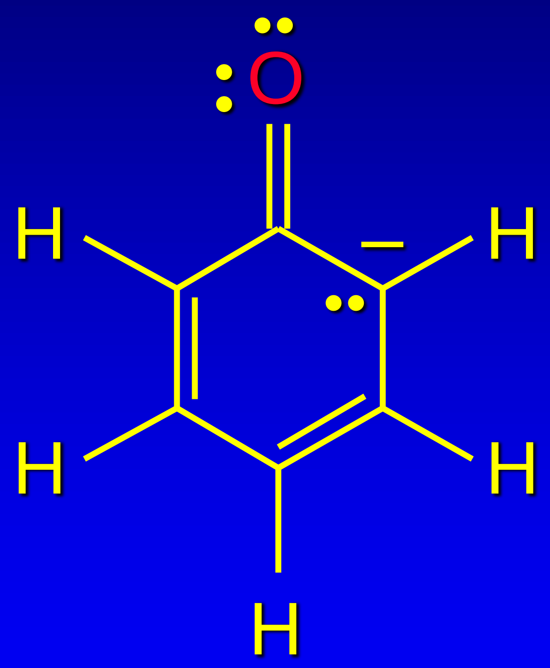
Delocalized negative charge in phenoxide ion



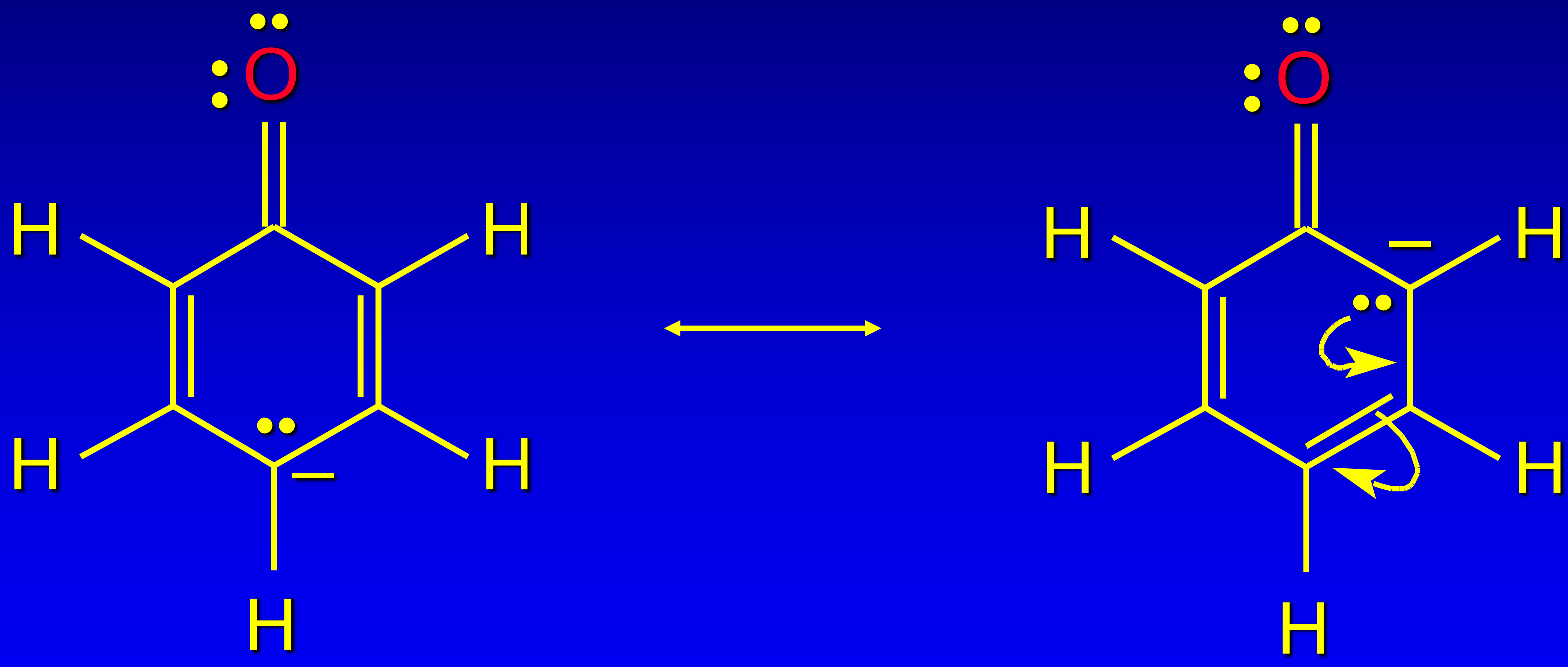
Delocalized negative charge in phenoxide ion



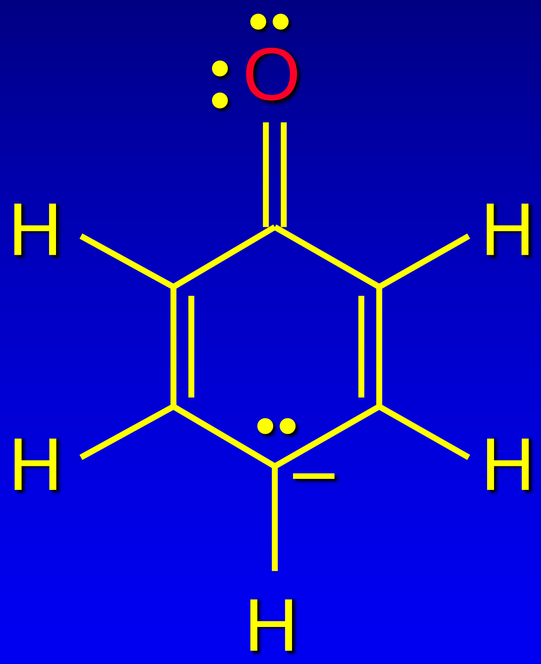
Delocalized negative charge in phenoxide ion



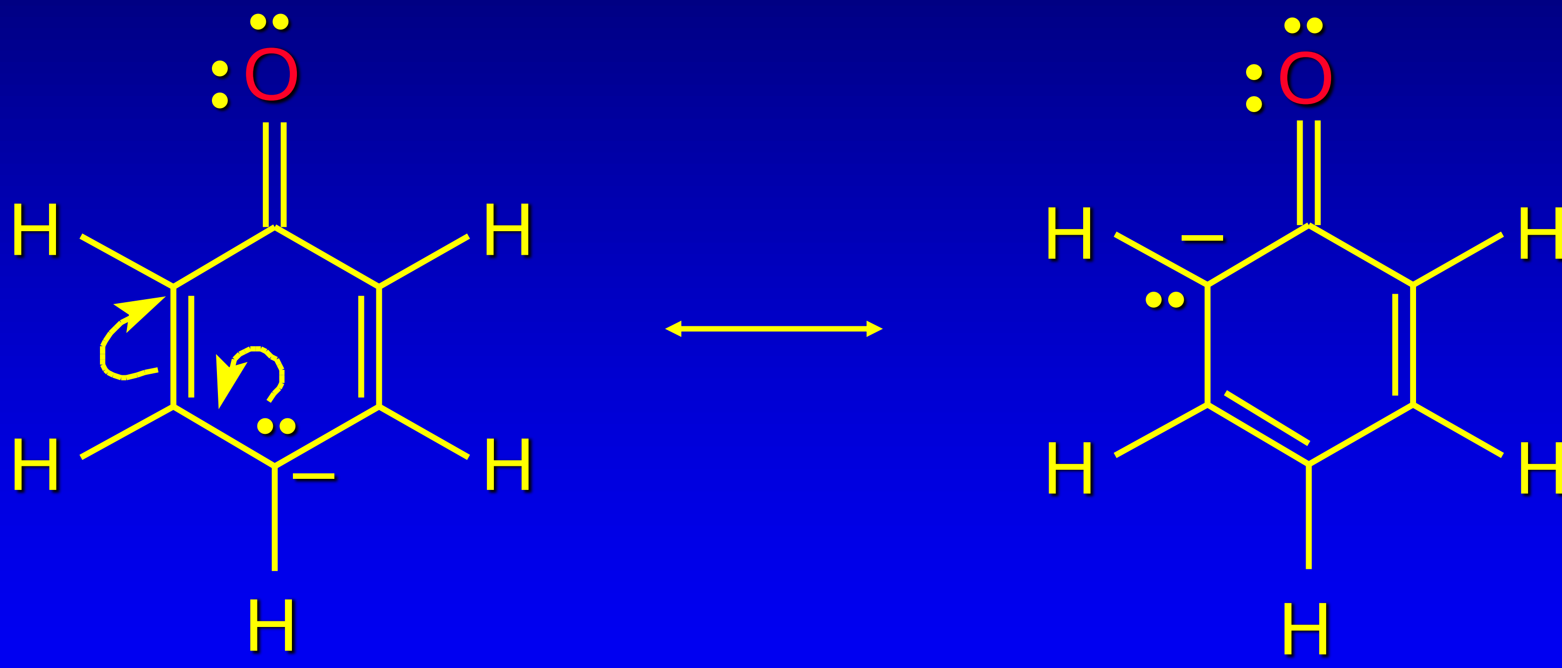
Delocalized negative charge in phenoxide ion



