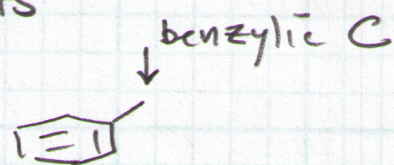


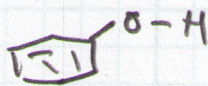
Chemistry of Benzene Substituents

Benzylic Resonance

|| Oxidat^{ns}/Reductions

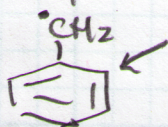
Phenols: Prep

Reactions

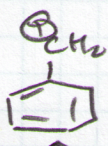
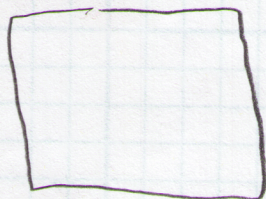


Claisen Rearr: Electrocyclic Rearr w/ benzene ring

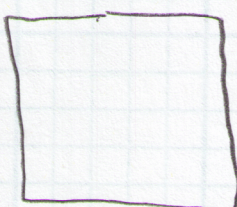
Benzylic



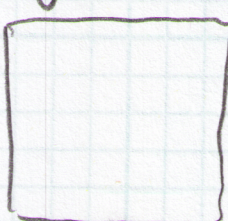
↑↓



↑↓



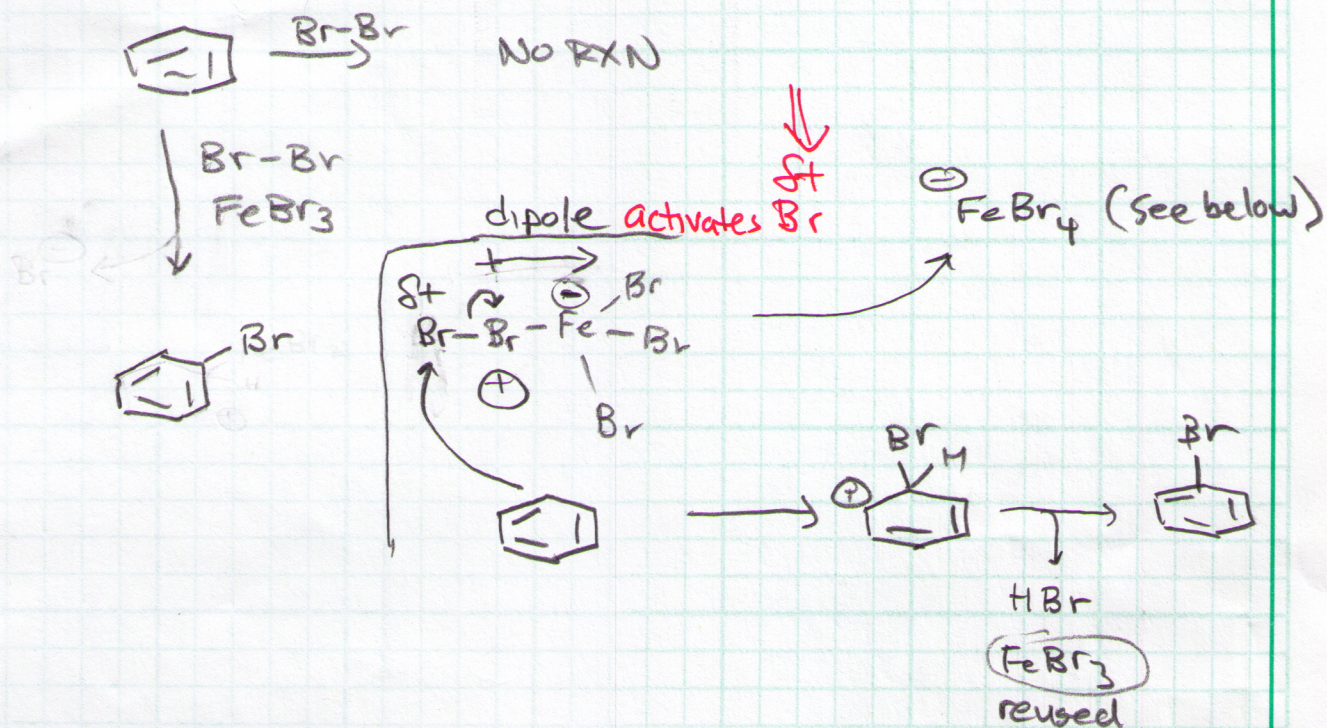
