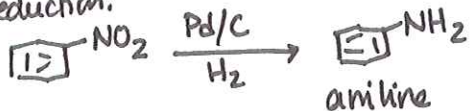
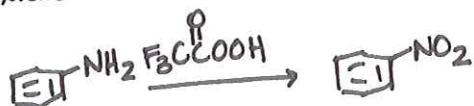


19 Interconversion of Nitrobenzene & Aniline

Reduction:



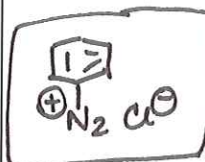
Oxidation:



20

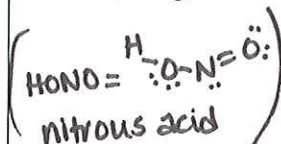
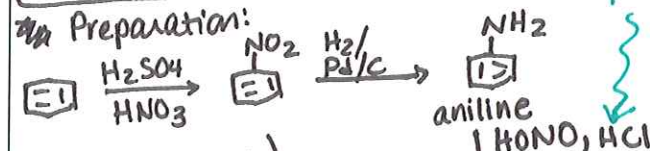
Benzene diazonium chloride

- key intermediate to substituted benzenes.



mechanism on p. 648.

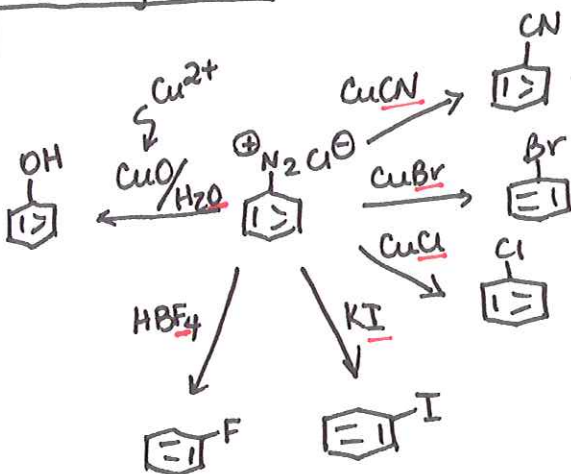
Preparation:



EXPLOSIVE WHEN DRY!!

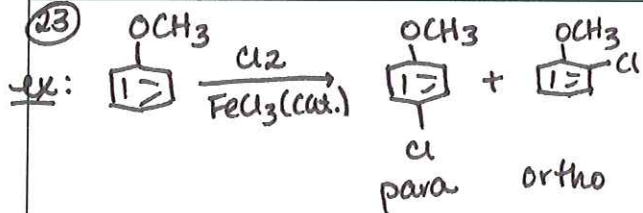
21

Sandmeyer Rxns:



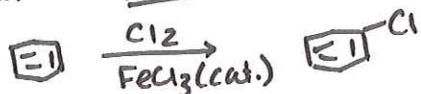
\*Mechanisms not fully known.\*

23

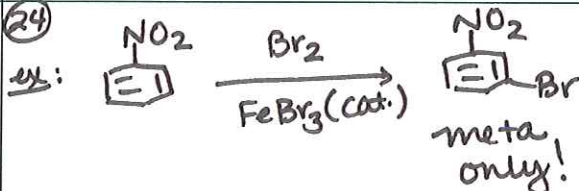


- No meta-substitution.

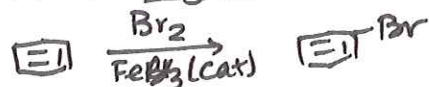
- Rxn is faster than



24



Rxn is very slow compared to



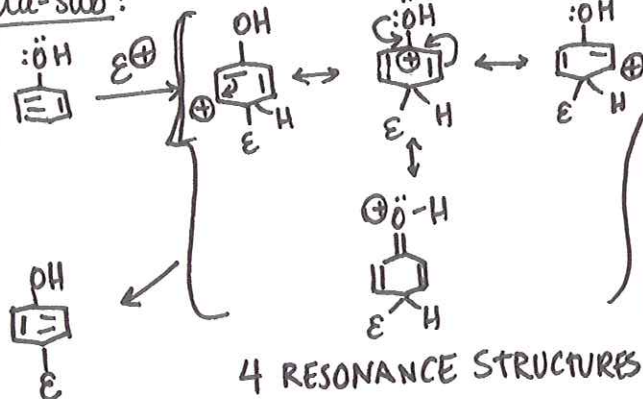
SEE HANDOUT

In general: o/p-directors are faster compared to benzene (except halides). m-directors are slower.

25) Why do o/p-directors direct substitution to the o/p-positions?

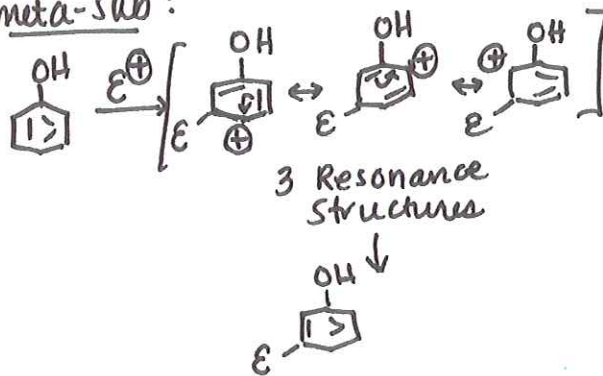
Examine c1ccc(O)cc1

para-sub:



26)

meta-sub:

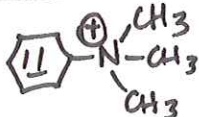


Conclusion: o/p director can participate in resonance stabilization of carbocation intermediate.

