LETTERS TO THE EDITOR

A STUDY OF THE REACTION MECHANISM OF THE CATALYTIC INTRAMOLECULAR CONVERSION OF HETEROCYCLES

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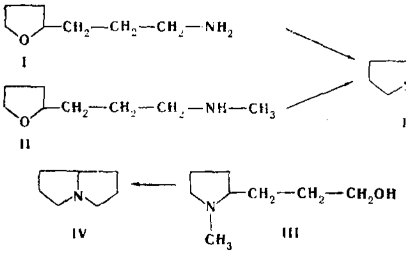
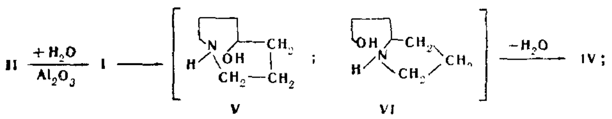
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 6, p. 1127, 1967

UDC 547.722.3'743.1:542.936:543.422.4

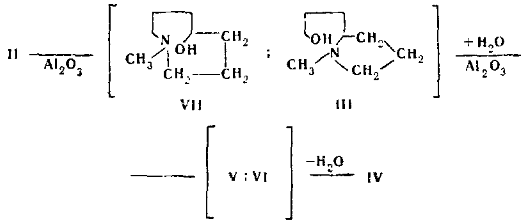
In order to study the reaction mechanism of the catalytic intramolecular conversion of heterocycles [1-3] and to broaden the field of their application, we have studied the dehydration over Al_2O_3 of 1-amino-3-(α-tetrahydrofuryl) propane (I), 1-methylamino-1-(α-tetrahydrofuryl) propane (II), and 2-(3-hydroxy-1-propyl)-1-methylpyrrolidine (III), leading in all three cases to pyrrolizidine (IV).



Bearing in mind the general laws given by Yu. K. Yur'ev [4], it is possible to envisage the formation of IV from II by two possible routes which do not exclude one another: 1) the conversion of II into I by catalytic demethylation of the secondary amino group with subsequent dehydration to IV through either or both of V and VI.



2) the catalytic isomerization of II into VII and III and their demethylation to V and VI with subsequent dehydration to IV.



To confirm the possibility of the second route via III, we have subjected the latter to dehydration. Of course, the successful dehydration of III does not exclude the variant II → [VII] → [V] → IV. The choice between the first and second routes requires further study.

IV (from I). Yield 65.9%. Bp 70.5-71.5° C (60 mm), 97-99° C (161 mm), 145-146.5° C (765 mm), d_4^{20} 0.9149; n_D^{20} $1.4700^{5 \cdot 6}$. Found, %: C 75.41; 5.64; H 11.86; 12.09%; MR_D 33.90. Calculated for $C_7H_{13}N$, %: C 75.61; H 11.79; MR_D 34.07. **Picrate:** mp 257.5-259° C (decomp, from ethanol) [5, 6]. Found, %: N 16.00; 16.03. Calculated for $C_7H_{13}N \cdot C_6H_2(NO_2)_3OH$, %: N 16.47. Compound **IV** was obtained from **II** with a yield of 58.6% and from **III** with a yield of 51.6%.

The IR spectrum of the samples of **IV** obtained from **I**, **II**, and **III** were identical and the picrates were identical (absence of a depression of the melting point in mixed samples).

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3 June 1966

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THE PREPARATION OF 1,3,4-OXADIAZOLES

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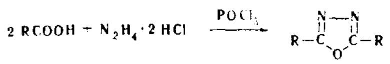
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 6, p. 1128, 1967

UDC 547.793:547.29:546.185

We have found that 2,5-dialkyl-1,3,4-oxadiazoles, which are difficult of access and have scarcely been studied, can be obtained in a single stage from carboxylic acids and hydrazine hydrochloride by heating them in boiling phosphorus oxychloride with subsequent fractional distillation of the reaction mixture.



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.

25 June 1966

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

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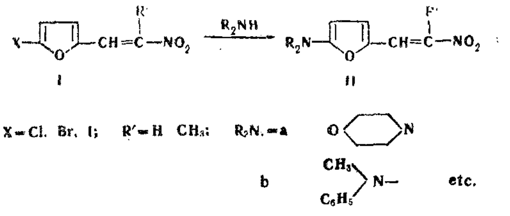
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 6, pp. 1128–1129, 1967

UDC 547.722.4.607:543.422.4.6:542.958.3

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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9 July 1966

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