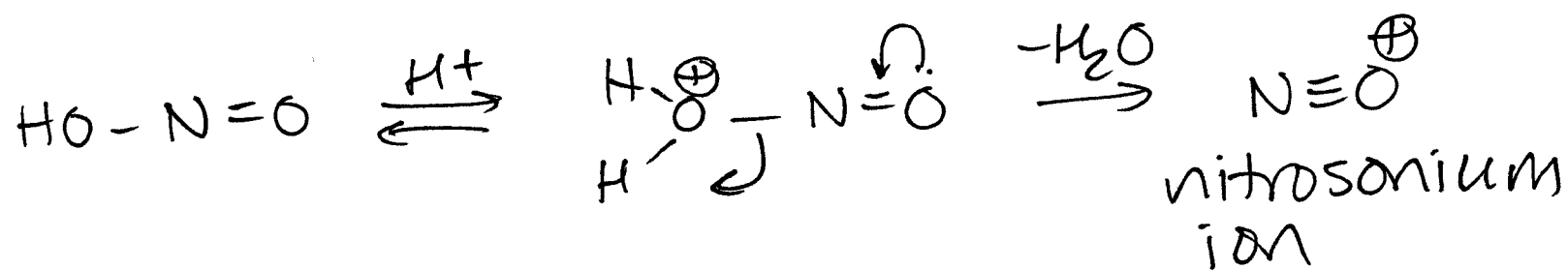


# Focus on amines - nitrosation

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

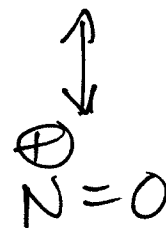
- unstable

- can be generated in situ + reacted immediately

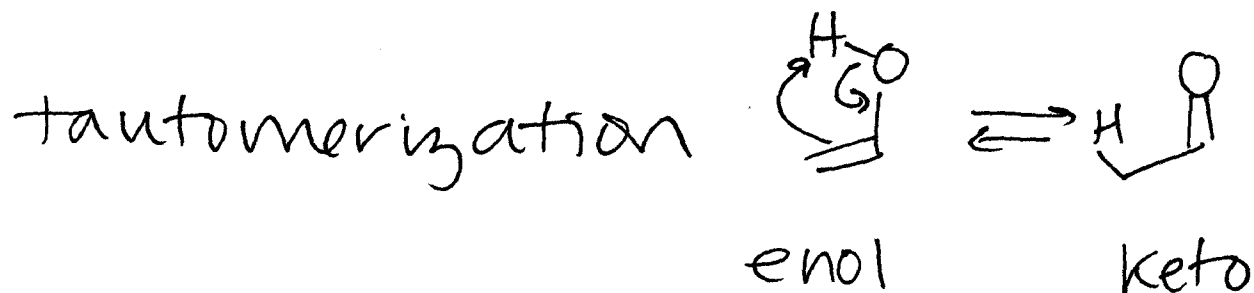
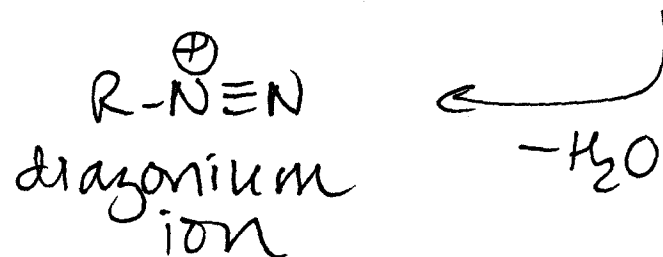
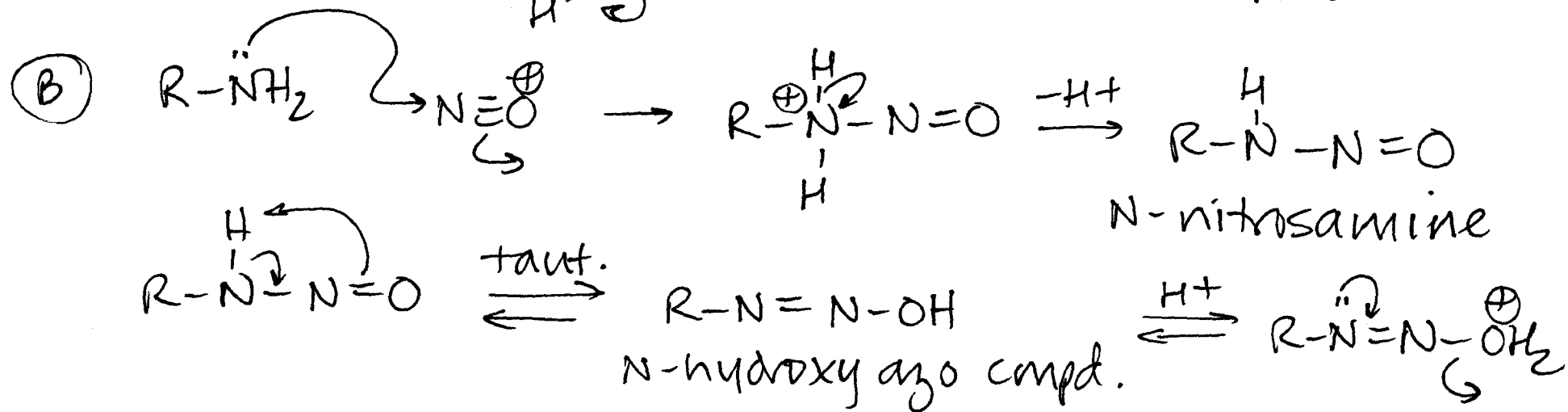
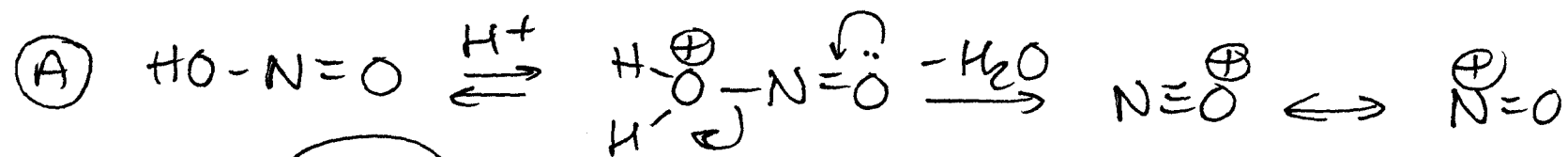



