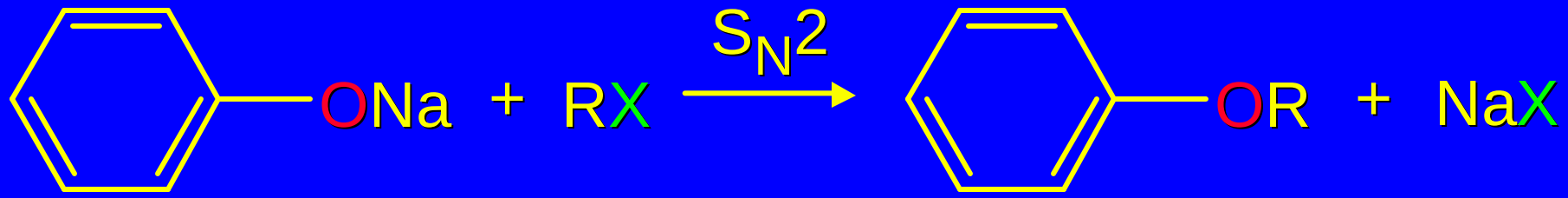
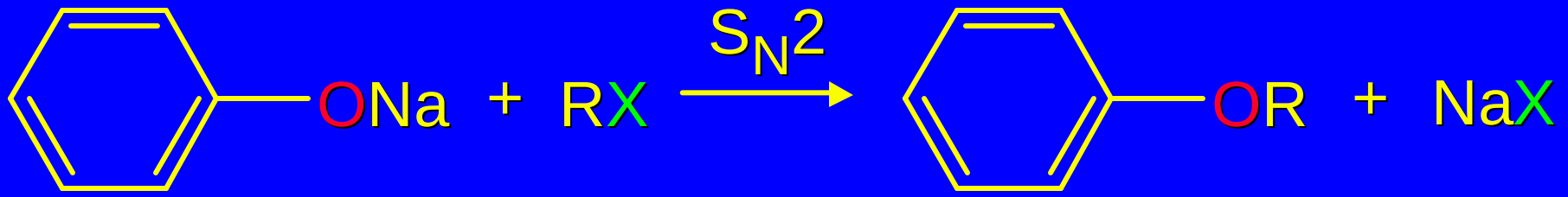
24.11
Preparation of Aryl Ethers

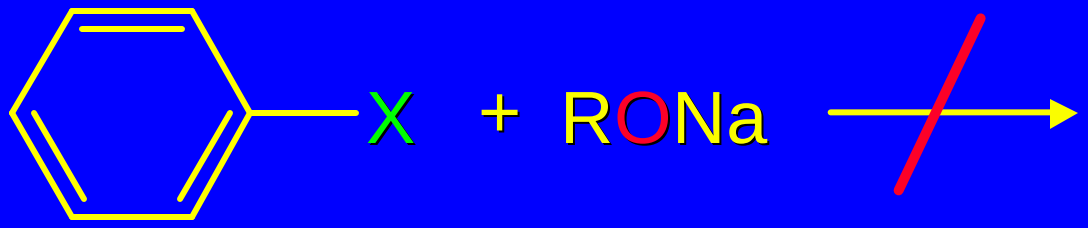
Typical Preparation is by Williamson Synthesis