↑↓



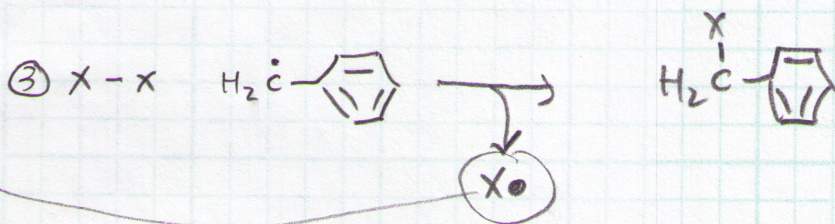
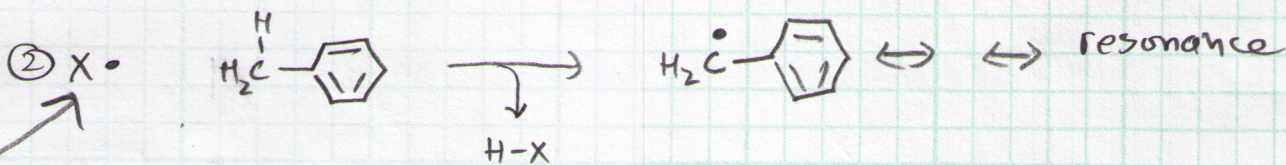
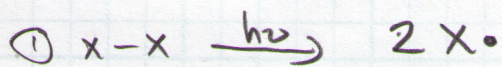
Draw a resonance structure of each where the arrow C has either the (•), (+), or (-) charge on it.

The benzylic C is ^{most} reactivity in the systems above so the aromaticity stabilization is NOT disrupted!

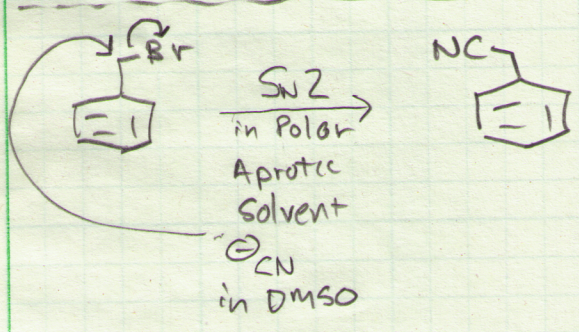
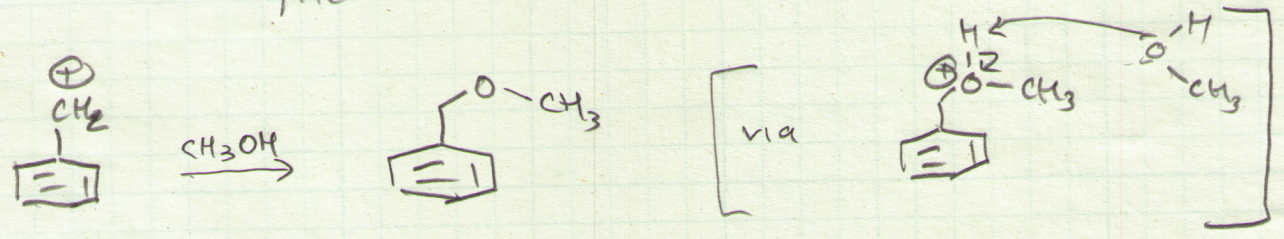
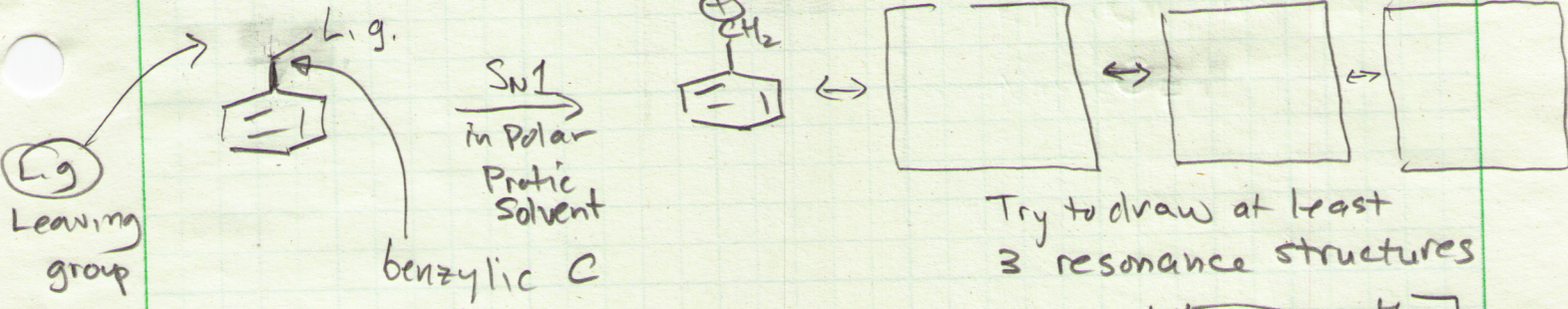
Stability of Aromaticity. Recall



