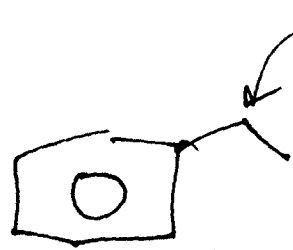
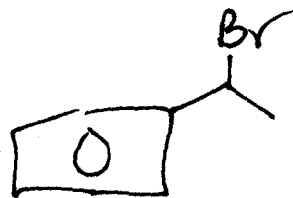
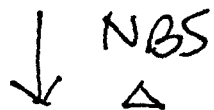


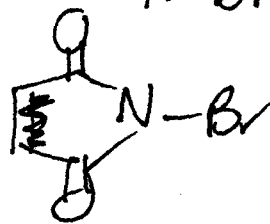
side chain rxns



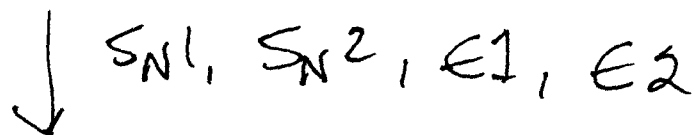
benzylic position — makes v. stable radical + v. stable cation (resonance stabilized)



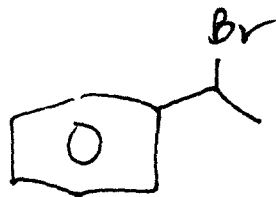
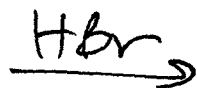
NBS = N-bromosuccinimide



source of $\cdot\text{Br}$

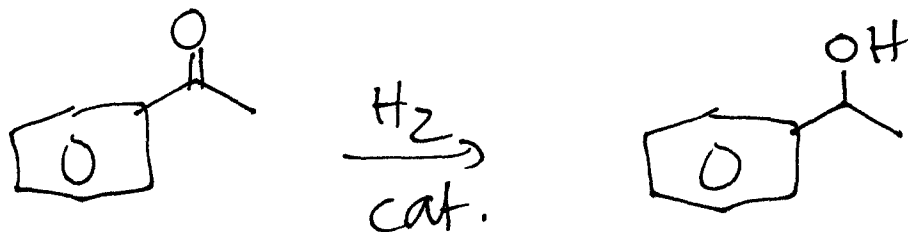
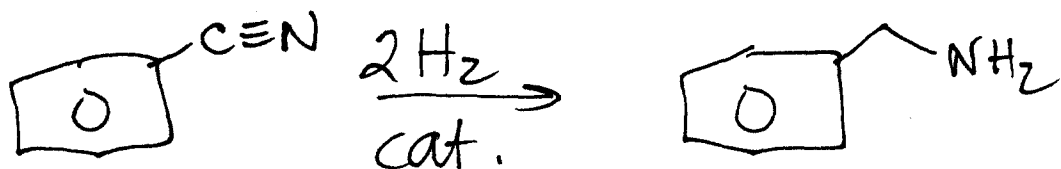


styrene

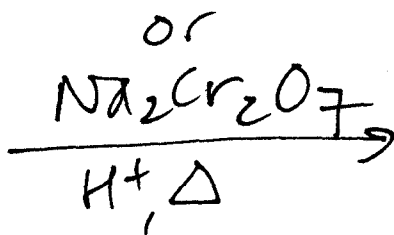
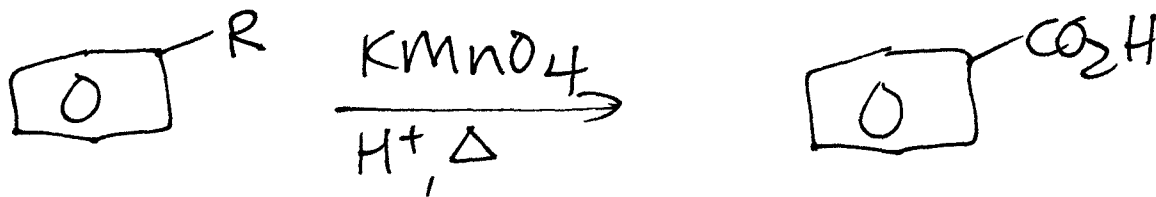