Typical Preparation is by Williamson Synthesis

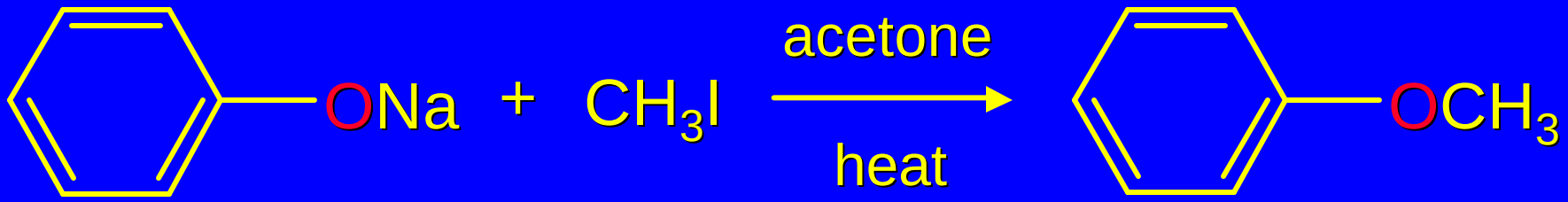


but the other combination



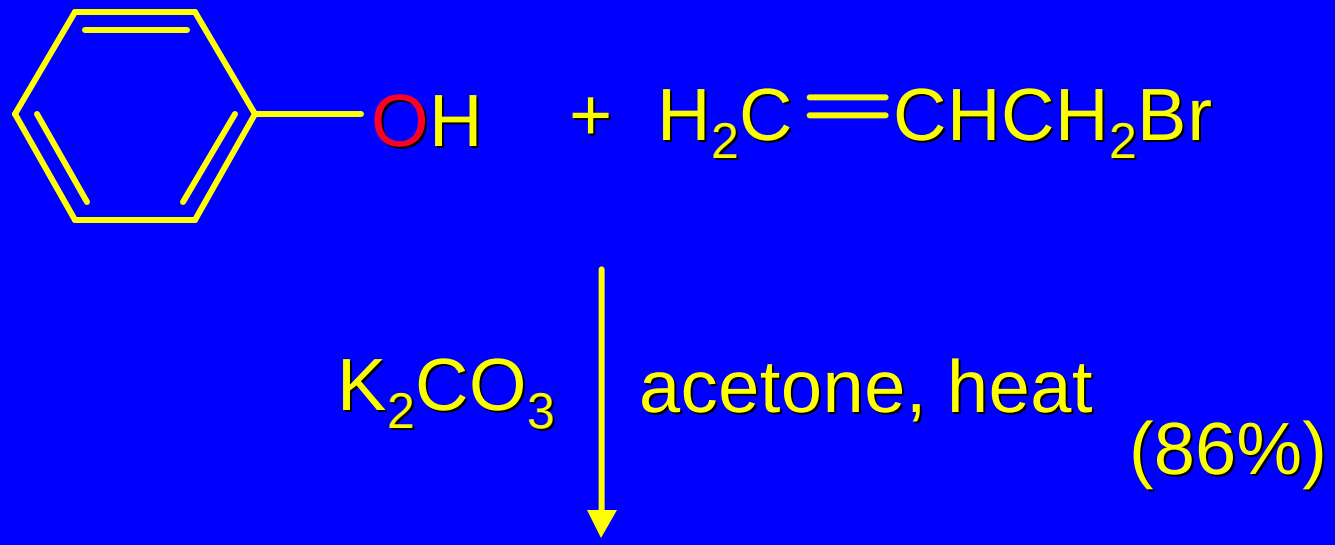
fails because aryl halides are normally unreactive toward nucleophilic substitution

