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RING-CHAIN TAUTOMERISM OF 1-BENZOYL-2-BENZYL-5-HYDROXYPYRAZOLIDINE

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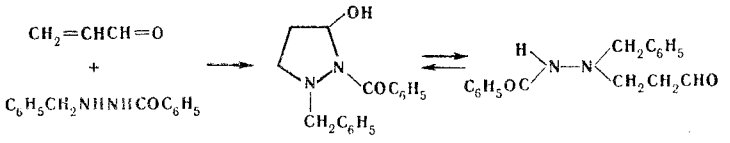
We have found that the product of the reaction of 1-benzoyl-2-benzylhydrazine with acrolein in nonpolar solvents (CCl_4, $CDCl_3$) has the cyclic 1-benzoyl-2-benzyl-5-hydroxypyrazolidine structure (A). The product was isolated in 80% yield and had mp 107°C and R_f 0.53 [activity II Al_2O_3, chloroform–methanol (50:1)]. Found: C 72.5; H 6.6; N 10.0%. $C_{17}H_{18}N_2O_2$. Calculated: C 72.3; H 6.4; N 9.9%. The IR spectrum of the product does not contain a band of vibrations of an aldehyde carbonyl group at 1700-1720 cm^{-1} but does contain a band of OH absorption at 3340 cm^{-1} and a band of "amide" carbonyl absorption at 1650 cm^{-1}. ^{13}C NMR spectrum (CFT-20, $CDCl_3$): 168.2 (s, C=O), 82.4 [d, J = 164 Hz, $C_{(5)}$], 61.7 (t, J = 142 Hz, CH_2Ph), 50.4 [t, J = 148 Hz, $C_{(3)}$], and 31.8 ppm [t, J = 136 Hz, $C_{(4)}$].* The carbon atoms of the aromatic rings give a group of signals at 127-136 ppm.

The same compound exists partially (∼10%) in linear tautomeric form B in polar solvents (d_6-DMSO, CD_3OD).



A B

The existence of the B form is proved by the appearance of an additional band of vibrations of an aldehyde carbonyl group at 1710 cm^{-1}, as well as by a set of signals corresponding to a linear structure in the PMR spectrum. PMR spectrum (Bruker WP-200, d_6-DMSO), δ: form A: 2.70-3.10 (4H, m, 3- and 4-H), 3.50 (AB system, J = 22 Hz, CH_2Ph), 5.85 (1H, broad s, OH), 6.40 (1H, m, 5-H), and 6.90-7.70 (10H, m, aromatic protons); form B: 2.55 (2H, dt, J_1 = 6 Hz, J_2 = 1.5 Hz, $COCH_2$), 3.22 (2H, t, J = 6 Hz, CH_2N), 4.08 (2H, s, CH_2Ph), 6.90-7.70 (10H, m, aromatic protons), 9.52 (1H, broad s, NH), and 9.68 ppm (1H, t, J = 1.5 Hz, CHO).

This is the first known example of tautomerism of a β-hydrazino carbonyl compound, viz., 5-hydroxypyrazolidine (A ⇄ B).

*Compare with the data presented by I. P. Bezhan, K. N. Zelenin, and V. V. Pinson in Zh. Org. Khim., 18, 493 (1982).

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