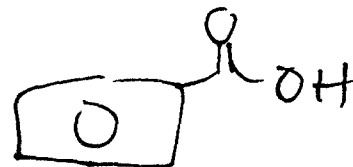
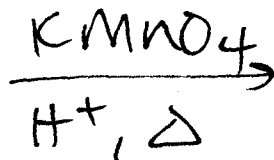
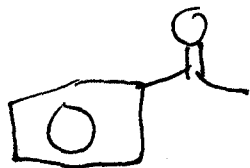
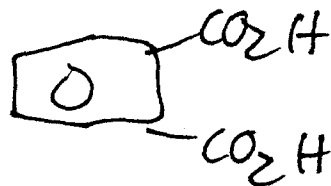
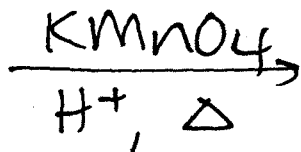
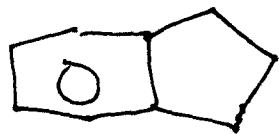
can hydrogenate (H_2 / cat.)

- side chain easily w/o affecting ring

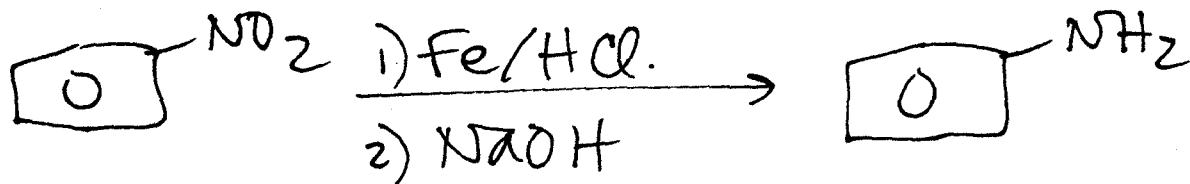


As long as there is a benzylic H....





Reduction of $\text{NO}_2 \rightarrow \text{NH}_2$



or: $\text{H}_2/\text{cat.}$

SKIP selective reduction when
more than one NO_2 present

How does a substituent interact with a benzene ring?

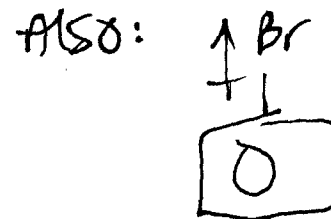
INDUCTION

Hyperconjugation



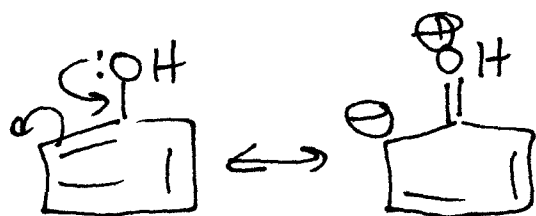
Alkyl gps. are e^- donors by induction.

Substituents more e^- neg than H/C

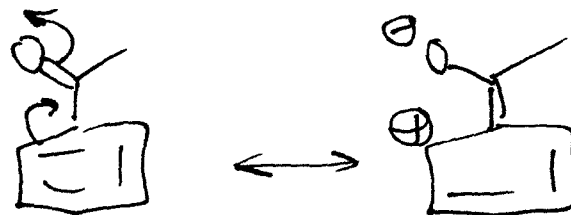


RESONANCE

Groups w/ lone pairs



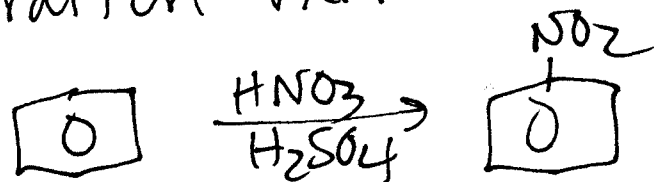
π bonds conjugated w/ benzene ring.



DONATING

WITHDRAWING

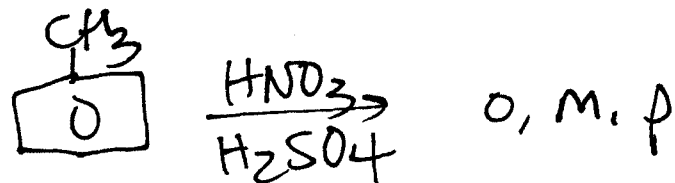
Nitration rxn.



