RECYCLIZATION OF 5-AMINO-1,2,3-THIADIAZOLE-4-CARBOTHIOAMIDES

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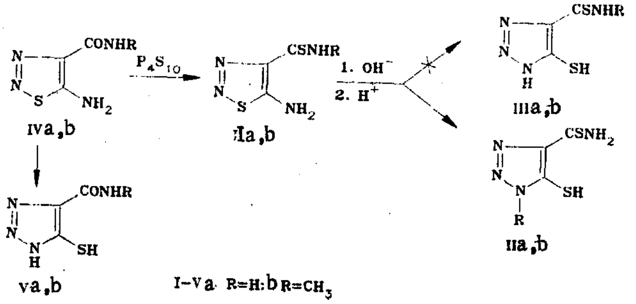
It is known that 5-amino-1,2,3-thiadiazoles undergo recyclization to 5-mercapto-1,2,3-triazoles in basic media [1, 2]. This rearrangement proceeds like the Dimroth reaction and includes deprotonation of the amino group, cleavage of the N—S ring bond, and 180° rotation about the $C_{(4)}-C_{(5)}$ bond with subsequent cyclization of the resulting α-diazo thioamides to mercaptotriazoles.



I–Va R=H; b R=CH_3

We have observed that 5-amino-1,2,3-thiadiazole-4-carbothioamide derivatives Ia,b are also converted to 5-mercapto-1,2,3-triazoles under these conditions. However, in contrast to the recyclization described above, this process takes place with the participation of the nitrogen atom of the carbothioamide group and leads to thioamides IIa,b rather than IIIa,b. The mechanism of the described transformation is under investigation.

Triazoles IIa,b and Va,b were obtained by the action of aqueous solutions of bases such as ammonia, carbonates, hydrocarbonates, and alkalies on the corresponding thiadiazoles Ia,b and IVa,b. After acidification of the reaction mass to pH 1, the precipitated triazole was removed by filtration and recrystallized from water.

The structure of thioamide IIb was confirmed by the PMR spectral data. In contrast to triazole Vb, the spectrum of which contains a doublet at 3.14 ppm, in the spectrum of IIb the protons of the methyl group show up in the form of a singlet at 3.9 ppm.

Starting 5-amino-1,2,3-thiadiazole-4-carbothioamides Ia,b were obtained by thionation of the corresponding carboxamides Ia,b [3] with P_4S_{10} in dioxane. The structures of Ia,b were confirmed by the IR, PMR, ^{13}C NMR, and mass spectra.

The individuality of the synthesized compounds was confirmed by thin-layer chromatography (TLC) on Silufol UV-254 plates. Compounds Ia,b and IIa,b had the following characteristics [compound, yield (%); mp (°C); IR spectrum (KBr) (cm^{-1}); PMR spectrum (in d_6-DMSO) (ppm); ^{13}C NMR spectrum (in d_6-DMSO) (ppm); mass spectrum (m/z) (relative intensity of four peaks, %)]: Ia, 32; 171-172; 3400, 3300, 3190 (NH_2), 1625; M^+ 160 (100), 132 (33), 105 (33), 67 (26); Ib, 25; 185-186; 3300, 3200 (NH_2), 1580; 3.14 (3H, d, J = 5.5 Hz, CH_3), 8.92 (2H, s, NH_2); 31.06 (CH_3), 136.92 [$C_{(4)}$], 167.24 [$C_{(5)}$], 184.66 (C=S); M^+ 174 (100), 117 (20), 105 (24), 74 (17); IIa, 80; 208; 3390, 3200 (NH_2), 1600; M^+ 160 (100), 143 (16), 127 (20), 60 (24); IIb, 98; 147-148; 3265; 3210 (NH_2); 3.90 (3H, s, CH_3); M^+ 174 (100), 105 (9), 81 (13), 60 (14).

The results of elementary analysis for Ia,b, IIa,b, and Va,b were in agreement with the calculated values.

LITERATURE CITED

1. G. L'Abbe, J. Heterocycl. Chem., 21, 627 (1984).

S.M. Kirov Ural Polytechnic Institute, Sverdlovsk 620002. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1429-1430, October, 1985. Original article submitted February 18, 1985.

0009-3122/85/2110-1180$09.50

2. M. Uher, A. Rybar, A. Martvon, and J. Leško, Collect. Czech. Chem. Commun., 41, 1551 (1976).
3. Yu. M. Shafran, V. A. Bakulev, V. S. Mokrushin, and Z. V. Pushkareva, Khim. Geterotsikl. Soedin., No. 12, 1696 (1982).

OPENING OF 6,7-DIHYDROIMIDAZO[1,2-f]XANTHINES BY THE ACTION OF HYDRAZINE HYDRATE

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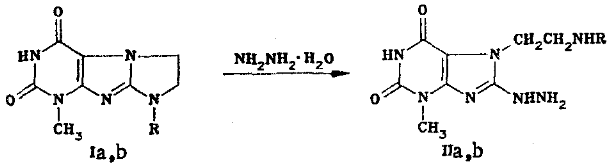
We have found that prolonged heating (for 10-30 h) of 1-methyl-3H-8-phenyl-6,7-dihydroimidazo[1,2-f]xanthine (Ia) and 1-methyl-3H-8-(p-tolyl)-6,7-dihydroimidazo[1,2-f]xanthine (Ib) [1] in excess hydrazine hydrate leads to opening of the imidazoline ring to give hydrazinoxanthines IIa,b.



I,II a R=Ph; b R=$C_6H_4CH_3$-p

Structure II was assigned to the products of the hydrazinolysis reaction on the basis of data from the IR and PMR spectra. The presence of a hydrazino group is also confirmed by the reaction of IIa,b with aromatic aldehydes, as a result of which brightly colored hydrazones are formed.

3-Methyl-7-(β-phenylaminoethyl)-8-hydrazinoxanthine (IIa). This compound, with mp 208-210°C (decomp., from water), was obtained in 78% yield. IR spectrum (mineral oil): 3350 (NH_2); 1690, 1680 (C=O); 1615 cm^{-1} (C=N). PMR spectrum (CF_3COOH): 3.21 (s, 3H, NCH_3), 3.73 (t, 2H, CH_2–NH), 4.41 (t, 2H, 7-N–CH_2), and 7.14 ppm (s, 5H, C_6H_5).

3-Methyl-7-[β-(p-tolylaminoethyl)]-8-hydrazinoxanthine (IIb). This compound, with mp 223-225°C (from dioxane), was obtained in 56% yield. IR spectrum (mineral oil): 3395 (NH_2); 3140 (NH); 1655, 1650 (C=O); 1600 cm^{-1} (C=N). PMR spectrum (CF_3COOH): 1.88 (s, 3H, CH_3), 3.10 (s, 3H, NCH_3), 3.63 (t, 2H, CH_2NH), 4.25 (t, 2H, 7-N–CH_2), and 6.83 ppm (s, 4H, aromatic).

LITERATURE CITED

1. B. A. Priimenko, N. I. Romanenko, S. N. Garmash, N. I. Gnatov, and A. K. Sheinkman, Khim. Prir. Soedin., No. 5, 623 (1980).

Zaporozhe Medical Institute, Zaporozhe 330074. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1430-1431, October, 1985. Original article submitted February 21, 1985.

0009-3122/85/2110-1181$09.50