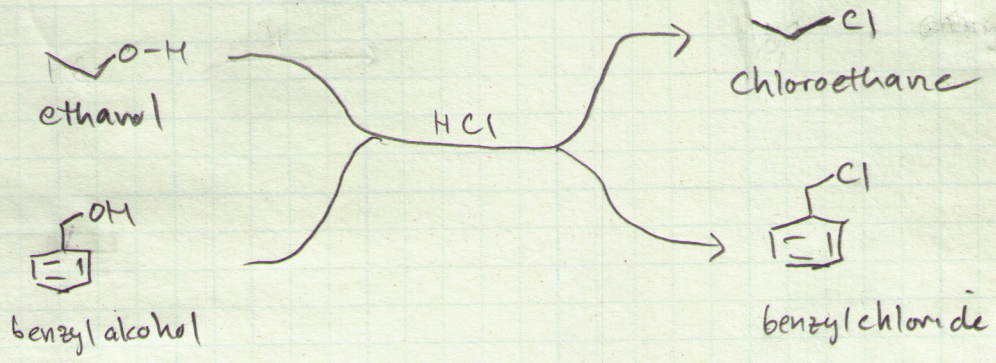
Halogenation X-X

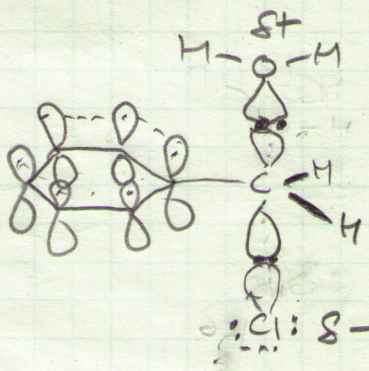


Nucleophilic Substitutⁿ Rxns at Benzylic Center.



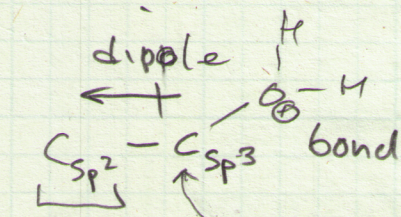
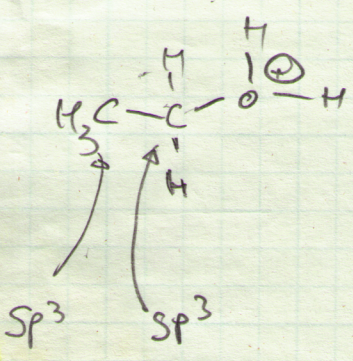
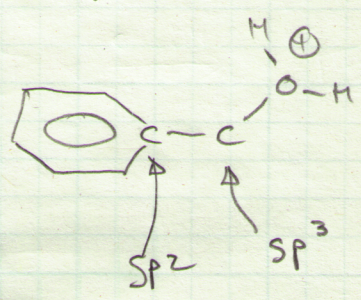
Which is faster? This question is asked as a prelude to understand why S_N2 rxns occur favorably at benzylic Cs.





