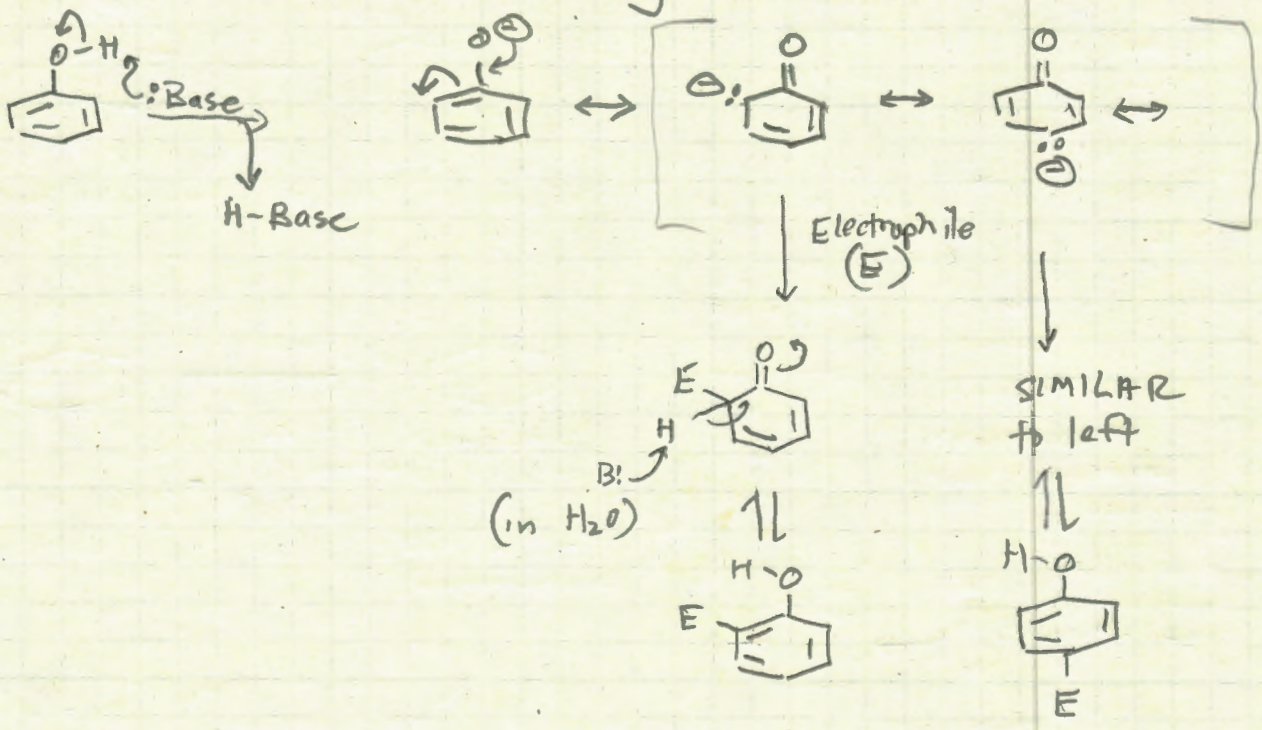
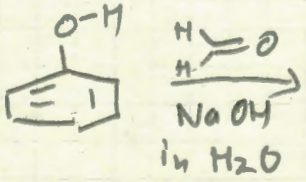
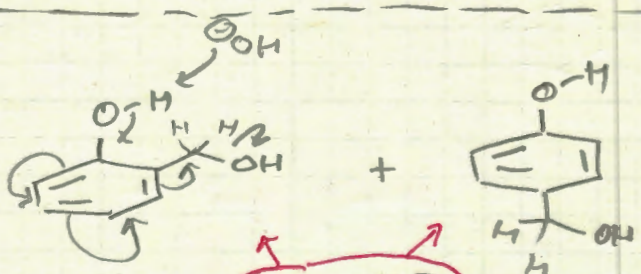
Electrophilic Add^n Involving Phenols

