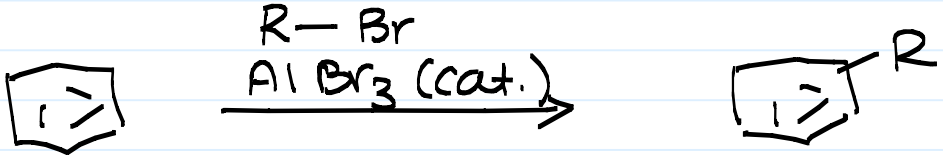
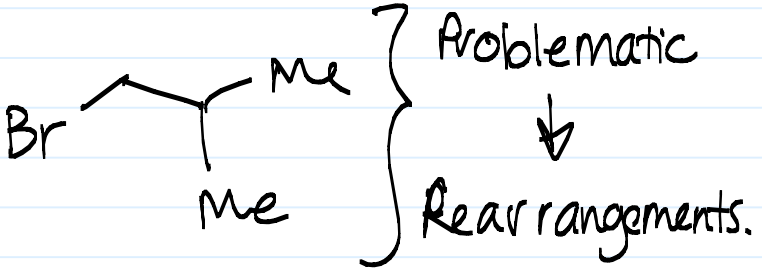
Aromatic Substitution

Note Title 2/27/2014

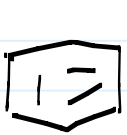
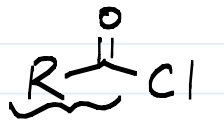
announcement: Old midterm posted on course website.



R = alkyl.

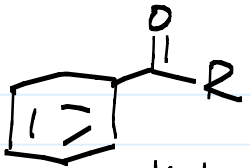


Friedel-Crafts Acylation

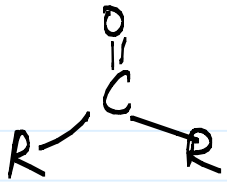
(a)  + 

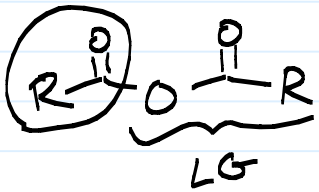
acyl chloride
(acid chloride)