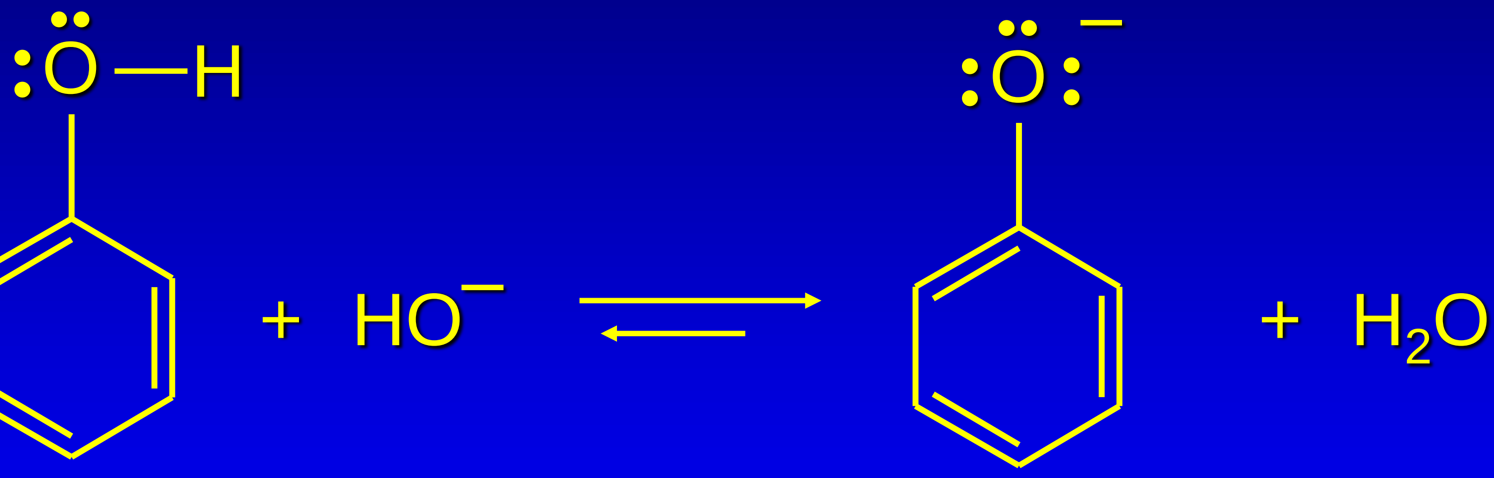
Delocalized negative charge in phenoxide ion



Delocalized negative charge in phenoxide ion



Phenols are converted to phenoxide ions in aqueous base

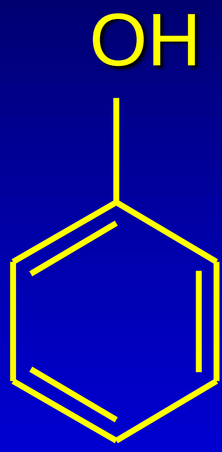


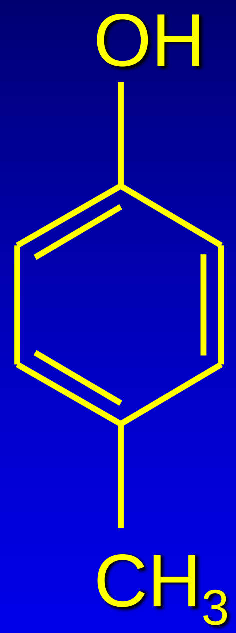
stronger acid

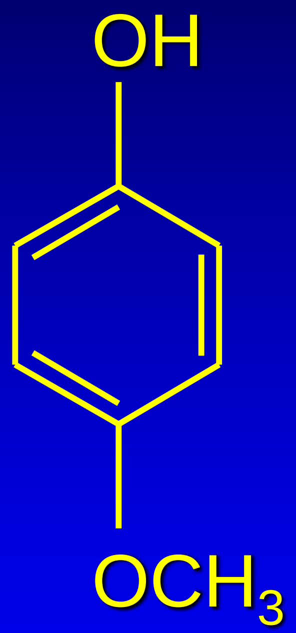
weaker acid

Substituent Effects on the Acidity of Phenols

Electron-releasing groups have little or no effect

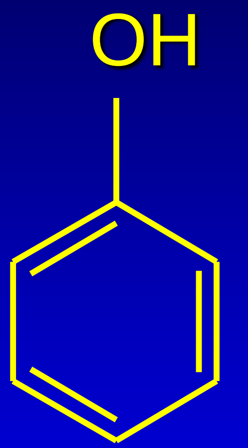


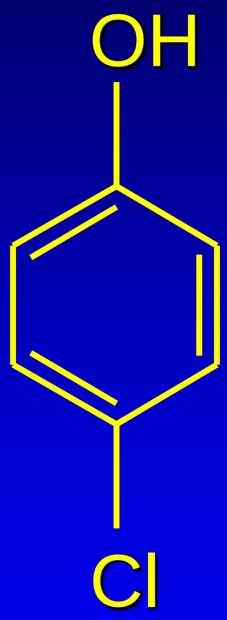


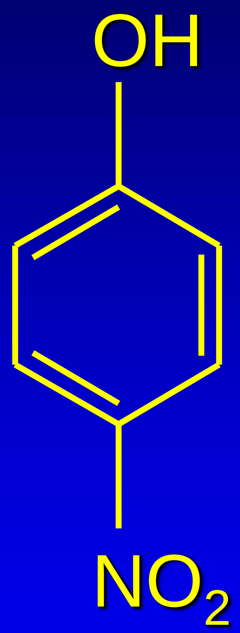


K_a: 1×10^{-10} 5×10^{-11} 6×10^{-11}

Electron-withdrawing groups increase acidity

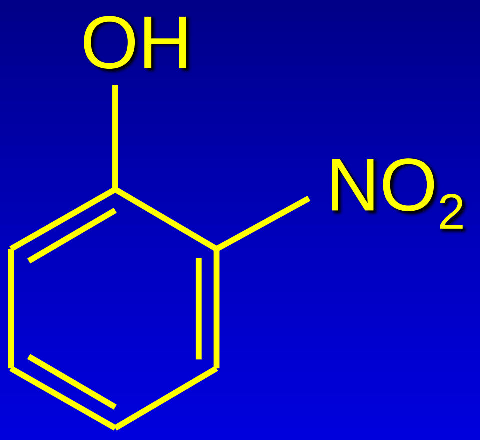


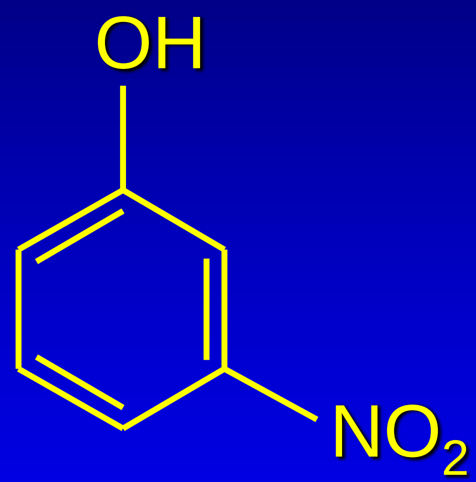


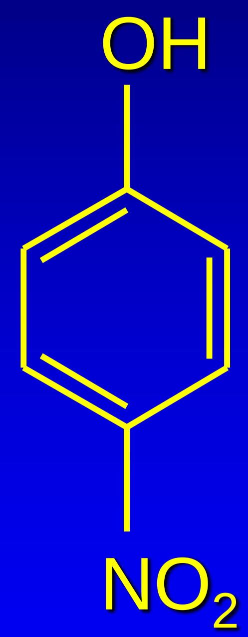


K_a: 1×10^{-10} | 4×10^{-9} | 7×10^{-8}

Effect of electron-withdrawing groups is most pronounced at ortho and para positions

