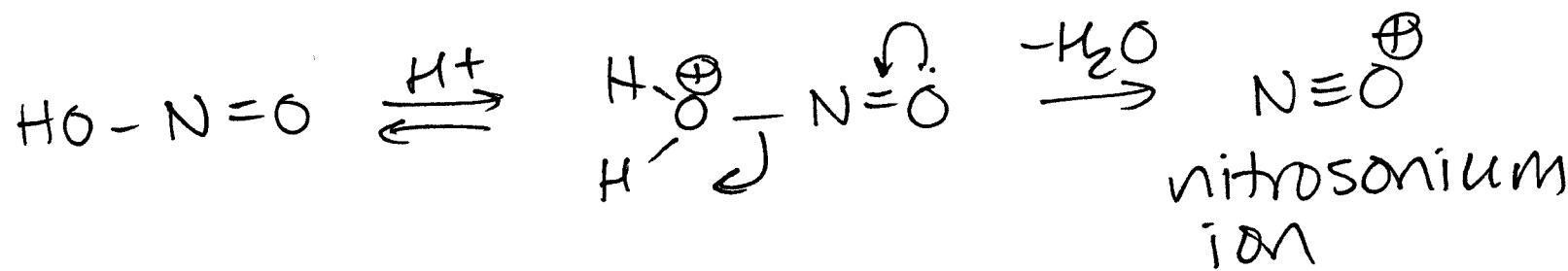


# Focus on amines - nitrosation

Nitrous acid -  $\text{HNO}_2$  - often written  $\text{HONO}$

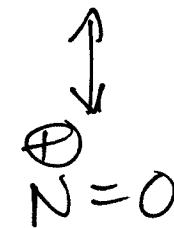
- unstable

- can be generated in situ + reacted immediately

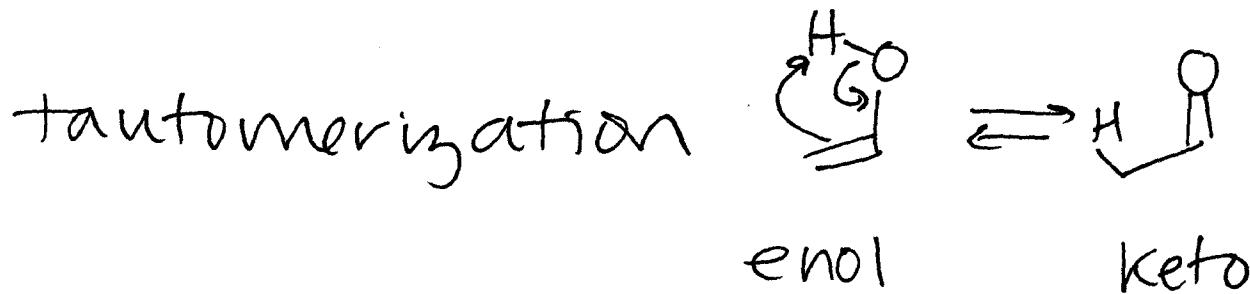
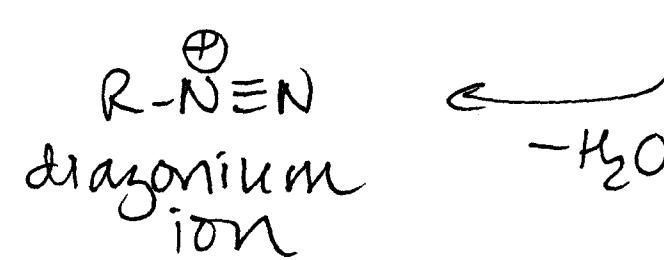
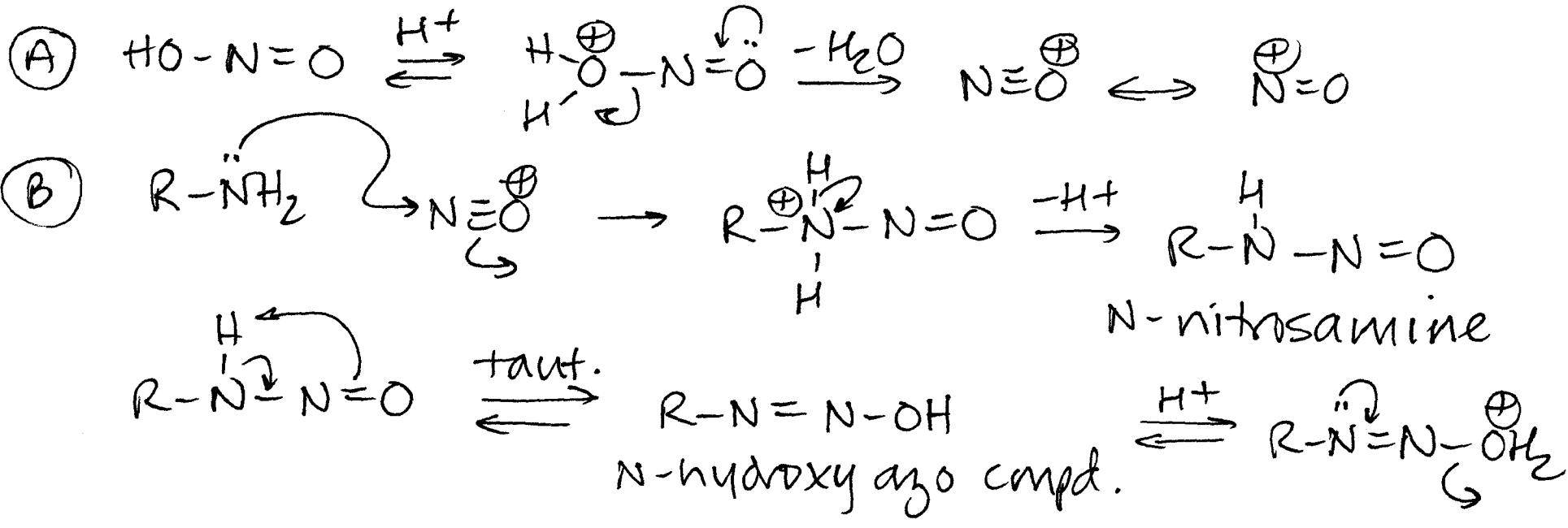