Example

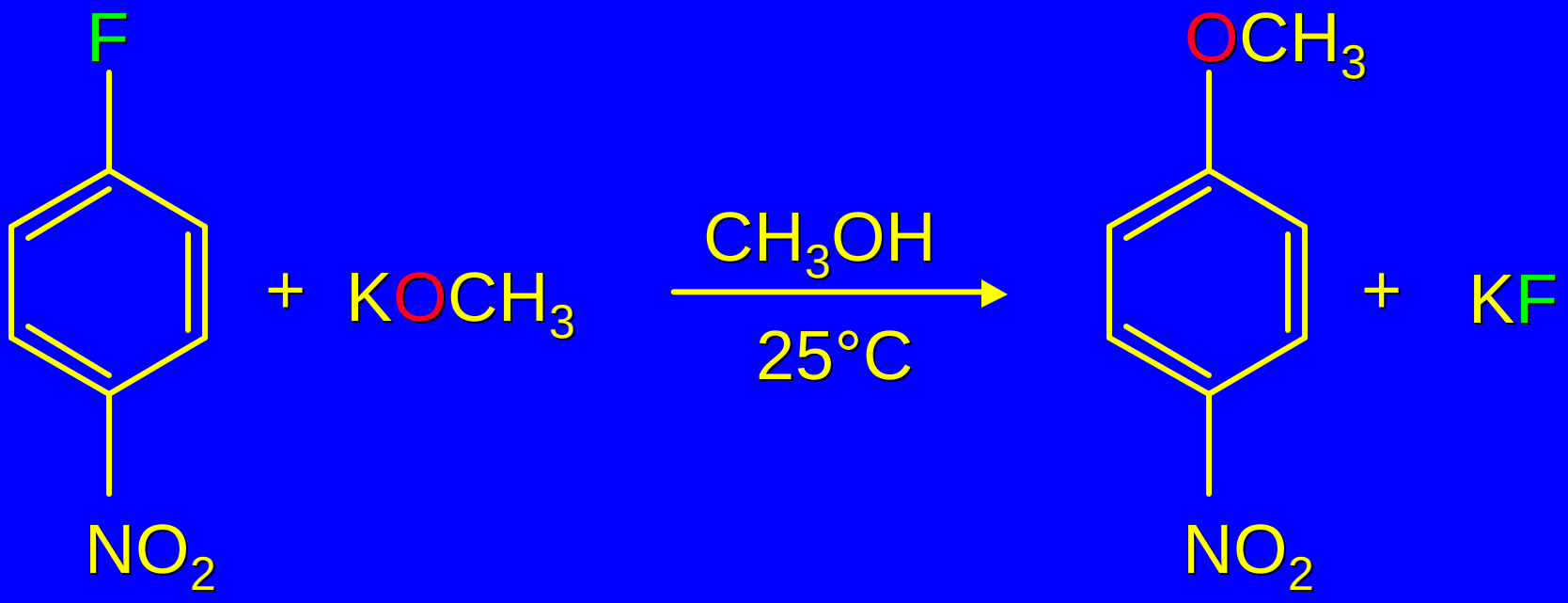


(95%)

Example



Aryl Ethers from Aryl Halides

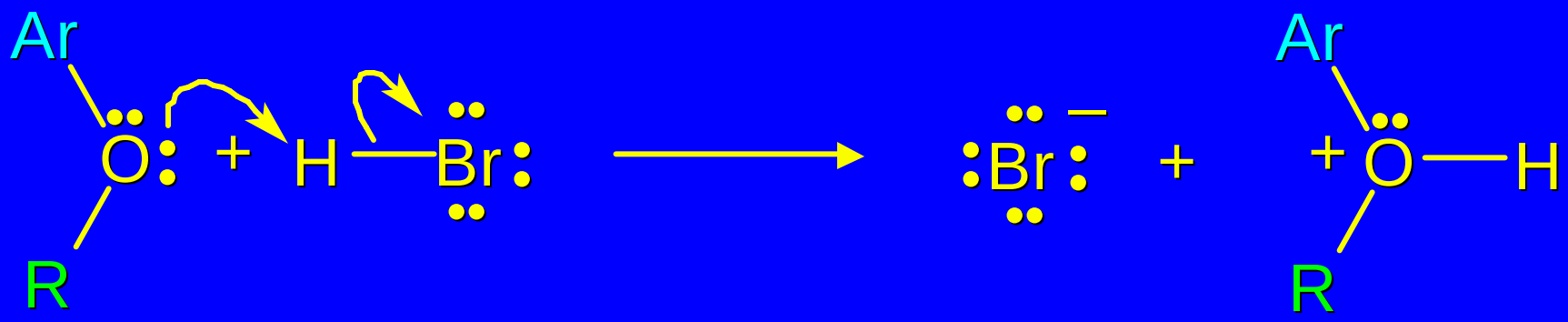


(93%)

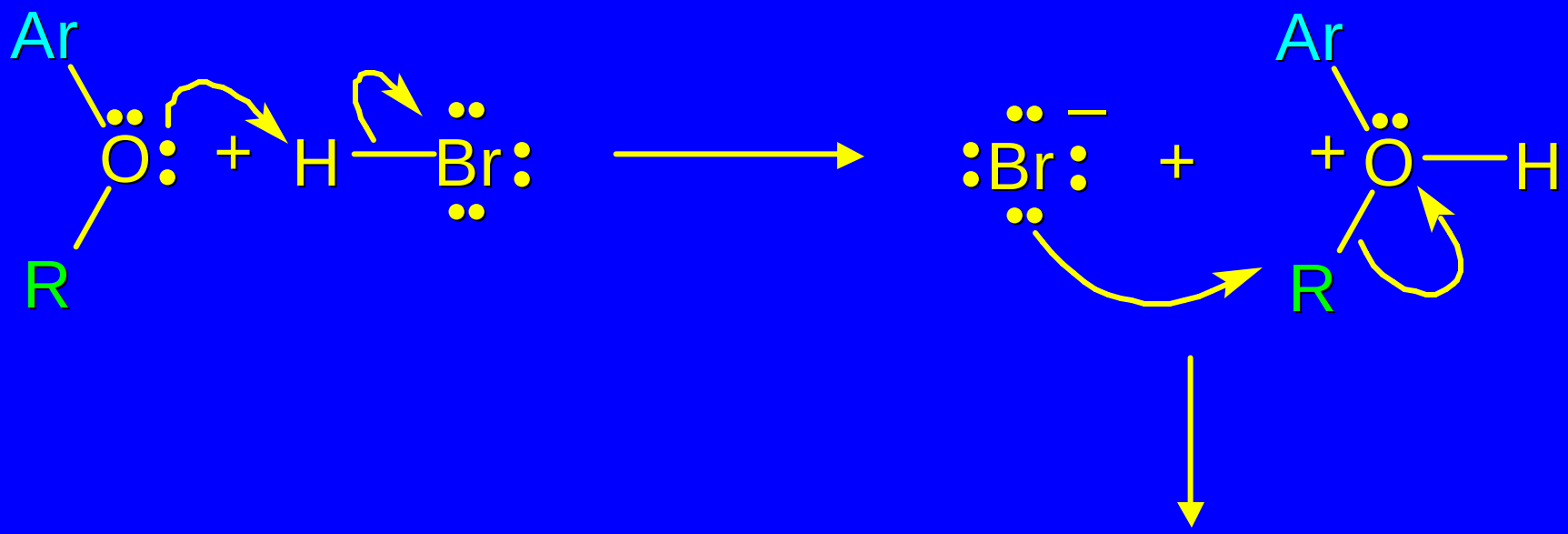
nucleophilic aromatic substitution is effective with nitro-substituted (ortho and/or para) aryl halides

