

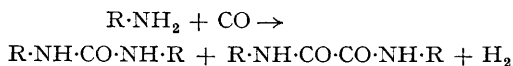
Organic Synthesis by Means of Noble-metal Compounds. Palladium-catalyzed Carbonylation of Amines

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It is known that carbonylation of amines catalyzed by various metal carbonyls gives rise to substituted formamides as main product, and in some cases the formation of disubstituted ureas has been reported.¹ A recent report of the reaction of amines with carbon monoxide in the presence of palladium chloride to give isocyanate² prompted us to disclose our results of the carbonylation of amines catalyzed by metallic palladium.

We found that primary amines can be carbonylated to form disubstituted ureas and oxamides with the evolution of hydrogen. The reaction can be shown by the following general scheme.



In a typical experiment, a mixture of n-decylamine (7.9 g.) and palladium chloride (0.5 g.) in benzene (30 ml.) was placed in a glass vessel equipped with a gas inlet capillary. The vessel was set in an autoclave (300 ml.) and carbon monoxide

was introduced (100 kg./cm.²). The reaction was carried out at 180° for 20 hours with shaking. After the usual work-up, *NN'*-didecylamide (3.8 g., m.p. 122°) and 1,3-didecylurea (2.2 g., m.p. 97—98°) were obtained. Formation of hydrogen was confirmed by gas chromatography.

Although the true catalytic entity seems to be metallic palladium, products are quite different depending on the nature of the catalyst and amine used. For example, when palladium on carbon was used, the yield of oxamide decreased considerably and formamide was formed instead. When a lower aliphatic amine was carbonylated, the yield of urea decreased and that of formamide increased. Only the urea was formed with aromatic amines.

The coupling of carbon monoxide to form oxamides is a new reaction, although coupling to form arils has been reported.³

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¹ F. Calderazzo, *Inorg. Chem.*, 1965, **4**, 293.

² E. W. Stern and M. L. Spector, *J. Org. Chem.*, 1966, **31**, 596.

³ N. L. Bauld, *Tetrahedron Letters*, 1963, 1841.