Transition state orbital overlaps with π system of Aromatic ring

Most important



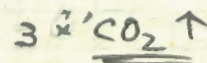
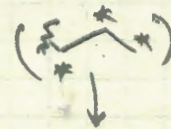
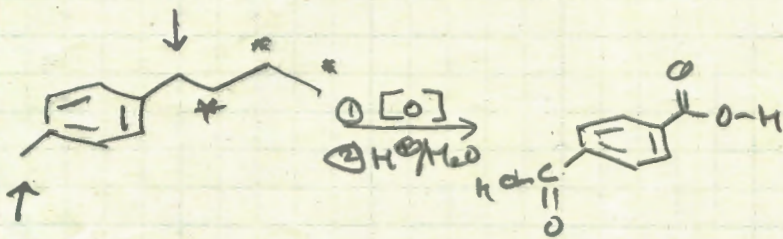
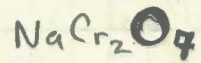
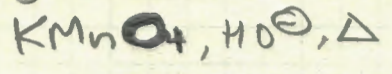
more electronegative than Cl^- is more reactive at this more electropositive C_{sp^3} center than due to inductive C_{sp^2} center.

vs

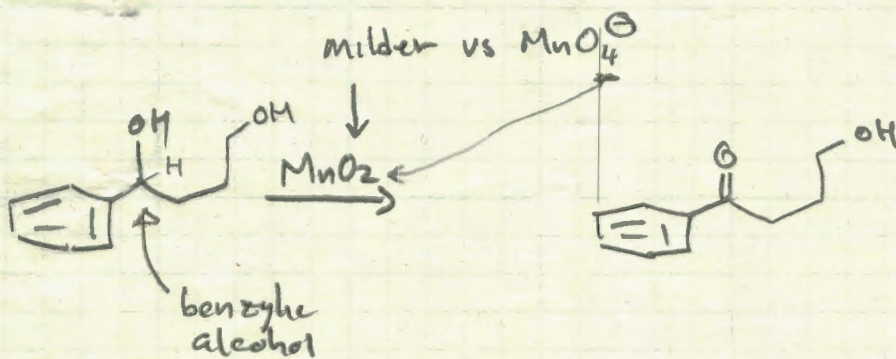
no dipole

Diagram showing a $\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}$ bond with a protonated hydroxyl group (O^+H_2) attached to the second carbon. The carbon atoms are labeled sp^3 and sp^3 .

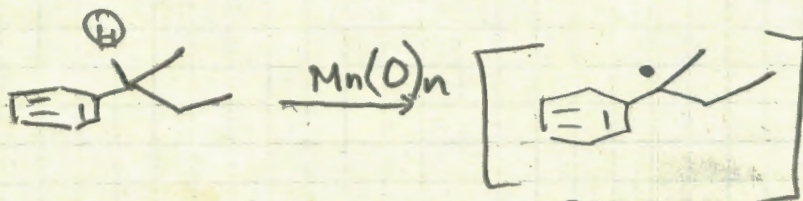
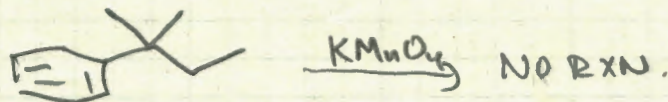
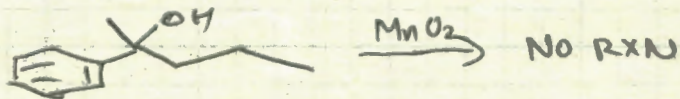
oxidation at benzylic sites with strong oxidants



via radical oxidatⁿ steps and $[MnO]_n$ addⁿ.



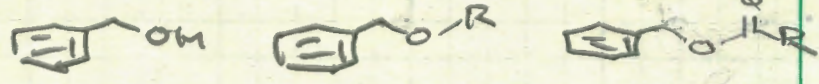
NOTE: these oxidatⁿ Rxns need AT LEAST 1 H ON THE BENZYLIC C.