Generate  $\text{NO}^+$  in the presence  
of an amine (good nucleophile)

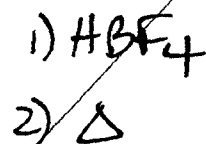
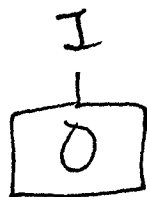
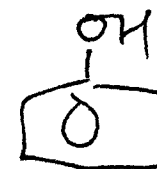
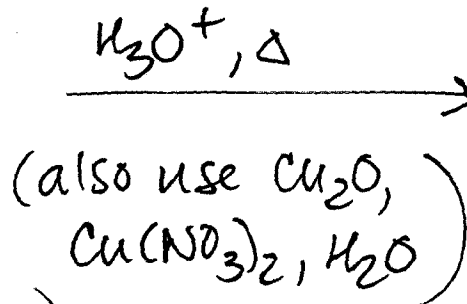
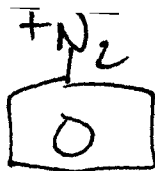
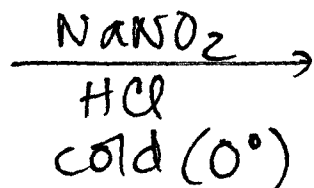
$\Rightarrow$  rxn.