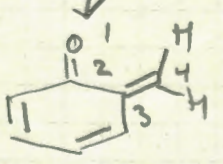


Examples

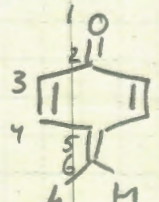




Δ Decomposition

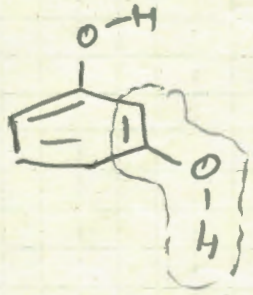


1,4-Michael Add^n
Reactant

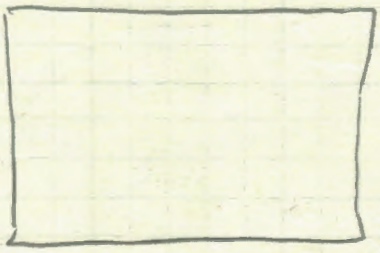


1,6-Add^n
Reactant

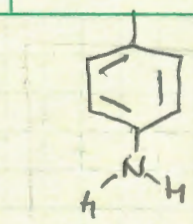
Learn by Doing

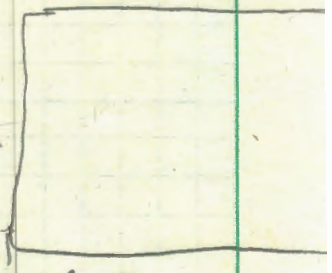


"enol"



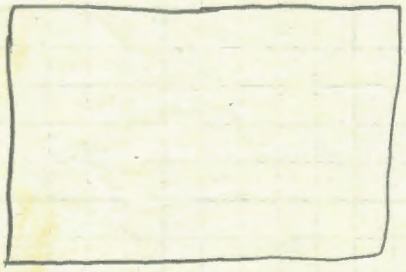
keto tautomer of circled region





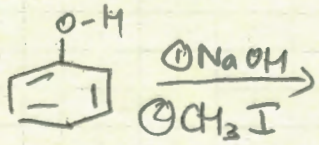
imino intermediate (A)

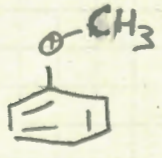
(A) ⇌



imino → enamine tautomer

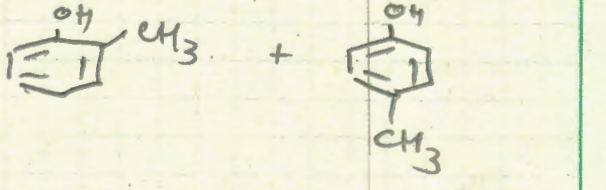
Earlier we saw



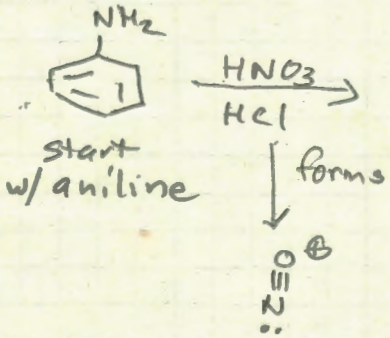


(B)

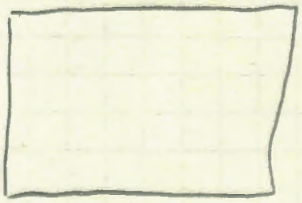
but now we know these conditions could also yield

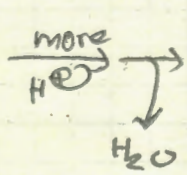


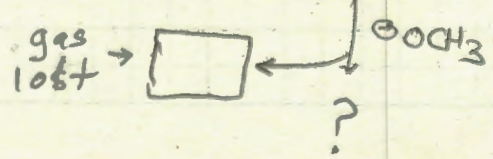
To avoid the side rxns, let's view an alternative route to (B)



