Orgo I Review

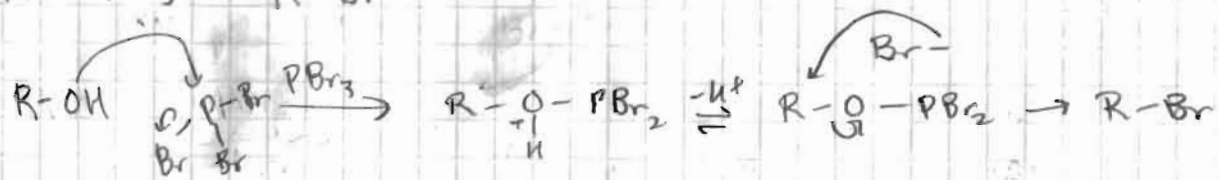
-ROH can act as

- acid
- nucleophile
- electrophile

S_N2, LG

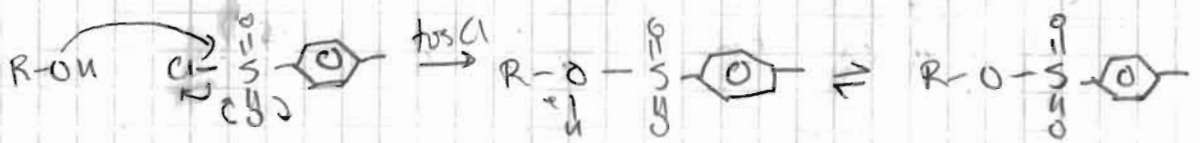
- can improve LG ability by using PBr_3, $SOCl_2$, tosCl, etc.
  (inverting) (noninverting)

- e.g. $ROH + PBr_3 \rightarrow R-Br$



1) O acts as nuc. 2) deprotonation w/ pyr. 3) S_N2

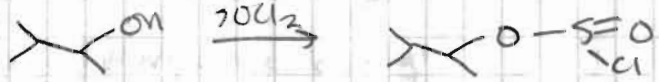
- e.g.



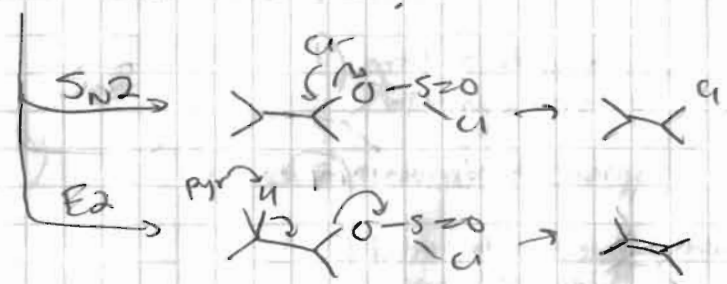
same steps as above

E2 - At high temperatures, pyr can act as a base, causing an elimination to occur

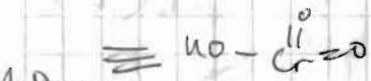
E2 - At high temperatures, pyr can act as a base, causing an elimination to occur

-e.g. workup: 

-note: Sulfur is more nucleophilic, strong nuc, weak base, will S_N2



Jones Oxidation - Converts alcohol to carbonyl (ROH → R=O)

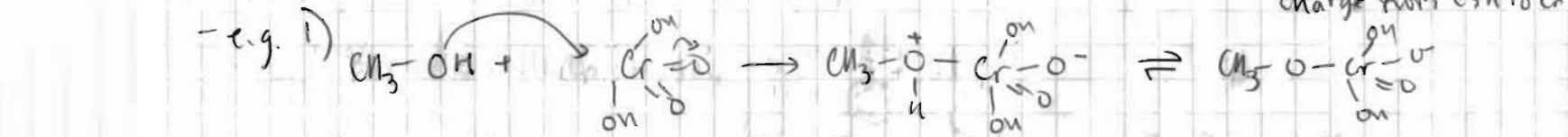
-requires: workup | CrO_3 / H_2SO_4 / H_2O ≡ 

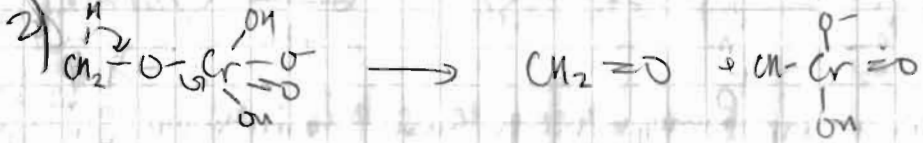
rxn | alcohol

-steps:

1) improve LG ability of OH

2) E2 by shifting charge from O's H to Cr

-e.g. 1) 

2) 

Epoxide Breaking

- in acidic, O^+ moves away from sterics, allowing for more sub. side to receive the ⊕

- e.g.

