

Phenols — Ar-OH

Phenols differ from alcohols in that the -OH is *directly* attached to the aromatic ring. [Ph-CH₂-OH is an alcohol.]

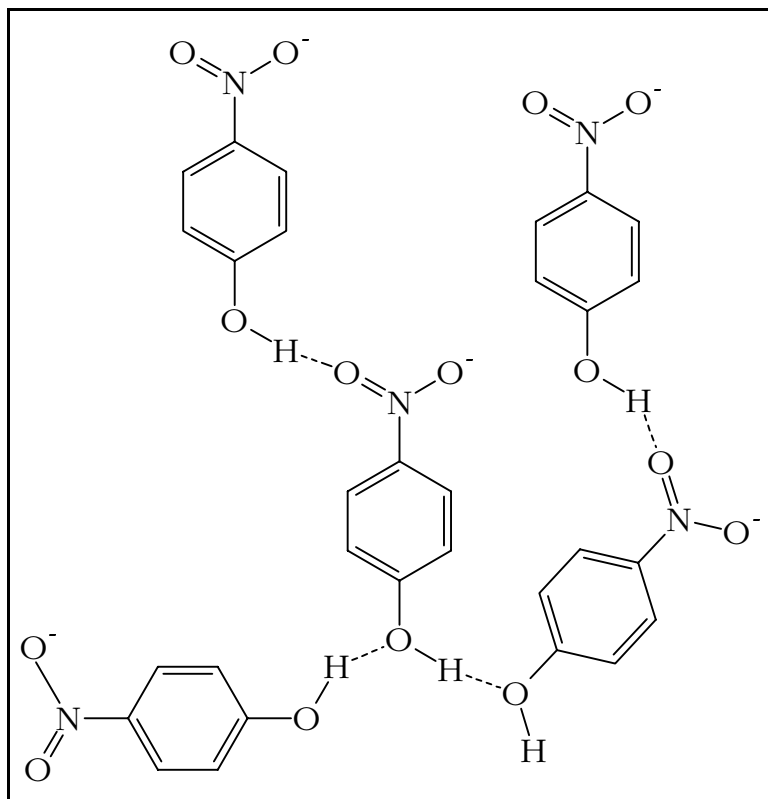
Physical Properties —

Phenol is somewhat soluble in water (hydrogen bonding); other phenols are not very soluble.

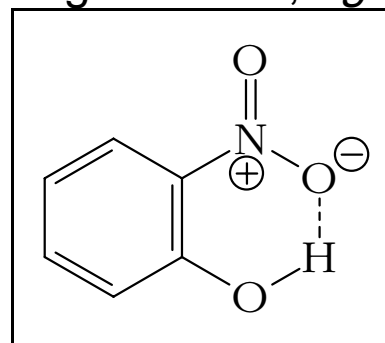
Boiling points are high compared to hydrocarbons owing to hydrogen bonding.

Hydrogen Bonding —

Most phenols form *intermolecular* hydrogen bonds, *eg*



However, some form *intramolecular* hydrogen bonds, *eg*



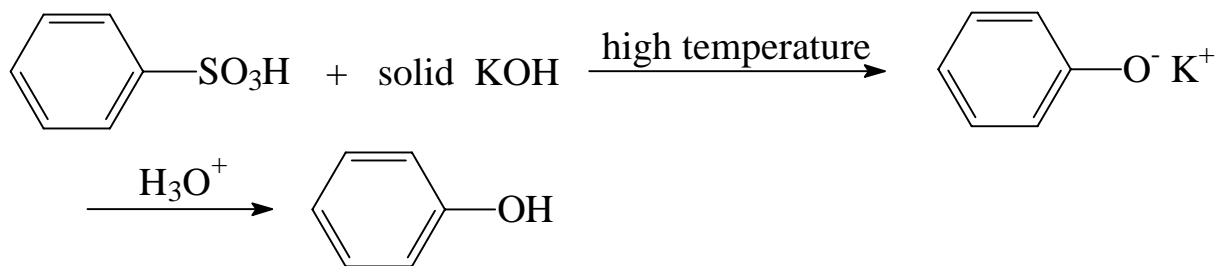
The geometry must be suitable for formation of intramolecular H-bonds.