24.12
Cleavage of Aryl Ethers by Hydrogen Halides

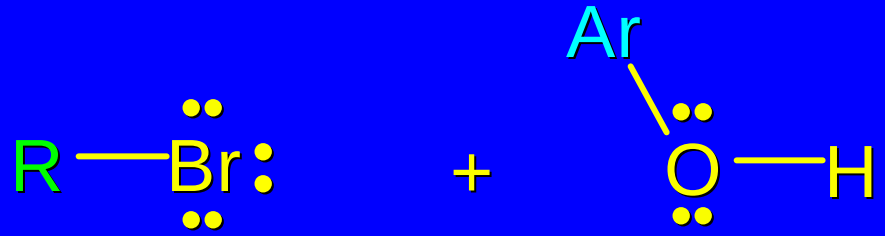
Cleavage of Alkyl Aryl Ethers



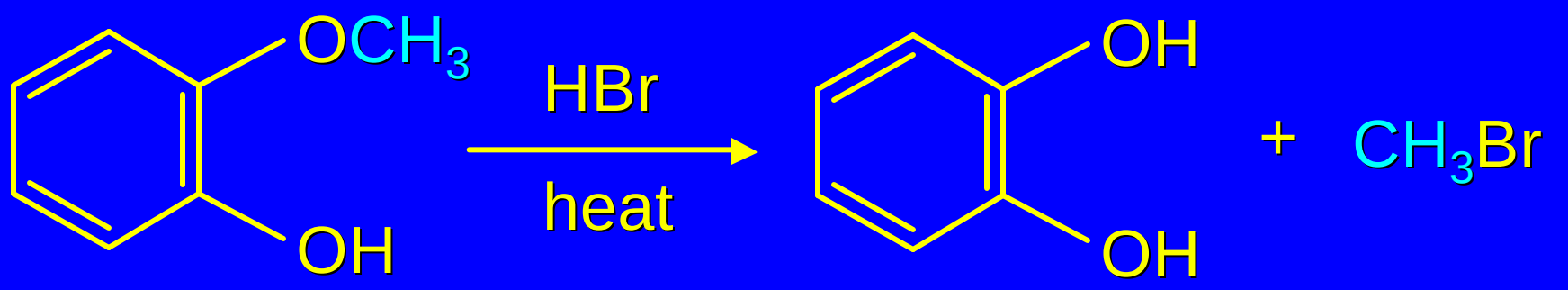
Cleavage of Alkyl Aryl Ethers



An alkyl halide is formed; never an aryl halide!



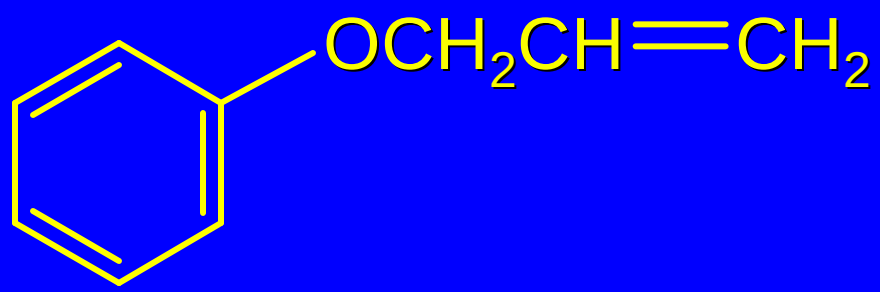
Example



(85-87%) (57-72%)

