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LETTERS TO THE EDITOR

ACID HALIDES OF 4-AMINOFURAZAN-3-CARBOHYDROXAMIC ACIDS

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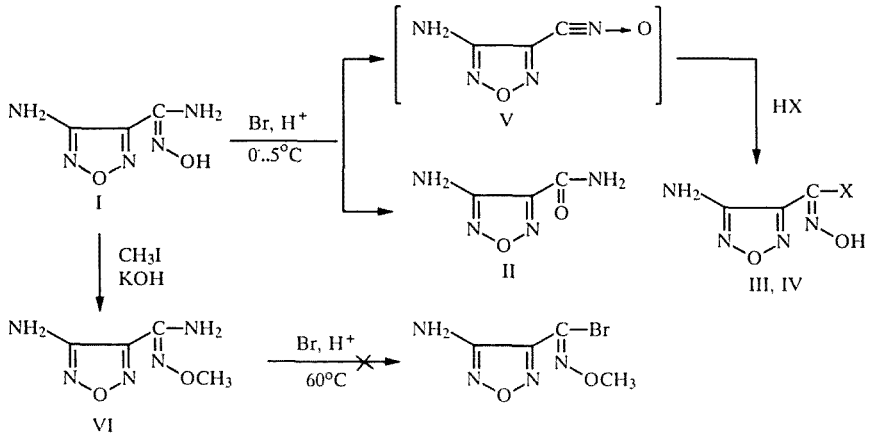
Reaction of benzamidoxime with bromine initially gives O-(N-acetylbenzimidoyl)benzamidoxime, further reaction of which may give 3,5-diphenyl-1,2,4-oxadiazole or benzonitrile [1-3].

We have established that reaction of 4-aminofurazan-3-carboxamidoxime I with bromine in sulfuric or hydrobromic acid solution initially gave two compounds. One — the product of deoximation of the original amidoxime — was 4-aminofurazan-3-carboxamide (II) while the second was 4-aminofurazan-3-carbohydroxamoyl bromide (IV).



III X = Cl, IV X = Br

The acid chloride III was obtained when the reaction was carried out in hydrochloric acid solution. In our view formation of the halogenooximes occurs via deamination of the initial amidoxime to give an intermediate nitrile oxide V which then adds a molecule of hydrogen halide to give the halogenooximes III and V. The suggestion that a nitrile oxide is formed as an intermediate is confirmed by the observation that the O-methylamidoxime VI did not react with bromine even at raised temperatures.

Compounds III and V contain both halogenooxime and primary amino groups which are normally very reactive towards one another. This also applies to the nitrile oxide V. Doubts had been raised previously [4] that nitrile oxides containing functional groups in the molecule could exist. The reason for the stability of halogenooximes III and IV is the low nucleophilicity of an amino group bonded to the electron accepting furazane ring.

Compound III. M.p. 200-201°C (from an ethanol water mixture). ^{1}H NMR Spectrum (here and below in DMSO-D_6): 5.69 (2H, s, NH_2), 12.38 (1H, s, OH). IR Spectrum: 3461, 3331 (NH_2), 3246 (OH), 1630 (C=N), 1012 (furazane).

Compound IV. M.p. 200-201°C (from an ethanol water mixture). ^{1}H NMR Spectrum: 5.69 (2H, s, NH_2), 12.38 (1H, s, OH). IR Spectrum: 3453, 3326 (NH_2), 3220 (OH), 1620 (C=N), 1010 (furazane).

Compound VI. M.p. 88-89°C (from water). ^{1}H NMR Spectrum: 3.72 (3H, s, CH_3), 6.24 (2H, s, NH_2), 6.39 (2H, s, NH_2). IR Spectrum: 3427, 3327, 3210 (NH_2), 1005 (furazane).

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