Hydrogen bonding is reflected in physical properties:

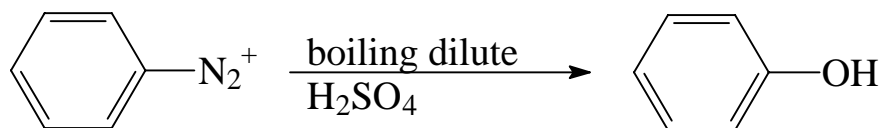
	BP °C/ 70 Torr	Solubility, g/100 g H ₂ O	H-bonding
<i>o</i> -nitrophenol	100	0.2	intra
<i>m</i> -nitrophenol	194	1.35	inter
<i>p</i> -nitrophenol	decomposes	1.69	inter

Preparation of Phenols —

* From Sulfonic Acids —



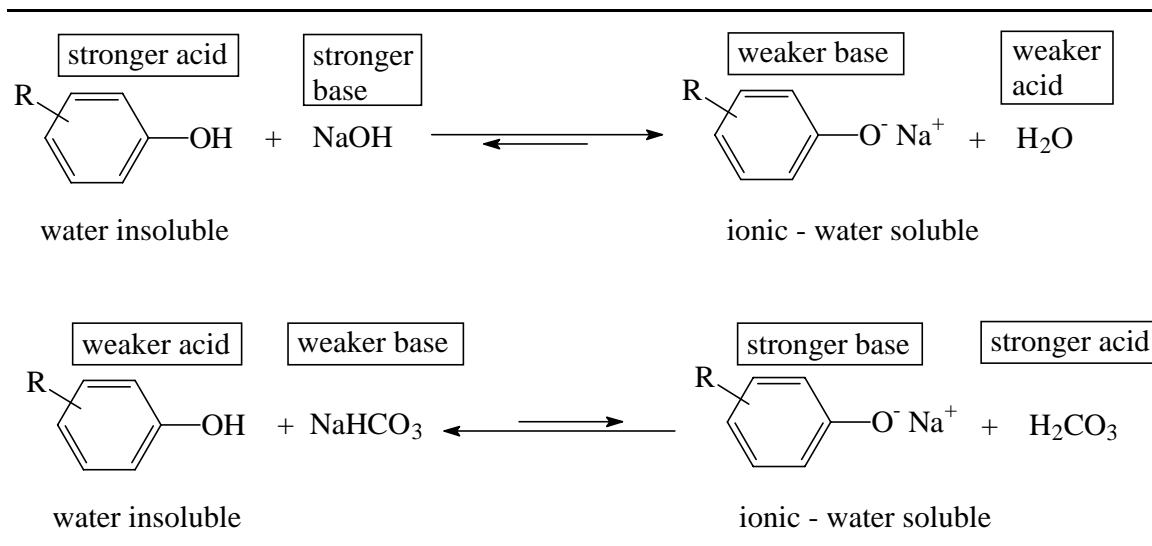
* From Diazonium Salts —



The function of the acid is to keep the phenol from forming phenoxide ion, which would rapidly couple with the diazonium salt.