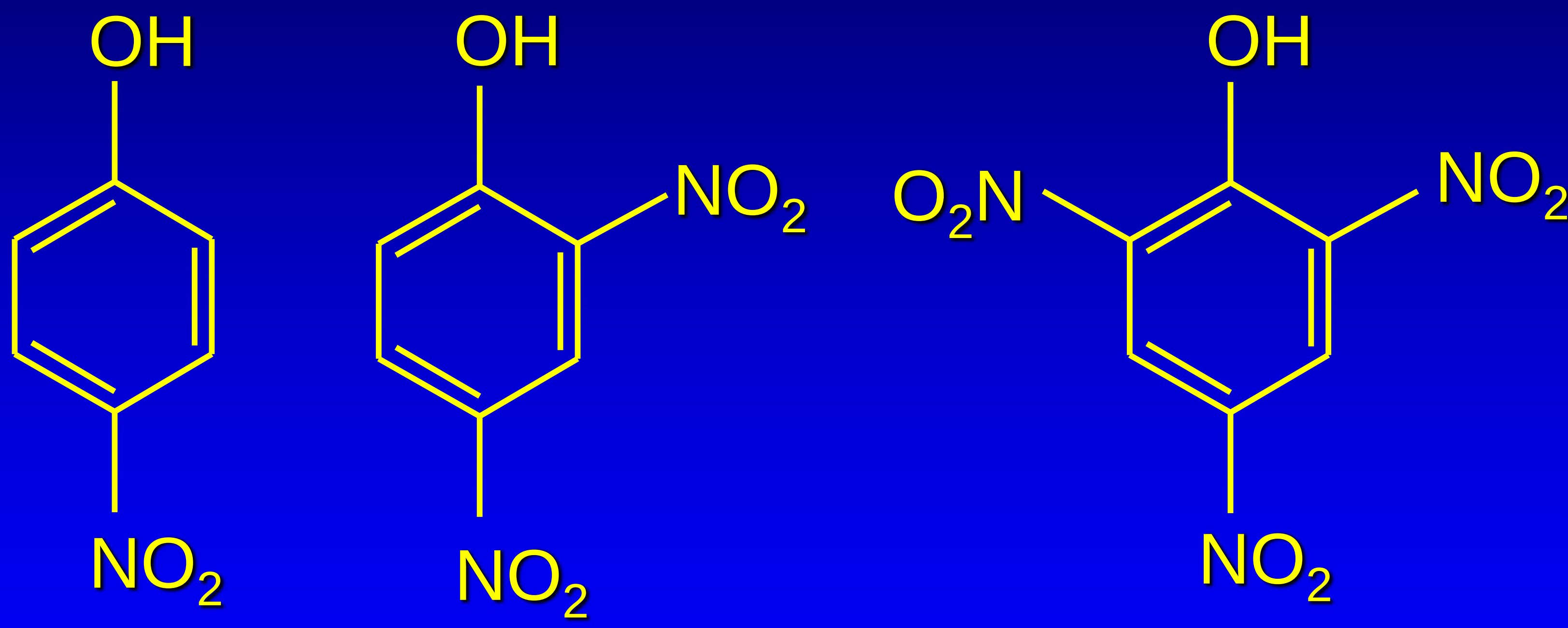






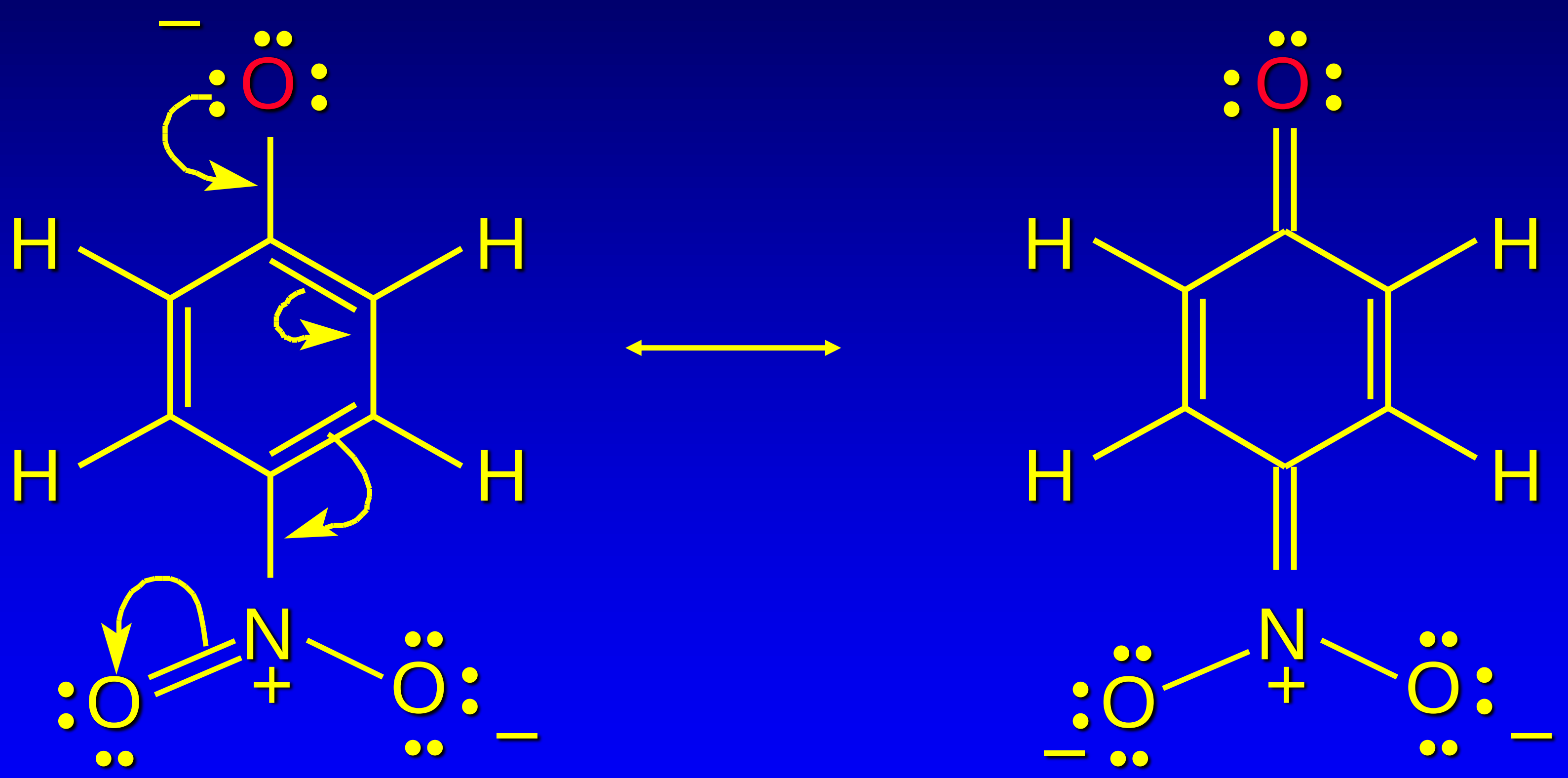
K_a:	6×10^{-8}	4×10^{-9}	7×10^{-8}

Effect of strong electron-withdrawing groups is cumulative



K_a: 7×10^{-8} 1×10^{-4} 4×10^{-1}

Resonance Depiction



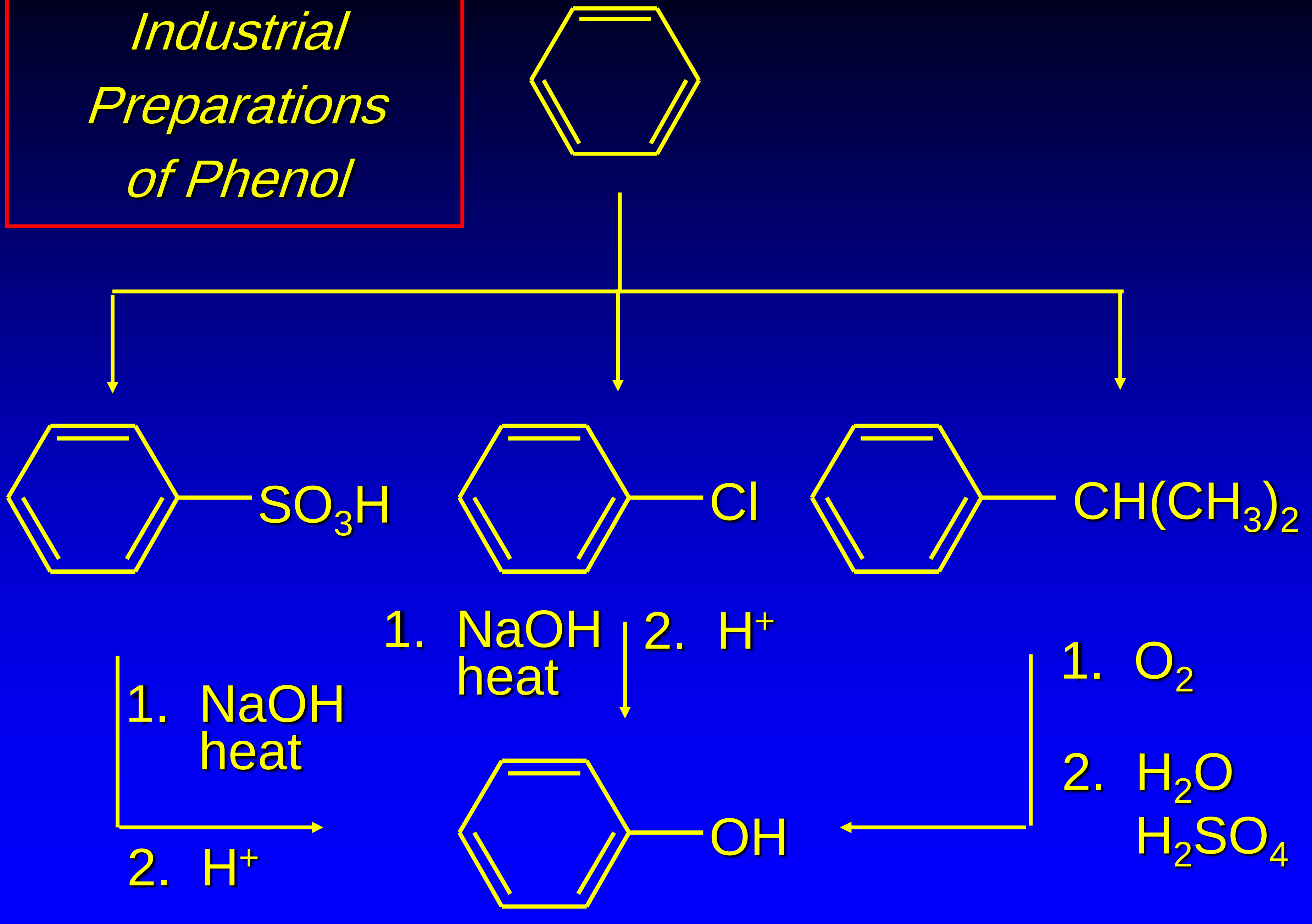
Sources of Phenols

Phenol is an important industrial chemical.

Major use is in phenolic resins for adhesives and plastics.