(i) $AlCl_3$ (stoich)
(ii) H_2O



ketone

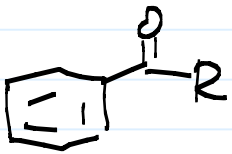


(b)  + 

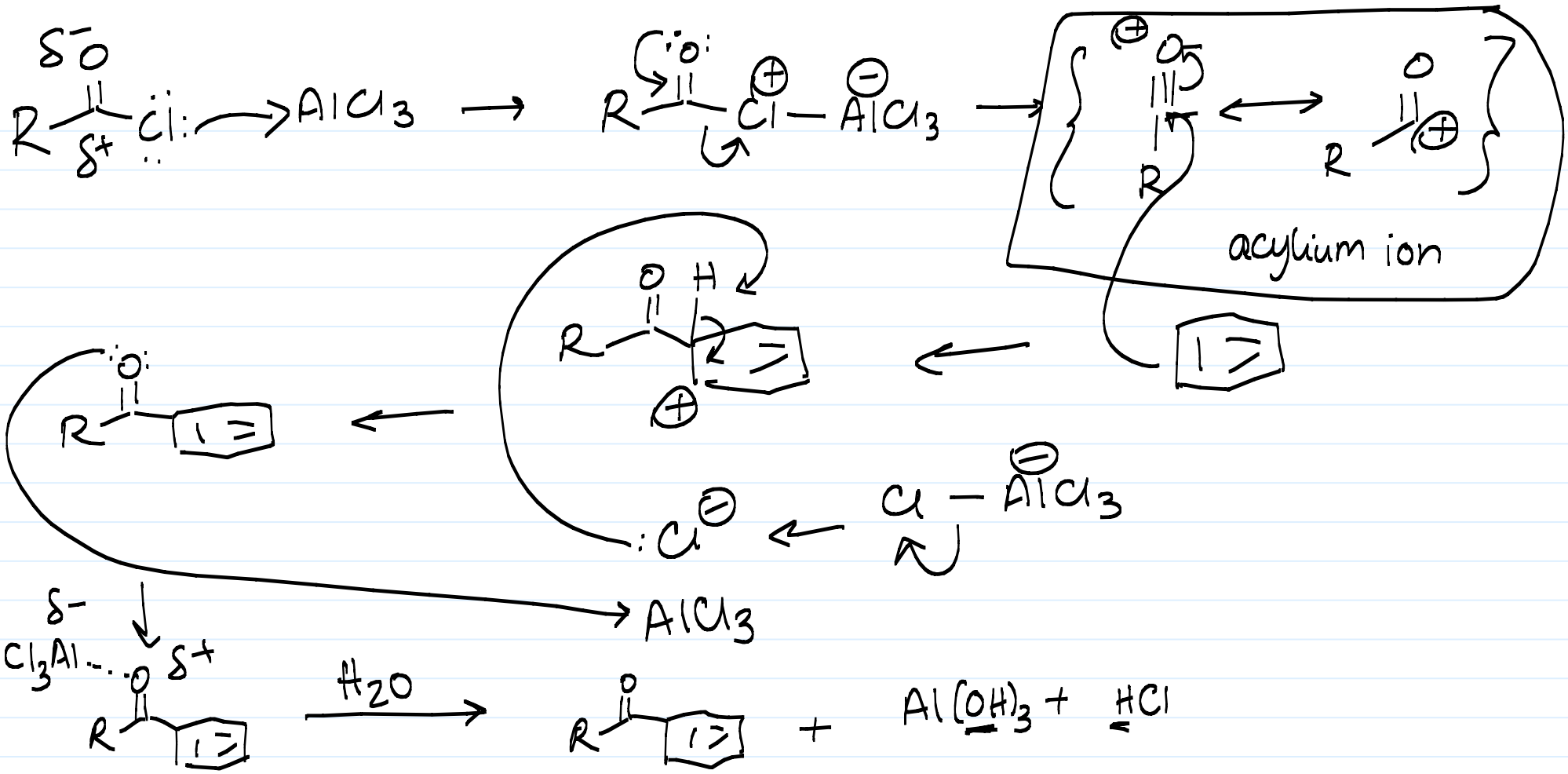
LG

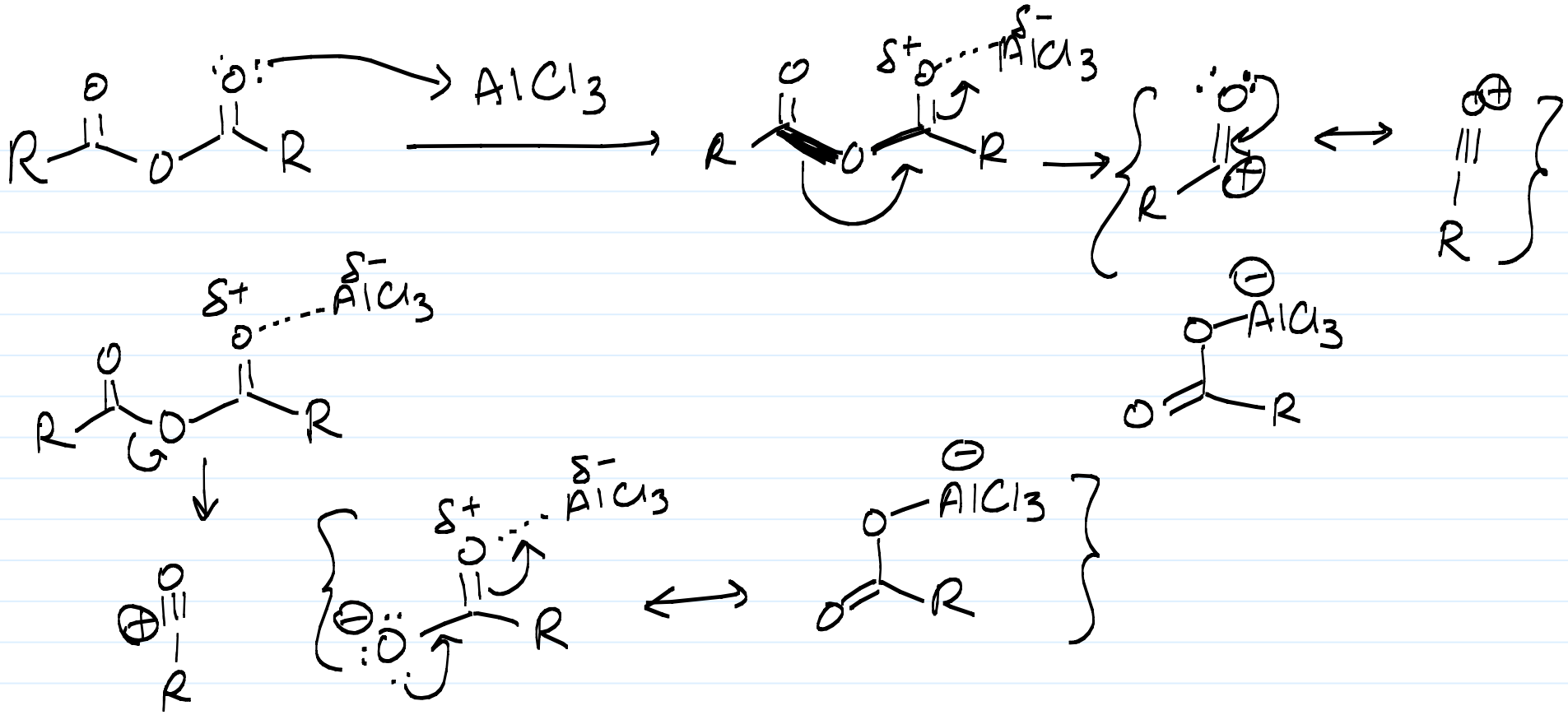
acyl anhydride

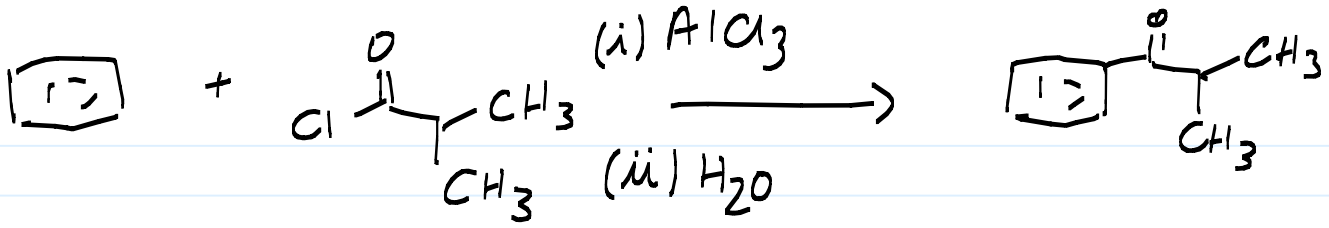