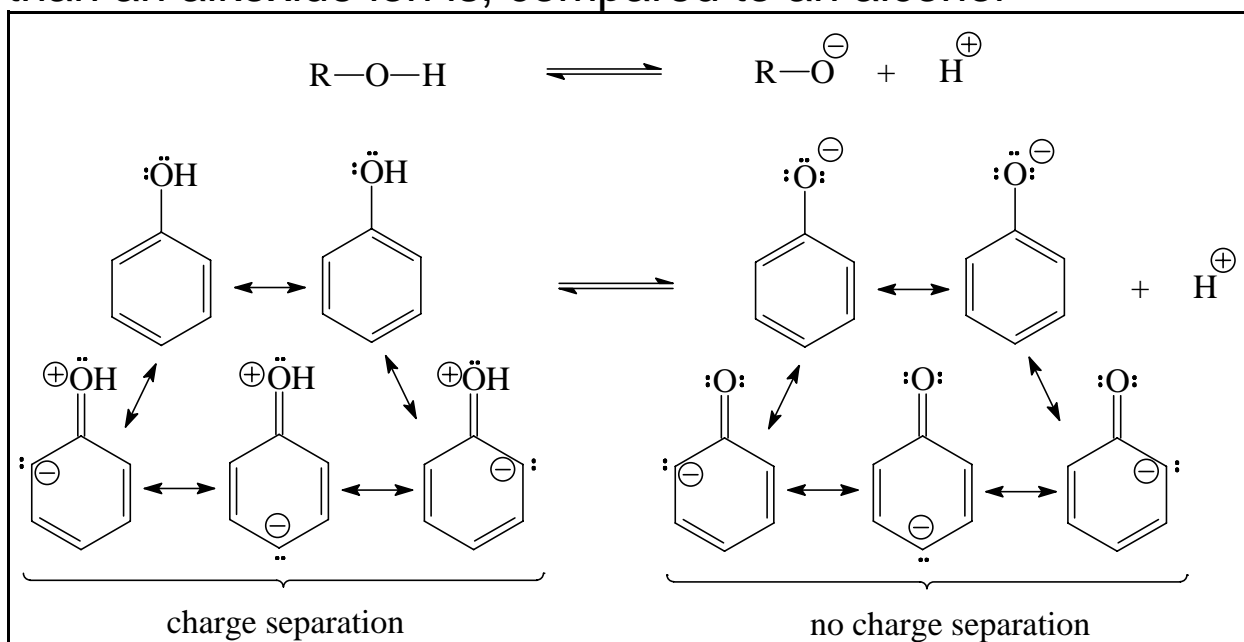
Reactions of Phenols —

Phenols are acidic. Typical phenols dissolve in aqueous hydroxide, OH^- , but not in aqueous bicarbonate, HCO_3^- .



Why are phenols acidic ($K_a \sim 10^{-10}$) compared to alcohols ($K_a \sim 10^{-16}$)?

Compared to a phenol, the phenoxide ion is more stable than an alkoxide ion is, compared to an alcohol —



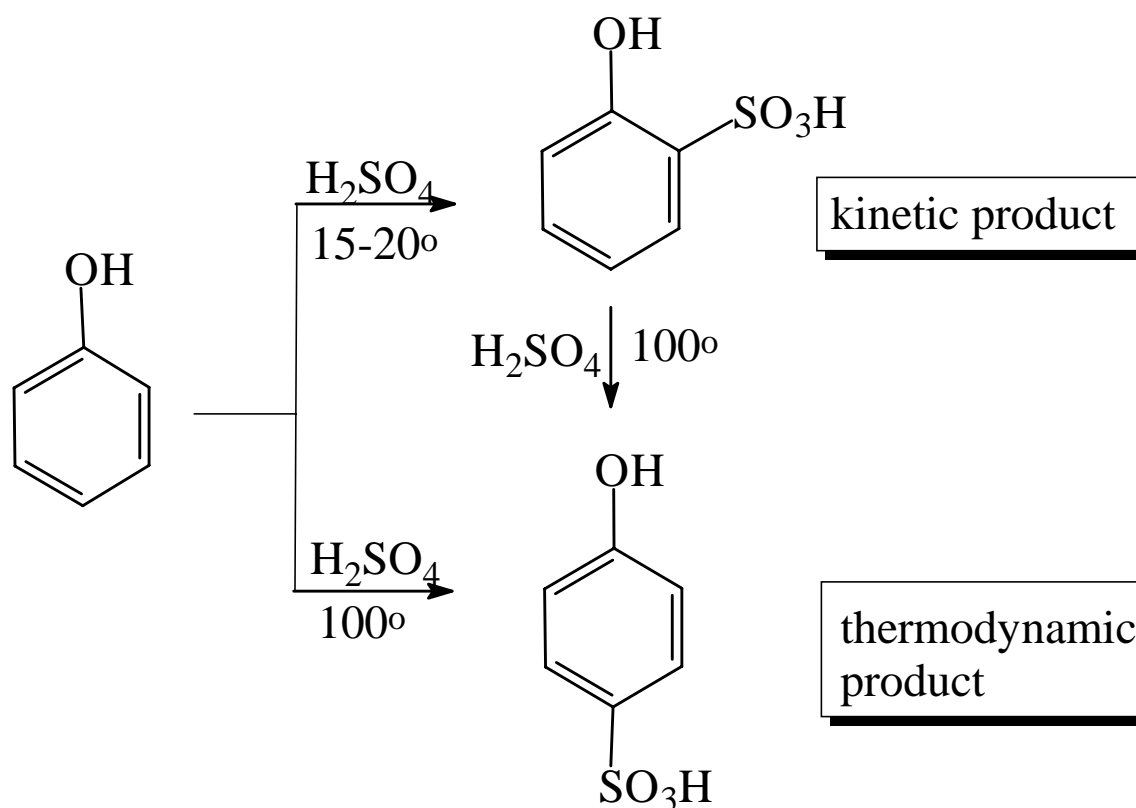
Effect of substituent groups on the ring —

Electron withdrawing groups increase acidity; electron donating groups decrease it.