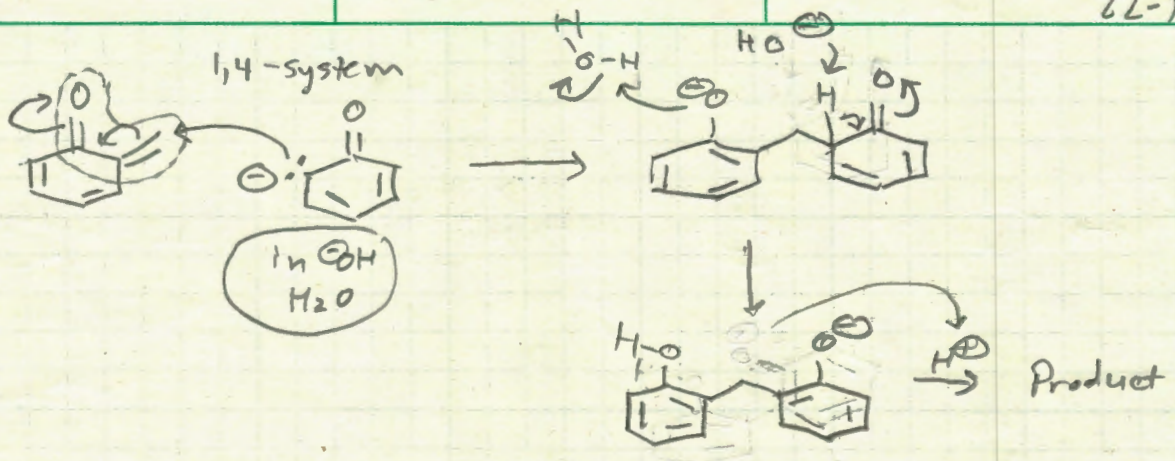
start w/ aniline

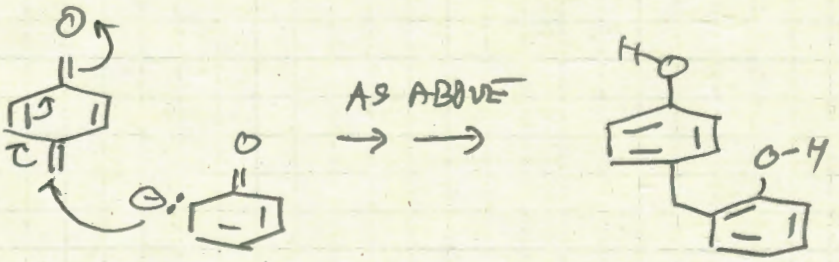






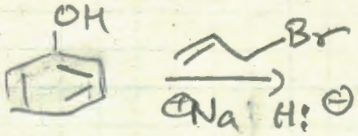
?



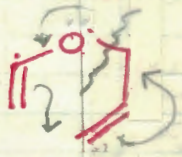


1,6-Addn

Claisen Rearrangement

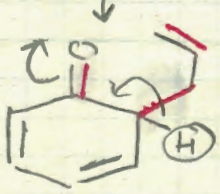


- 6-atoms are involved
- THEME



6 e⁻ movement provide aromatic transition state (TS)

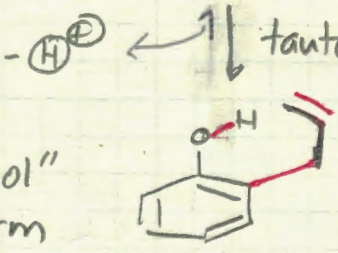
"Aromatic" stable TS



Thermodynamically favored! "keto" form

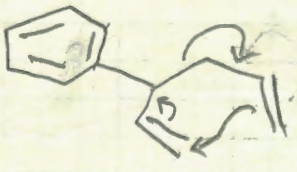
compared to

new bonds in (red)

