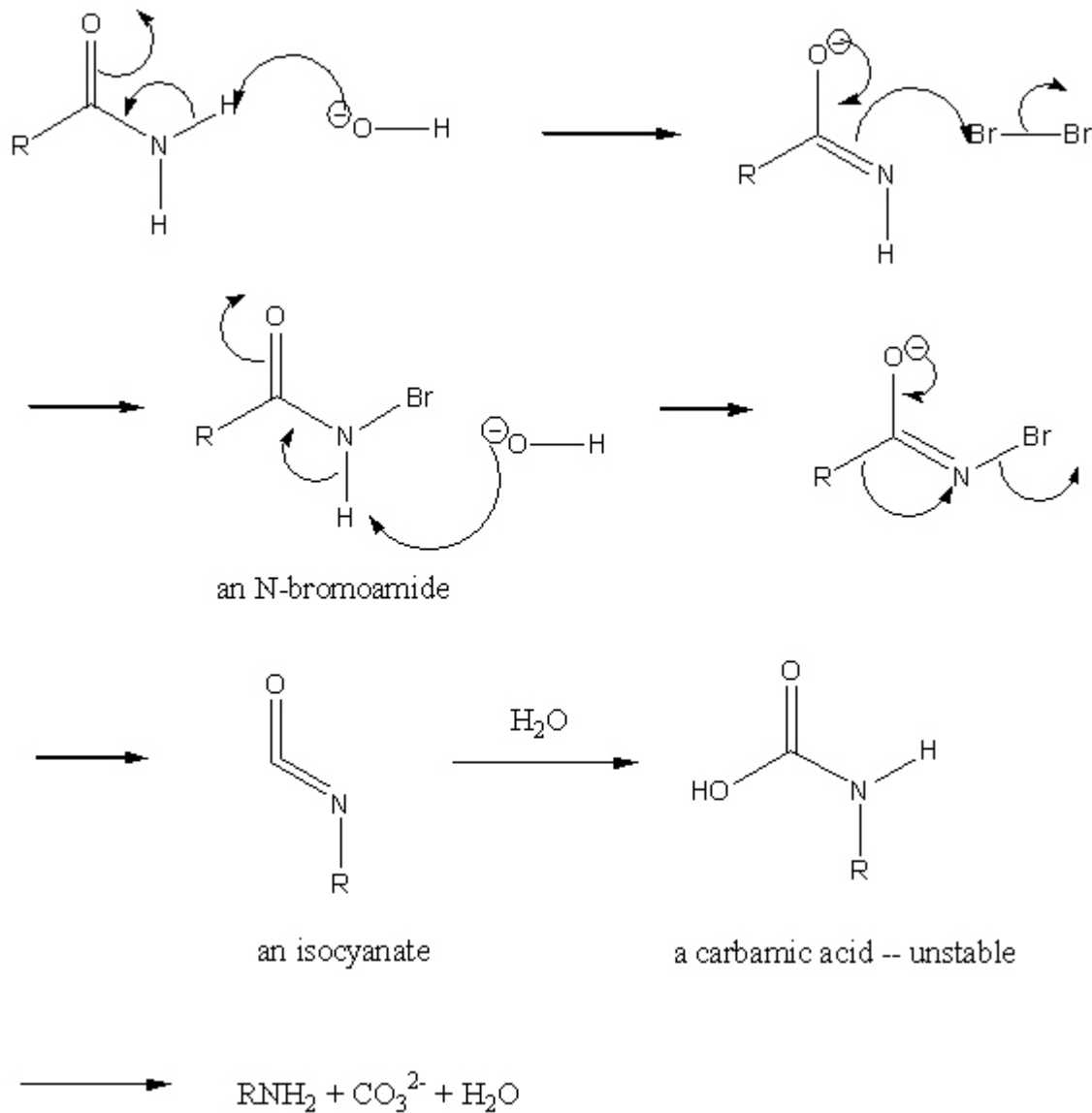
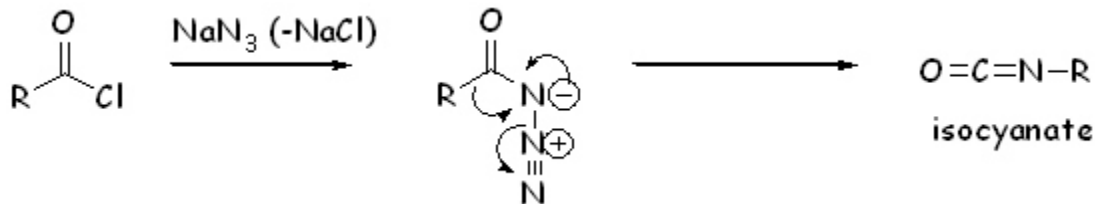


