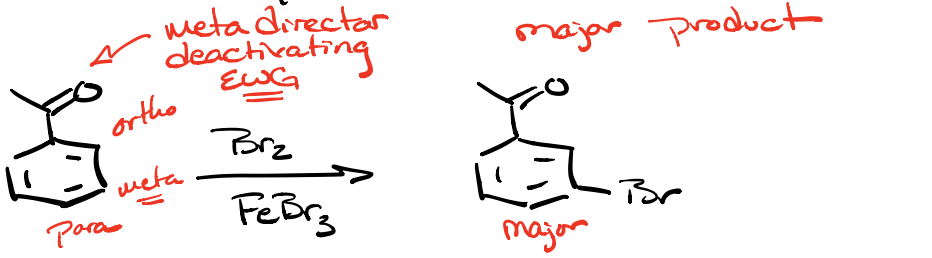
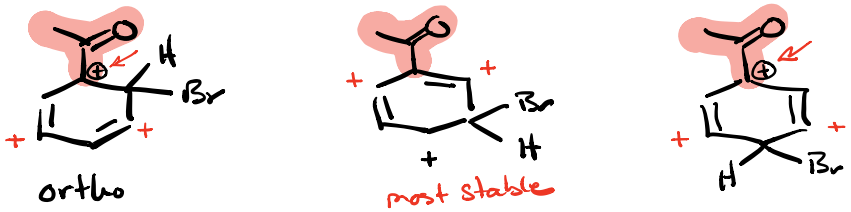
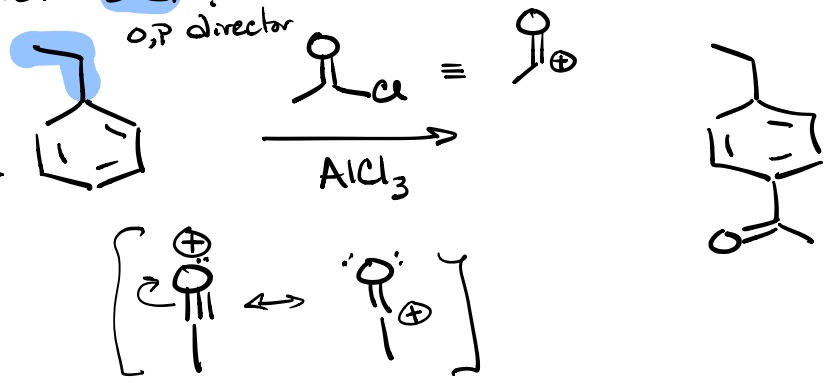
Electrophilic Aromatic Substitution