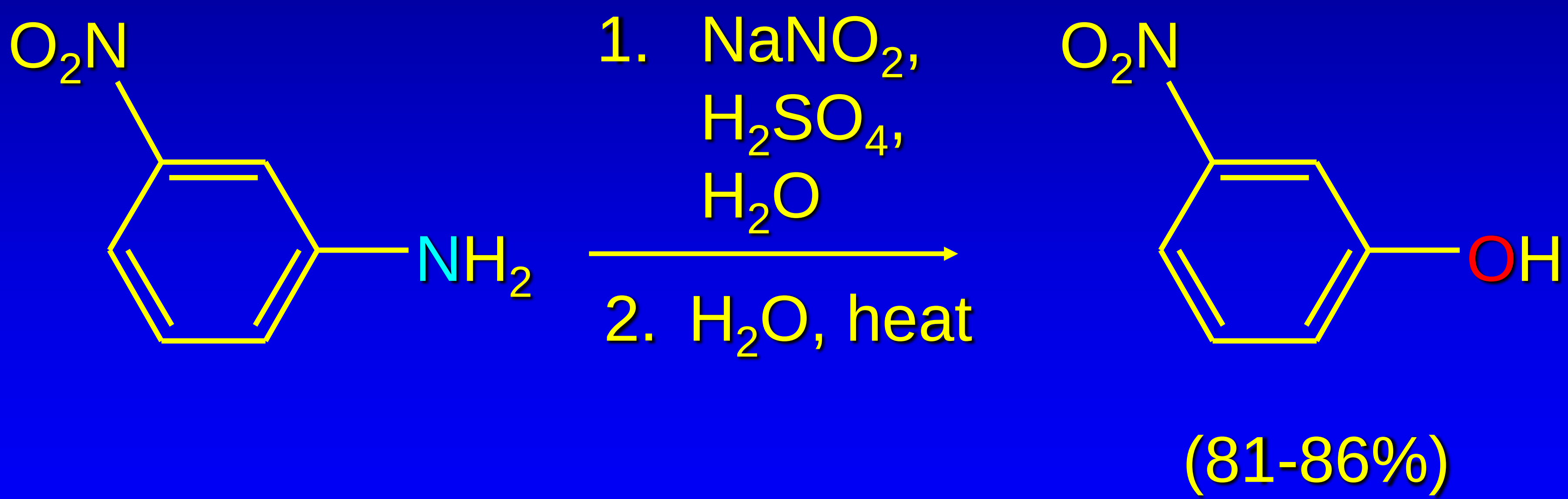
Annual U.S. production is about 4 billion pounds per year.

Industrial Preparations of Phenol



Laboratory Synthesis of Phenols

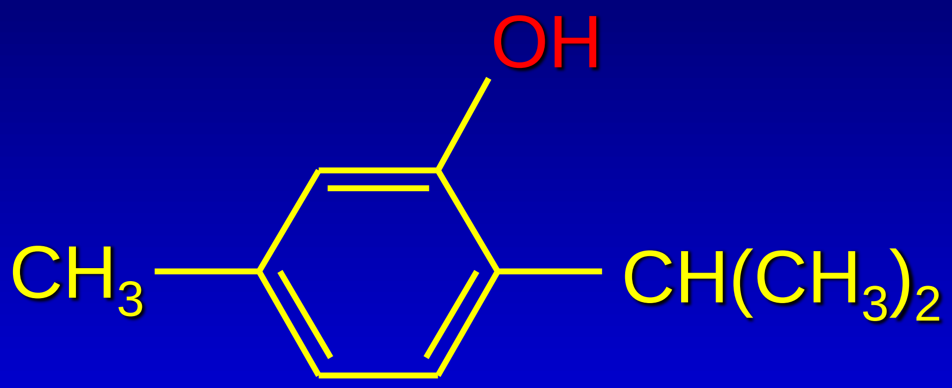
from arylamines via diazonium ions



Naturally Occurring Phenols

Many phenols occur naturally

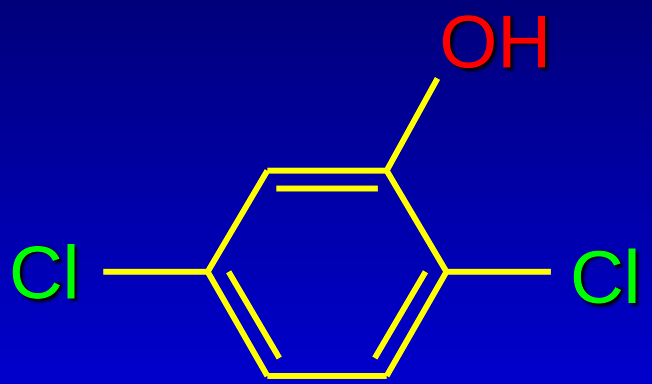
Example: Thymol



Thymol

(major constituent of oil of thyme)