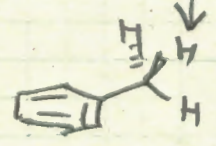
RADICAL INTERMEDIATE STARTS REDⁿ SEQUENCE

Reduction/Oxidatⁿ

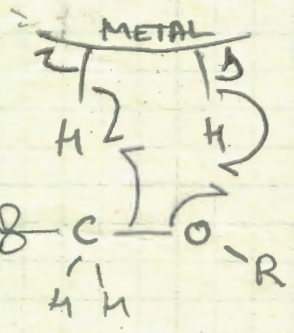
Reduction of BENZYLIC ALCOHOL ETHERS ESTERS



H₂, Metal



via



Convert



① What is lost?
one carbon

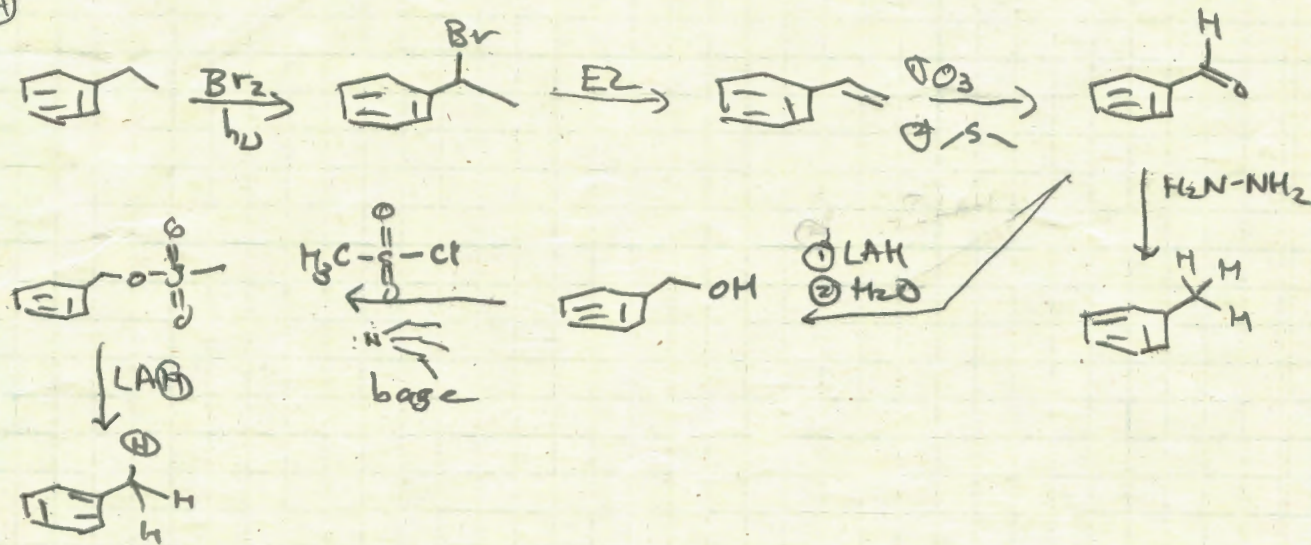
② What are some ways to do
C-C bond cleavage?

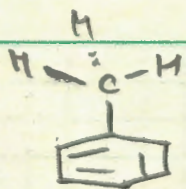
(A) O_3, Zn (B) -S-

OR

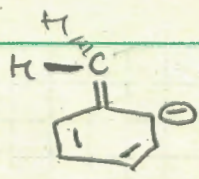
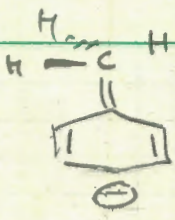
(B) $\text{KMnO}_4, \text{HO}^-$

④

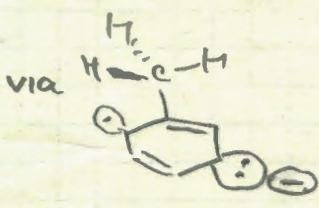




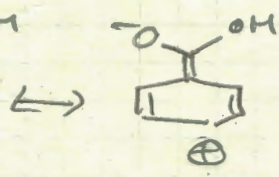
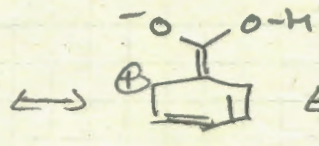
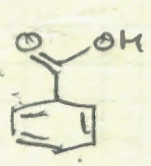
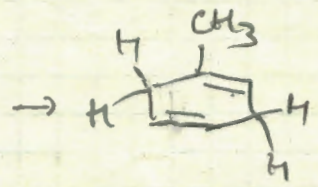
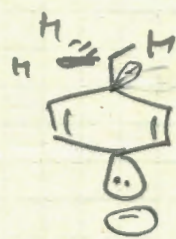
hyperconjugation



