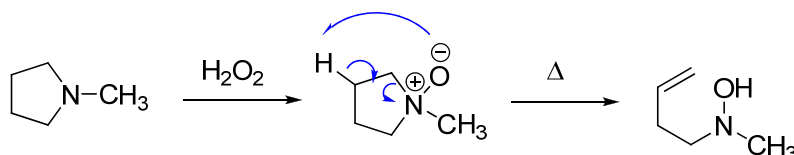


Chapter 20 Information

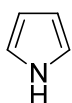
Cope elimination – treat a tertiary amine with peroxide, get an amine N-oxide. (This also works on primary and secondary amines.) Heat up the tertiary amine N-oxide, get an intramolecular E2 elimination. It is a *syn* elimination, and if there is more than one possible product, the oxygen generally pulls off a proton from the less substituted carbon.



Aromatic Heterocycles



furan



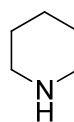
pyrrole



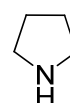
thiophene



pyridine



piperidine



pyrrolidine

(those last two are in there just for comparison)

Aromatic heterocycles undergo electrophilic aromatic substitution reactions just like benzene does. There are some differences, however. For instance, all positions on a heterocyclic ring are not equivalent. Five-membered rings have the “2” position (next to the heteroatom) and the “3” position. Substitution at the “2” position is preferred, because the sigma complex is more stable (has three resonance contributors) as compared to the sigma complex for substitution at the “3” position (two resonance contributors). If the “2” position is blocked, then substitution will occur at the “3” position.

5-membered heterocycles are more reactive towards EAS than benzene, because they can stabilize the positive charge in the sigma complex better. Pyrrole > furan > thiophene > benzene; different Lewis acid catalysts are used as well. Pyrrole doesn't require a catalyst (just use the anhydride); furan uses BF_3 ; thiophene uses SnCl_4 ; benzene uses AlCl_3 .

Pyridine also undergoes EAS, preferably at the “3” position (this gives the most stable sigma complex; the other positions wind up with nitrogen having both an incomplete octet AND a positive charge). Pyridine is less reactive to EAS than nitrobenzene; it requires vigorous conditions, gives relatively low yields, and does not undergo Friedel-Crafts reactions.

SKIP nucleophilic aromatic substitution of heterocycles.