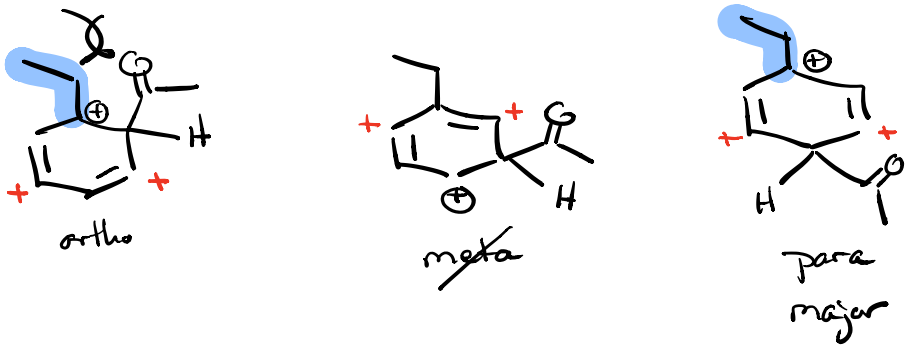


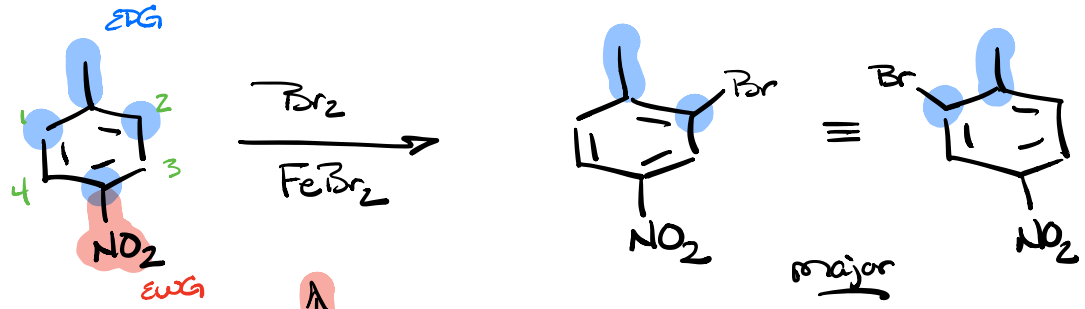


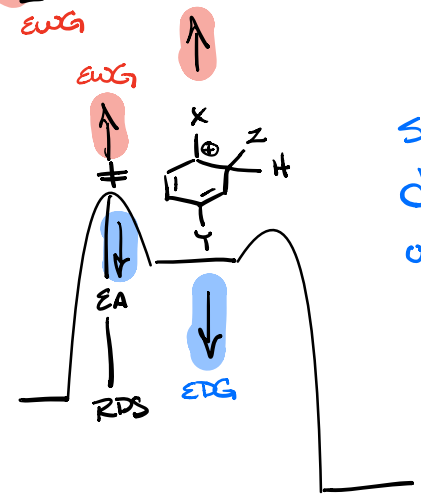
-NH_3
-OH
Cl
CH_3 ortho
Et
Pr para
ipr
-Br
-I

EWG or EDG ?
o,p director



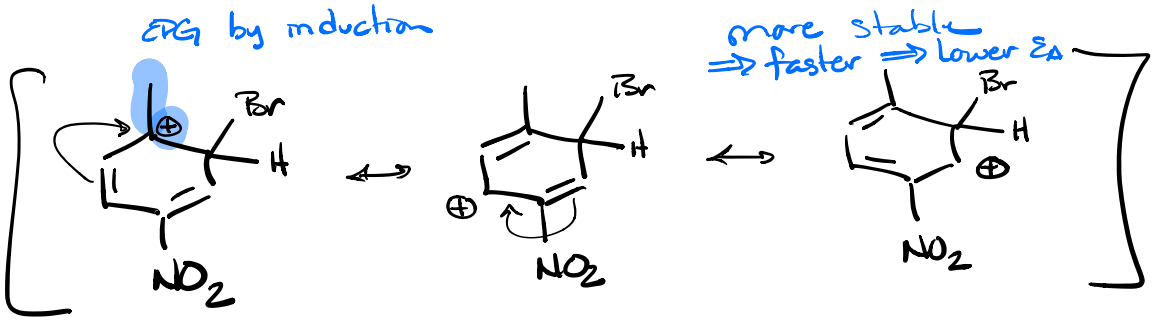


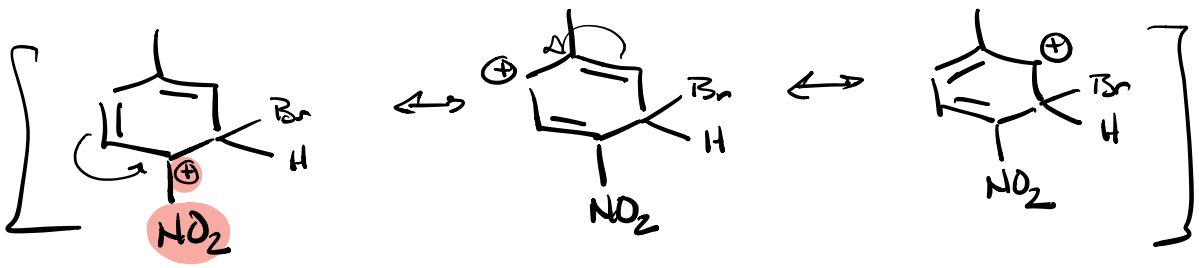


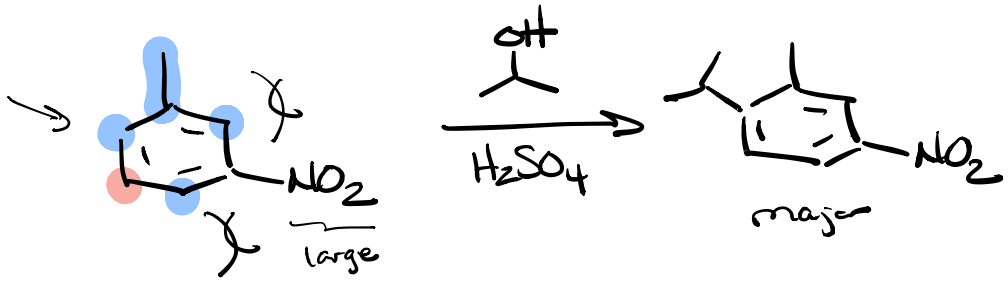


strongest donating group directs the location of the addition Rxn.