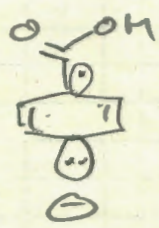
Birch anion will NOT form here because ξ CH₃ is an ortho/para director placing (-) chrg here



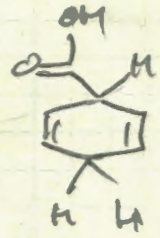
preferred over



(-) chrg favorable posits here!



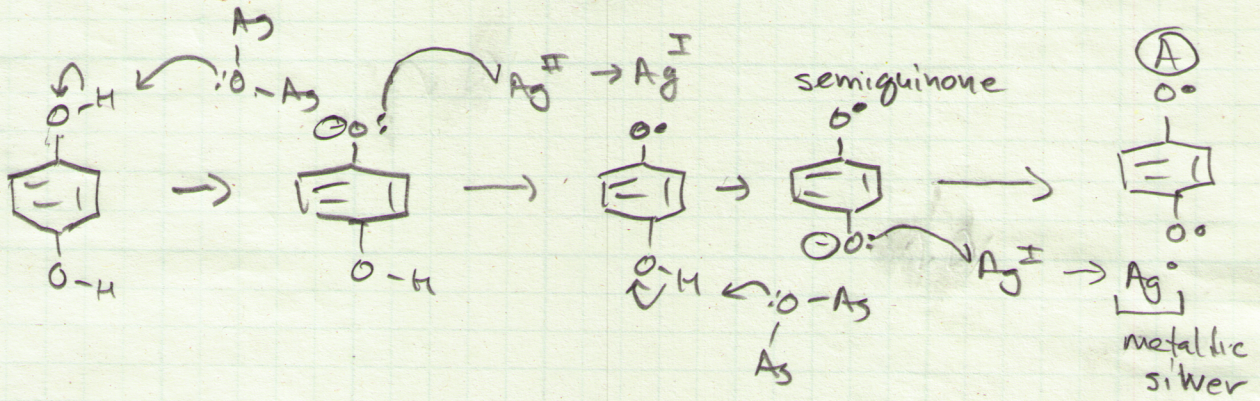
preferred \therefore



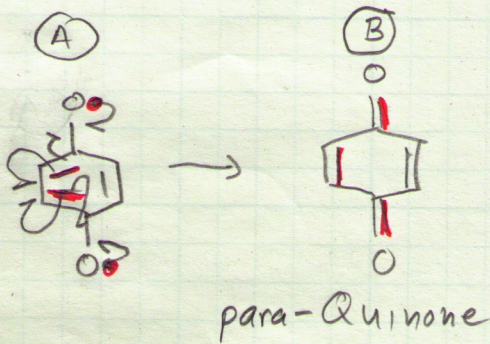
90% Birch product

Oxidation of Hydroquinone to Quinone