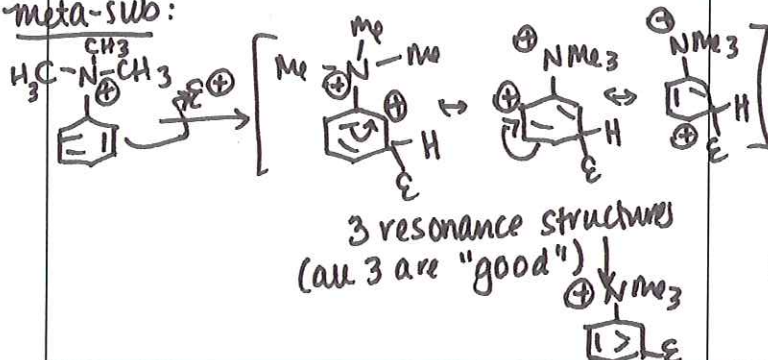
∴ o/p substitution is favored!

27) Why do m-directors direct substitution to m-positions?

Examine:

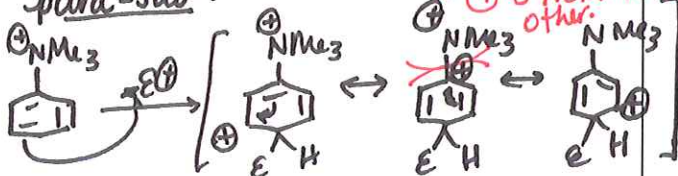


meta-sub:



28)

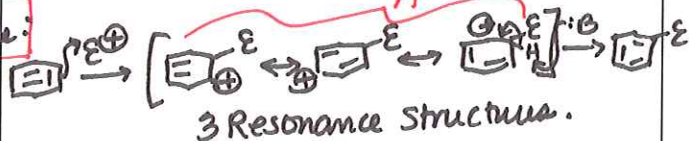
para-sub:



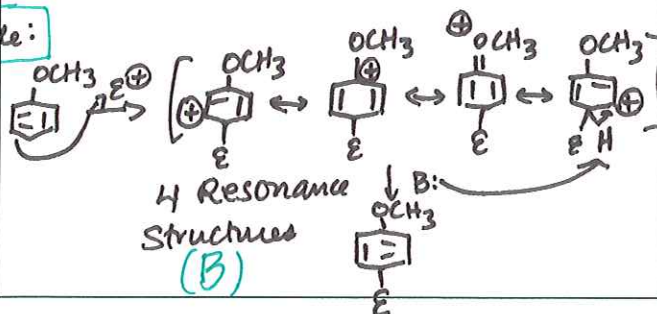
∴ meta is favored.

29) Why do most o/p-directing monosubstituted benzenes undergo substitution rxns faster than benzene?

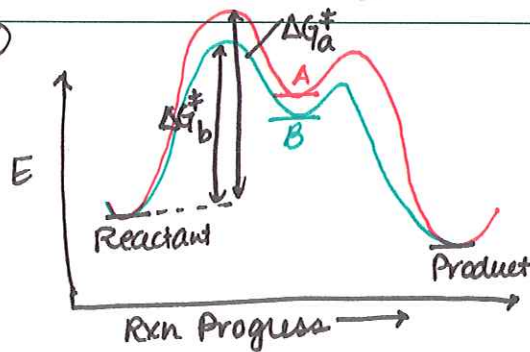
Benzene:



Anisole:



30)

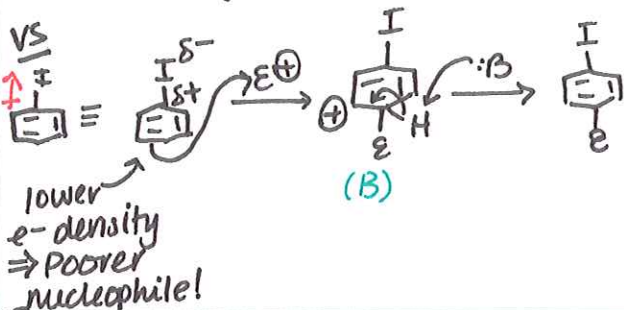
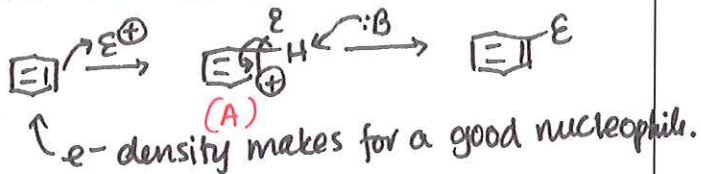


Intermediate B more stable.