Generate  $\overset{\oplus}{\text{NO}}$  in the presence  
of an amine (good nucleophile)

$\Rightarrow$  rxn.



# Mechanism:



alkyl

1°

- goes all the way to diazonium ion
- v. unstable!

aromatic

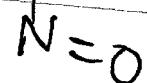
stable at low temp. ( $0^{\circ}\text{C}$ ) \*

2°

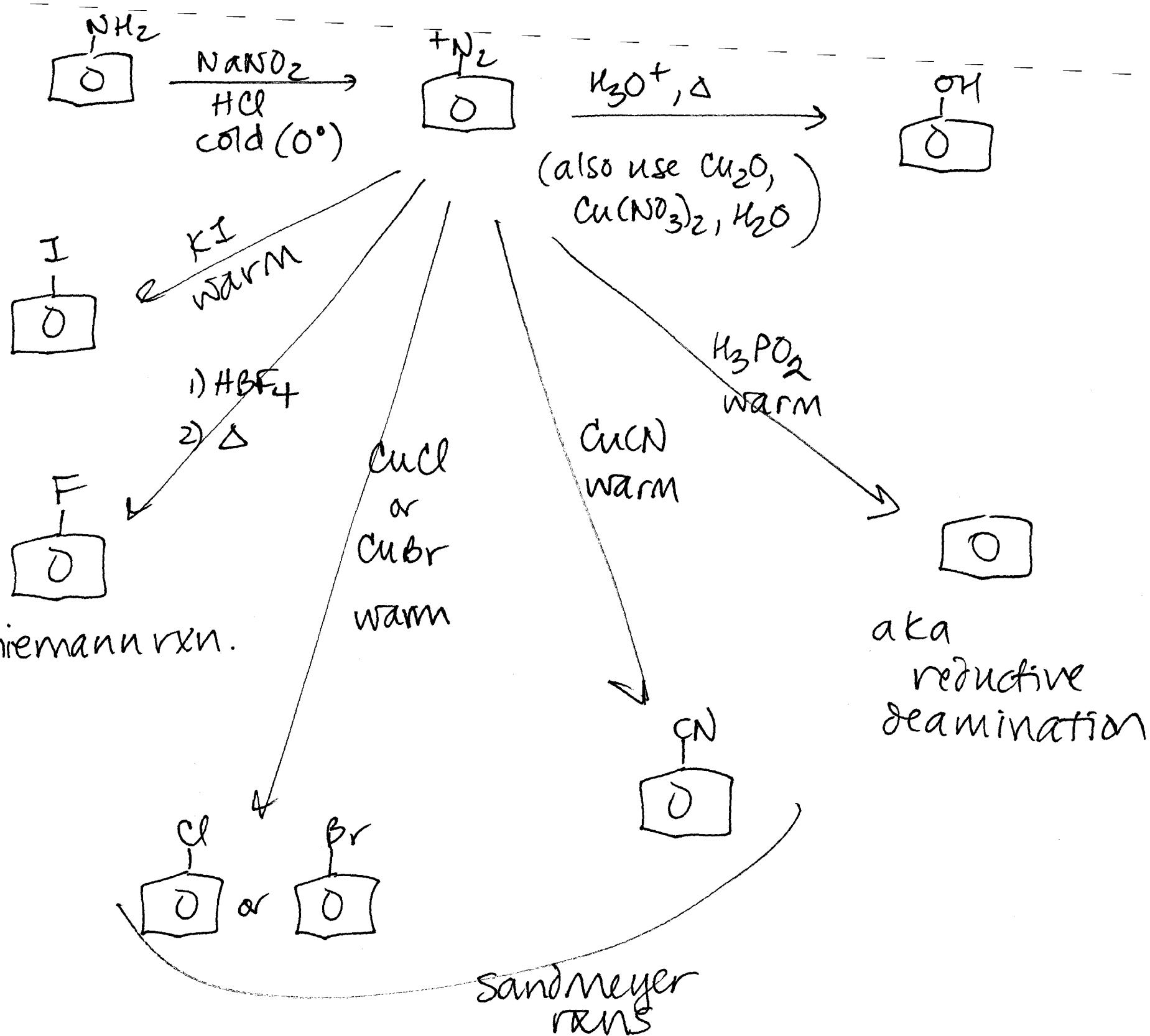
stop @ N-nitrosamine stage  
(carcinogens) - doesn't have  $\alpha^{+}$  for tautomerization step.