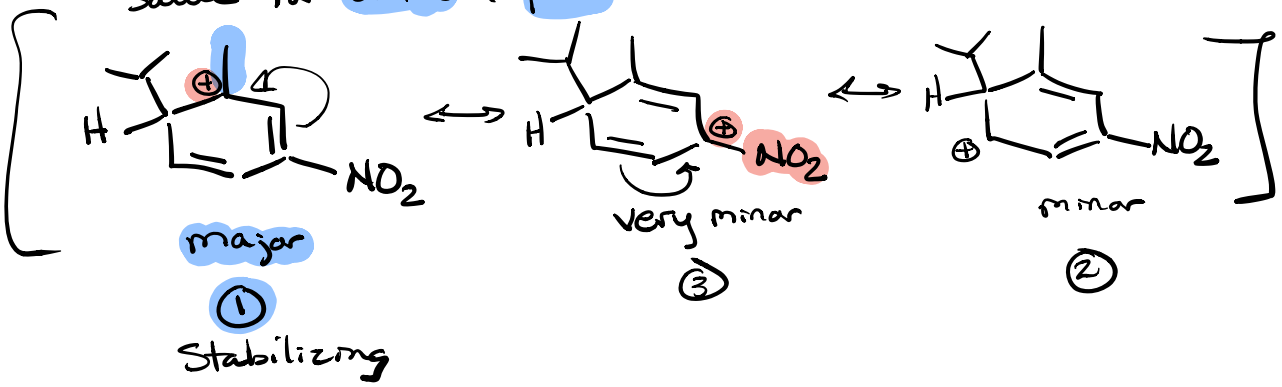
1. Donating
2. Sterics

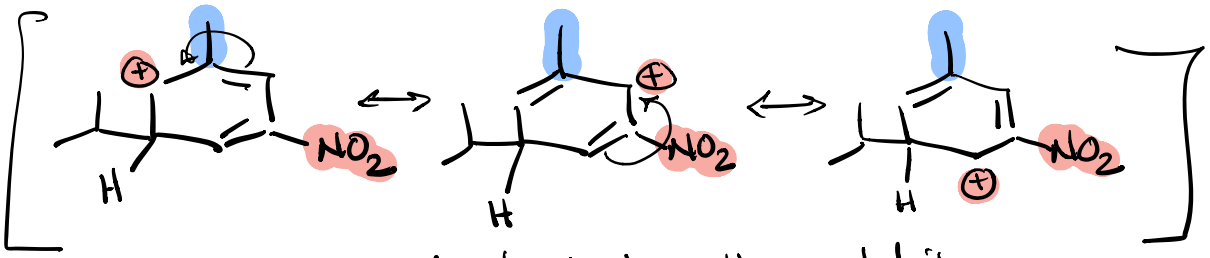




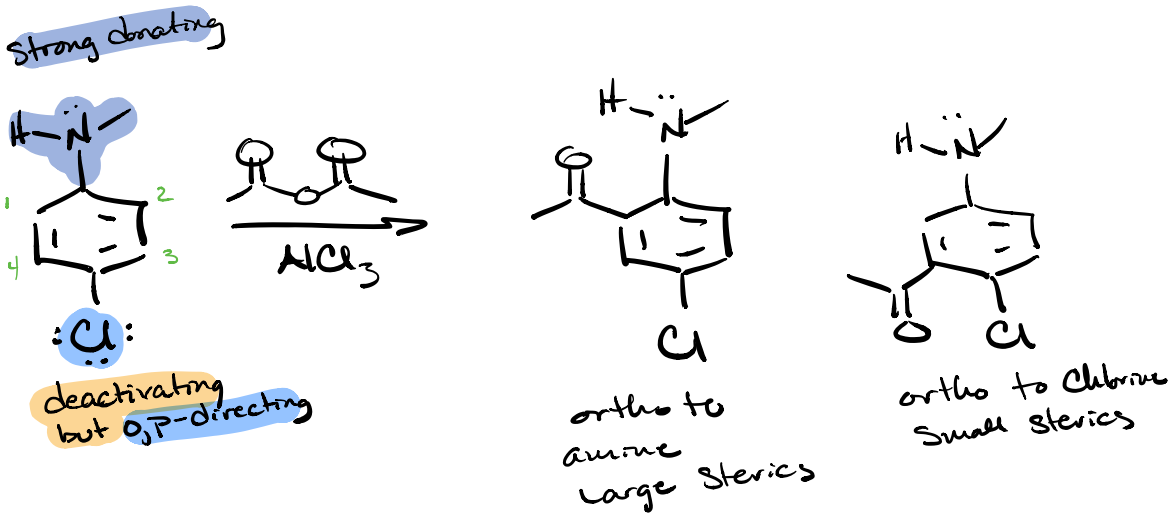


same for ortho & para

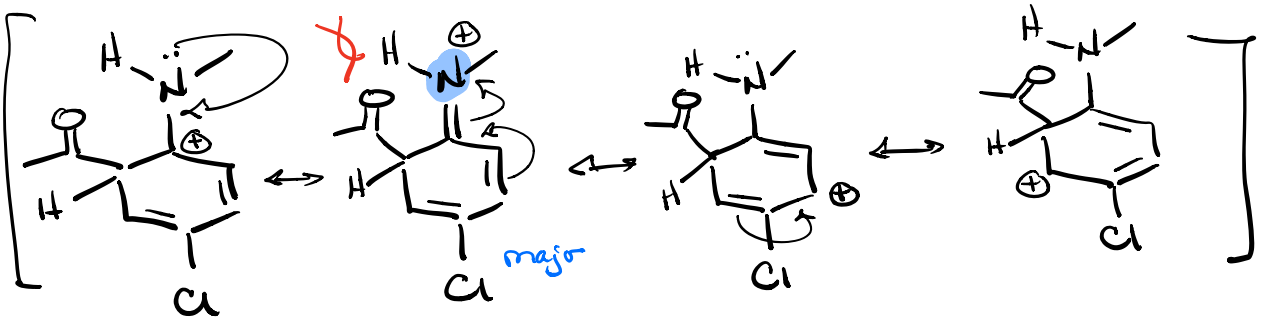


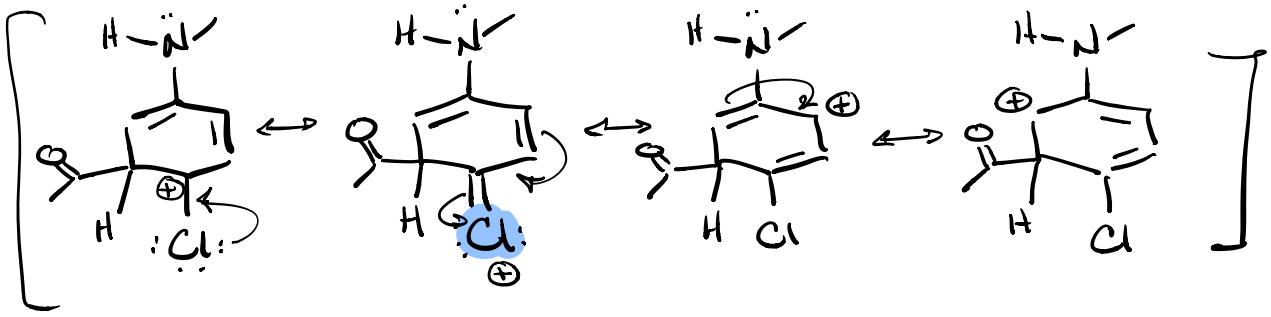


Equivalent, but nothing stabilizing



