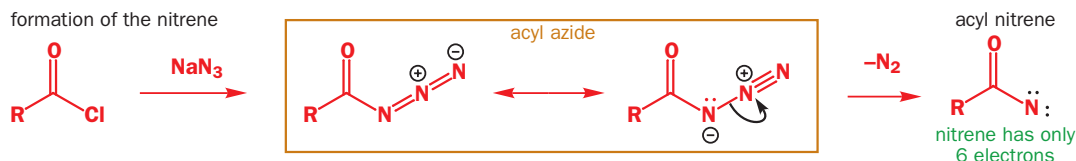
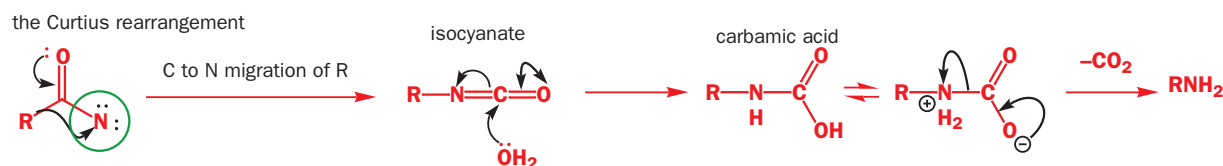


Nitrenes are the nitrogen analogues of carbenes

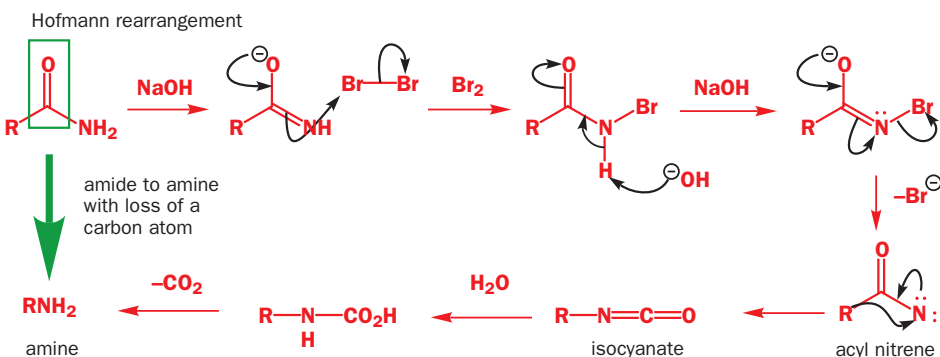
The Wolff rearrangement has some important cousins that we must now introduce to you—they deserve a mention because they bear a family likeness even though they do not, in fact, involve carbenes. They are a group of reactions that proceed through an intermediate **nitrene**—the nitrogen analogue of a carbene. The simplest to understand, because it is the direct nitrogen analogue of the Wolff rearrangement, is the **Curtius rearrangement**. It starts with an acyl azide—which can be made by nucleophilic substitution on an acyl chloride by sodium azide. The acyl azide is what you would get if you just replaced the $-\text{CH}=\text{N}_2$ of a diazoketone with $-\text{N}=\text{N}_2$. And, if you heat it, it is not surprising that it decomposes to release nitrogen (N_2), forming the nitrene. The nitrene has two bonds fewer (1) than a normal amine and has two lone pairs making six electrons in all.



Nitrenes, like carbenes, are immensely reactive and electrophilic, and the same Wolff-style migration takes place to give an isocyanate. The substituent R migrates from carbon to the electron-deficient nitrogen atom of the nitrene. Isocyanates are unstable to hydrolysis: attack by water on the carbonyl group gives a carbamic acid which decomposes to an amine.



Overall, then, the Curtius rearrangement converts an acid chloride to an amine with loss of a carbon atom—very useful. Also useful is the related **Hofmann rearrangement**, which turns an amide into an amine with loss of a carbon atom. This time we start with a primary amide and make a nitrene by treatment with base and bromine. Notice how close this nitrene-forming reaction is to the carbene-forming reactions we talked about on p. 000. The nitrene rearranges just as in the Curtius reaction, giving an isocyanate that can be hydrolysed to the amine.



Attack of carbenes on lone pairs

Wolff rearrangements, involving shifts of alkyl groups, are effectively intramolecular insertions into C–C bonds. Carbenes will also insert into other bonds, especially O–H and N–H bonds, though the mechanism in these cases involves initial attack on the lone pair of the heteroatom.