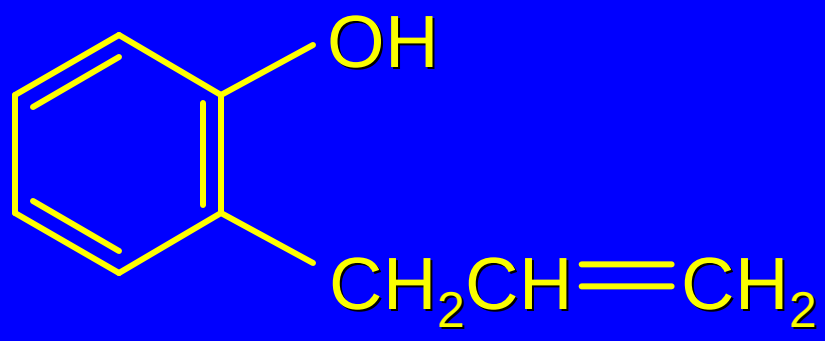
24.13
Claisen Rearrangement of Allyl Aryl Ethers

Allyl Aryl Ethers Rearrange on Heating



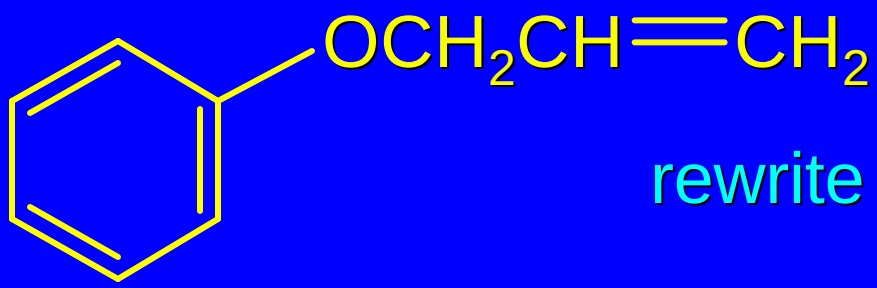
200°C

allyl group migrates to ortho position

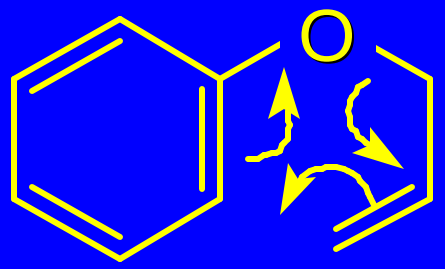


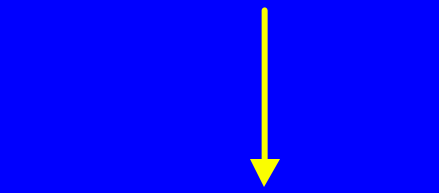
(73%)

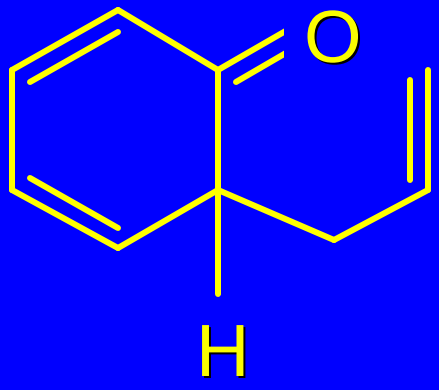
Mechanism



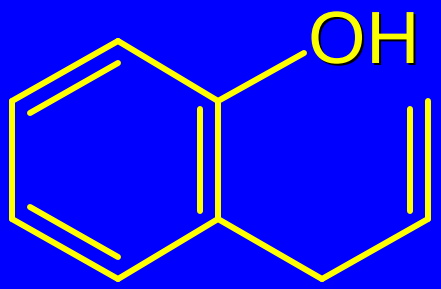
rewrite as





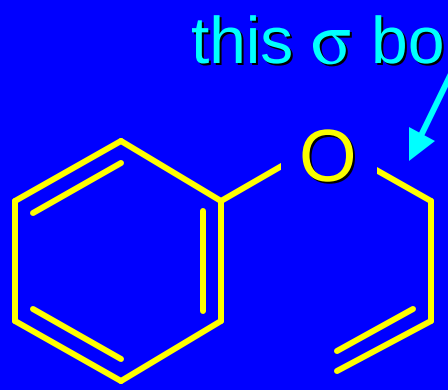


keto-to-enol
isomerization

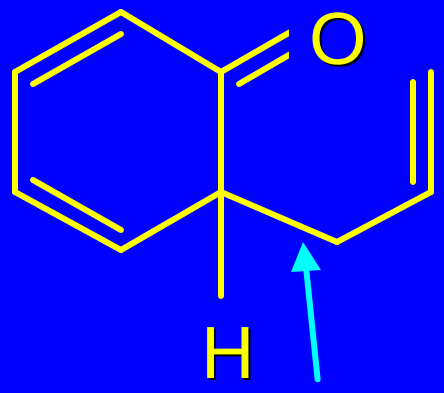


Sigmatropic Rearrangement

Claisen rearrangement is an example of a sigmatropic rearrangement. A σ bond migrates from one end of a conjugated π electron system to the other.