Compound	phenol	<i>p</i> -cresol	<i>p</i> -nitrophenol
K_a	1.1×10^{-10}	0.67×10^{-10}	690×10^{-10}

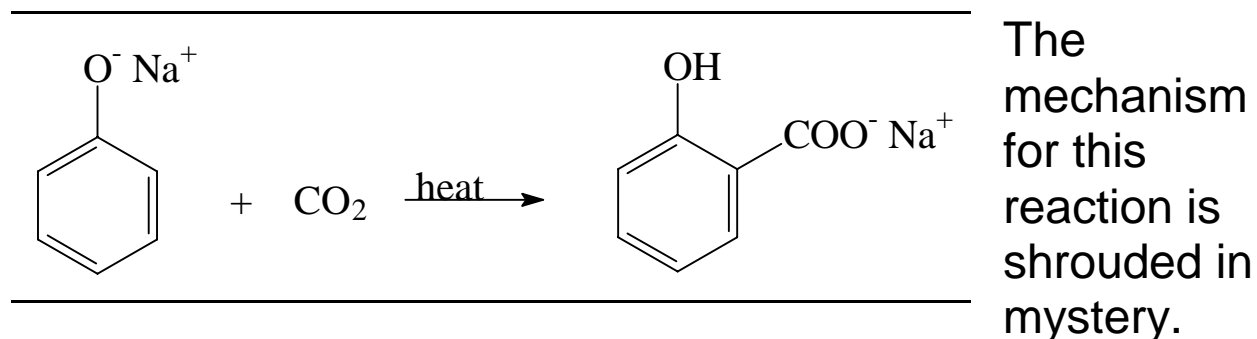
Electron withdrawing groups stabilize the phenoxide ion by dispersing the negative charge; electron donating groups destabilize the phenoxide ion by intensifying the negative charge.