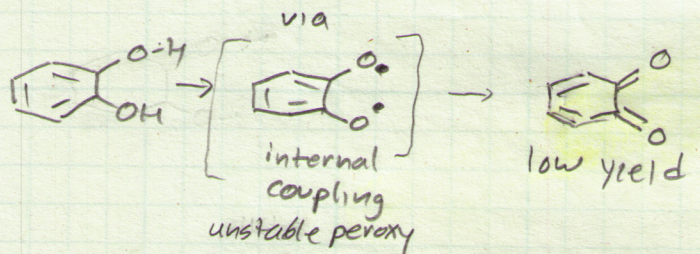
Oxidants [O]: Ag_2O or $Na_2Cr_2O_7$



Half-barbed arrows

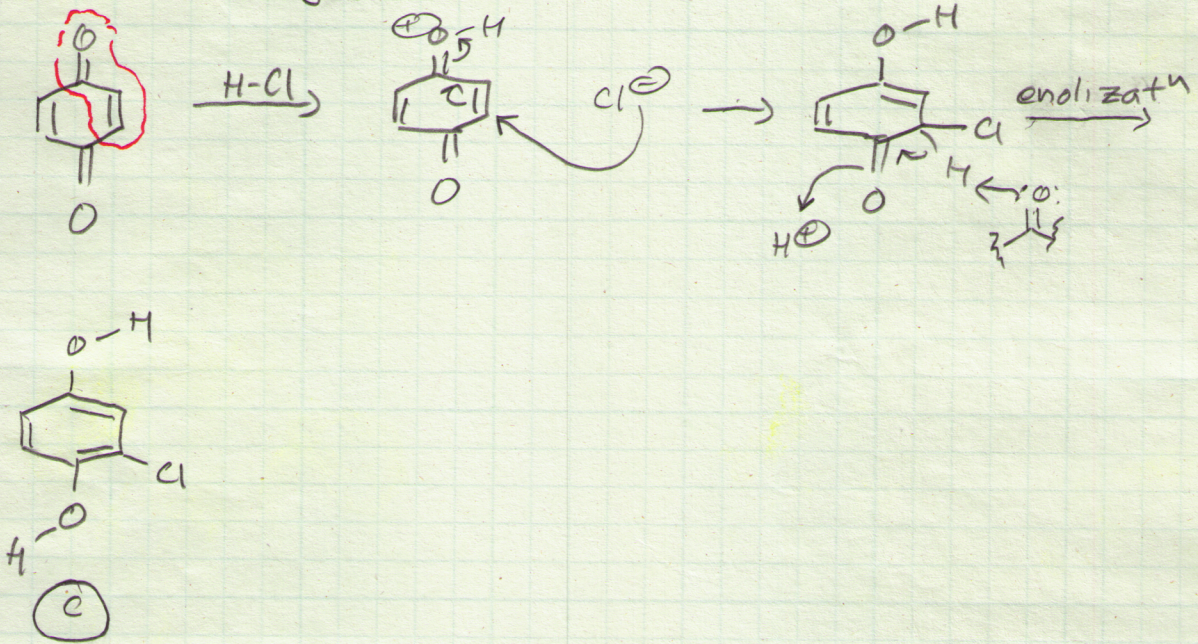


ortho-Quinone production slow (electronic unstable; thus, side rxns)

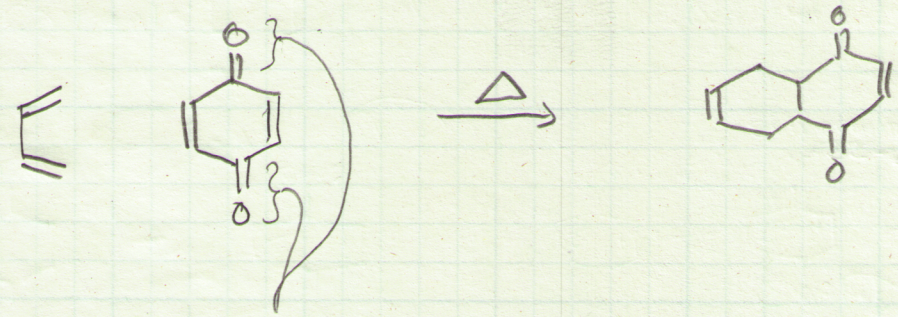


Quinone (B)

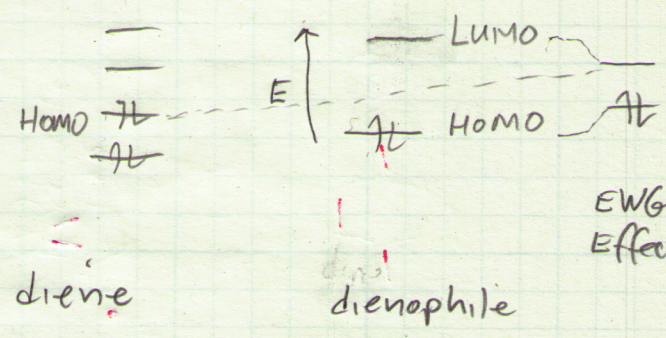
1,4 - Michael Conjugate Addⁿ



Diels - Alder Rxn with Quinone (B)