3°

NRX

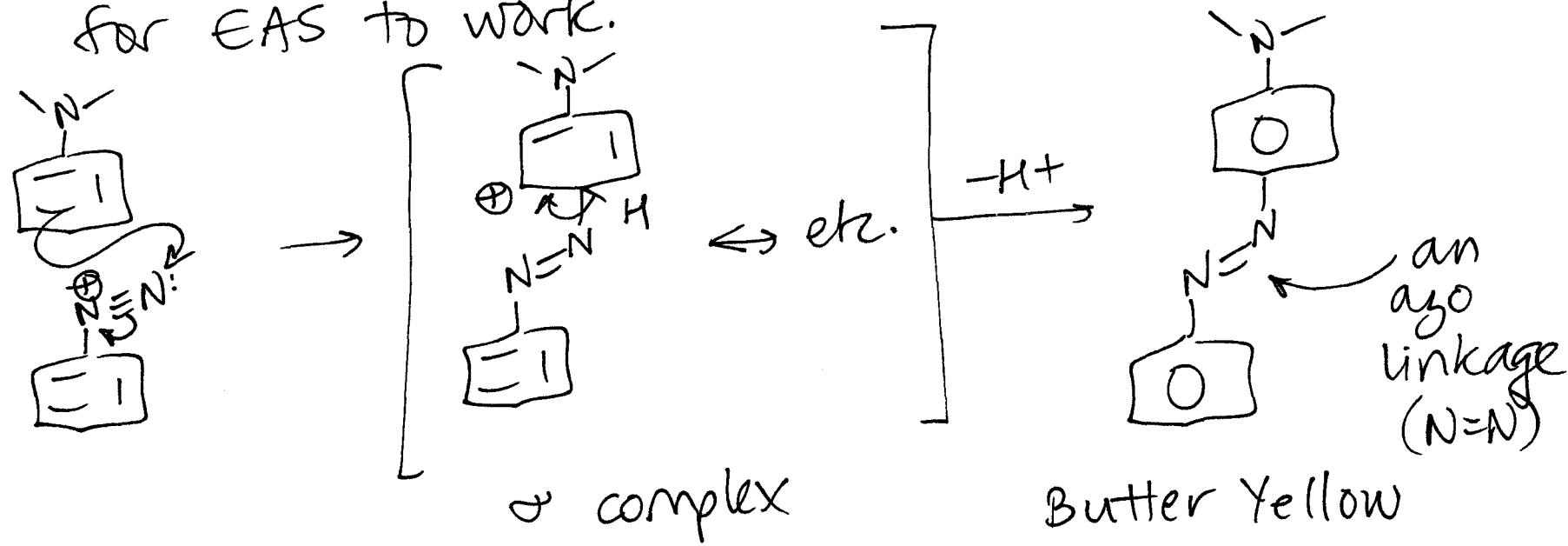


$+\text{N}=\text{O}$  is  
the electrophile



arene diazonium ions as EAS e'philes

\* because these are only stable at low temp  
need aromatics w/ strong activators in order  
for EAS to work.