- in basic, nuc will attack less sterically hindered side

- e.g.

- this concept is generalizable (⚠)

Aromatic Reactions

Aromatic Reactions

Electrophilic Aro sub

- Adds an electrophile to an aromatic ring

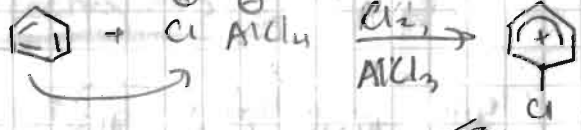
- requires: workup: | enough nuc. on ring
  enough elec. on ephile

- steps:
  1) grab electrophile by breaking a bond
  2) resonate + charge
  3) Elimination using H from C on C⁺, this removes ⊕ charge.

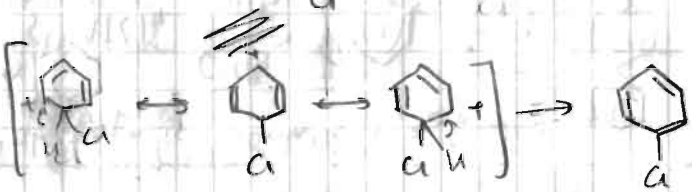
- eg. Using Al/Fe/B/Zn to ↑ electrophilicity

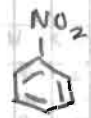
- workup: $AlCl_3 + Cl_2 \rightarrow Cl^{\oplus}\ {}^{\ominus}AlCl_4$

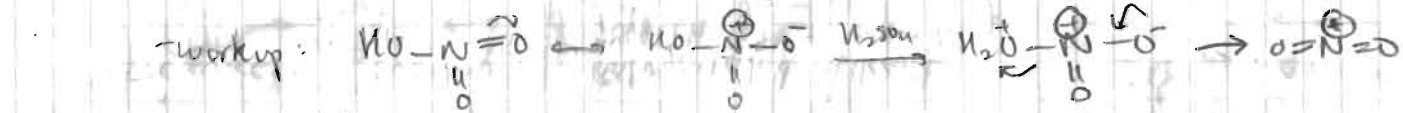
- rxn:

1) 

2)
3)



- e.g. Benzene + $HNO_3/H_2SO_4 \rightarrow$ 

- workup: 

- rxn: same process as above

Friedel Crafts

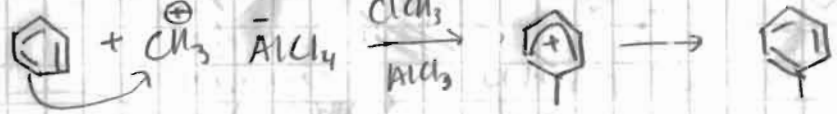
-Alkylation - Benzene + Cl–R + $AlCl_3$

requires: workup | halogenated molecule, something to r. ephilicity | rxn: | aromatic ring

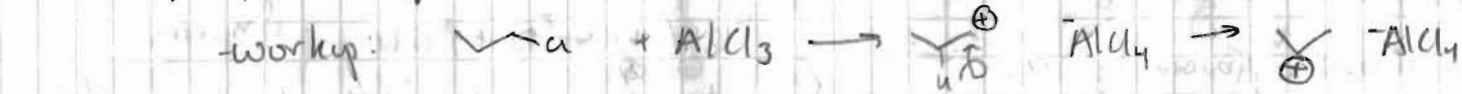
-e.g. w/out rearrangement: benzene + chloromethane + $AlCl_3$

-workup: $Cl-CH_3 + AlCl_3 \rightarrow {}^{\oplus}CH_3 \; {}^{-}AlCl_4$

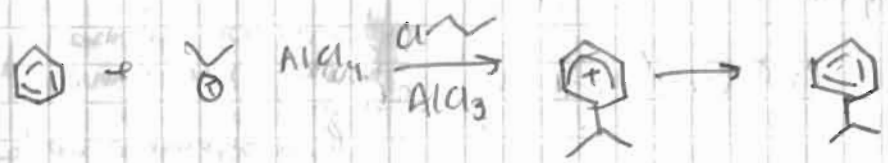
-rxn: same as electrophilic aromatic sub.