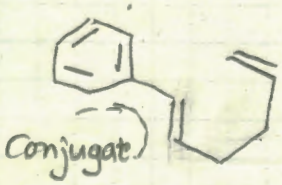


"enol" form

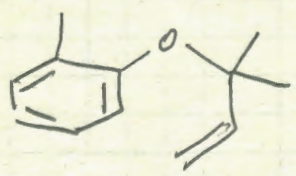
Similar: Cope Rearr

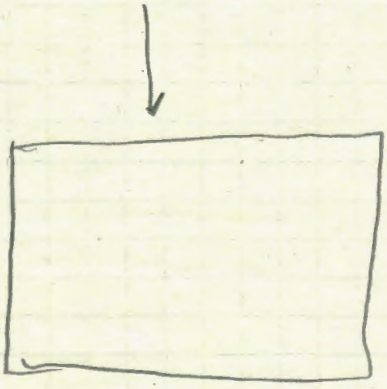


SEE THEME ABOVE



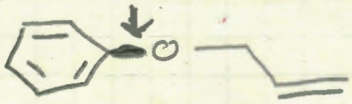
Conjugate



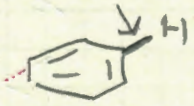


Draw the Claisen rearr product.

Given the bde values of



53 kcal mol^{-1}

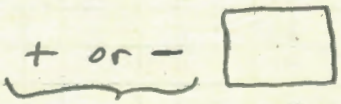


112 kcal mol^{-1}

88 kcal mol^{-1}

87 kcal mol^{-1}

estimate the ΔH of the rearr

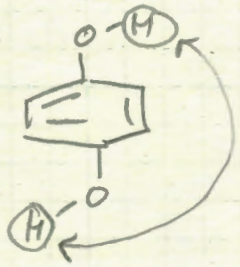


Hint: Redraw the product from above and bold the broken bonds in the phenyl ether reactant and the Claisen product you drew above

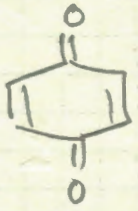
embolden the broken bonds

Claisen product complete structure embolden the made bonds!

Single electron oxidation of hydroquinone

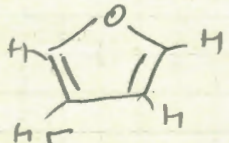


hydro form of ⇓ reduced form

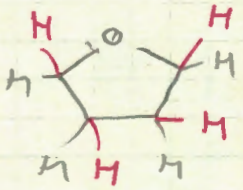


quinone!

e.g.