Hofmann Rearrangement - primary amides only. Mechanism:



(Carbamic acid effectively falls apart to give the primary amine, CO_2 and hydroxide, which combine to give bicarbonate anion)

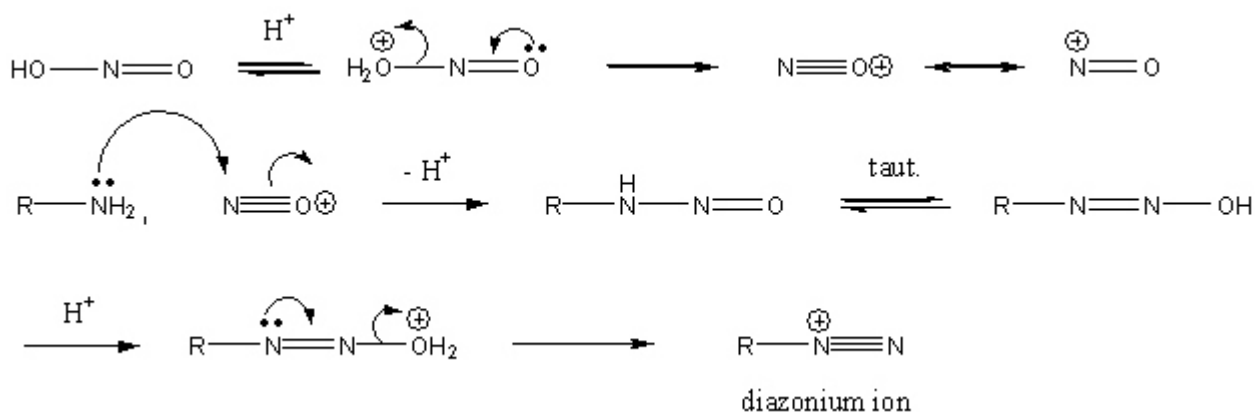
Curtius Rearrangement: rearrangement of acyl azides. Similar to the Hofmann rearrangement in that an R group migrates to the nitrogen and a leaving group leaves.



This initially gives an isocyanate, which can then be hydrolyzed to a primary amine + CO_2 . (See mechanism for Hofmann rearrangement for details.)

Nitrosation. Nitrous acid (HONO) itself is fairly unstable, but it can be generated in solution from NaNO_2 and HCl . Under these conditions, it is protonated and loses water (analogous to nitration in EAS) to form the nitrosonium ion, which is a very good electrophile. If this is done in the presence of an amine (a good nucleophile), you get a reaction.

Primary alkylamine: here's the mechanism.

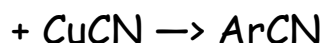
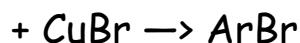
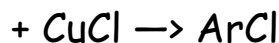
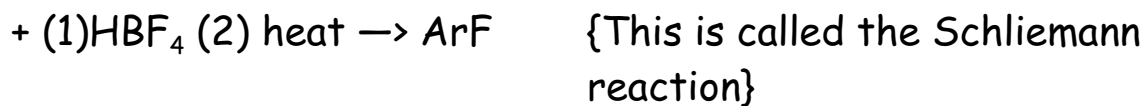
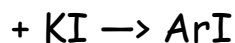
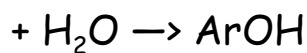


Primary alkylamines go all the way to the diazonium ion, which is unstable, loses nitrogen to form the alkyl cation, which does all the things cations normally do, and you get a total mess.

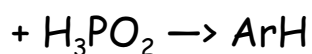
Secondary alkylamines stop at the N-nitroso compound, which can't tautomerize to go any further. N-nitroso compounds are frequently potent carcinogens, and are present in things like beer, herbicides, fried bacon, and tobacco smoke.

Tertiary alkylamines don't do anything as they don't even have one proton to lose.

Primary arylamines form the diazonium salts, which are stable when kept cold. Aryl diazonium ions undergo a variety of reactions:



{The copper ones are Sandmeyer rxn}



{can also use EtOH in place of H_3PO_2 ; reaction is called reductive deamination}

When making aryl diazonium salts, generally use sulfuric acid instead of HCl, since it's nonnucleophilic.

Secondary arylamines make the N-nitroso compounds as well.

Tertiary arylamines undergo electrophilic aromatic substitution with the nitrosonium ion acting as the electrophile.