Sulfonation —

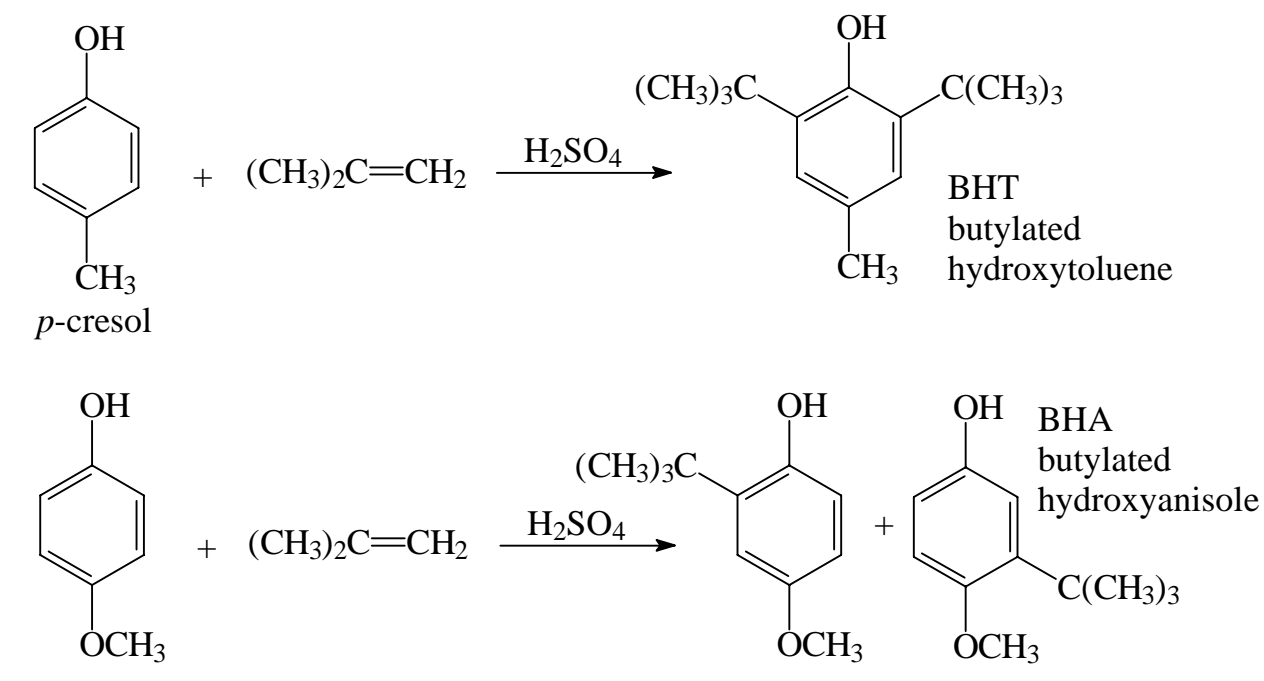


The usual story here. At low temperature more collisions have enough energy to form the kinetic product (lower ΔG^\ddagger). The sulfonation reaction is reversible. At higher temperature many collisions have enough energy to form either product. The kinetic product is still formed faster, but, since the reaction is reversible, and it is the less stable compound, it is unformed faster. Thus, the more stable product predominates.

Kolbe-Schmitt Reaction —



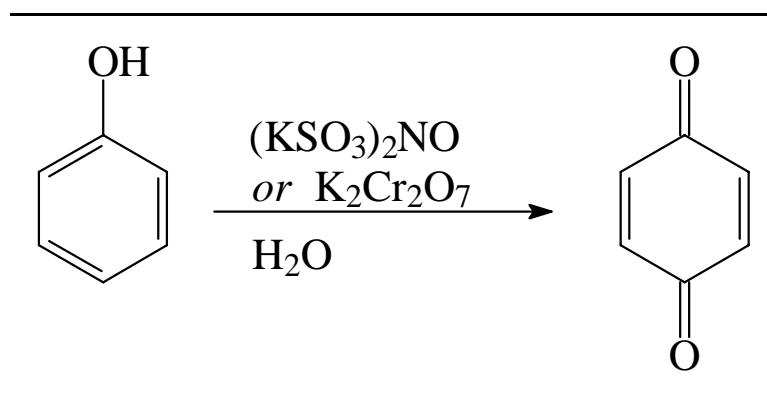
Friedel-Crafts — -OH is a powerful activating group.



Phenols can act as antioxidants by functioning as free radical scavengers: $\text{Ar-O-H} + \text{R}\cdot \rightarrow \text{Ar-O}\cdot + \text{RH}$. $\text{Ar-O}\cdot$ is a relatively stable radical and will cause chain termination.

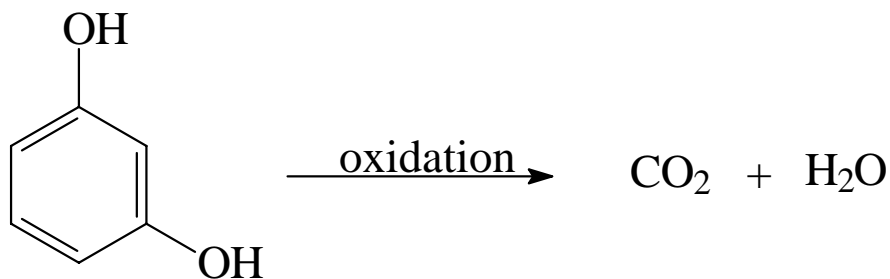
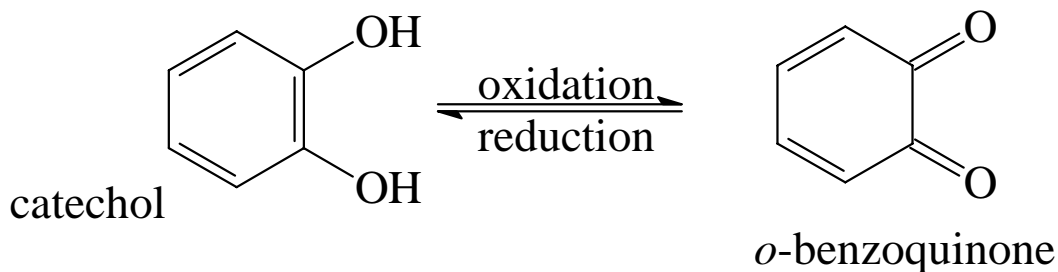
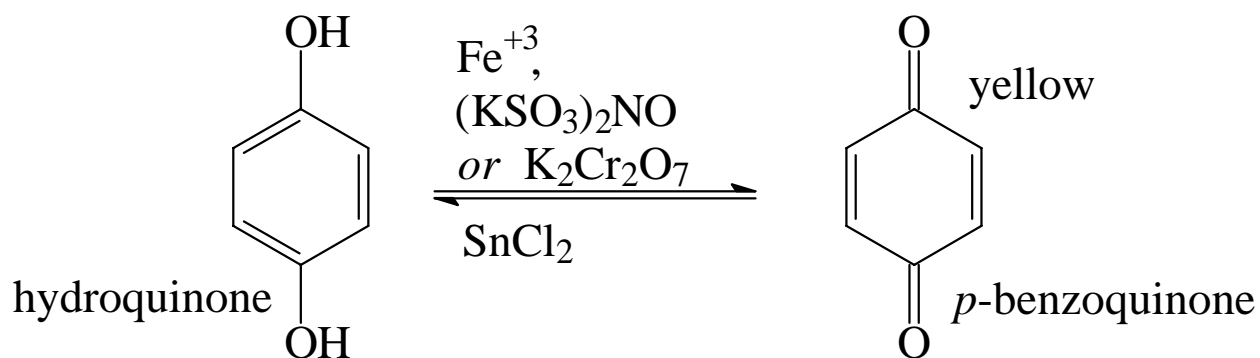
Oxidation of Phenols —