(i) $AlCl_3$ (stoich)
(ii) H_2O

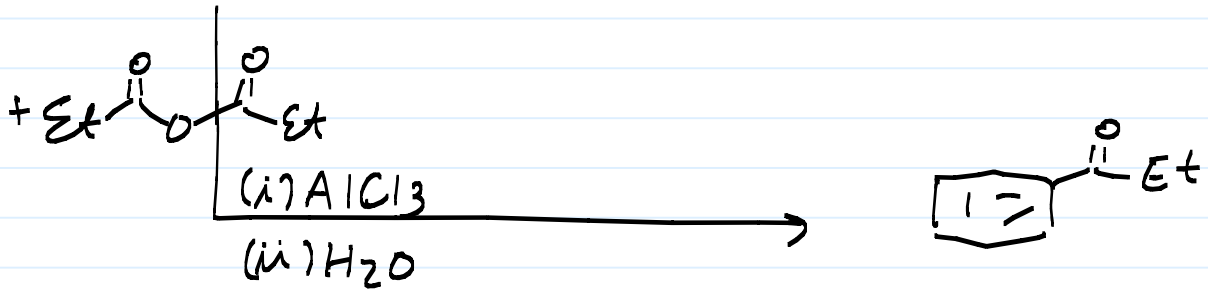


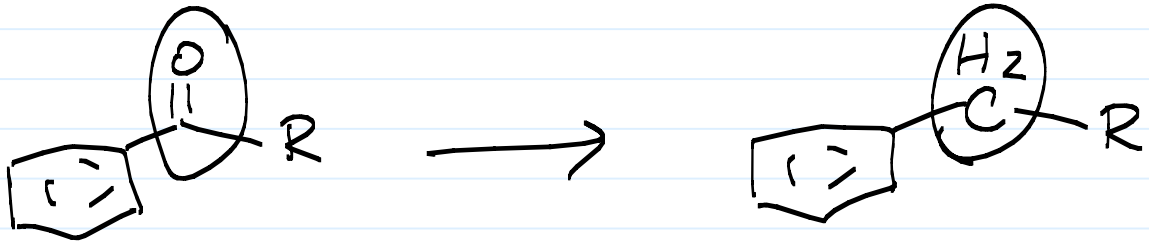
ketone


AlCl3
acylium ion
AlCl3
H2O
Al(OH)3 + HCl

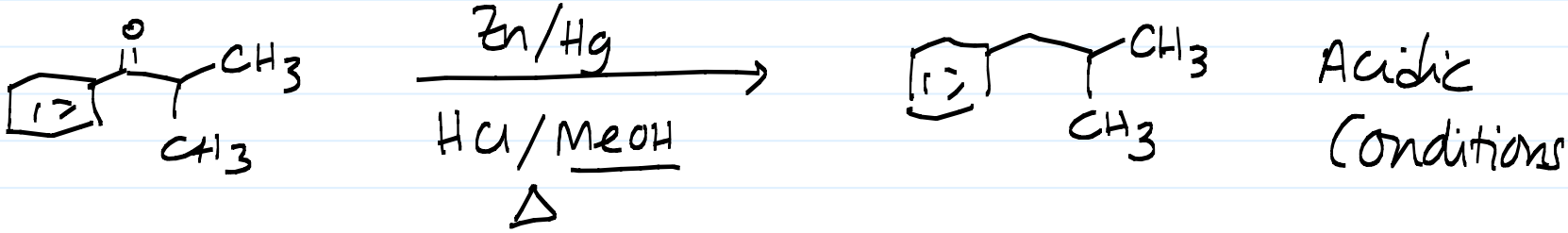

AlCl3
δ+
δ−
