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σ-ADDUCTS IN THE 1,2,4-OXADIAZOLE SERIES

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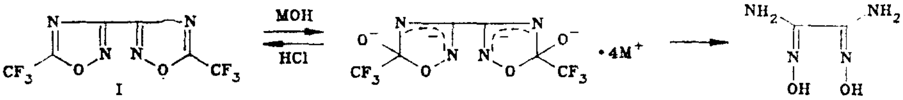
It is known that the 5-trichloromethyl group in 1,2,4-oxadiazoles is readily replaced under the influence of nucleophiles, particularly alkalis [1]. We have established that, in contrast to the trichloromethyl derivative, bis(5-trifluoromethyl-1,2,4-oxadiazol-3-yl) reacts with alkalis to give stable anionic σ-adducts, which were previously unknown in the 1,2,4-oxadiazole series [2].



I

M = Na, K

Owing to the strongly expressed electron-acceptor properties of the oxadiazole ring and the trifluoromethyl group, the acidities of the hydroxy groups in the σ adduct are so high that they are ionized in alkaline solution. Thus a precipitate of the tetrapotassium or tetrasodium salt of bis(5-hydroxy-5-trifluoromethyl-1,2,4-oxadiazol-3-yl) is formed in 67% of 73% yield, respectively, in the reaction of 5 mmoles of I with a solution of 30 mmoles of KOH or NaOH in 50 ml of alcohol for several minutes. The salts melt above 300°C. The results of elementary analysis for C, H, and N were in agreement with the calculated values.

The reaction involving the formation of the adduct is reversible: the starting bis(oxadiazolyl) I, with mp 138°C (from alcohol), is formed in 55% yield when a solution of 5 mmole of the adduct in 5 ml of water is treated with hydrochloric acid to pH 3-4. The adduct gradually decomposes during storage; the process takes place faster in aqueous solution – in a few days. However, products of ordinary nucleophilic substitution are not formed in this case, since cleavage of the ring C–O bond, which ultimately leads to a diaminoglyoxime, rather than cleavage of the C–CF_3 bond occurs.

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