REARRANGEMENTS OF 5-TRIFLUOROMETHYL-1,2,4-OXADIAZOLES BY ACTION OF AMMONIA AND AMINES

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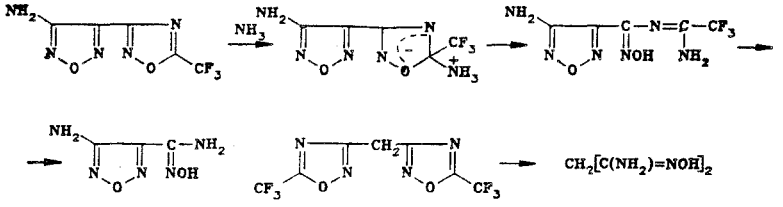
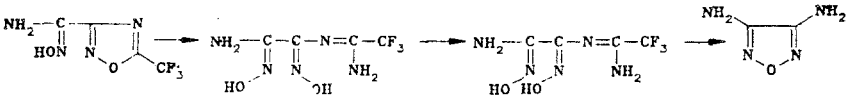
It is known that the trichloromethyl group at the 5-position of the 1,2,4-oxadiazole ring is readily substituted by the action of amines with the formation of 5-amino-1,2,4-oxadiazoles [1]. In the study of the properties of 5-trifluoromethyl derivatives, we found that the trifluoromethyl group is not substituted under these conditions, but that splitting of the oxadiazole ring takes place:



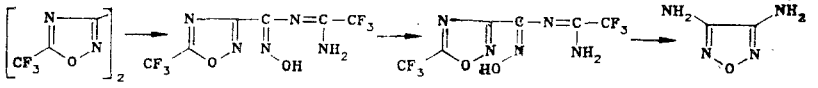
The reaction with morpholine and hydrazine proceeds similarly. It is possible that while in the case of trichloromethyl derivatives, the intermediate complex splits through rupture of the C-CCl_3 bond, in the case of trifluoromethyl analogs a rupture of the C–O bond takes place with consequent formation of amidoximes.

If there is an amidoxime group in the 3-position of the oxadiazole ring, the reaction leads to diaminofurazan:



This reaction resembles a monocyclic rearrangement [2]. However, a monocyclic rearrangement proceeds via the stage of an acid-catalyzed isomerization of the oxime group, followed by a synchronous opening of the oxadiazole, and closure of the furazan ring. In the case of a trifluoromethyl derivative, it is most probable that first the oxadiazole ring opens by the action of an amine, and then the oxime group Z, E-isomerizes with closing of the furazine ring. A substantial difference between the schemes is the fact that in the first case an oxygen atom from the oxime group appears in the furazane ring, and in the second case the oxygen atom comes from the oxadiazole ring.

Under similar conditions, the diaminofurazane is also formed from bis(5-trifluoromethyl-1,2,4-oxadiazol-3-yl)



In this case after opening of one of the oxadiazole rings, the reaction may proceed by a monocyclic rearrangement mechanism.

LITERATURE CITED

1. L. B. Clapp, Adv. Heterocycl. Chem., 20, 65 (1976).
2. M. Ruccia, N. Vivona, and D. Spinelli, Adv. Heterocycl. Chem., 29, 141 (1981).

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