Phenol can be oxidized to *p*-benzoquinone by several oxidizing agents, including Fremy's salt or potassium dichromate.

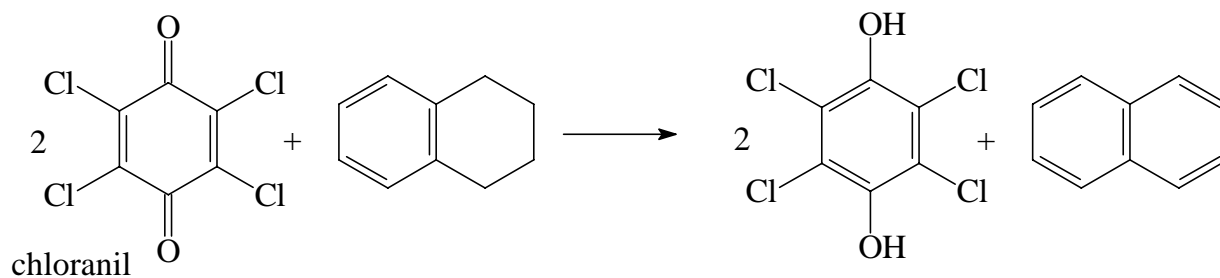


Quinones —

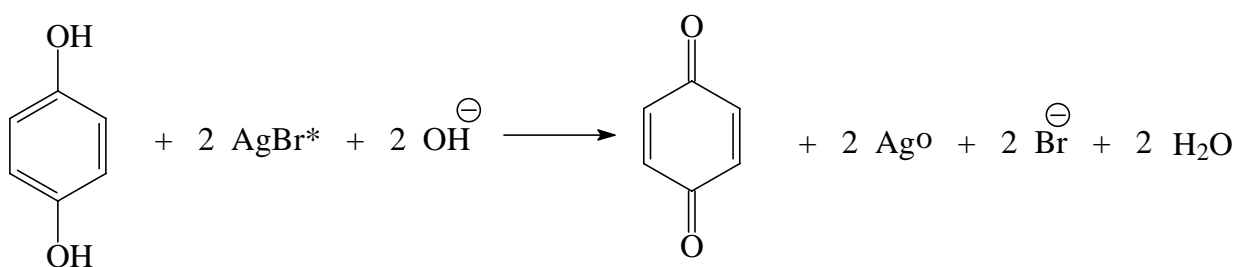
Quinones can also be formed by mild oxidation of 1,2- or 1,4-dihydroxy aromatic compounds. In turn, the quinones can be reduced back to these compounds.