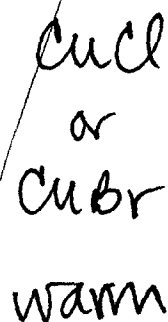
Mechanism:



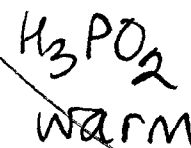
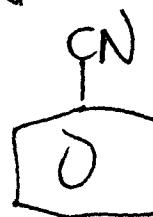
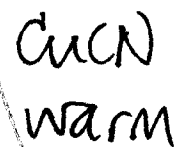
	alkyl	aryl
1°	<ul style="list-style-type: none"> <li>- goes all the way to diazonium ion</li> <li>- v. unstable!</li> </ul>	stable at low temp. (0°C) *
2°	stop @ N-nitrosamine stage (carcinogens) - doesn't have 2 <sup>nd</sup> H for tautomerization step.	
3°	NRX	EAS $\rightarrow$ <div style="display: inline-block; vertical-align: middle; text-align: center;">  <p>N=O</p> </div> P- <del>NO</del> NO + N=O is the electrophile



Schriemann rxn.



or

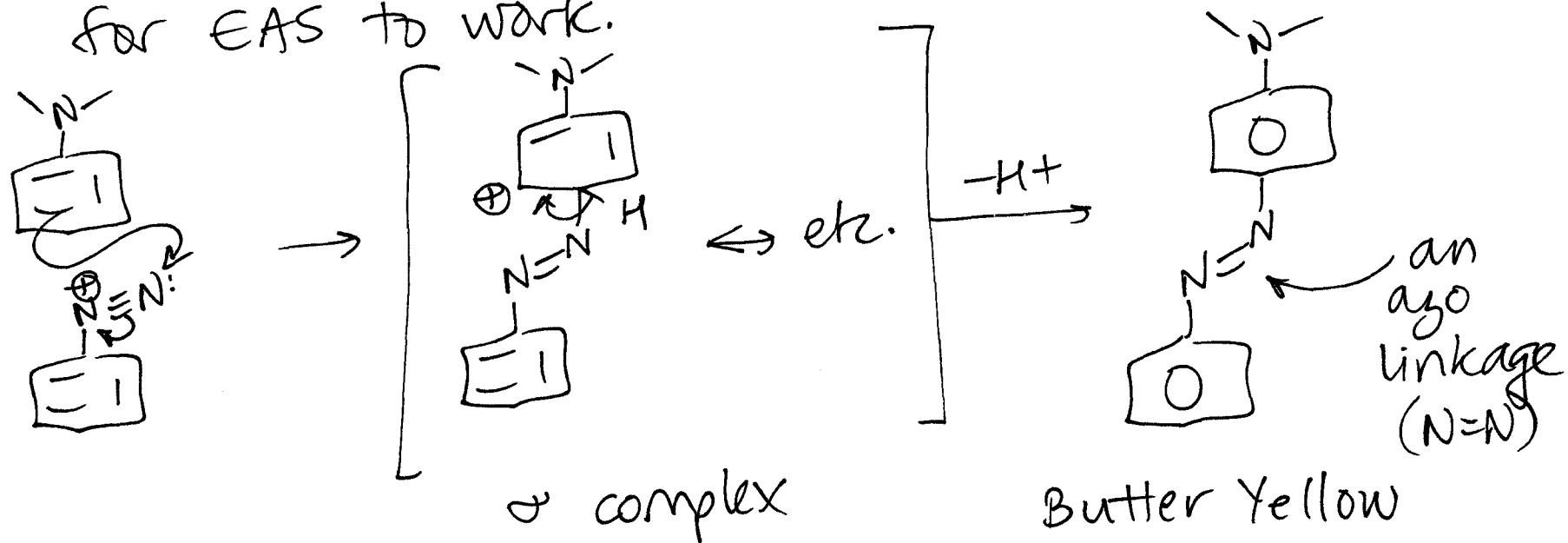


aka reductive deamination

Sandmeyer rxns