Azo compounds can be cis or trans -

- usually trans
- usually highly colored (extended conjugated system)
- often dyes



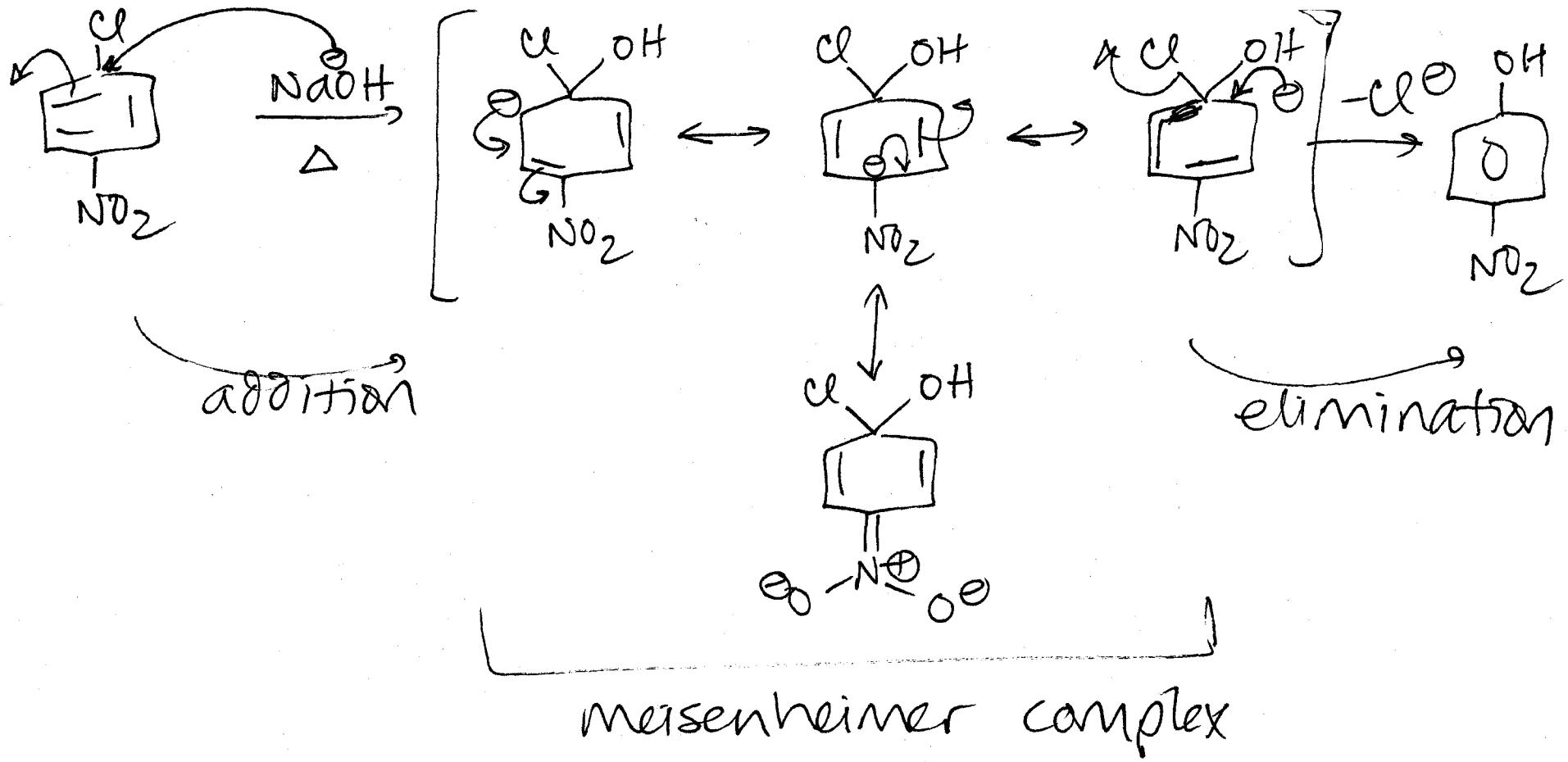
Any halides do not react w/ nucleophiles because the large e' cloud repels any incoming nucleophile.

But... If the following conditions are satisfied:

1. Good LG. (generally a halogen)
2. Strong nucleophile ( $\text{OH}^-$ ,  $\text{OR}^-$ ,  $\text{NH}_2^-$ ,  $\text{R}_2\text{NH}/\Delta$ )
3. A strong e' withdrawing group ( $\text{NO}_2$  or  $\text{CF}_3$ ) ortho and/or para to the LG.

Then we do get a rxn.  $\text{S}_{\text{N}}\text{Ar}$   
substitution, nucleophilic, aromatic.  
aka addition-elimination





only works because strong e' withdrawer  
o/p help stabilize the  $\ominus$  charge.

p-NO <sub>2</sub>	pH 14, 160°
o,p-NO <sub>2</sub>	pH 10, 100°
o,o,p-NO <sub>2</sub>	pH 7, 40°