EWG groups
Lower E of LUMO

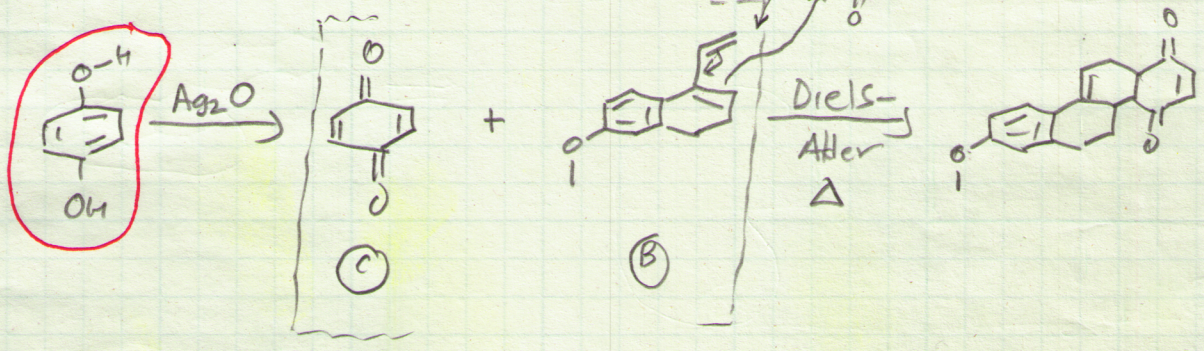
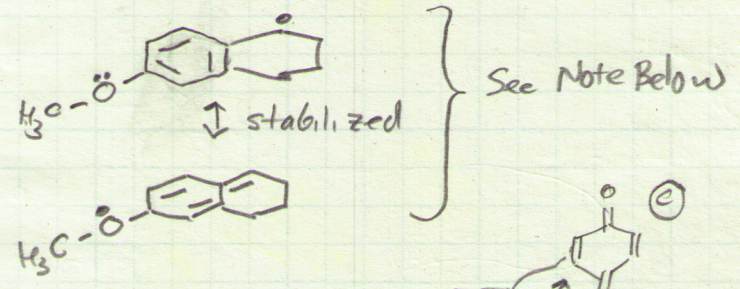
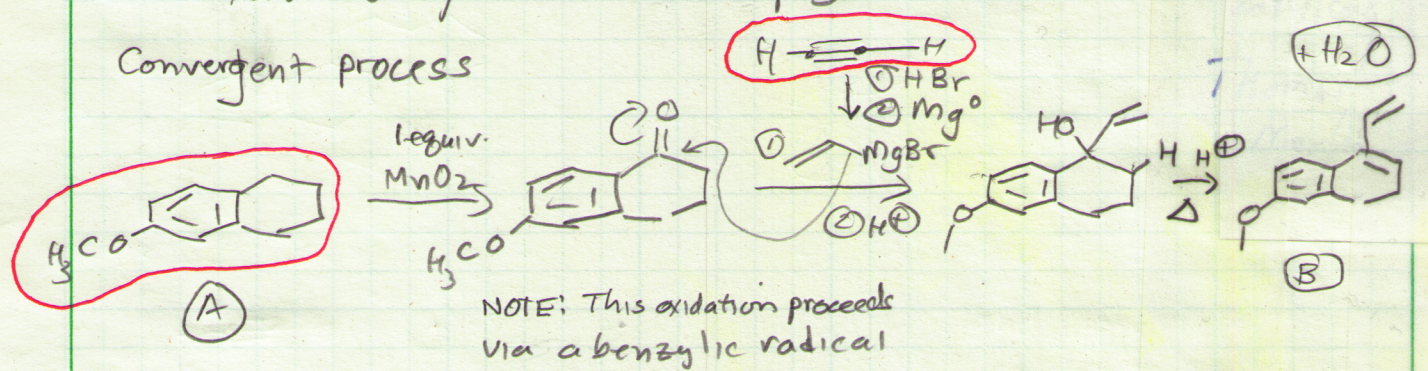


diene dienophile
HOMO/LUMO E are closer

Thermal transition
is more allowable

Show forward synthesis on this page

Convergent process



What about the other benzylic C