Example: 2,5-Dichlorophenol



2,5-Dichlorophenol

(from defensive secretion of

a species of grasshopper)

Reactions of Phenols: Electrophilic Aromatic Substitution

Hydroxyl group strongly activates the ring toward electrophilic aromatic substitution

Electrophilic Aromatic Substitution in Phenols

Halogenation

Nitration

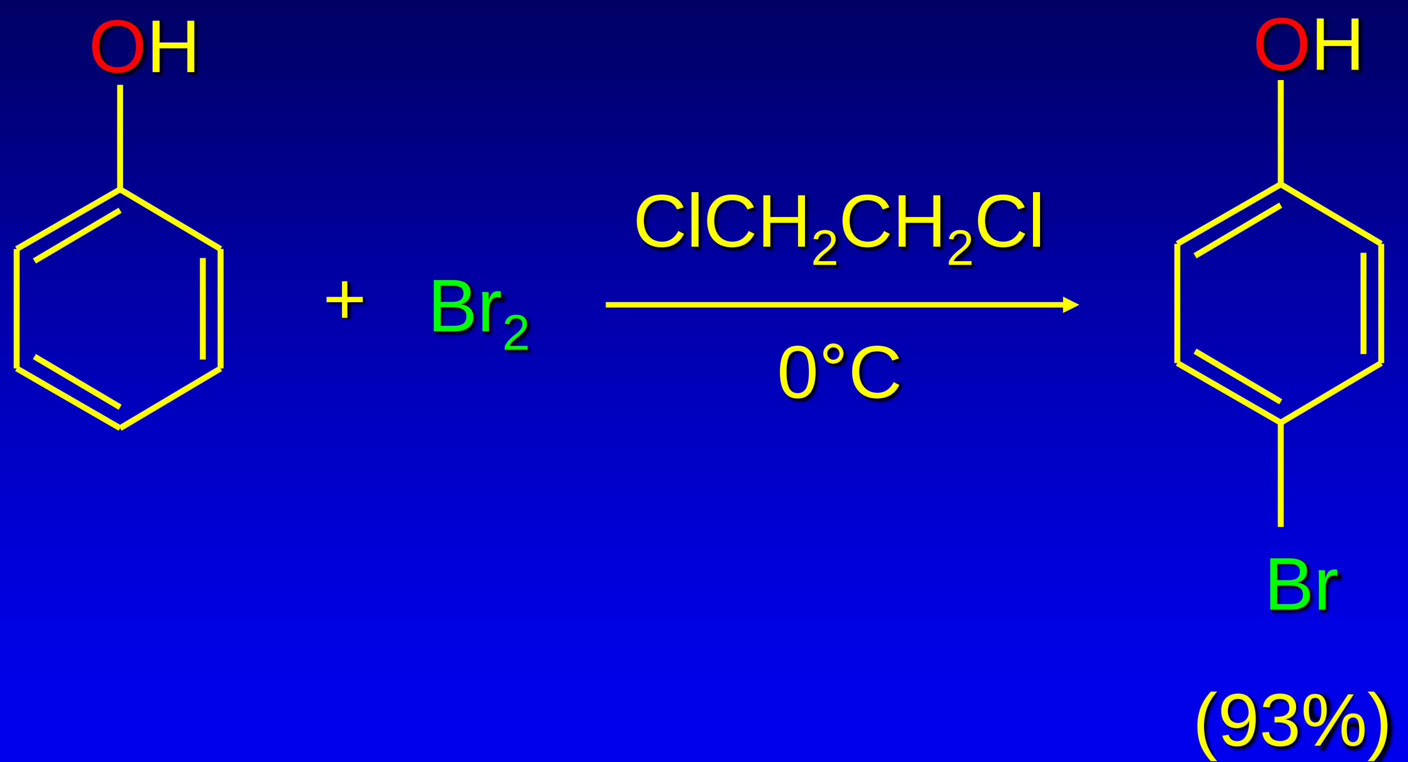
Nitrosation

Sulfonation

Friedel-Crafts Alkylation

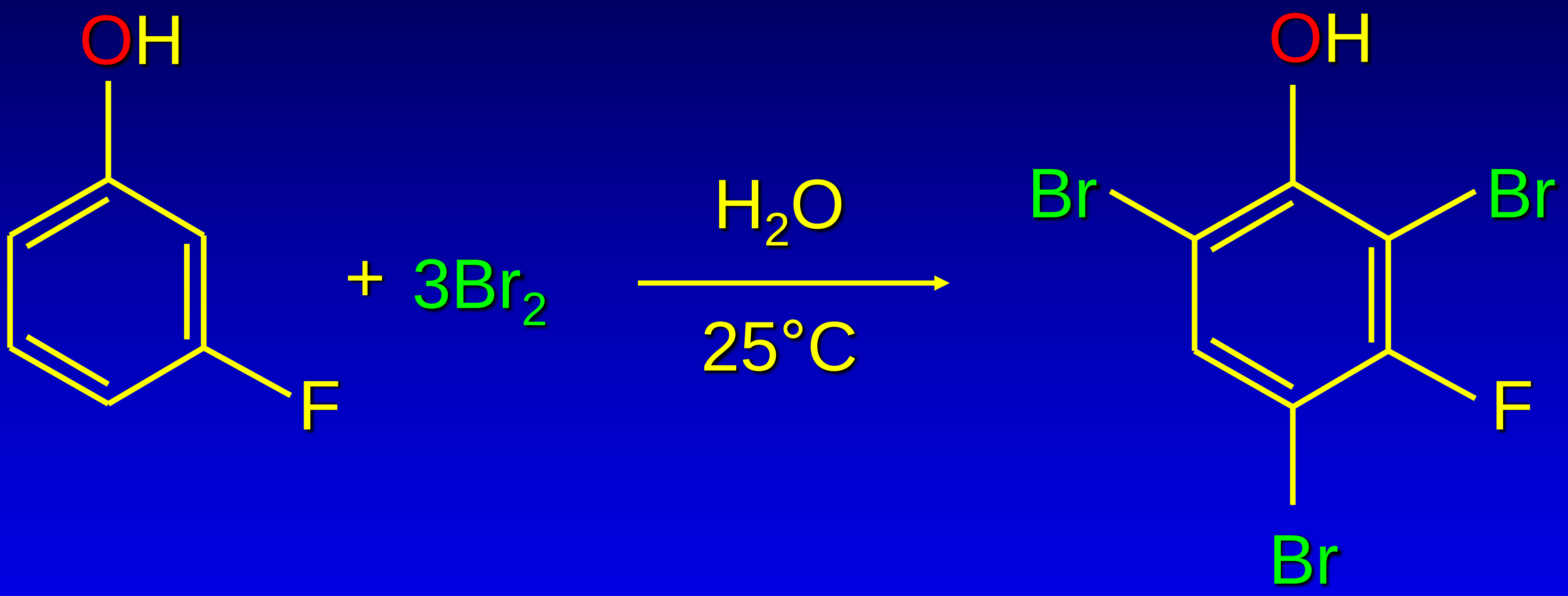
Friedel-Crafts Acylation

Halogenation



monohalogenation in nonpolar solvent (1,2-dichloroethane)

Halogenation



(95%)

multiple halogenation in polar solvent (water)

