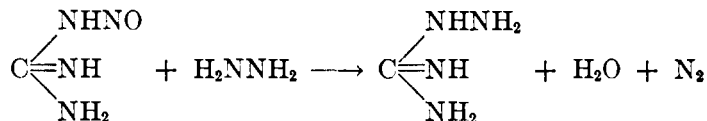


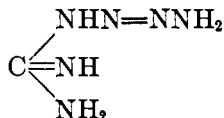
*C. Hydrazinolysis*

## 1. Nitrosoguanidine

Thiele (149), in 1893, discovered that equimolecular proportions of nitrosoguanidine (125) and hydrazine hydrate react readily, with evolution of nitrogen, to form aminoguanidine:



The intermediate, a tetrazene,



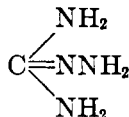
was considered to form, and immediately lose nitrogen. However, when the reaction was conducted with the ratio of 2 moles of nitrosoguanidine to 1 mole of hydrazine hydrate, a much slower reaction took place, and the product was hydrazodicarbamidine:



The first substance formed is aminoguanidine, as indicated above. This in turn reacts with additional nitrosoguanidine to form the tetrazene



in which loss of nitrogen results in the formation of hydrazodicarbamidine. Thiele considered that this was proof that aminoguanidine did not have the "symmetrical" form:



Thiele (149) suggested as an alternative mechanism for the formation of hydrazodicarbamidine that the nitrosoguanidine first "dearranged" (25, 26) to water, nitrogen, and cyanamide; that cyanamide combined with the hydrazine to form aminoguanidine; and that this compound in turn reacted with a second mole of cyanamide to form hydrazodicarbamidine. About the same time, Pellizzari (101) found that the reaction of cyanamide and hydrazine hydrochloride led to the formation of aminoguanidine.