Rearrangement of Cyclic Amines Catalysed by Palladium

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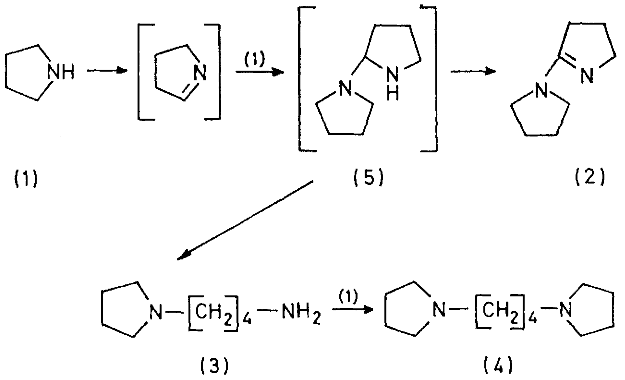
Summary Rearrangement of cyclic amines catalysed by palladium afforded *N*-substituted cyclic amines (**2**)—(**4**), while heterocyclic amines were converted into *N*-formyl cyclic amines (**6**)—(**7**).

Although considerable attention has been paid to dehydrogenation of secondary amines, catalysed by metals, to give Schiff bases,[1] little is known of the reaction between the resulting Schiff base and further amines.[2] We now report a general rearrangement of cyclic amines catalysed by palladium, and a new formylation of heterocyclic amines.

Suspension of a catalytic amount of palladium in pyrrolidine (**1**) gave (**2**)[3] (65%) and (**3**)[4] (24%) after heating for 10 h at 80°, (**3**) (85%) after heating for 5 h at 150°, and (**4**)[2] (75%) after heating to 200°. These results can be rationalized in terms of either a reductive cleavage or dehydrogenation of intermediate (**5**). Analogously, piperidine was converted into α,ϵ-dipiperidinylpentane (86%) at 200°.



In contrast, reaction of heterocyclic amines with palladium afforded *N*-formylamines. Thus, morpholine gave *N*-formylmorpholine (**6**)(95%)[5] and *N*-methylpiperazine gave (**7**) (96%).[5]†‡ The oxygen of the formyl group does not come from molecular oxygen. Catalytic oxidation of *N*-methylpiperidine by palladium has been reported to give *N*-formylpiperidine.[6] This formylation can be interpreted in terms of nucleophilic attack of OH$^-$ from moisture on the intermediate (**8**), corresponding to (**5**), to give (**9**) as a transient intermediate which could then lead to the product

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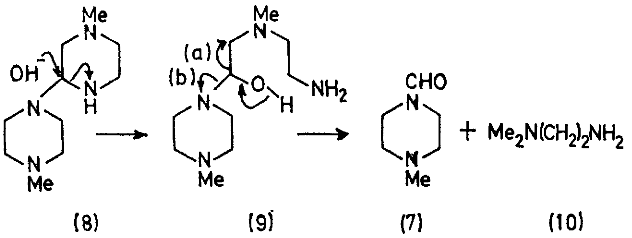
† Satisfactory spectroscopic and analytical data have been obtained.

‡ Yields were calculated stoicheiometrically based on unrecovered amines.

by cleavage (a) of (**9**) (Scheme). Alternatively cleavage (b) leads to the starting amine or the intermediate imine. Indeed, in the reaction of *N*-methylpiperazine, the diamine (**10**) was obtained as a fragment of cleavage (a) of (**8**). Wanzlick demonstrated ready reaction of imidazoline with moist solvents or chromatography on moist Al_2O_3.[7] This new formylation seems to be general for heterocyclic amines. 2-Ethylhexahydropyrimidine was smoothly converted into *NN'*-diformyl-2-ethylhexahydropyrimidine at 100° for 2 h.



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