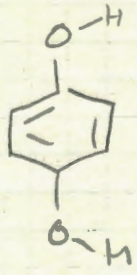


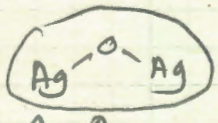
Furan



tetrahydrofuran

Oxidation of hydroquinone



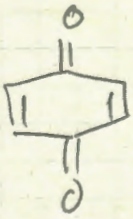


Ag_2O

OR

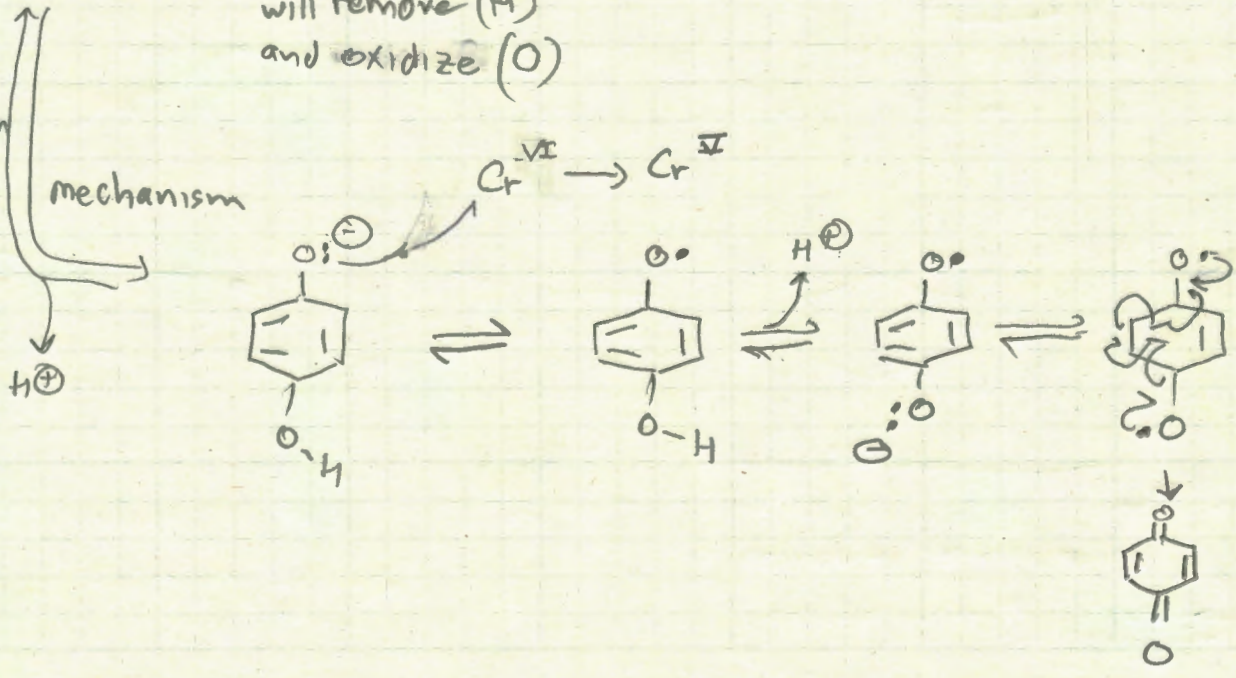
$NaCr_2O_7, H_2SO_4$

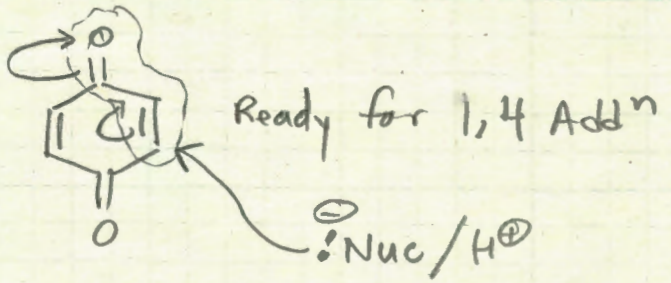
oxidant will remove (H) and oxidize (O)

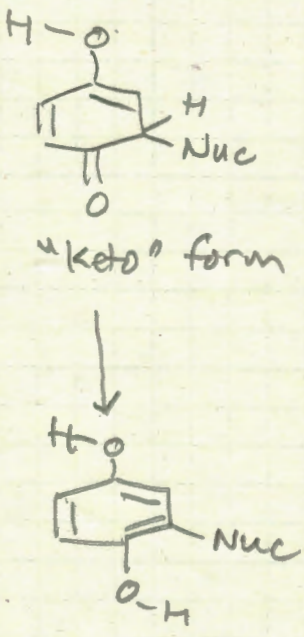


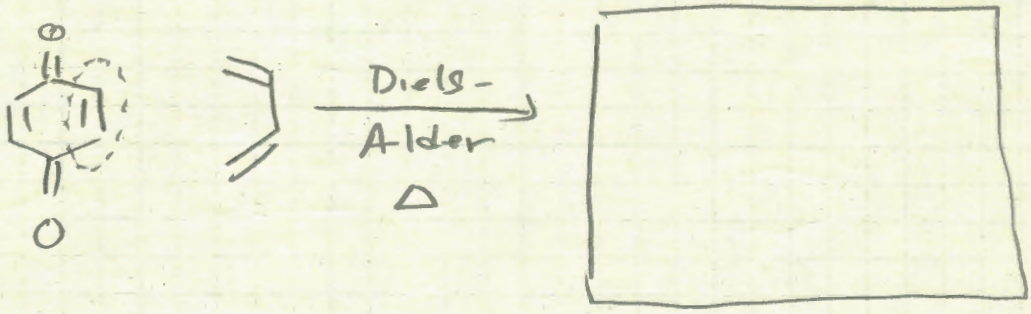
equilibrium

mechanism




Ready for 1,4 Addn
Nuc/H⊕


H
Nuc
"keto" form
Nuc


Diels-
Alder
Δ