RING—CHAIN TAUTOMERISM OF 2-ALKYLAMINOTETRAHYDROPYRANS AND -FURANS

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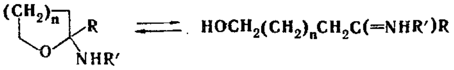
Up until recently, a 2-alkylaminotetrahydropyran structure of the Ia type was assigned to the products of the reaction of primary alkylamines with 5-hydroxypentanal [1]. We have established by means of PMR spectroscopy that in the absence of a solvent or in polar solvents these compounds actually exist in the form of a mixture of tautomers Ia and the corresponding imines Ib. Similar tautomerism is also characteristic for 2-alkylaminotetrahydrofurans (IIa, for example), which we have obtained for the first time.



I–Va I–Vb

I $n=2$, $R=H$, $R'=CH_3$; II $n=1$, $R=H$, $R'=CH_3$; III $n=2$, $R=R'=CH_3$; IV $n=1$, $R=R'=CH_3$; V $n=1$, $R=H$, $R'=$tert-C_4H_9

The position of the equilibrium depends markedly on the nature of the solvent, the ring size, the character of the substituent in the 2 position, and, to a lesser extent, on the structure of the N-alkyl group.

Thus the product of the reaction of methylamine with 4-hydroxybutanal [bp 59-59.5° (31 mm), d_4^{20} 0.9843; n_D^{20} 1.4590] in the absence of a solvent contains, at the equilibrium point, equal amounts of tetrahydrofuran IIa and imine IIb (here and subsequently all of the data pertain to 30°); in CCl_4 the concentration of the open imine form is ~15%. An increase in the ring size leads to high stability of the cyclic form (the fraction of tetrahydropyran Ia in the tautomeric mixture Ia $\rightleftharpoons$ Ib is 90% in the absence of a solvent and 100% in CCl_4). The introduction of a methyl group in the 2 position of the heteroring leads to its destabilization because of nonbonded interactions and an increase in the equilibrium concentration of the imine. Thus the ratio of IIIa and IIIb for the product of the reaction of methylamine with 6-hydroxy-2-hexanone [bp 59-60° (15 mm), d_4^{20} 0.9352, and n_D^{20} 1.4572] is 55:45, whereas the ratio of IVa and IVb is 1:2 for the analogous derivative obtained from 5-hydroxy-2-pentanone [bp 60-62° (17 mm), d_4^{20} 0.9431, and n_D^{20} 1.4585] (the data obtained in the absence of a solvent are presented). An increase in the volume of the N-alkyl group also leads to a certain destabilization of the cyclic tautomer. Thus the ratio of Va and Vb for tert-butyl-substituted V [bp 72-73° (14 mm), d_4^{20} 0.9033, and n_D^{20} 1.4495] is 1:4.

LITERATURE CITED

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