Rate

$$K = 1$$

Products



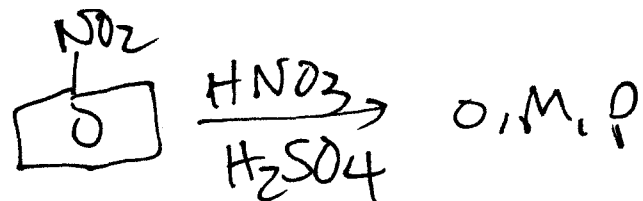
$$K = 30$$

\Rightarrow R activate

94% o/p

6% m

\Rightarrow R o, p dir.





$$K = 10^{-4}$$

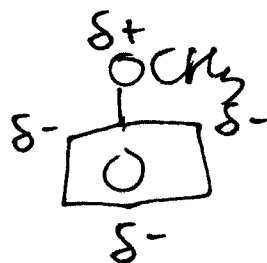
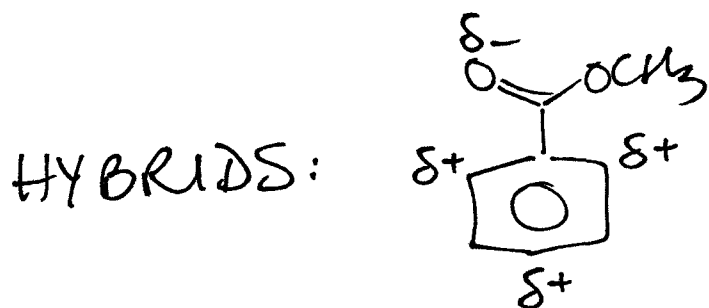
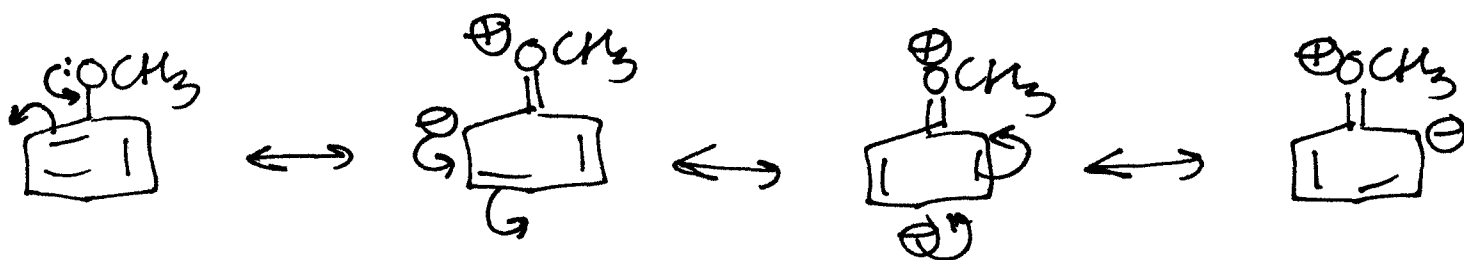
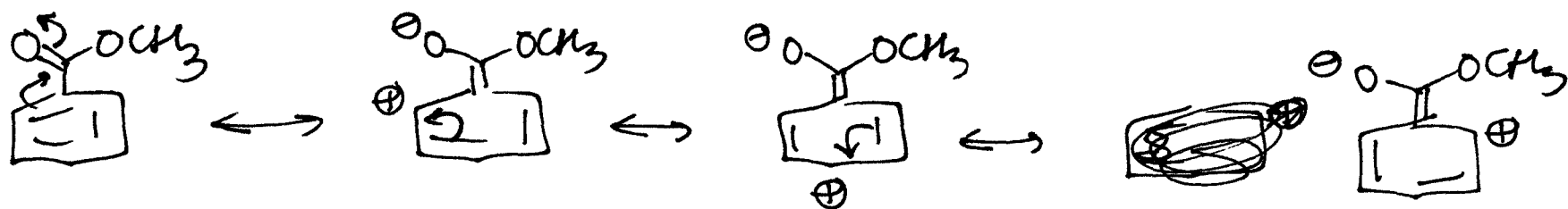
\Rightarrow O=[N+]([O-]) deactivates

7% o/p

93% m

\Rightarrow O=[N+]([O-]) m dir.

Substituent	Activator/Deactivator	Directing Effects
NH ₂ , NHR, NR ₂	Strong Activator	Ortho/para
OH, OR		
NHCOR 	Moderate Activator	
O ₂ CR 		
R, Ar, CH=CH ₂	Weak Activator	
H	Neutral	
* F, Cl, Br, I	Weak Deactivator	
All carbonyls	Moderate Deactivator	Meta
CN, SO ₃ H	Strong Deactivator	
Positively charged N		
NO ₂		
	kinetics	products



e^- withdrawer pulls
more e^- density from
o/p \Rightarrow incoming e^+ goes m

e^- donor puts
extra e^- density
onto o/p positions
 \Rightarrow incoming e^+
goes there.

What about halogens?

Deactivators (by induction)

o, p directors (by resonance)

It turns out that from a kinetic perspective, the inductive effect is more efficient.

But for product distribution, resonance wins out.