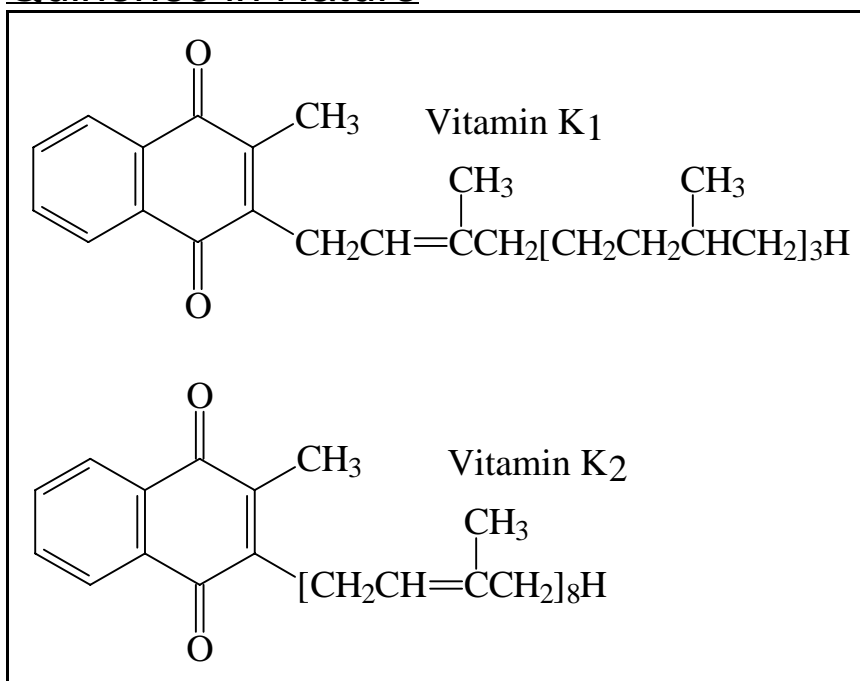
Quinones are oxidizing agents, *eg*



Hydroquinones are reducing agents, *eg*

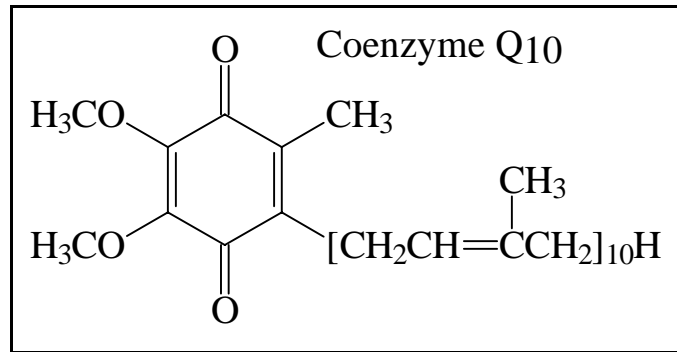


Quinones in Nature



The K vitamins are involved in blood clotting and are synthesized by intestinal bacteria in mammals. K₁ is found in alfalfa leaves and K₂ in fish meal.

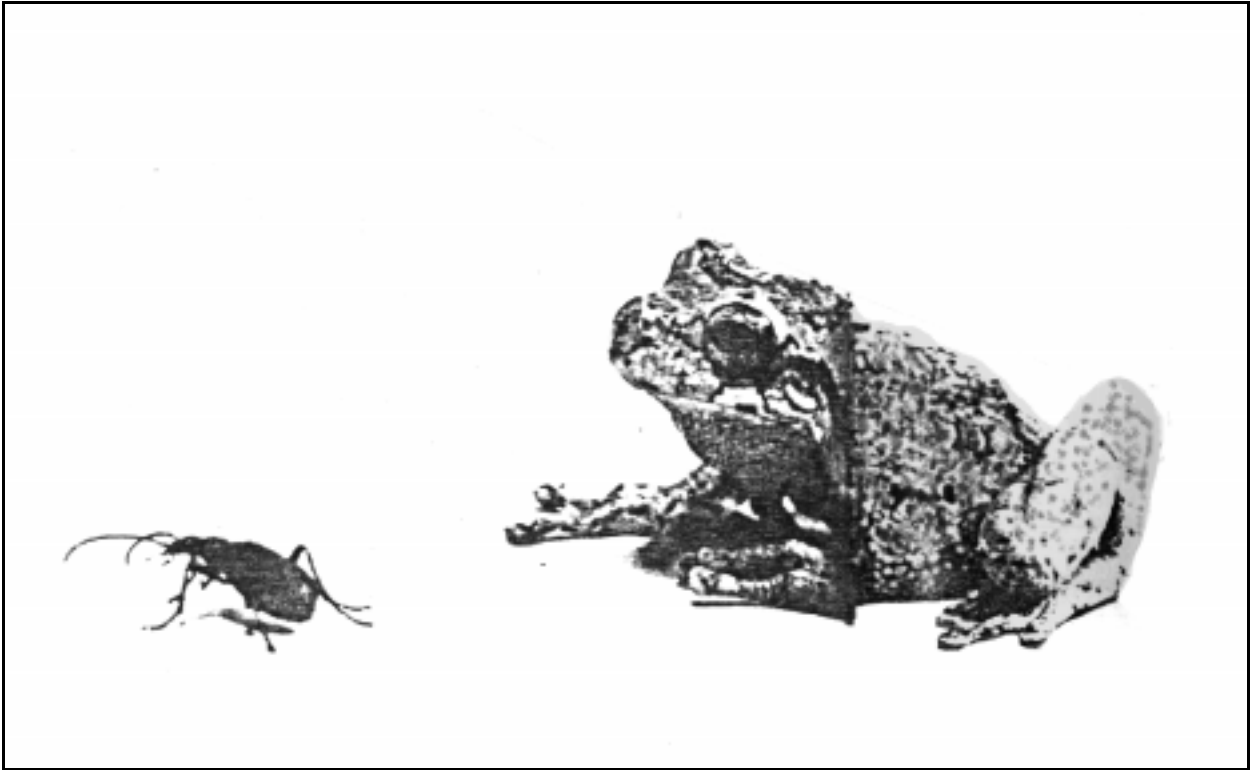
Coenzyme Q₁₀, aka ubiquinone is an electron transfer agent, involved in the oxidative phosphorylation reaction.