Electrophilic Aromatic Substitution in Phenols

Halogenation

Nitration

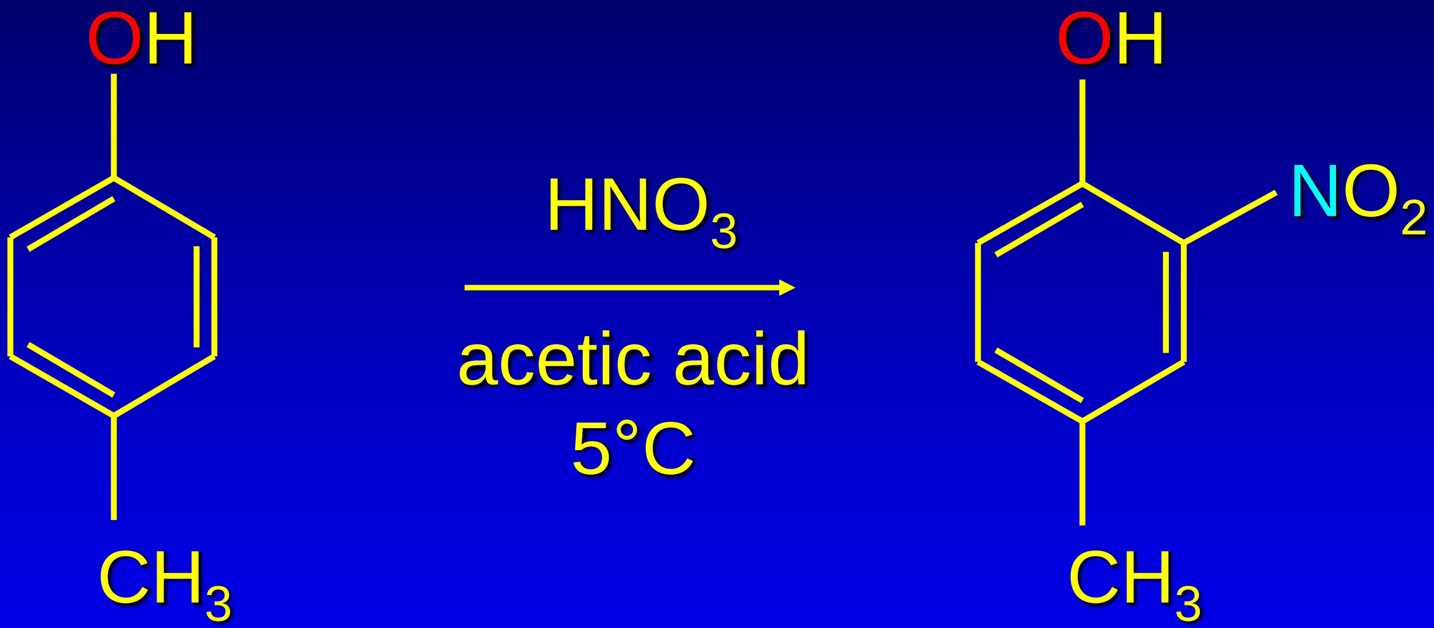
Nitrosation

Sulfonation

Friedel-Crafts Alkylation

Friedel-Crafts Acylation

Nitration



OH group controls regiochemistry

(73-77%)

Electrophilic Aromatic Substitution in Phenols

Halogenation

Nitration

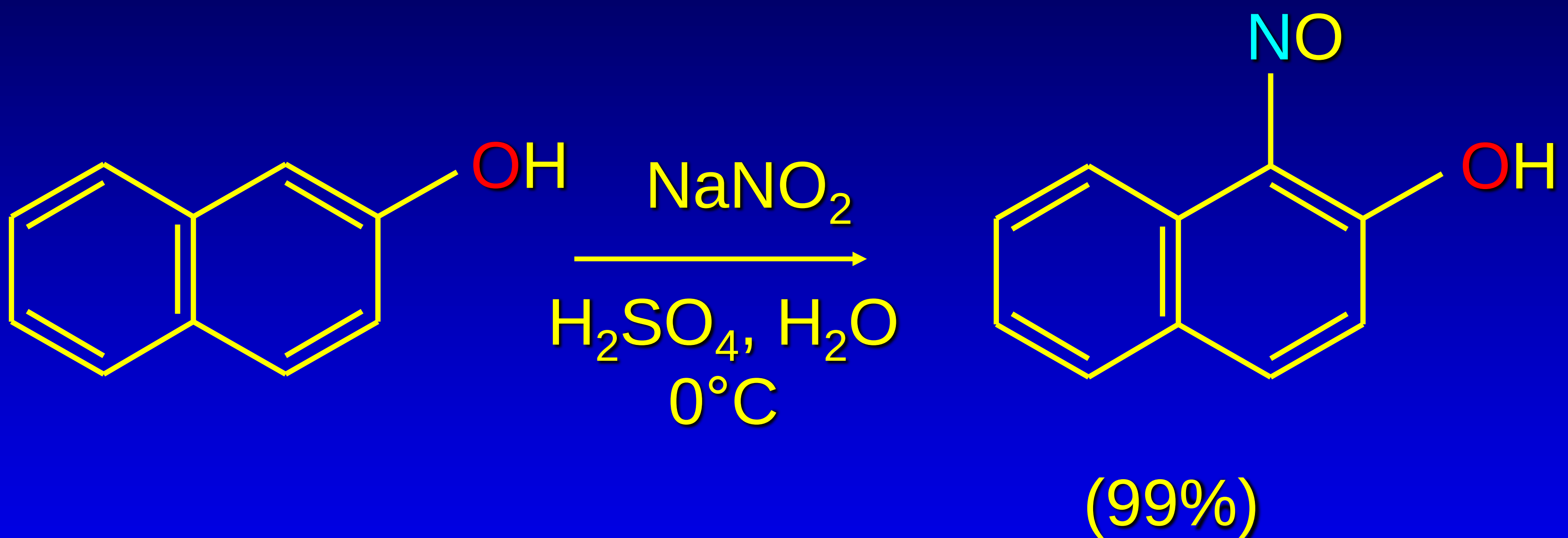
Nitrosation

Sulfonation

Friedel-Crafts Alkylation

Friedel-Crafts Acylation

Nitrosation



only strongly activated rings undergo nitrosation when treated with nitrous acid

Electrophilic Aromatic Substitution in Phenols

Halogenation

Nitration

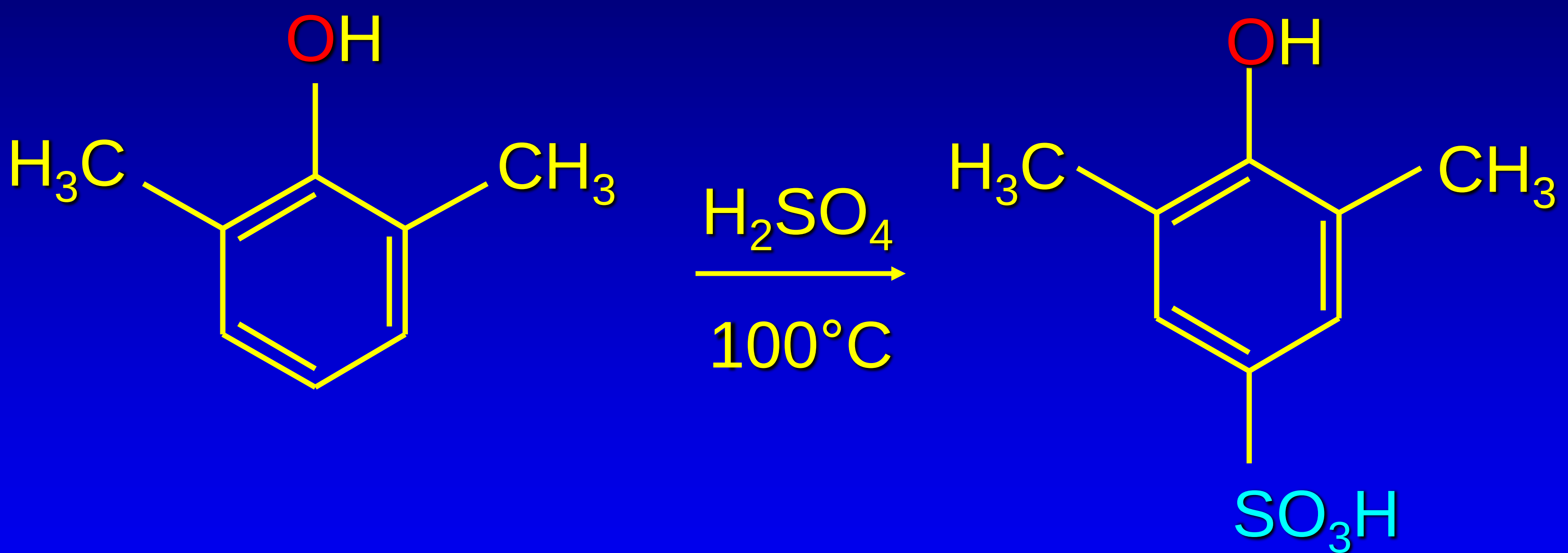
Nitrosation

Sulfonation

Friedel-Crafts Alkylation

Friedel-Crafts Acylation

Sulfonation



OH group controls regiochemistry

(69%)