Electronics > Sterics





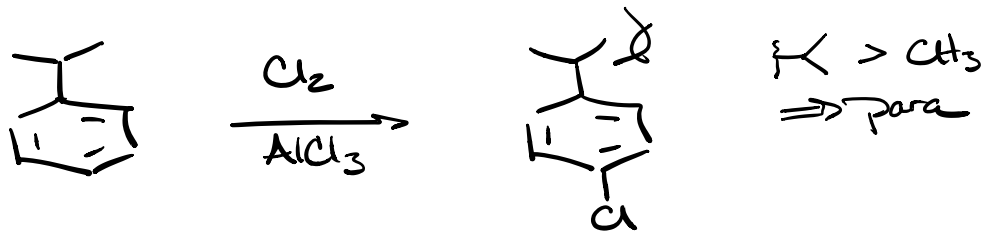
EN/hybridization

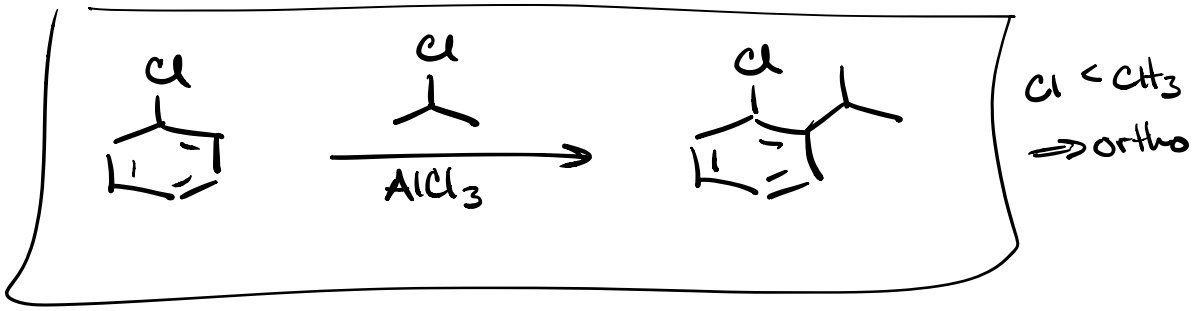
Resonance

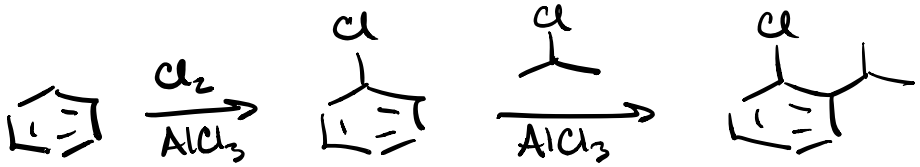
Size

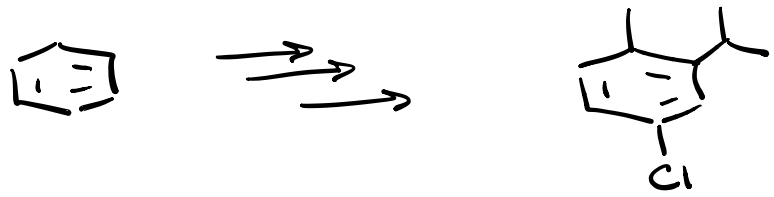
Induction

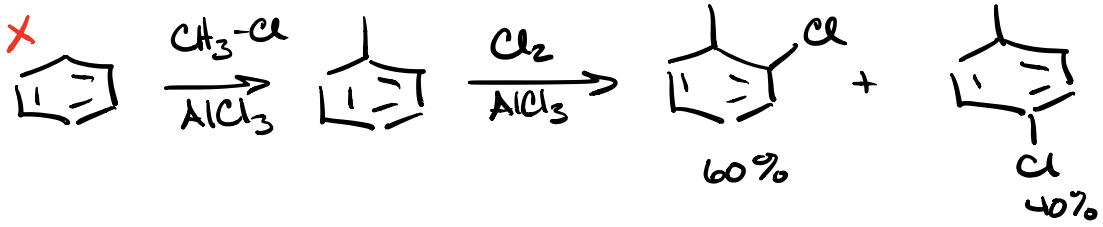