# Arenediazonium Ions as EAS e<sup>-</sup>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

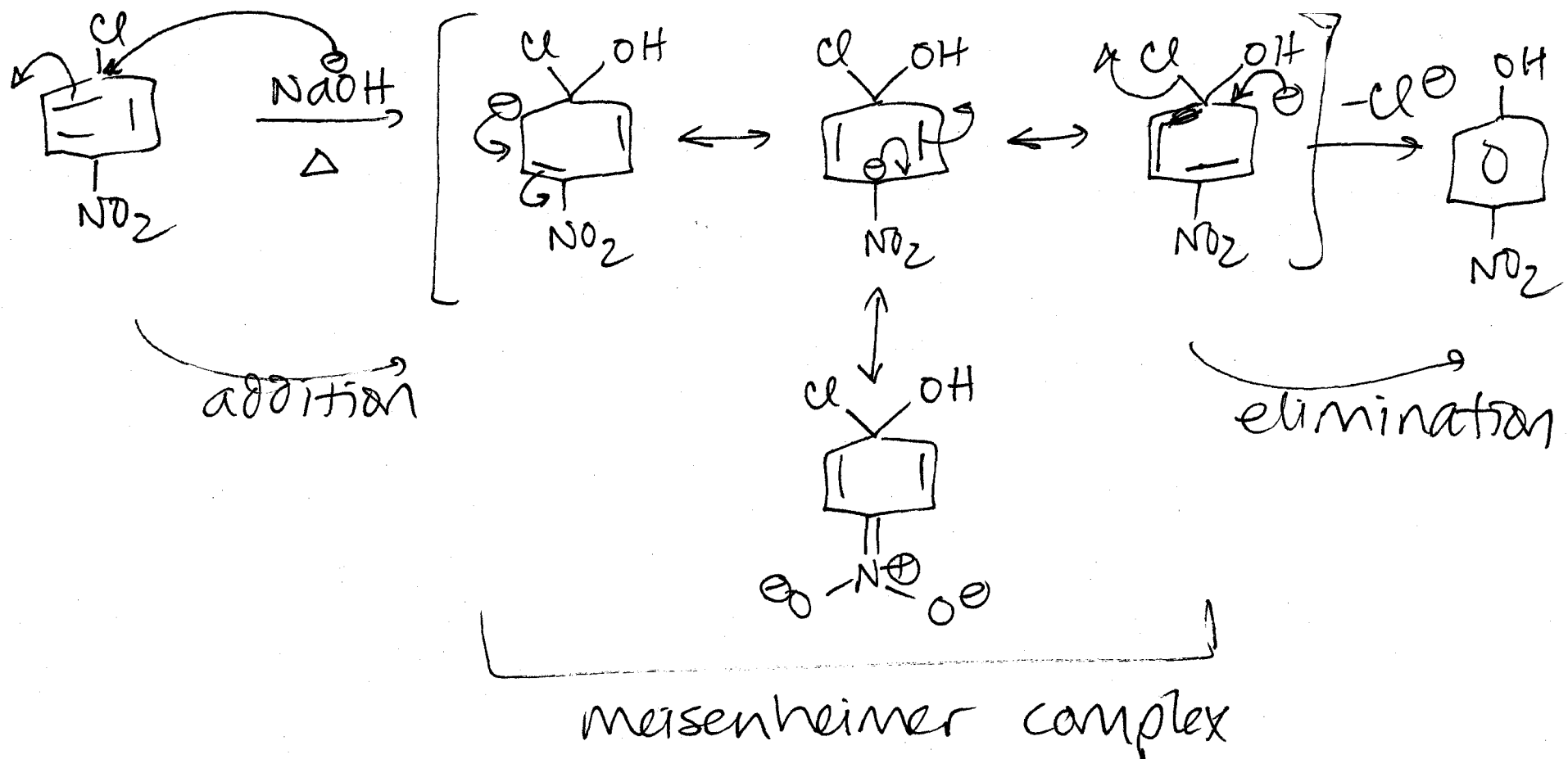


Aryl halides do not react w/ nucleophiles because the large  $e^-$  cloud repels any incoming nucleophile.

But... If the following conditions are satisfied:

1. Good LG. (generally a halogen)
2. Strong nucleophile ( $OH^-$ ,  $OR^-$ ,  $NH_2^-$ ,  $R_2NH/\Delta$ )
3. A strong  $e^-$  withdrawing group ( $NO_2$  or  $CF_3$ ) ortho and/or para to the LG.

Then we do get a rxn.  $S_NAr$   
 substitution, nucleophilic, aromatic.  
 aka addition-elimination



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

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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°