Electrophilic Aromatic Substitution in Phenols

Halogenation

Nitration

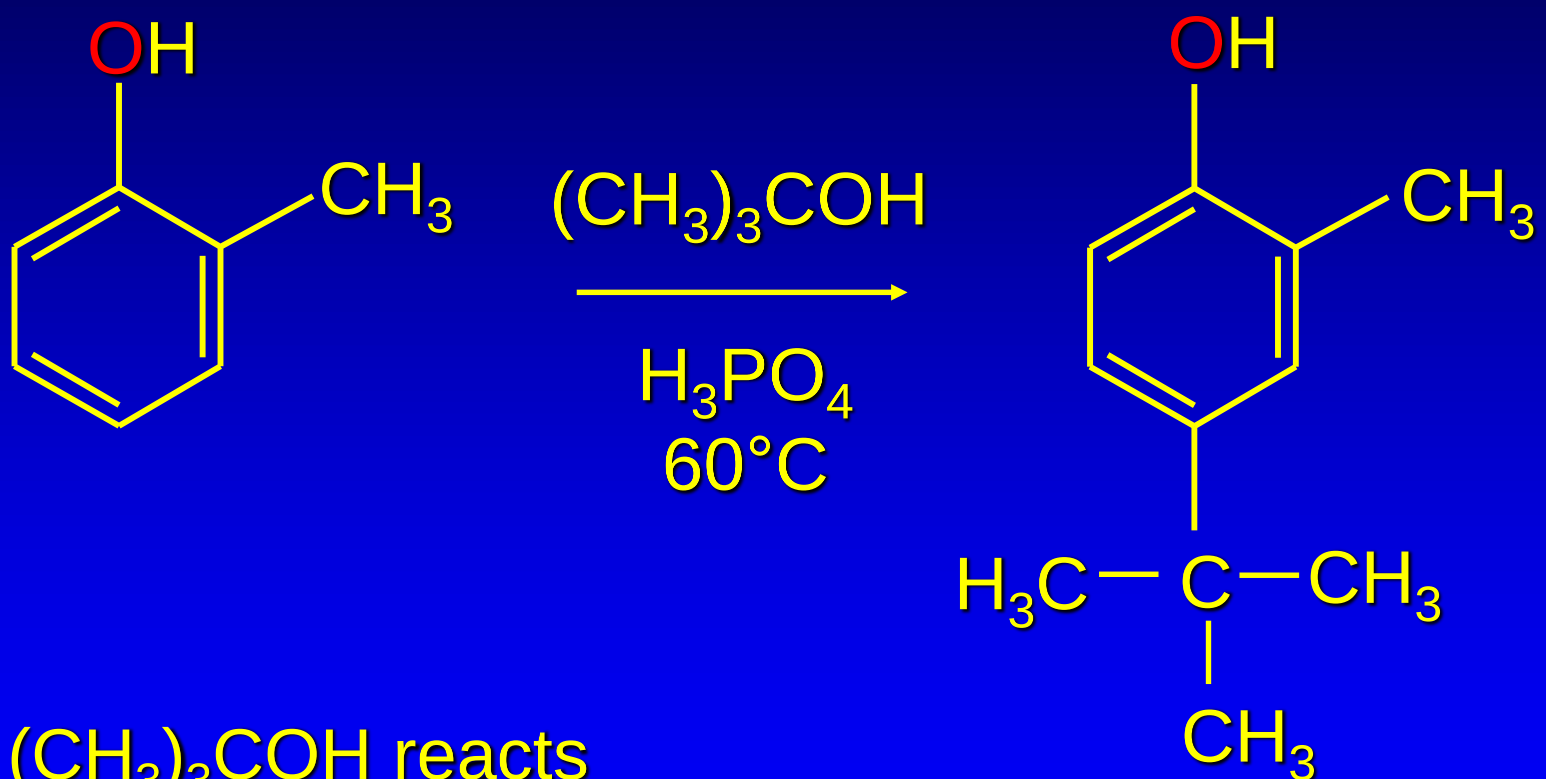
Nitrosation

Sulfonation

Friedel-Crafts Alkylation

Friedel-Crafts Acylation

Friedel-Crafts Alkylation



(63%)