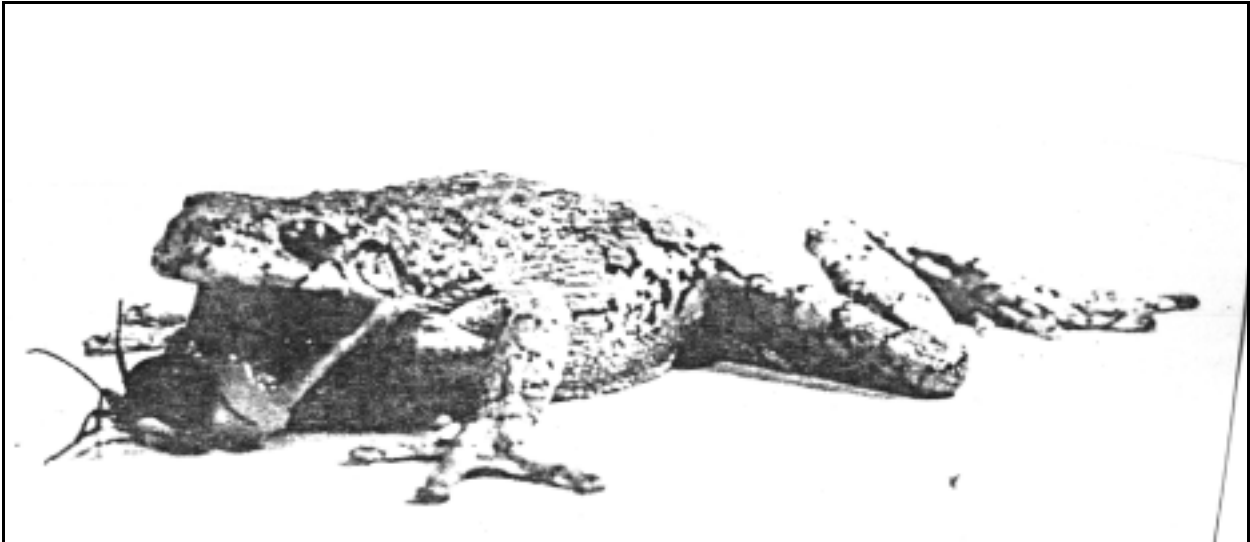
Isolated from pig hearts:

1 ton pig hearts -----> 37 grams coenzyme Q₁₀.

Quinones are used in insect defense mechanisms, *eg*, the bombardier beetle mixes H₂O₂, hydroquinones, and enzymes to give O₂, H₂O and quinones. The reaction mixture gets so hot (100°C) the mixture is vaporized and shot from the beetle in a jet.



Ummmmm. A Tasty Looking Treat!



Gotcha. A bombardier blast! Oh, oh.



Poor Mr. Froggie!