Cl

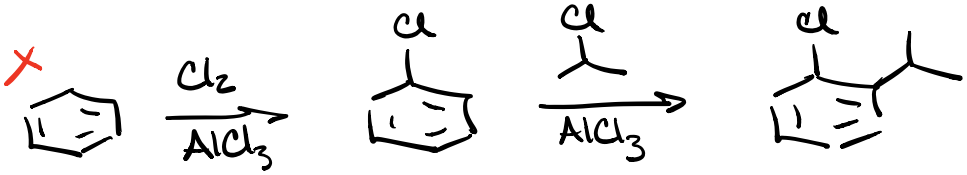

Cl2
AlCl3
Cl
> CH3
⇒ para


Cl
Cl
AlCl3
Cl
Cl < CH3
⇒ ortho

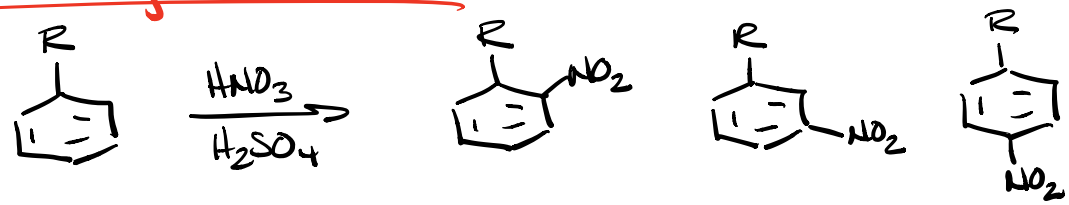

Cl2
AlCl3
Cl
Cl
AlCl3
Cl



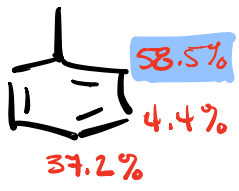




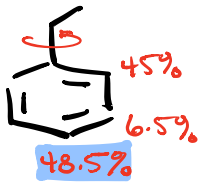