R
O


(i) AlCl3
(ii) H2O

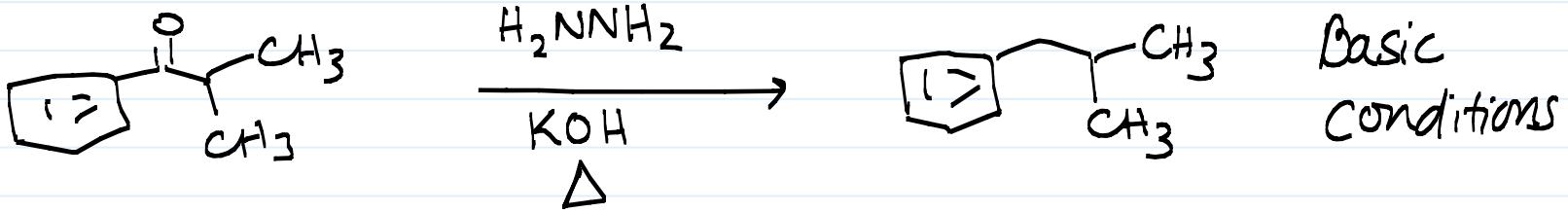

(i) AlCl3
(ii) H2O

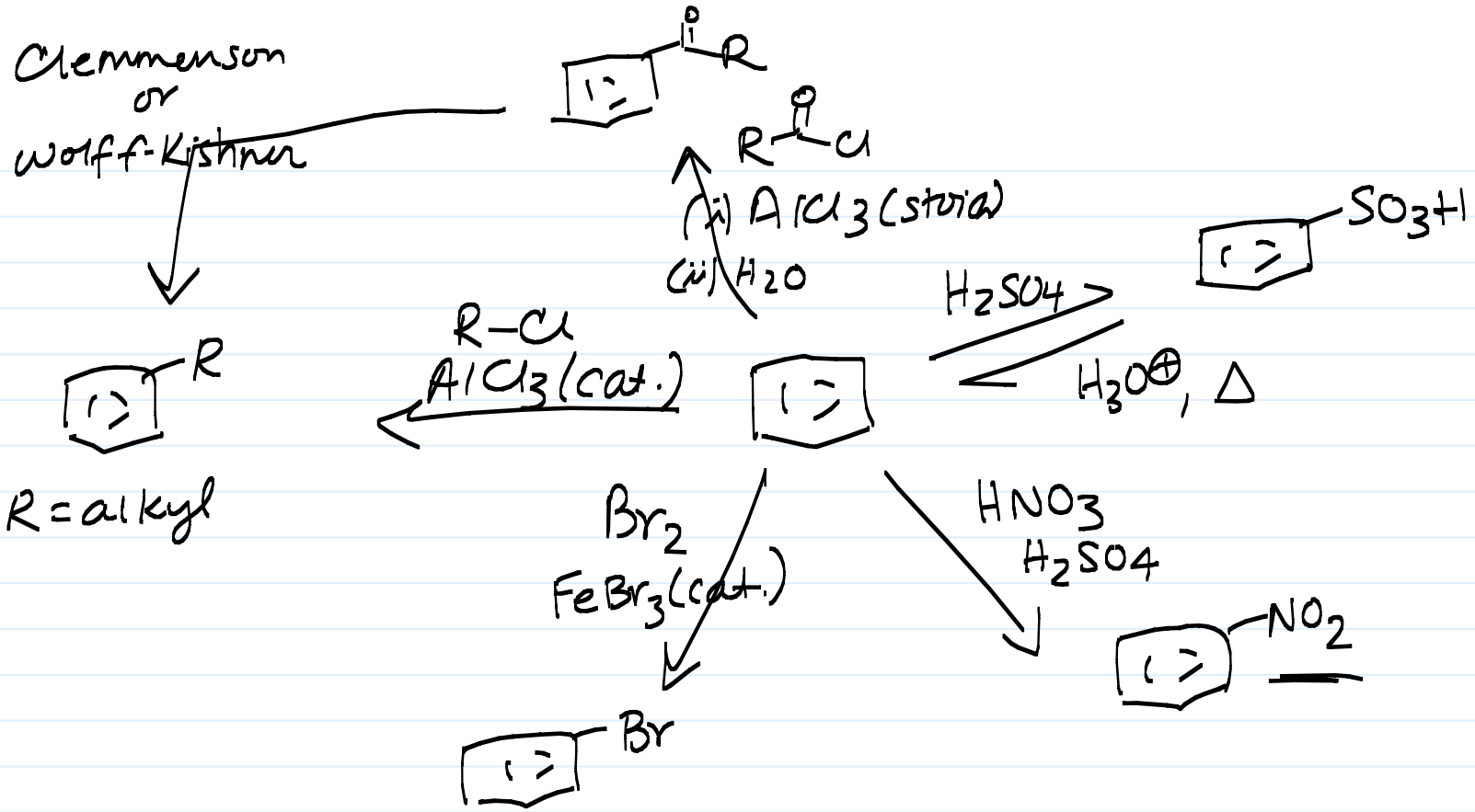

H2

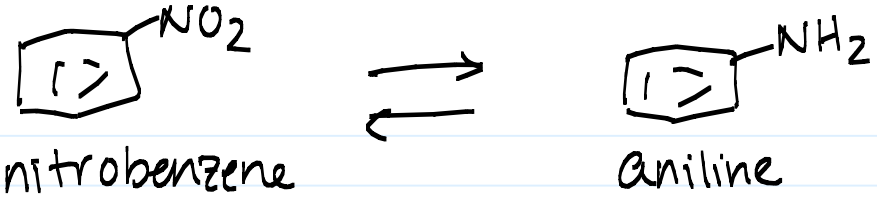
(1) Clemmenson Reduction



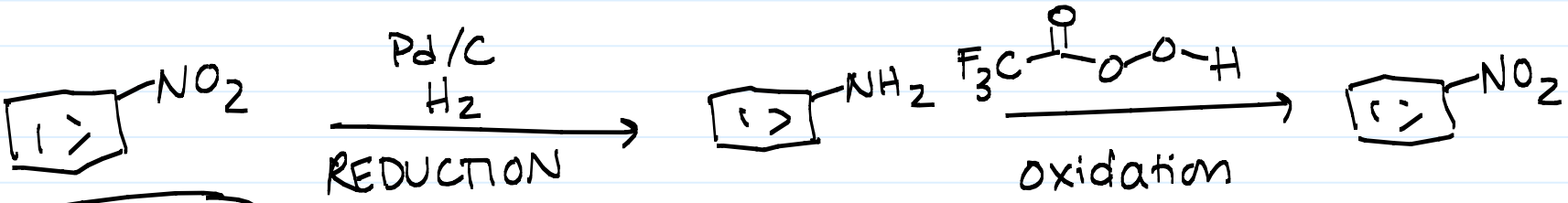
(2) Wolff-Kishner Reduction

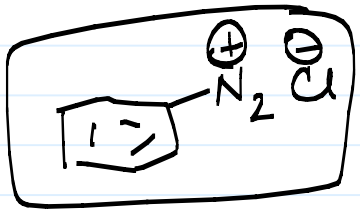



Clemmenson
or
wolff-Kishner
R
R = alkyl
R–Cl
AlCl3 (cat.)
(i) AlCl3 (stoich)
(ii) H2O
R
Cl
H2SO4
H3O⊕, Δ
SO3H
Br2
FeBr3 (cat.)
Br
HNO3
H2SO4
NO2

