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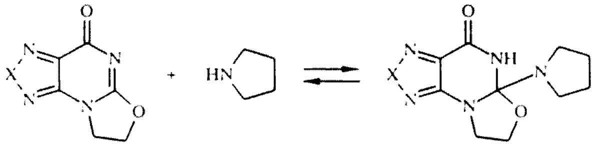
σ-COMPLEXES OF PYRROLIDINE WITH HETEROANALOGS OF PURINE

A. A. Yavolovskii, E. A. Kuklenko, V. Ya. Gorbatyuk,
É. I. Ivanov, and R. Yu. Ivanova

We have discovered that 7,8-dihydro-1,2,5-thiadiazolo[3,4-*d*]oxazolo[2,3-*b*]-7H-pyrimidin-4-one (Ia) [1] and its selenium analog (Ib) form covalent σ-complexes with secondary cyclic amines (pyrrolidine, morpholine, piperidine). The complexes with pyrrolidine (IIa and IIb), which were isolated in quantitative yield, are stable in the crystalline state.



Ia, b   IIa, b

I, II a X = S, b X = Se

^{1}H NMR spectroscopic results show that the reaction is reversible: after 7 h, a solution of complex II in $CDCl_3$ shows the spectra of free pyrrolidine and about 23% of the starting material I.

Comparison of the ^{1}H and ^{13}C NMR spectra of the starting compound Ia (DMSO-D_6): 4.47 (2H, t, J = 8 Hz, CH_2), 4.95 (2H, t, J = 8 Hz, CH_2), 44.1 and 63.42 (CH_2CH_2), 141.1 (C_5), 152.8 (C_2), 162.8 (C_4), 163.5 (C_6) with those of its σ-complex IIa: 1.95 (4H, m, $2CH_2$), 3.68 (4H, m, $2CH_2$), 3.73 (2H, t, J = 5 Hz, CH_2), 25.2 and 50.9 $(CH_2)_4$, 51.6 and 57.4 (CH_2CH_2), 142.5 (C_5), 156.7 (C_2), 158.0 (C_6), 160.3 (C_4) permits the conclusion that, apart from the effect resulting from charge transfer to the π-electron deficient heterocycle, addition of the nucleophile is accompanied by considerable redistribution of the structural deformation of the conjugated tricyclic system. Changes in the ^{13}C NMR spectrum with nucleophilic association in mono- and bicyclic structures is much simpler [2, 3].

5a-Pyrrolidino-5,5a,7,8-tetrahydro-1,2,5-thiadiazolo[3,4-*d*]oxazolo[2,3-*b*]-(7H)-pyrimidin-4-one (IIa). A two-fold excess was added to compound Ia (0.2 g, 1 mmole) in methanol (30 cm^3). During 30 min a precipitate appeared, followed by white acicular cyrstals. The precipitate was filtered off, washed with a small amount of methanol, and air-dried to give IIa (0.25 g, 95%), mp 180-182°C, M^+ 267. IR spectrum (Nujol): 3360, 1660, 1650 cm^{-1}. ^{1}H NMR spectrum (DMSO-D_6): 1.95 (4H, m, $2CH_2$), 3.68 (4H, m, $2CH_2$), 3.73 (2H, t, J = 5 Hz, CH_2), 4.37 ppm (2H, t, J = 5 Hz, CH_2). Found, %: C 44.90, H 4.90, N 26.26. Calc. for $C_{10}H_{13}N_5O_2S$, %: C 44.94, H 4.87, N 26.22.

5a-Pyrrolidino-5,5a,7,8-tetrahydro-1,2,5-selenadiazolo[3,4-*d*]oxazolo[2,3-*b*]-(7H)-pyrimidin-4-one (IIb). An excess of pyrrolidine was added to compound Ib (0.24 g, 1 mmole) in methanol (20 cm^3). After the precipitate had dissolved diethyl ether was added and the mixture was cooled. The yellowish acicular crystals which separated were filtered off and air-dried to give IIb (0.28 g, 90%), mp 180-185°C. M^+ 314. IR spectrum (Nujol): 3300, 1630, 1620 cm^{-1}. ^{1}H NMR spectrum (DMSO-D_6): 1.99 (4H, m, $2CH_2$), 3.70 (4H, m, $2CH_2$), 4.07 (2H, t, J = 5 Hz, CH_2), 4.47 (2H, t, J = 5 Hz, CH_2). Found, %: C 38.26, H, 4.20, N 22.23. Calc. for $C_{10}H_{13}N_5O_2Se$, %: C 38.22, H 4.14, N 22.29.

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A. V. Bogatskii Physico-Chemical Institute, National Academy of Sciences of Ukraine, Odessa 270080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1001-1002, July, 1996. Original article submitted May 25, 1996.

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