THE CARBONYLATION OF α,β'-BIPIPERIDYL WITH CARBON MONOXIDE

Ya. Yu. Aliev, I. B. Romanova, and Z. F. Panfilova

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The previously unreported N, N'-diformyl-α,β'-bipiperidyl has been synthesized by the reaction of α,β'-bipiperidyl with carbon monoxide under pressure.

The present work is a continuation of investigations of the carbonylation of nitrogen-containing heterocyclic compounds [1-3]. In a study of the influence of the steric factor on the interaction of heterocyclic amines with carbon monoxide, it was established that with respect to ease of carbonylation the heterocyclics studied can be arranged in the sequence: piperidine > > β-pipecoline > anabasine > α-pipecoline. In other words, the more remote the substituents are from the nitrogen atom, and the less they screen its free electron pair, the more easily does the reaction of carbon monoxide with the corresponding amine take place. We have hydrogenated anabasine to α,β'-bipiperidyl. Its structure permitted the assumption of a different capacity of the two amino groups for the catalytic addition of carbon monoxide.

Influence of the Amount of Catalyst on the Yield of N, N'-Diformyl-α,β'-bipiperidyl (I) (Pressure of CO 130 atm, Temperature 100° C, Time of Heating 2 hr, Molar Ratio of α,β'-Bipiperidyl to Solvent = 1 : 12)

Expt. No.	Molar ratio of α,β'-bipiperidyl to catalyst	Yield of I, %
1	1 : 0.2	Traces
2*	1 : 0.4	74
3	1 : 0.4	98
4	1 : 0.6	Traces
5	1 : 1	0

* Time of heating 80 min.

α,β'-Bipiperidyl was carbonylated with carbon monoxide under pressure in methanolic solution in the presence of sodium methoxide. The reaction took place smoothly; at 100° C, 130 atm of CO, and with heating for 2 hours in the autoclave, we obtained the previously unreported N, N'-diformyl-α,β'-bipyridyl (I) at a yield of 98%. The formation of monoformyl derivatives of α,β'-bipiperidyl did not take place, since the conditions that we used did not favor the expression of a difference in the reactivity of the two amino groups. Shortening the time of heating (experiment 2 in the table) or reducing the pressure to 100 atm led to a decrease in the yield of compound I and, correspondingly, to the incomplete conversion of the initial compound. A further lowering of the pressure led to the cessation of the process.

The influence of the amount of catalyst and the time of the reaction on the carbonylation of α,β'-bipiperidyl can be judged from the data given in the table. Thus, in the presence of the same amounts of CH_3ONa, with a reaction time of 80 min (experiment 2), the yield of N, N'-diformyl-α,β'-bipiperidyl was 74%, and with two hours' heating (experiment 3) it was 98%. At a molar ratio of α,β'-bipiperidyl to sodium methoxide of 1 : 0.2, only traces of carbonylation product were formed, and the starting material was recovered almost unchanged (experiment 1). An increase in the amount of catalyst led to the complete resinification of the reaction mixture (experiments 4 and 5).

EXPERIMENTAL

Starting materials. α,β'-Bipiperidyl was obtained by hydrogenating anabasine on Raney nickel by the method of Sadykov and Otroshchenko [4]. Mp 68°-69° C (in a sealed capillary). The carbon monoxide was obtained by the reaction of sulfuric and formic acids; the purity of the CO was 99.8%.

N, N'-Diformyl-α,β'-bipiperidyl. A rotating autoclave with a capacity of 0.25 *l* was charged with 8.4 g (0.05 mole) of α,β'-bipiperidyl and 30 ml of absolute methanol containing 1.08 g (0.02 mole) of sodium methoxide, and carbon monoxide was forced in to a pressure of 130 atm. The autoclave was heated and kept at a temperature of 100° C for 2 hr. The catalyzate was filtered from the sodium carbonates that had deposited, and the elimination of the methanol gave 11.1 g (98%) of N, N'-diformyl-α,β'-bipiperidyl, mp 135° C (from benzene). Found, %: C 64.17; H 9.28; N 12.55; Mol. wt. 226. Calculated for $C_{12}H_{20}N_2O_2$, %: C 64.25; H 8.90; N 12.60; Mol. wt. 224.3.

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Institute of Chemistry AS Uzbek SSR, Tashkent