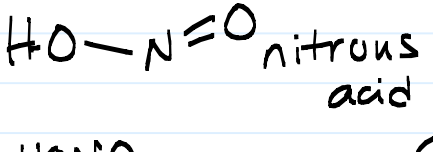


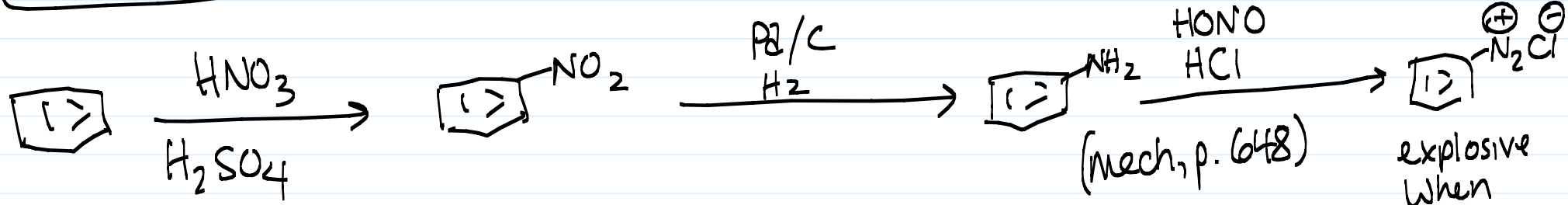
nitrobenzene ⇌ aniline





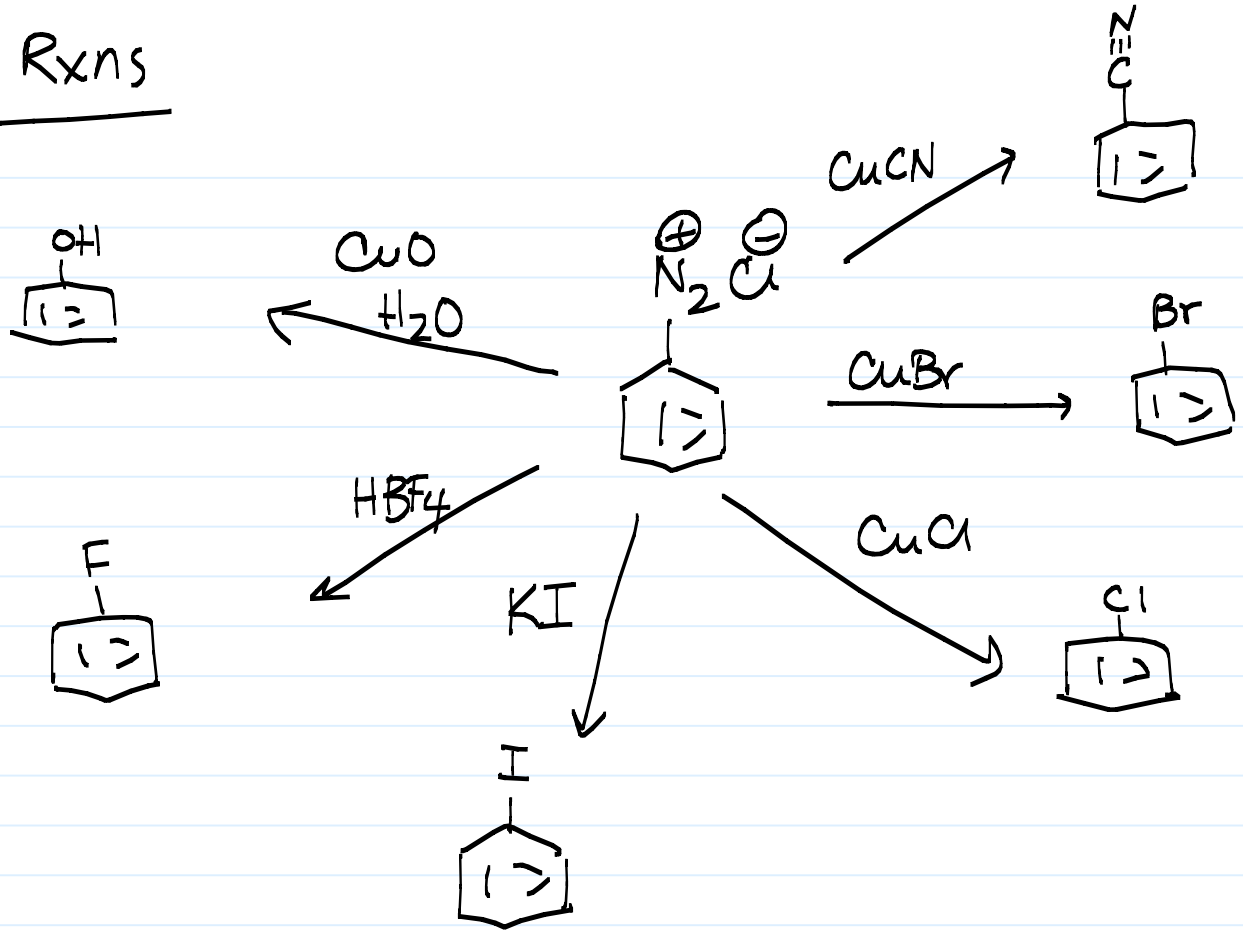
Benzene diazonium chloride



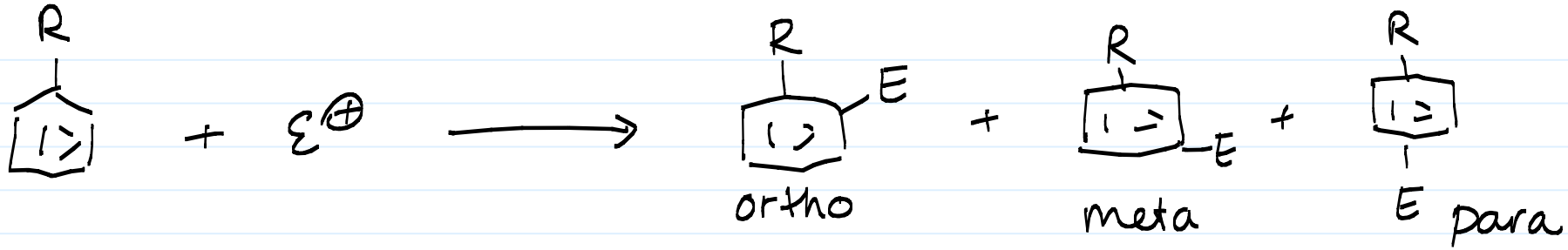


(mech, p. 648)

Sandmeyer Rxns



Disubstituted Benzenes



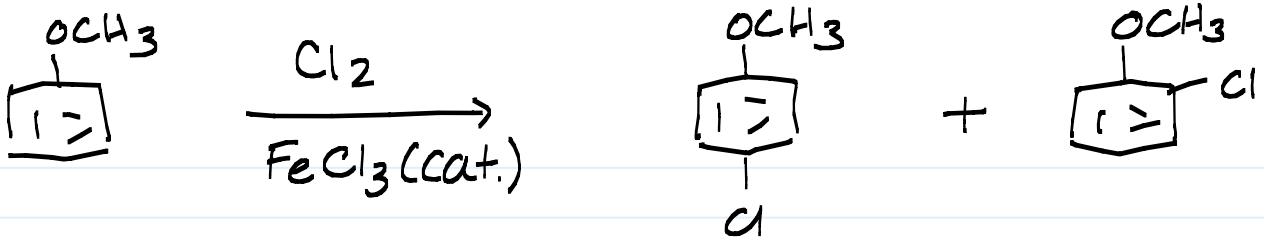
R influences: (1) substitution pattern : o, m, p