Selectivity vs. Sterics



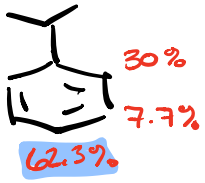
Methyl



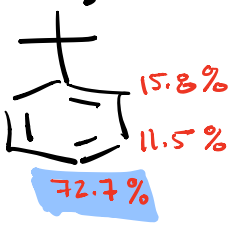
Ethyl

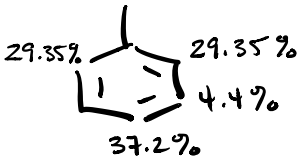


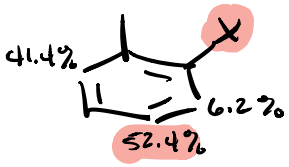
Isopropyl



Tert-butyl





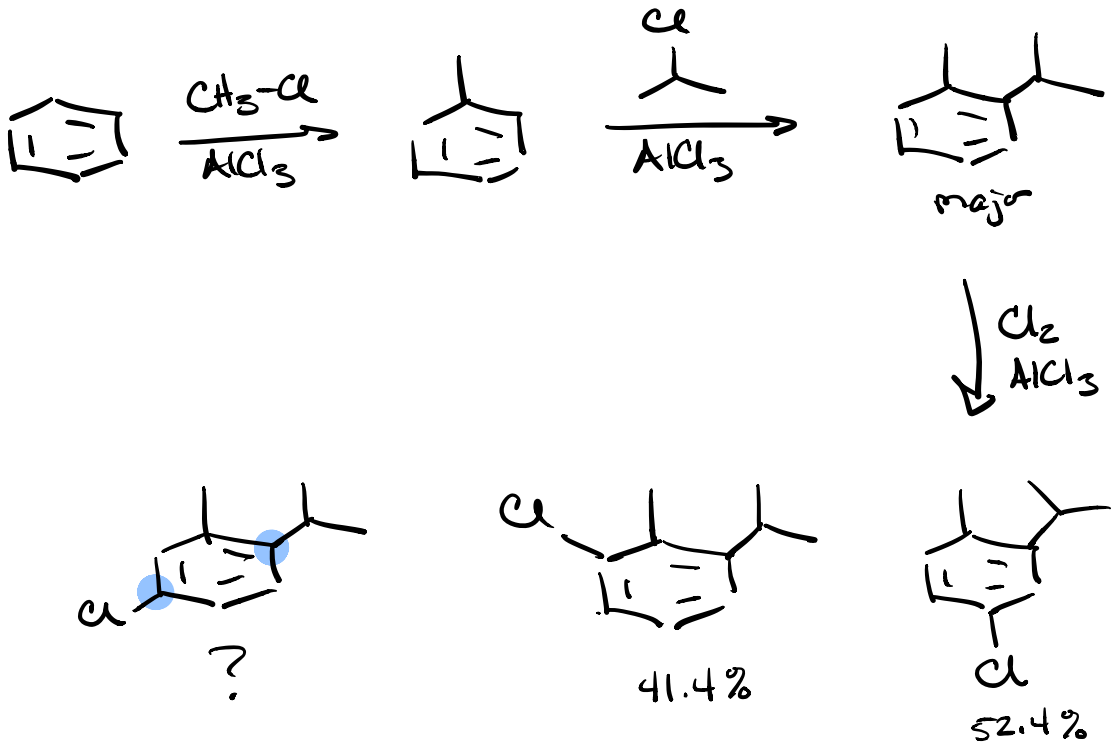


