5-AMINO-2,3-DIHYDRO-1,3,4-SELENADIAZOLIUM CATIONS — THE PROTONATED FORM OF SELENOSEMICARBAZONES

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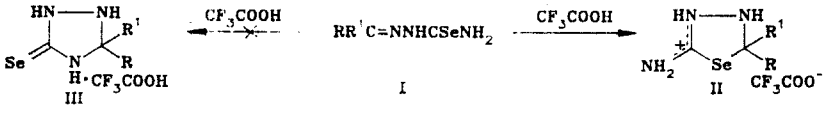
It is known that thiosemicarbazones in acidic media undergo cyclization to 1,3,4-thiadiazoline derivatives, which was proved by ^{15}N NMR spectroscopy [1]. Information regarding the structure of selenosemicarbazones in acidic media is not available, whereas they readily lose selenium under the influence of moisture in the presence of acids [2]. We have found that in anhydrous CF_3COOH selenosemicarbazones Ia,b, like their thio analogs, undergo cyclization to 1,3,4-selenadiazole derivatives IIa,b. The fact of cyclization is confirmed by the strong-field shift of the signals of substituents R and R^1 as compared with the PMR spectra of the free bases, as well as by the appearance of a C_2 signal at 74-77 ppm in the ^{13}C NMR spectra in place of the C=Se signal at 173.6 ppm. The choice between alternative structures II and III in favor of isomer II is based on the appearance of the absorption of a C=N bond in the IR spectra at 1635-1640 cm^{-1}, on the presence of the signal of a $C=N^+$ carbon atom at 180-182 ppm in the ^{13}C NMR spectra, and on the analogy between the spectral data for cations II and the data for the products of cyclization of thiosemicarbazones in CF_3COOH [1].



I—III a R=H, R^1=Ph; b R=R^1=Me

Compound Ia. This compound had mp 161-163°C [3]. PMR spectrum ($CDCl_3$): 7.11 (2H, broad s, NH_2), 7.30-7.74 (5H, m, H_{arom}), 8.12 (1H, s, CH=N), 10.57 ppm (1H, s, NH). ^{13}C NMR spectrum [$CDCl_3$ + d_6-DMSO (1:1)]: 127.2, 128.3, 130.2, 132.8 (C_{arom}); 145.0 (C=N); 173.6 ppm (C=Se).

Compound Ib. This compound had mp 178°C [4]. PMR spectrum ($CDCl_3$): 1.93 and 1.97 (6H, s, CH_3); 7.68 (2H, broad s, NH_2); 9.29 ppm (1H, s, NH).

Salt IIa. PMR spectrum (CF_3COOH): 6.87 (1H, s, CH), 7.32-7.64 ppm (5H, m, C_6H_5). ^{13}C NMR spectrum (CF_3COOH): 77.1 (C_2); 127.6, 129.3, 130.8, 131.7 (C_{arom}); 180.6 ppm ($C=N^+$).

Salt IIb. PMR spectrum (CF_3COOH): 1.96 (6H, s, $2CH_3$). ^{13}C NMR spectrum (CF_3COOH): 26.9 (CH_3), 74.0 (C_2), 181.9 ppm ($C=N^+$).

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