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 Nformylmorpholine (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

[†] Satisfactory spectroscopic and analytical data have been obtained.

[‡] Yields were calculated stoicheiometrically based on unrecovered amines.

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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 Al₂O₃.⁷ 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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