"conjugated π electron system" is the allyl group

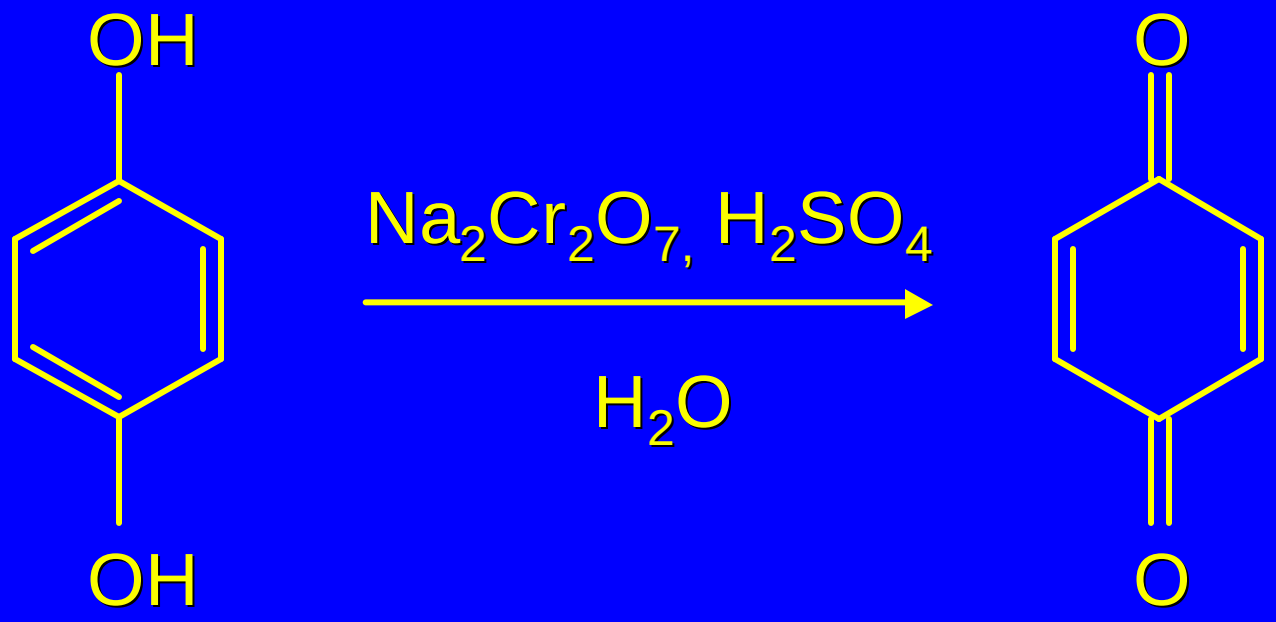


this σ bond forms

24.14
Oxidation of Phenols: Quinones

Quinones

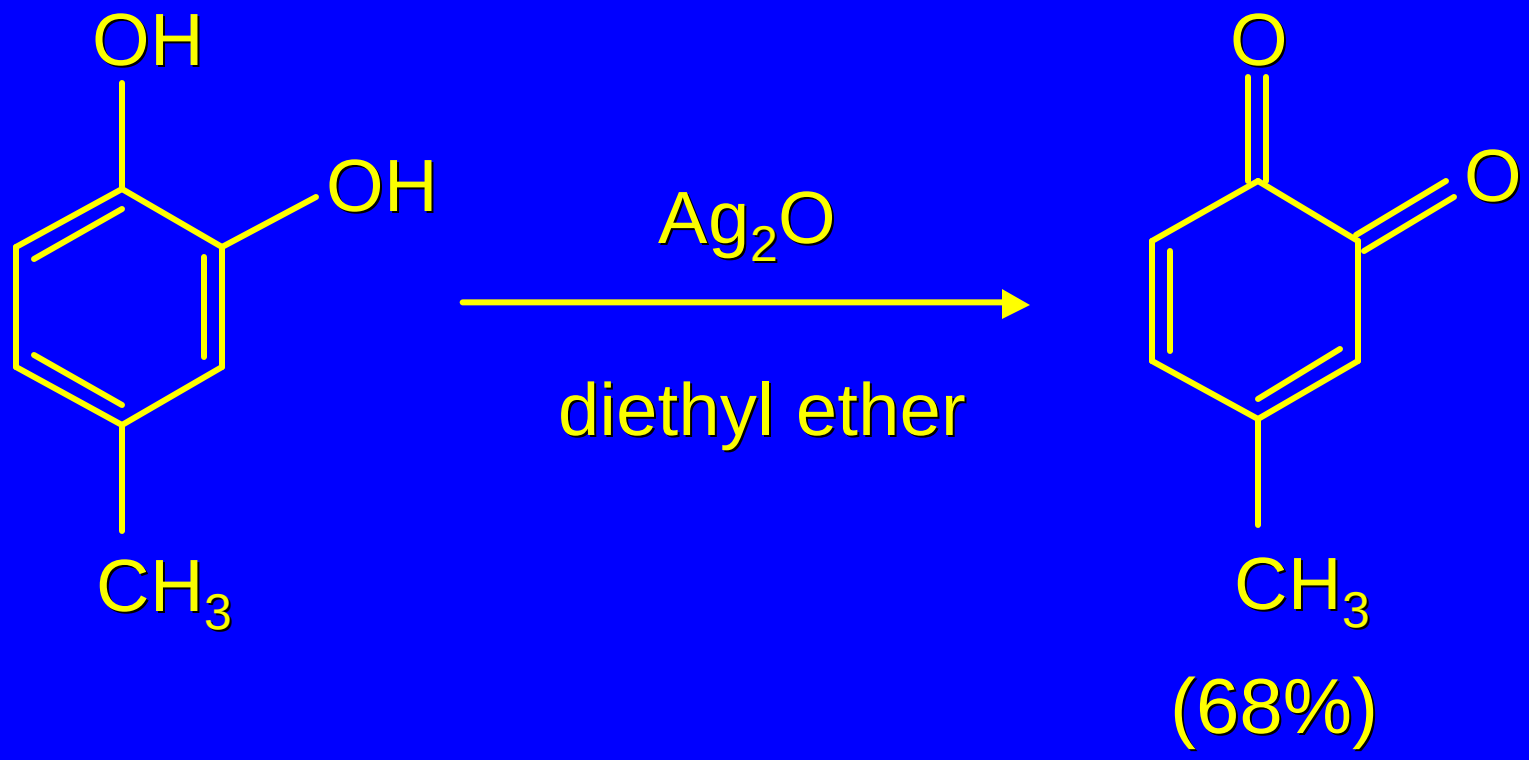
The most common examples of phenol oxidations