-e.g. w/ rearrangement: benzene +  + $AlCl_3$

-workup: 

-rxn: same as above.

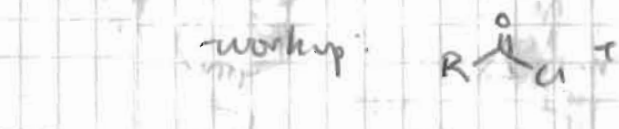


-Acylation - Benzene +  + $AlCl_3$ (prohibits rearrangement)

- Acylation - Benzene +  + $AlCl_3$ (prohibits rearrangement)

- requires workup: | halogenated carbonyl | non-/anomatic ring
| something to ↑ e⁻ philicity

- e.g.

- workup: 

- Adding multiple electrophiles

ortho & para: 1)  (activating b/c donates)

2)  (deactivating b/c induction)

meta: 1)  (deactivating b/c withdraws)

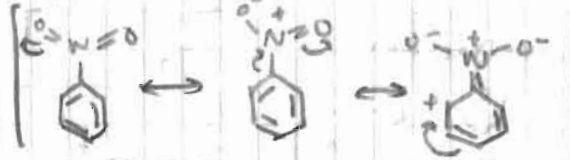
note: watch for steric

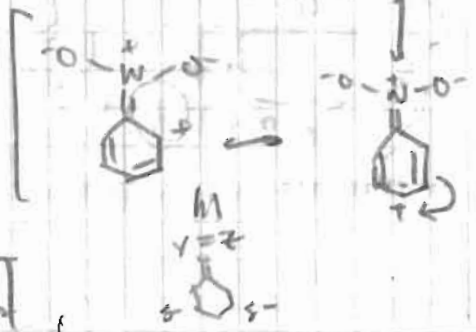
- e.g. NH_2, OH, halogens

ortho para

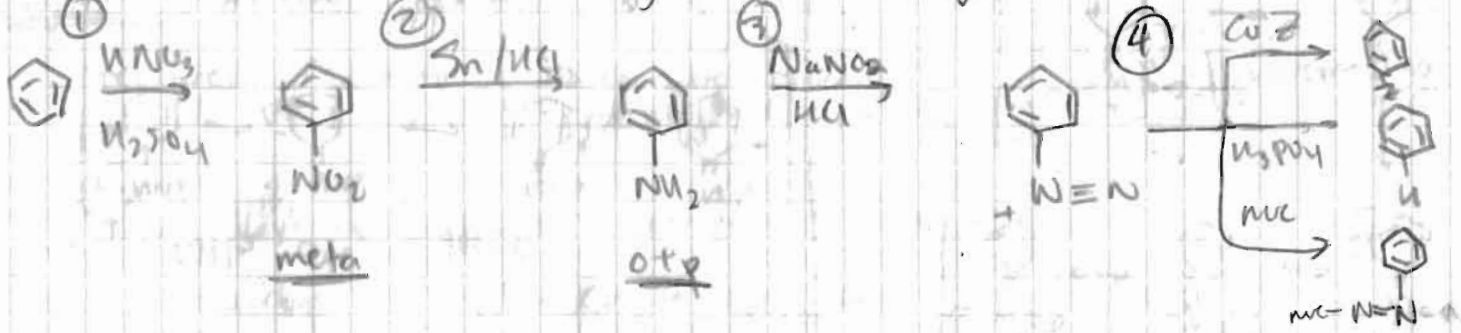
← legit. δ⁻ weakly/relative δ⁻

- e.g. NO_2





$NO_2 \rightarrow NH_2 \rightarrow \dot{N}\equiv N$ — A commonly used pathway to switch between o+p/m



- rxn for ③ aka diazotization aka ON NO+ rxn (HONO) aka Sandmeyer

- workup: Na^+ $O=\overset{\ominus}{N}-O$ $\xrightarrow{HCl}$ $HO-N=O \overset{+H^+}{\rightleftharpoons} H_2\overset{+}{O}-N=O$

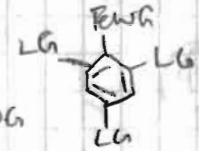
- rxn:

