ISOMERIZATION OF 1,2,4-OXADIAZOLE-3-CARBOXAZIDOXIMES

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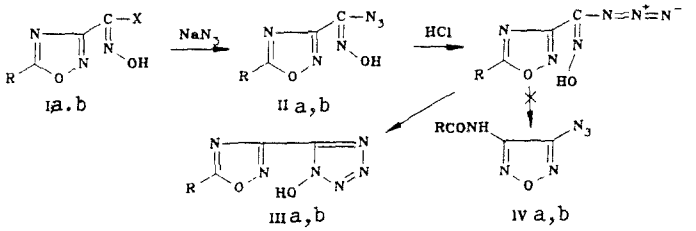
UDC 547.793.3'796.1.07

We have previously shown that Z,E-isomerization of functionally substituted oximes, which are formed upon reaction of 1,2,4-oxadiazole-3-carbohydroxamic acid halides (Ia, b) with nucleophiles, is accompanied by rearrangement involving cleavage of the 1,2,4-oxadiazole ring and ring closure to a 1,2,5-oxadiazole [1, 2]. Studying the behavior under the same conditions of azidoximes II, which are obtained via the reaction of halooximes I with sodium azide, we have found that Z,E-isomerization of the oxime group, which occurs upon treatment with hydrogen chloride in ether solution, is not accompanied by rearrangement, but rather leads to ring closure to give a tetrazole:



I–IV a R=H, X=Cl; b R=CF_3, X=Br

The structures of the new products were established on the basis of their IR and PMR spectral data, which were missing signals due to the amide and azide groups, but which contained signals indicative of the presence of oxadiazole [3] and tetrazole rings [4].

1,2,4-Oxadiazole-3-carboxazidoxime (IIa, $C_3H_2N_6O_2$). mp 154-156°C. IR spectrum: 3000-3200 (OH), 3105 (cycl CH), 2143 (N_3), 1612 (C=N), 895 cm^{-1} (oxadiazole). PMR spectrum (DMSO-D_6): 9.56 (1H, s, CH), 12.58 ppm (1H, s, OH).

5-Trifluoromethyl-1,2,4-oxadiazole-3-carboxazidoxime (IIb, $C_4HF_3N_6O_2$). mp 118-120°C. IR spectrum: 3330 (OH), 2175 (N_3), 1615 (C=N), 1150-1250 (CF_3), 898 cm^{-1} (oxadiazole). PMR spectrum (DMSO-D_6): 12.87 ppm (1H, s, OH).

5-(1,2,4-Oxadiazolyl-3)-1-hydroxytetrazole (IIIa, $C_3H_2N_6O_2$). mp 129-131°C. IR spectrum: 3120 (cycl CH), 3050 (OH), 1408 and 1352 (tetrazole), 912 cm^{-1} (oxadiazole). PMR spectrum (DMSO-D_6): 9.91 ppm (1H, s, CH).

1-Hydroxy-5-(5-trifluoromethyl-1,2,4-oxadiazolyl-3)tetrazole (IIIb, $C_4HF_3N_6O_2$). mp 107-109°C. IR spectrum: 3180 (OH), 1420 and 1341 (tetrazole), 1150-1250 (CF_3), 916 cm^{-1} (oxadiazole).

LITERATURE CITED

1. V. G. Andrianov, V. G. Semenikhina, and A. V. Eremeev, Khim. Geterotsikl. Soedin. (in press, 1990).
2. V. G. Andrianov, V. G. Semenikhina, and A. V. Eremeev, Khim. Geterotsikl. Soedin. (in press, 1990).
3. L. B. Clapp, Adv. Heterocycl. Chem., 20, 65 (1976).
4. K. Schofield, M. R. Grimmett, and B. R. T. Keane, The Azoles, Cambridge University Press, Cambridge (1976), p. 14.

Institute of Organic Synthesis, Academy of Sciences of the Lativan SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1700-1701, December, 1989. Original article submitted May 30, 1989.

0009-3122/89/2512-1419$12.50