The process probably takes place through the stage of the formation of the carboxylic acid chloride, which acylates the hydrazine hydrochloride to the diacylhydrazine which then cyclodehydrates under the action of the phosphorus oxychloride with the formation of the oxadiazole.

We have obtained, by this method, for example 2, 5-diethyl-1, 3, 4-oxadiazole [yield 50%, mp 78°—79° C, (12 mm), d_4^{20} 1.0180, n_D^{20} 1.4463. Found, %: C 57.00; H 7.88%. Calculated for $C_6H_{10}N_2O$, %: C 57.12; H. 7.99] and 2, 5-di(n-amyl)-1, 3, 4-oxadiazole [yield 67%, bp 150°—152° C (10 mm), d_4^{20} 0.9308, n_D^{20} 1.4528. Found, %: C 68.79; H 10.83. Calculated for $C_{12}H_{22}N_2O$, %: C 68.53; H 10.54]. The corresponding oxadiazoles have also been obtained from butyric, isobutyric, and valeric acids.

When the reaction mixture was treated with phosphorus pentachloride, the amount of undistillable residue was reduced through the regeneration of the phosphorus oxychloride from the product of its partial hydrolysis and the yields of the oxadiazoles were increased.

The application of this method to acetic acid was unsuccessful, evidently because of the high volatility of acetyl chloride. However, 2, 5-dimethyl-1, 3, 4-oxadiazole can be obtained by the action of phosphorus oxychloride on N, N'-diacetylhydrazine, but satisfactory yields (about 86%) can be achieved only when the reaction mixture is treated with phosphorus pentachloride. The 2, 5-dimethyl-1, 3, 4-oxadiazole obtained had bp 63° C (10 mm), d_4^{20} 1.0963, n_D^{20} 1.4441. Found, %: C 48.82; H 6.09. Calculated for $C_4H_6N_2O$, %: C 48.96; H 6.16. This compound was also obtained in low yield by boiling a solution of diacetylhydrazine and thionyl chloride in dioxane. In this case, the diacetylhydrazine can be replaced by a mixture of anhydrous hydrazine and acetic acid.

The method described of the one-stage conversion of carboxylic acids into oxadiazoles can also be applied to aromatic acids. Thus, benzoic acid gave a 47% yield of 2, 5-diphenyl-1, 3, 4-oxadiazole with mp 136°—137° C. It was isolated by pouring the residue from the distillation of the excess of phosphorus oxychloride into water.

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THE SYNTHESIS OF N-SUBSTITUTED β-(5-AMINO-2-FURYL) NITROOLEFINS

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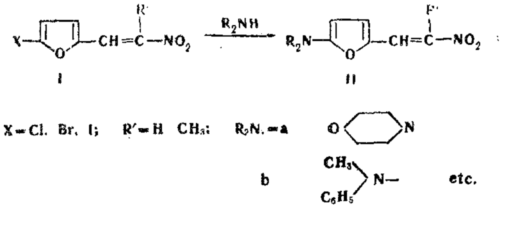
Studying nucleophilic substitution reactions in a number of β-(5-halo-2-furyl)nitroolefins (I) with secondary amines, we have shown for the first time the possibility of synthesizing the previously unknown N-substituted β-(5-aminofuryl)nitroolefins (II). We have found that the smoothest substitution reaction takes place in the case of the 5-halofurylnitropropenes (I, R = CH_3) with morpholine and methylaniline when their alcoholic solutions are heated.



1-(5-Morpholino-2-furyl)-2-nitro-1-propene (IIa), lustrous dark red needles, mp 170°—171° C (from ethanol). Found, %: C 56.27; 56.50; H 6.05; 6.04; N 11.92; 12.02. Calculated for $C_{11}H_{14}N_2O_4$, %: C 56.46; H 5.92; N 11.76. λ_{max} 480 nm, log ε 4.33.

1-[5-(N-Methyl-N-phenylamino)-2-furyl]-2-nitro-1-propene (IIb), almost black lustrous crystals with a green tinge, mp 128° C (from ethanol). Found, %: C 65.33; 65.27; H 5.70; 5.59; N 10.97; 10.92. Calculated for $C_{14}H_{14}N_2O_3$, %: C 65.09; H 5.46; N 10.84. λ_{max} 490 nm, log ε 4.26.

The structure of the substitution products was also confirmed by indirect synthesis from the corresponding N-substituted-5-aminofuraldehydes [1]. The products were shown to be identical by comparing their UV and IR spectra.

With pyridine, dimethylamine, and diethylamine, the double bond of the olefin also underwent nucleophilic attack.

In the case of 5-bromofurylnitroethylene, the reaction with amines (dimethylamine, diethylamine, piperidine, and morpholine), like the reaction with $Na_2S_2O_3$ [2, 3], leads to products of the polymerization of the initial olefin. The reaction takes place so vigorously that the reaction mixture sometimes spontaneously inflames. The amines mentioned also cause the polymerization of unsubstituted furylnitroethylene (I, R = = X = H).

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