TAUTOMERISM OF 2-ACYL-3-HYDROXYISOXAZOLIDINES

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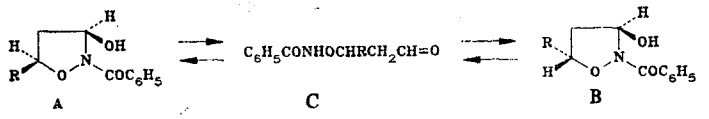
Only one example of the reaction of hydroxamic acids with α, β-unsaturated carbonyl compounds, viz., the reaction of acrolein with benzhydroxamic acid, which is used as one of the steps in the synthesis of the growth-regulating preparation canavanine, is known [1]. Cyclic structure A was assigned to this product (Ia) on the basis of the IR and PMR ($CDCl_3$) spectra, whereas, as for other 3-hydroxyisoxazolidines, A ⇄ C ring-chain tautomerism is possible for it in principle.

In slightly polar solvents (CCl_4, $CDCl_3$, d_6-acetone) Ia is actually 3-hydroxyisoxazolidine A; however, in polar solvents (CD_3OD, d_7-DMF, d_6-DMSO, d_5-pyridine) it displays a capacity for A ⇄ C tautomerism (~10-15% of form C).



Ia R = H; b R = CH_3

Compound Ia. PMR spectrum (d_7-DMF): form A: 2.20-2.65 (m, 2H, 4-H), 3.80-4.20 (m, 2H, 5-H), 5.88 (ddd, 1H, 3-H, $J_{H,OH}$ = 2, J_{34} = 5, J_{34} = 6 Hz), and 6.61 ppm (d, 1H, OH); form C: 2.14 (dt, 2H, α-CH_2, J_1 = 3.1, J_2 = 3.9 Hz), 4.12 (t, 2H, β-CH_2), 9.76 (t, 1H, CHO, J = 1.5 Hz), and 11.65 ppm (broad s, 1H, NH). A multiplet of aromatic protons of forms A and C is found at 7.1-7.9 ppm. ^{13}C NMR spectrum (d_7-DMF): form A: 37.6 (t, 4-C), 69.15 (t, 5-C), 84.6 (d, 3-C), 171.8 ppm (s, C=O); form C: 72.8 (t, α-C), 70.3, (t, β-C), 163.8 (s, NC=O), 192.4 ppm (HC=O). Six signals of C atoms of the aromatic rings of both tautomers are found at 128-135 ppm.

Chain tautomer C was not detected spectrally for Ib, which we synthesized under the same conditions as Ia (isolated in 60% yield as an oil by column chromatography; the results of analysis were in agreement with the calculated values); however, the dependence of the amounts of stereoisomers A-B on the nature of the solvent (according to the PMR data, 1:1 in $CDCl_3$ and 3:2 in d_6-DMSO) constitutes indirect evidence for its development. Equilibrium is reached instantaneously and is insensitive to temperature changes. PMR spectrum ($CDCl_3$): forms A and B: 1.3 (d) and 1.4 (d), CH_3; 1.92-2.18 (m) and 2.4 (qd, J_1 = 12.5, J_2 = 5, J_3 = 1 Hz) + 2.72 (tt, J_1 = 12.5, J_2 = 6, J_3 = 1 Hz), 4-H; 4.18 (m) and 4.67 (m), 5-H; 5.1 (broad s, OH); 6.08 (m, 3-H); 7.2-7.9 (5H, Ar). ^{13}C NMR spectrum ($CDCl_3$): forms A and B: 17.6 and 17.8 (qd, CH_3); 42.2 and 43.0 (tdd, 4-C); 76.3 and 77.9 (dm, 5-C); 81.0 and 81.6 (dd, 3-C); 166.1 and 167.3; (s, C=O); 127.5-132.6 (five signals, Ar).

The establishment of the configurations of the stereoisomers requires additional study.

LITERATURE CITED

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