$(CH_3)_3COH$ reacts with H_3PO_4 to give $(CH_3)_3C^+$

Electrophilic Aromatic Substitution in Phenols

Halogenation

Nitration

Nitrosation

Sulfonation

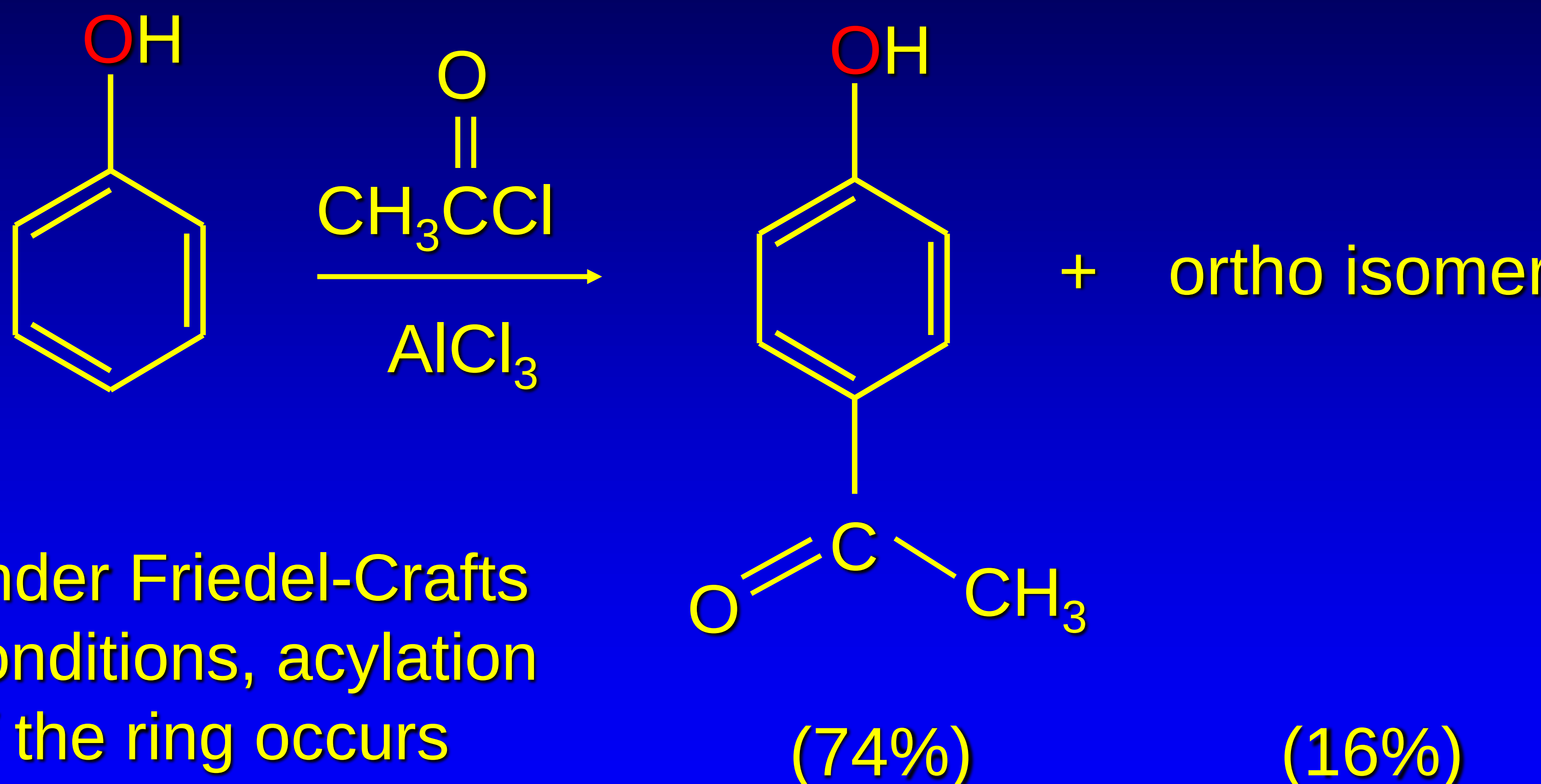
Friedel-Crafts Alkylation

Friedel-Crafts Acylation

Acylation of Phenols

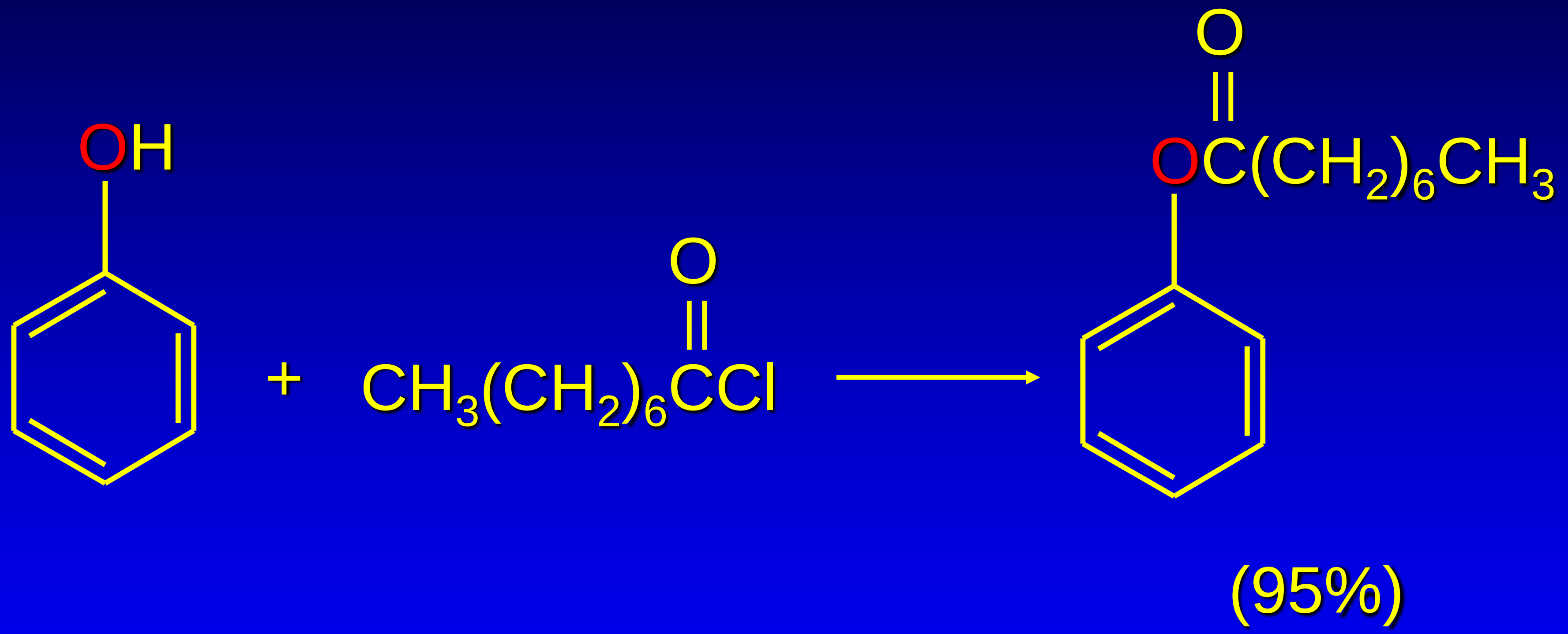
Acylation can take place either on the ring by electrophilic aromatic substitution or on oxygen by nucleophilic acyl substitution

Friedel-Crafts Acylation



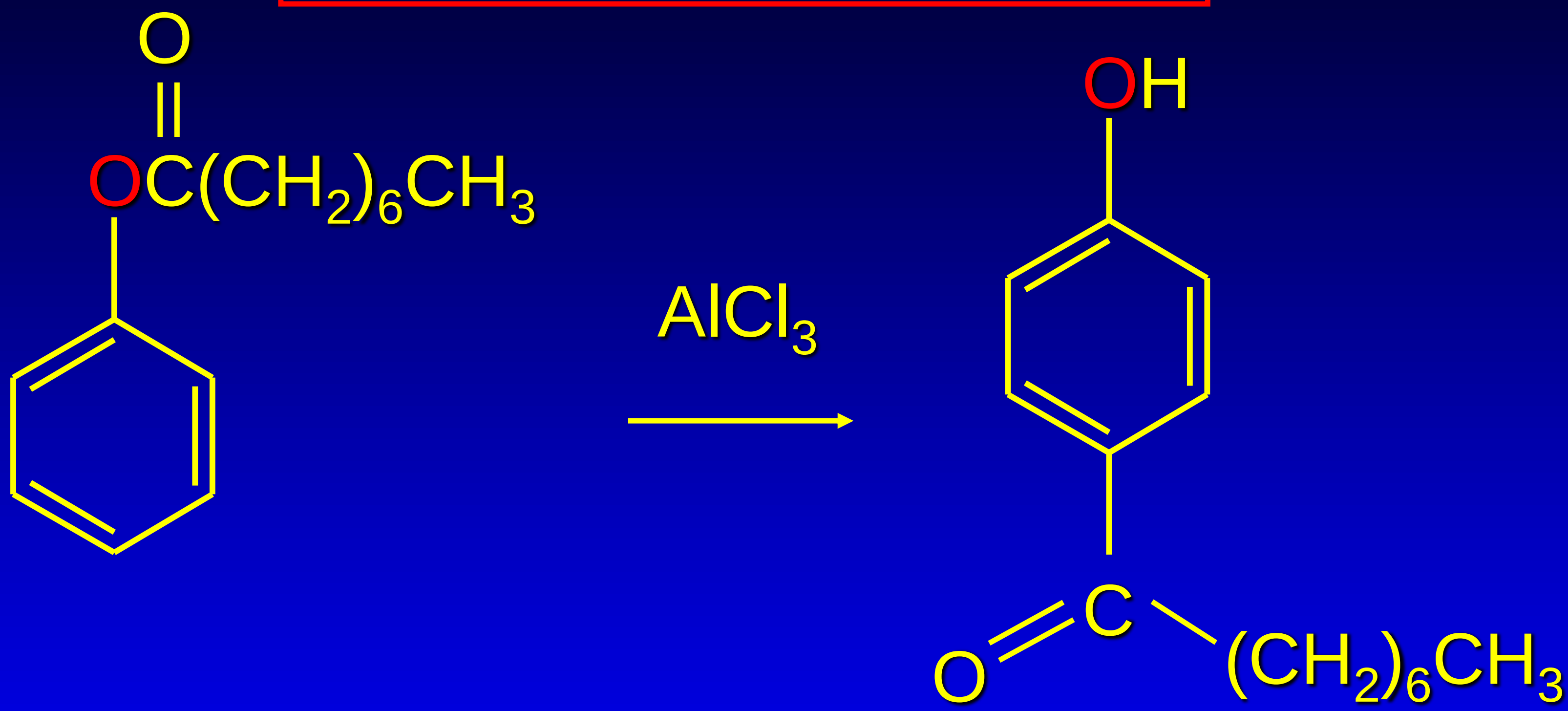
under Friedel-Crafts conditions, acylation of the ring occurs (C-acylation)

O-Acylation



in the absence of $AlCl_3$, acylation of the hydroxyl group occurs (O-acylation)

O- versus C-Acylation



formed faster

more stable

O-Acylation is kinetically controlled process; C-acylation is thermodynamically controlled

$AlCl_3$ catalyzes the conversion of the aryl ester to the aryl alkyl ketones; this is called the Fries rearrangement