FORMYLATION OF SECONDARY AMINES BY THE USE OF DMFA UNDER THE ACTION OF LOW-VALENCE

NICKEL COMPLEXES

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We have established that secondary amines of various structures react with DMFA in the presence of complexes of catalysts containing nickel with the formation of N-formyl derivatives of the respective amines:

$$RR^{1}NH + (CH_{3})_{2}NC(O)H \xrightarrow{NI-L} RR^{1}NC(O)H + (CH_{2})_{2}NH$$

$$(I-V)$$

Thus, piperidine is formylated by use of DMFA on catalysts of the type $Ni(acac)_2-L-Al(C_2H_5)_3$ [L = $P(OPh)_3$, $P(OC_6H_{11})_3$, and PPh_3 , $60^{\circ}C$, 5 h, toluene], being converted into N-formylpiperidine (I) with yield of ~65%. Under analogous conditions, the N-formyl derivatives (II)-(IV) are obtained with DMFA with yields of 31, 20, and 34%, respectively, from diethylamine, morpholine, and hexamethylenimine. During reaction of piperazine with DMFA, predominantly mono-N-formylpiperazine (V) is formed, and the content of the diformyl derivative in the catalyzate does not exceed 8%.

It should be noted that a stoichiometric amount of dimethylamine was isolated along with the N-formyl derivatives in all experiments. The structures of the amides (I)-(VI) which were obtained were confirmed by comparison with known preparates [1-5].

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