(2) Rate of Rxn

Slower rxn => R = Deactivating Group

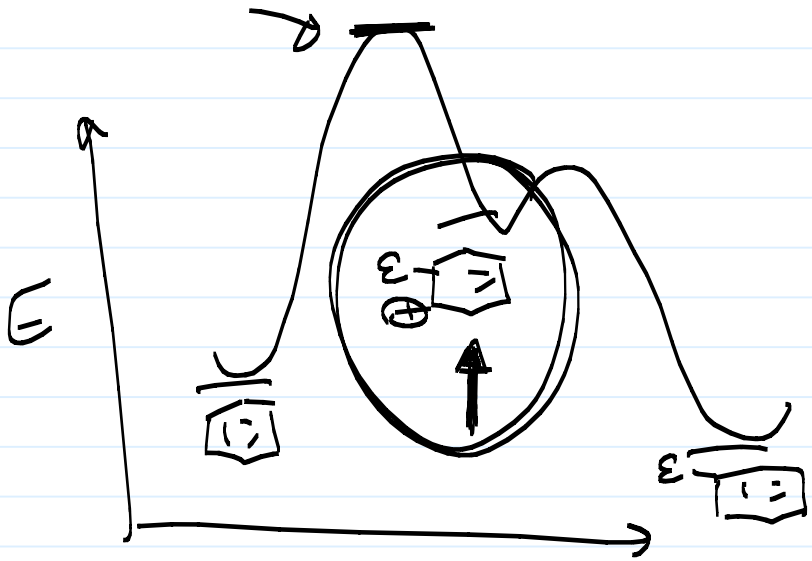
Faster rxn => R = Activating Group

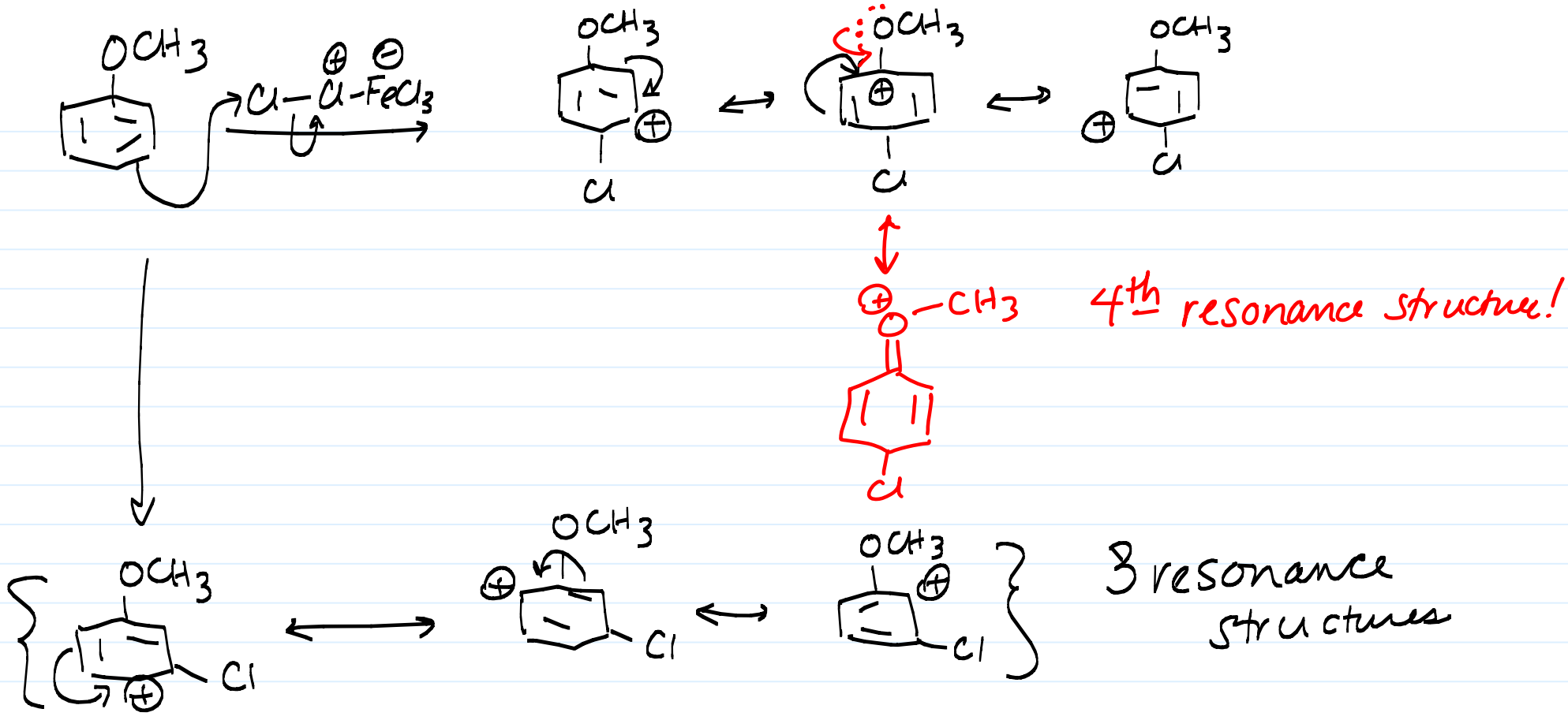
ex:

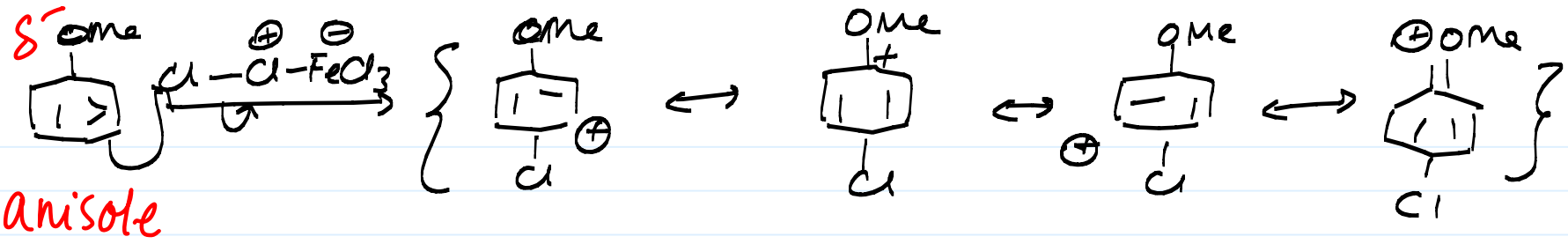


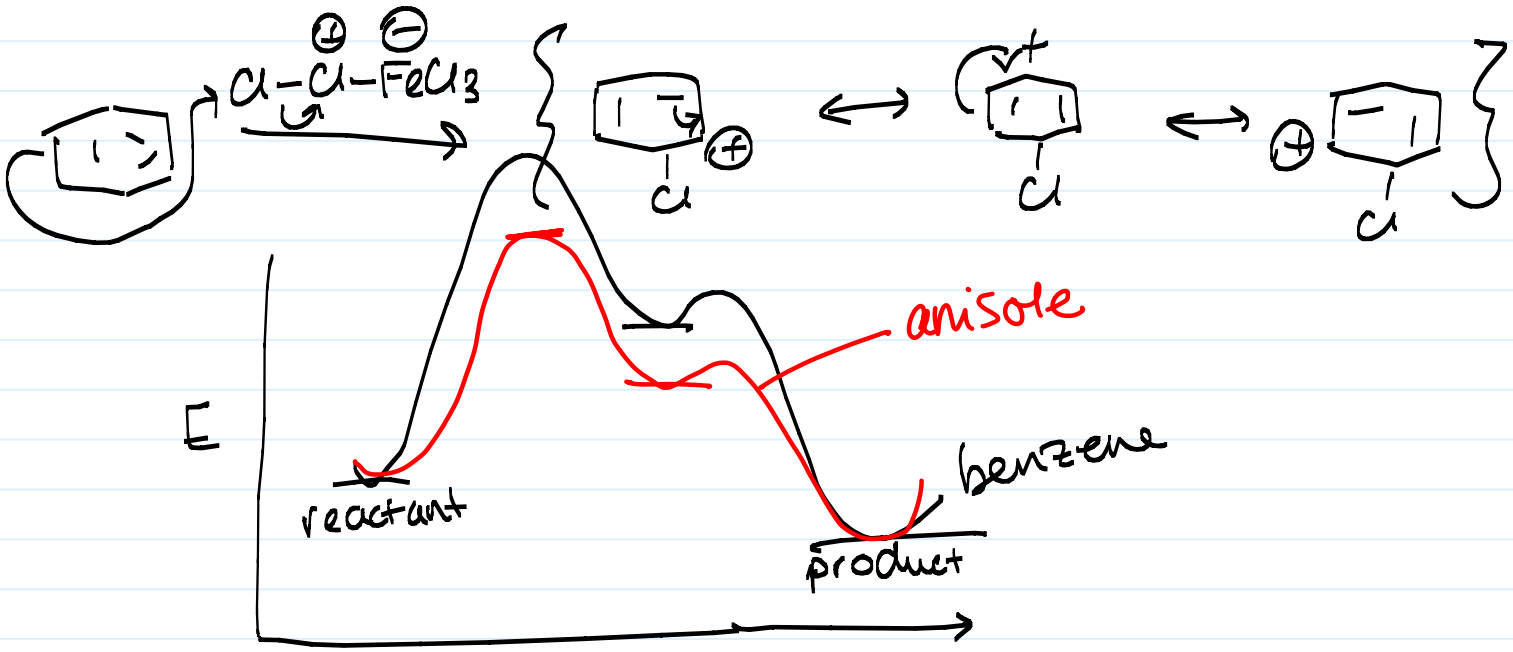
- No meta substn.
- Faster than rxn of benzene

WHY?




OCH3
Cl–Cl–FeCl3
Cl
CH3
4th resonance structure!
3 resonance structures


δ⁻
OMe
Cl–Cl–FeCl3
anisole


Cl–Cl–FeCl3
anisole
E
reactant
product
benzene