are the oxidations of 1,2- and 1,4-benzenediols to give quinones.



(76-81%)

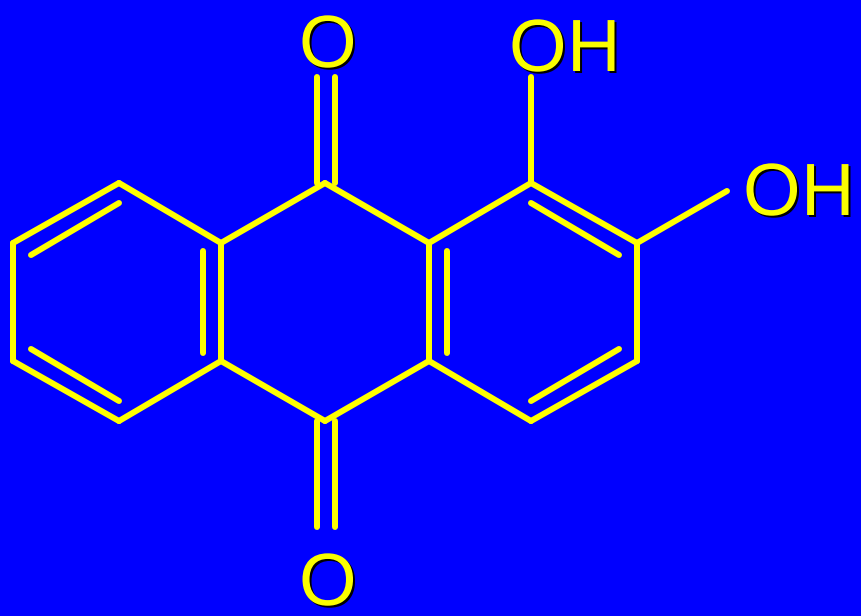
Quinones

The most common examples of phenol oxidations are the oxidations of 1,2- and 1,4-benzenediols to give quinones.



