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LETTERS TO THE EDITOR

N–C=O ↔ N=C–O Rearrangement in the Heteroring of 4-Methyl-1-phenyl-2-(trimethoxysilylmethyl)-3-pyrazolidone

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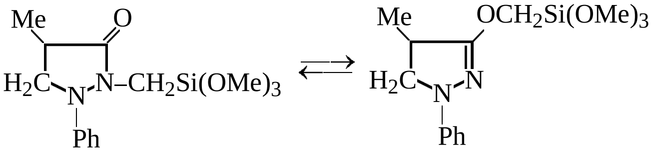
Proceeding with studies on the mutual effect of nitrogen-containing aromatic heterocycles and organosilicon substituents SiX_3 bound with them [SiX_3 = $Si(OMe)_3$, SiF_3, $Si(OCH_2CH_2)_3N$] [1], we have prepared previously unknown 4-methyl-1-phenyl-2-(trimethoxysilyl)-3-pyrazolidone (**I**) and 4-methyl-1-phenyl-2-(silatranylmethyl)-3-pyrazolidone (**II**). In the IR spectrum of the starting 4-methyl-1-phenyl-3-pyrazolidone (**III**), the band of stretching vibrations of the (N)C=O carbonyl is at 1682 cm^{-1}. The UV spectrum of compound **III** contains a strong $\pi \rightarrow \pi^*$ band of the 1-phenylpyrazolidone heteroring at 248 nm (ε 10 700). Vacuum distillation of compound **I** gave a low-boiling and a high-boiling fractions [bp 164 and 182°C (4 mm), respectively] in a 1 : 4 ratio. The IR spectra of both fractions show the above carbonyl stretching band at 1699 cm^{-1} and a new band at 1636 cm^{-1}. In the IR spectrum of the high-boiling fraction the latter band is much stronger than the carbonyl band. The UV spectrum of a solution of the low-boiling fraction in acetonitrile shows two π-π^* bands at 249 and 275 nm (2 : 1). The UV spectrum of the high-boiling fraction contains mainly a band at 275 nm (ε 11 700). The appearance of the band at 1636 cm^{-1} in the IR spectrum and of the long-wave band at 275 nm in the UV spectra of both fractions of compound **I** can be explained either by rearrangement of the –N–C=O fragment to –N=C-O– or by formation of a Si ← O(=C) donor-acceptor bond. The second assumption should be ruled out, since the UV spectra of solutions of the high-boiling fraction of compound **I** in heptane, acetonitrile, and DMSO practically coincide. The highly nucleophilic DMSO should cleave the Si ← O(=C) bond and lead to coordination of DMSO with the silicon atom. These effects would lead to a hypsochromic rather than a bathochromic shift of the $\pi \rightarrow \pi^*$ band in the UV spectrum.

The presence of the N=C–O moiety in compound **I** is caused by the n,σ^*-hyperconjugation effect in the $N–CH_2–Si(OMe)_3$ fragment, which attenuates the electron-donor power of the nitrogen atom [2]. Such rearrangement without isolation of the tautomers was detected by $^1H–(^{29}Si)$ INDOR spectroscopy in 1-(trimethylsilyl)-2-piperidone (4 : 1 N : O tautomeric ratio) [3].

The resulting data allow us to state that in compound **I** the following rearrangement takes place, favored by the n,σ^*-hyperconjugation effect.



Ia **Ib**

Treatment of the high-boiling fraction of compound **I** with triethanolamine gave silatrane **II** in 88% yield. The observation of a single C=O stretching band at 1679 cm^{-1} in the IR spectrum of compound **II** and of a band at 253 nm (ε 9500) in the UV spectrum of its acetonitrile solution gives unequivocal evidence for the formation of an *N*-substituted heteroring containing an N–C=O group. That means that in the absence of n,σ^* interaction the equilibrium for compound **II** is shifted to the left, i.e. the N–C=O ↔ N=C–O rearrangement is reversible.

4-Methyl-1-phenyl-2-(trimethoxysilylmethyl)-3-pyrazolidone (I) was obtained by the previously described procedure [4]. The total yield of the mixture of tautomers **Ia** and **Ib** was 76%. Found, %: C 57.15, 57.45; H 7.50, 7.80; N 10.10, 10.09; Si 9.52, 9.60. $C_{14}H_{22}N_2O_3Si$. Calculated, %: C 57.11; H 7.53; N 9.52; Si 9.54.

4-Methyl-1-phenyl-2-(silatranylmethyl)-3-pyrazolidone (II). Yield 88%, mp 229°C. Found, %: C 56.14, 55.99; H 6.82, 6.98; N 11.58, 11.38; Si 7.71, 7.95. $C_{17}H_{25}N_3O_4Si$. Calculated, %: C 56.17; H 6.93; N 11.56; Si 7.73.

The UV spectra of **I** and **II** in 2×10^{-3} M acetonitrile solutions were recorded on a Specord UV-Vis spectrophotometer in the range 200–350 nm. The IR spectra of compound **I** in thin layer and compound **II** in KBr pellets were measured on a Specord IR-75 spectrometer in the range 400–4000 cm^{-1}.

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