Steps
1) add HONO
H^+
$-H_2O$

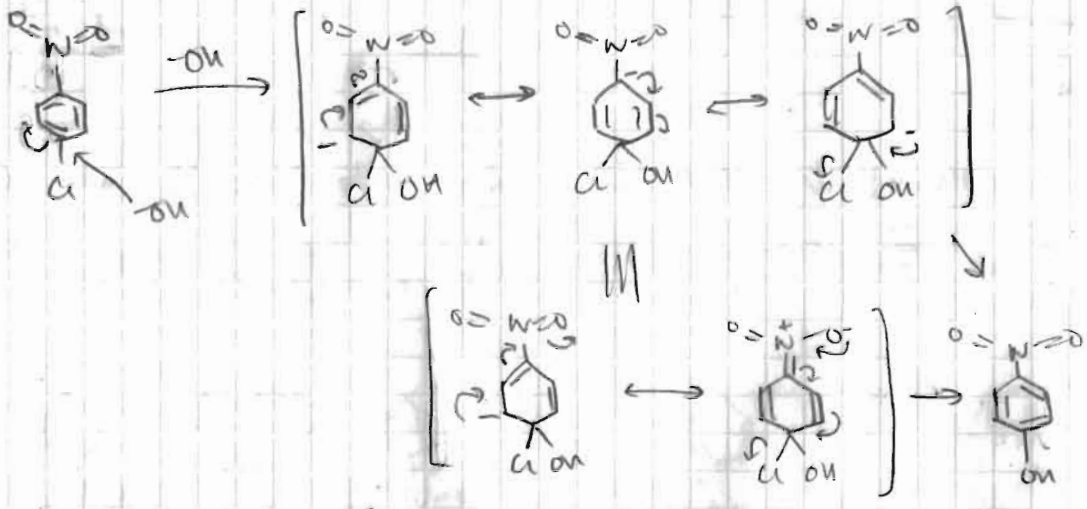
2) deprotonate N–H to neutralize ⊕
↑ bond order by using e⁻ from N
protonate O
repeat 2× until N≡N and H_2O (G)

Nucleophilic Aromatic Substitution (SnAr) – Adds on nucleophile to aromatic ring

- requires conditions:
  1) EWG
  2) a. good LG
     b. that is o/p to EWG



- e.g. $Cl-\phi-NO_2 + -OH \rightarrow HO-\phi-NO_2$



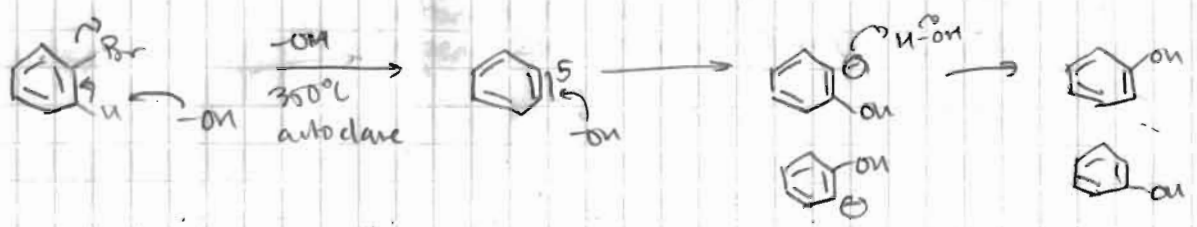
Benzyne – Racemic nucleophilic addition of aromatic ring

- requires:
  - benzene w/ good LG vicynil to a C–H
  - base
  - heat, pressure (harsh conditions)

steps: 1) Elimination 2) Nuc-esque addition

note:
discovered w/:
+ trapping using diels alder
- isotopic labelling

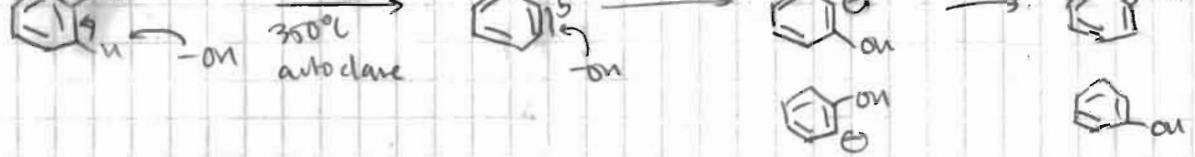
- e.g.



1

Aromatic summary:

-isotopic labelling



Aromatic summary

1) Electro Aro Sub

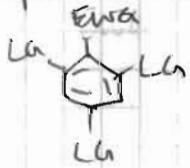
ortho + para vs. meta

X/AlX$_3$

HNO$_3$/H$_2$SO$_4$ → Sn/HCl → NaNO$_2$/HCl → Sandmeyer

Friedel Crafts Alkylation/Acylation

2) Nucleophilic Aro Sub



3) Benzyne rxn