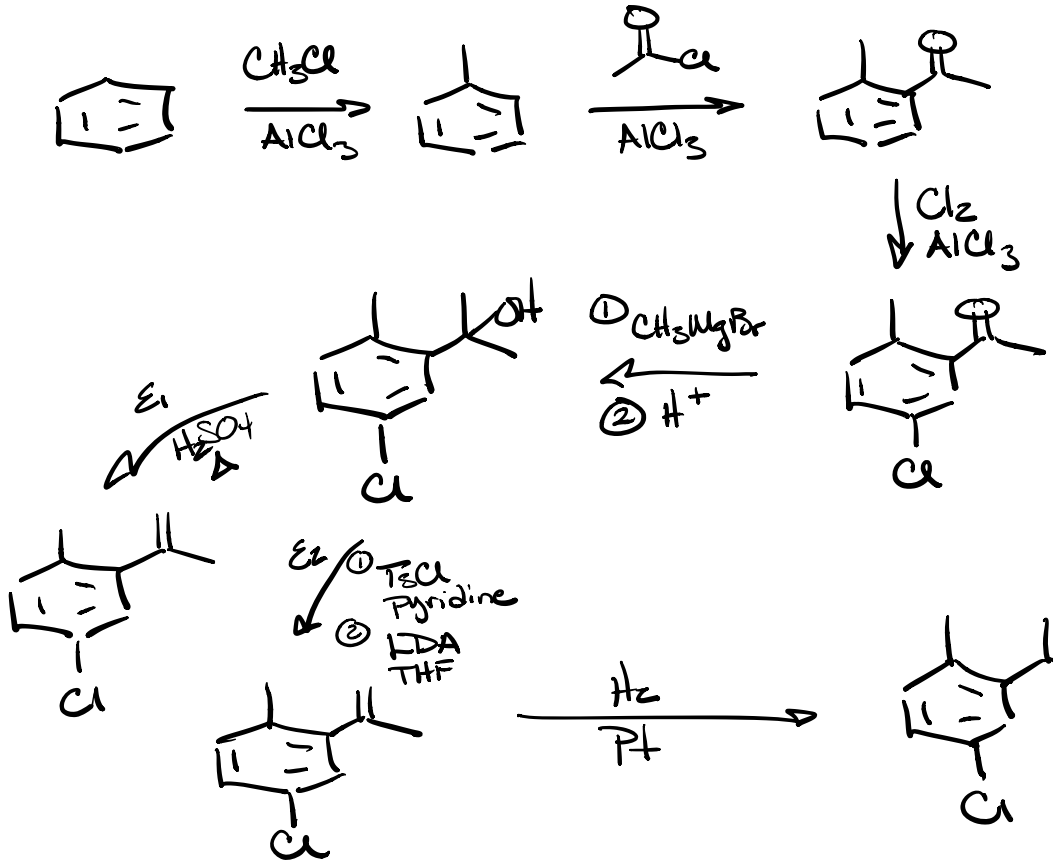
29.35 → 41.4%

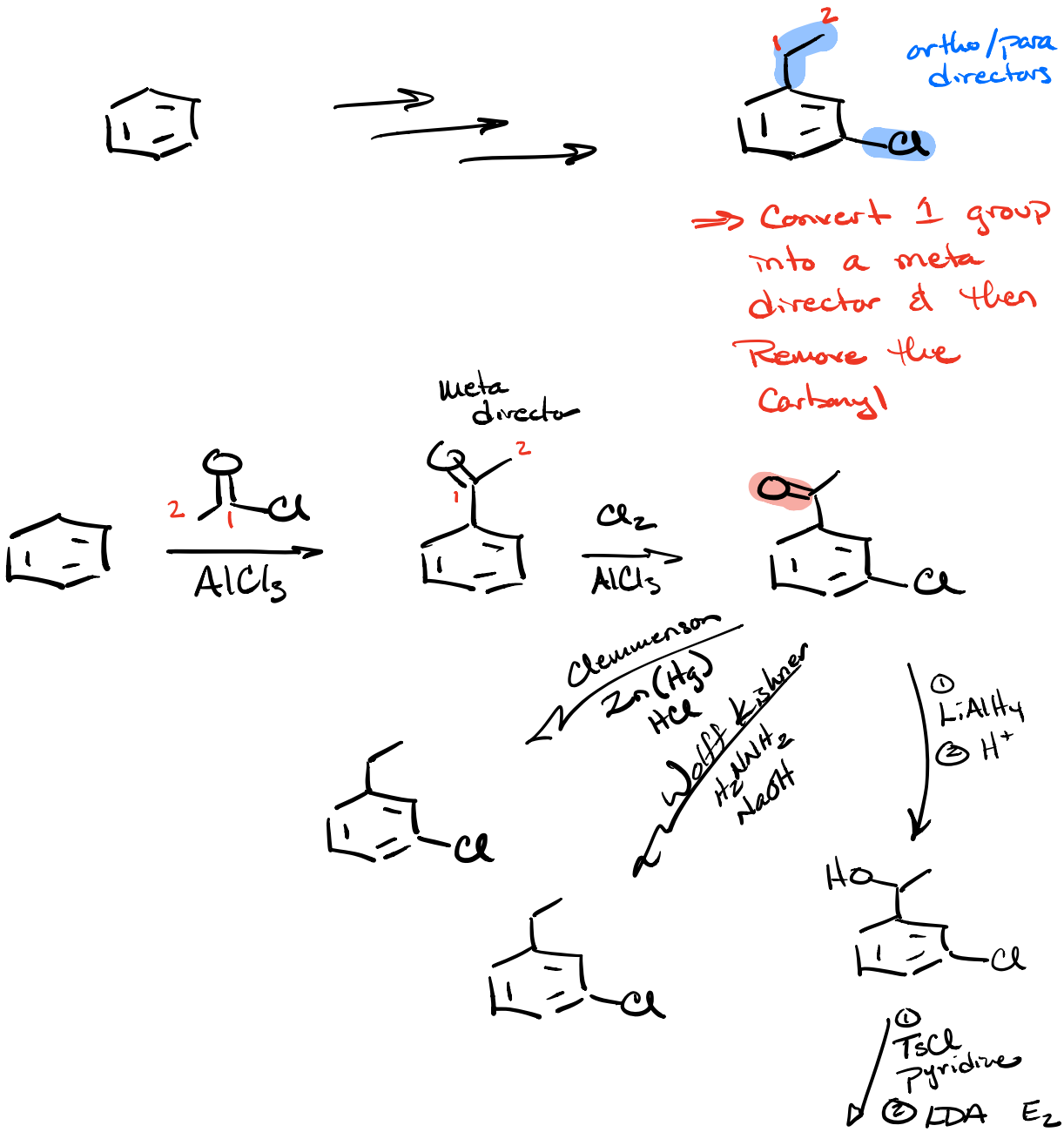
4.4 → 6.2%

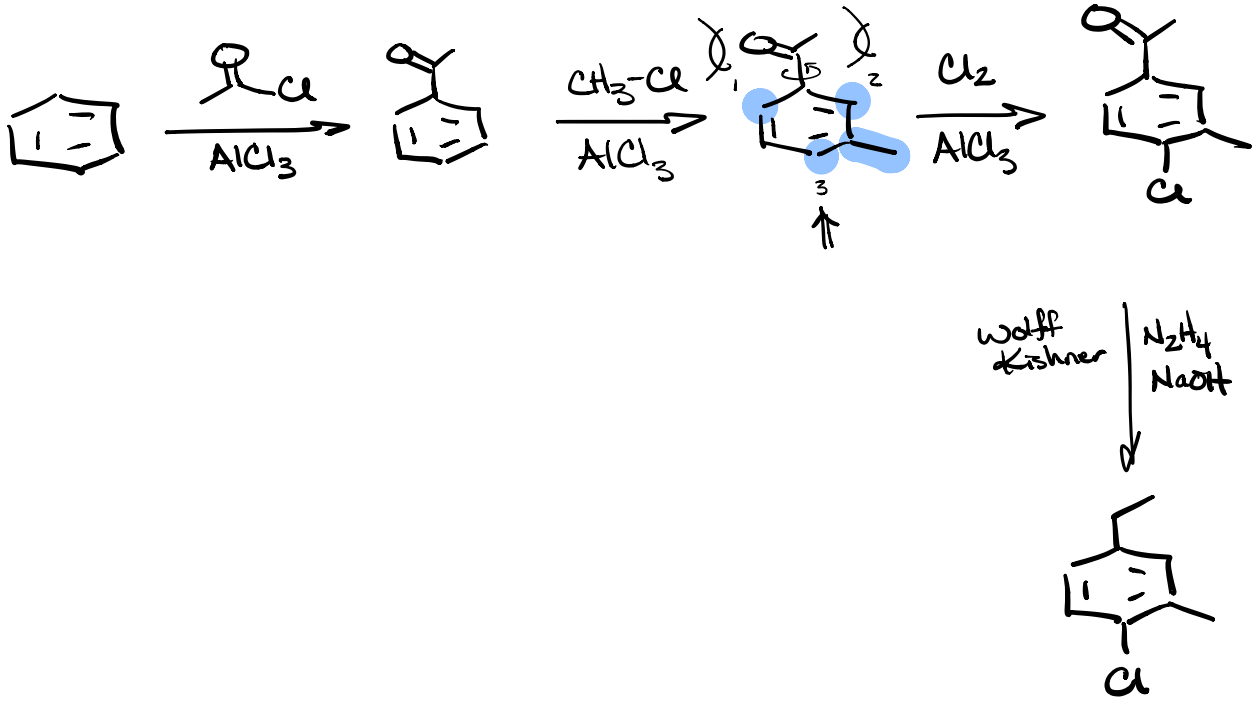
37.2 → 52.4% Major

70.95


CH3-Cl
AlCl3
major
Cl2
AlCl3
?
41.4%
52.4%


CH3Cl
AlCl3
Cl2
AlCl3
E1
H2SO4
Δ
1) CH3MgBr
2) H+
E2
1) TsCl
Pyridine
2) LDA
THF
H2
Pt


ortho/para directors
⇒ Convert 1 group into a meta director & then Remove the Carbonyl
meta director
AlCl3
Cl2
AlCl3
Clemmenson
Zn(Hg)
HCl
Wolff Kishner
H2NNH2
NaOH
1 LiAlH4
2 H+
1 TsCl
Pyridine
2 LDA E2
H2
Pt


AlCl3
CH3-Cl
AlCl3
1
2
3
Cl2
AlCl3
Cl
Wolff Kishner
N2H4
NaOH
Cl