Transition states resemble intermediates. ∴ TS B more stable &  $\Delta G_b^\ddagger$  is smaller  $\Rightarrow$  Rxn is faster! These substituents = Activating Groups.

31) Why do halobenzenes & meta-directors undergo slower rxns?

Inductive effect:



32)

Intermediate B is higher in energy b/c we are forming  $\oplus$  charge on an electron-deficient ring.

If TS's resemble intermediates, then TS B is higher in energy than TS A  $\Rightarrow$  Rxn is slower.

$$\Delta G_b^\ddagger > \Delta G_a^\ddagger$$

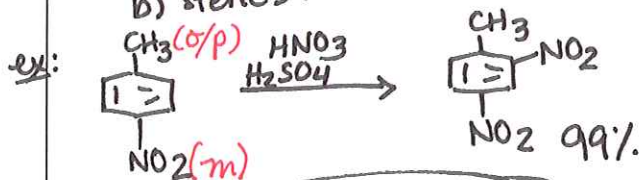
These substituents  $\Rightarrow$  Deactivating Groups.

33)

Polysubstitution: Where will substitution occur?

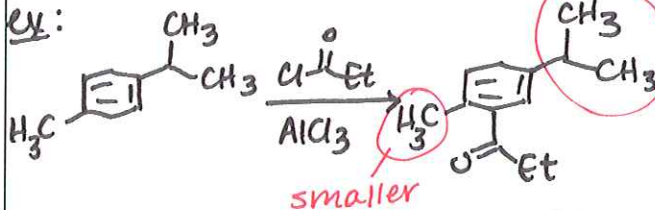
Outcome of aromatic subst'n rxns is determined by both

- a) electronics &
- b) sterics.



Electronics dominate.

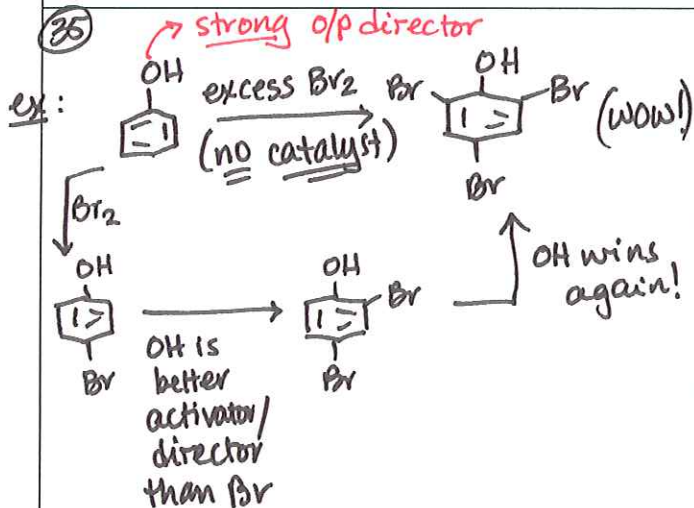
34)



iPr & Me = equal directing ability

Sterics dominate.

35)

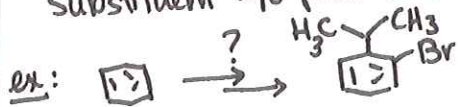


36)

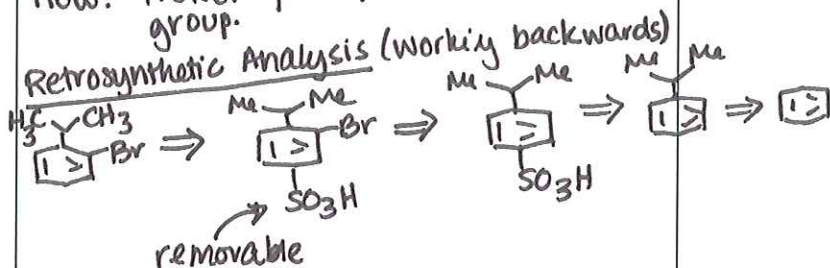
37

### Multistep Aromatic Polysubstitution

Classic Problem: Install ortho-substituent w/o para-substituent.

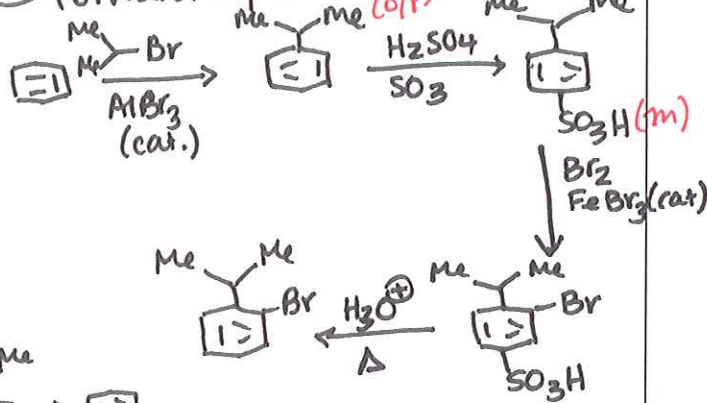


How? Protect para-position w/ removable group.



38

### Forward synthesis:



39

40

41

42