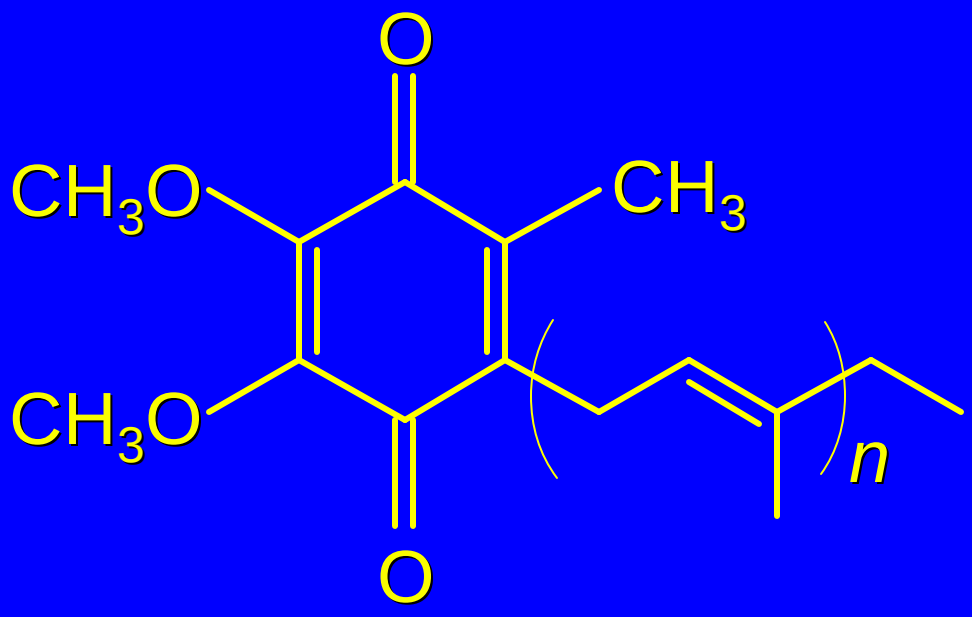
(68%)

Some quinones are dyes



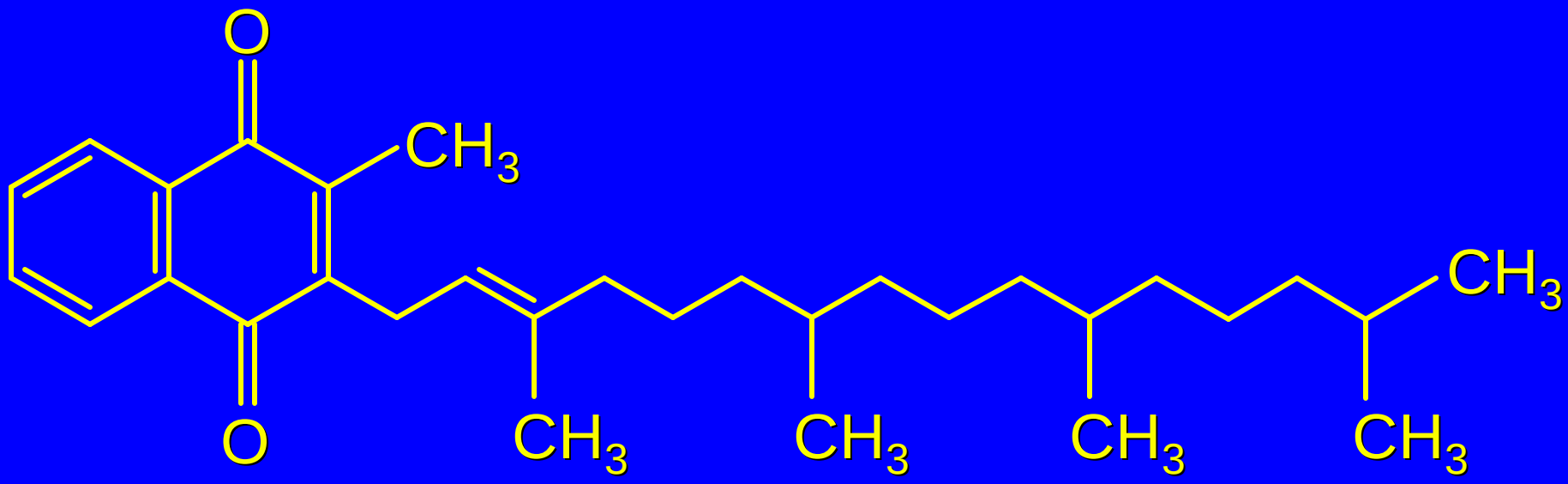
Alizarin
(red pigment)

Some quinones are important biomolecules



Ubiquinone (Coenzyme Q)
n = 6-10
involved in biological electron transport

Some quinones are important biomolecules



Vitamin K
(blood-clotting factor)