SYNTHESIS OF 1-SUBSTITUTED TETRAZOLES BY HETEROCYCLIZATION OF PRIMARY AMINES, ORTHOFORMIC ESTER, AND SODIUM AZIDE

P. N. Gaponik, V. P. Karavai, and Yu. V. Grigor'ev UDC 547.796.1.07

It has been shown that the reaction of heterocyclization of primary amines with orthoformic acid and sodium azide in acetic acid has a rather general character and is a convenient method for the synthesis if 1-substituted tetrazoles. On the basis of experimental data, a probable reaction mechanism is proposed.

Methods for preparing 1-substituted tetrazoles, which are valuable intermediates in the synthesis of pharmaceuticals [1, 2], have not been worked out adequately [3]. The procedures are generally tedious and they require the use of volatile, toxic substances. It has recently been shown in certain examples [4-6] that the interaction of a primary amine, orthoformic ester, and sodium azide leads rapidly and smoothly to a 1-substituted tetrazole.

In the present work, we have attempted to extend this method to a broad circle of amines, and we have shown that the reaction has a rather general character and is a convenient preparative route for the synthesis of various 1-substituted tetrazoles:

$$R-NH_2 + HC(OC_2H_5)_3 + NeN_3 \xrightarrow{CH_3COOH} N_N Ia-m$$

In the case of a bifunctional amine, as shown in the example of ethylenediamine, the interaction involves both NH_2 groups, forming 1,2-bis(1-tetrazoly1)ethane (In). Even when the process parameters were varied, we could not restrict the reaction to one amino group only, which would have given 1-(2-aminoethy1)tetrazole. Also, with hydroxylamine, melamine, or hydrazine, we were unable to obtain clear-cut results or to isolate any individual substances, even though the benzaldehyde derivative of hydrazine readily gives 1-aminotetrazole in a side reaction [7].

The same as in the case of ethanolamine [6], a slow reaction begins even at room temperature; however, in order to obtain a rapid, controlled reaction, temperatures of $80-100^{\circ}$ are required for most of the amines; at these temperatures, the interaction is completed in 2-3 h, with good yields (Table 1). Studies of the yields of the tetrazoles in relation to the reaction temperature showed that the less basic amines, under otherwise equal conditions, are more resistant to reaction (see Fig. 1 for typical curves). In such cases, the yields of the desired tetrazoles can be increased by extending the time of interaction (up to 5-6 h) and by raising the temperature ($100-110^{\circ}$). Amine salts such as nitrates, sulfates, oxalates, and hydrochlorides can be used in place of the free amines and are preferable, since the isolation of the tetrazole product is easier when the salts are used. The course of the reaction and the product yields are influenced by the order in which the components are introduced. The optimal sequence is the addition of the acid to a mixture of the amine and azide in the ortho ester, as this avoids clotting of the reaction mixture and loss of the aziding agent in the form of HN₃; the best results are obtained with 6-8 moles of acid per mole of amine.

With the aim of studying the mechanism of this reaction, we carried out a detailed investigation of the process in the examples of aniline and ethanolamine; we found that in

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31259,04 $\binom{0,01}{(c_{15},H)}, \binom{1,11}{5,34m}, \binom{1,11}{5,3m}, \binom{1,11}{2,3m}, \binom{1,11}{2,$	1021, 1069, 1107 1011, 1081, 1102	1107 1102	3070 3123	9,08 8,92	(2H), 1,64 t (α 2H), 1,96 n 1,80 n (γ 2H	37,0 47,2	6,3 8,0	56,5 44,7	C ₃ H ₆ N ₄ C ₅ H ₁₀ N ₄	36,8 47,7	6,1 7,9	57,1 44,4	88
3150 9.25 $\frac{3.22}{1.50}$ d (27H), 3,80 t 34,4 5,1 39,4 C,4H_6N,O_2 33,9 4,2 39,4 3130 9,28 4,84 t (22H), 3,60 t 42,6 7,6 49,7 C_6H_1N_5 42,6 7,8 49,6 3137 9,51 4,73 t (22H), 3,80 t 42,6 7,8 42,6 7,8 49,6 3137 9,51 4,27 t (32H), 2,68 s (6H) 26,0 3,7 70,1 C_6H_1N_5 25,9 3,6 70,5 3155 9,80 4,36 s (6H) 2,6,0 3,0 24,6 C_6H_5N_4 26,1 3,1 24,4 3143 9,24 4,47 s (H), 4,24 s (6H) 34,2 5,6 3,2,5 C_6H_0N_0S 34,5 5,7 32,2 3143 9,24 4,47 s (H), 4,24 s (6H) 34,2 5,6 3,6,7 C,H_5N_6 34,5 5,7 32,2 3156 9,48 8,00 m (4H) 34,2 5,7 23,2 34,5 5,7 32,2 36,6 3156 9,54 9,56 2,1 7,1,4 1,5 6,1,0N_0S 34,5 <td>1013, 1100</td> <td></td> <td>3125</td> <td>9,04</td> <td>0,90 t (201) 6,01 d (H), 5,42 m (cis-H), 5,34m (trans-H),</td> <td>43,5</td> <td>5,5</td> <td>51,1</td> <td>C4H6N4</td> <td>43,6</td> <td>5,5</td> <td>50'3</td> <td>84</td>	1013, 1100		3125	9,04	0,90 t (201) 6,01 d (H), 5,42 m (cis-H), 5,34m (trans-H),	43,5	5,5	51,1	C4H6N4	43,6	5,5	50'3	84
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3143 9,24 4,47 s (H), 4,24 s (6H) 34,2 5,6 32,5 CeH ₀ N ₄ O ₃ 34,5 5,7 32,2 3156 9,97 7,36-7,64 m (5H) 57,8 4,2 38,0 CH ₆ N ₄ 57,5 4,1 38,4 3156 9,48 8,00 m (4H) 57,8 4,2 26,6 36,7 CH ₉ N ₅ O ₂ 4,4,0 2,6 36,6 36,6 36,6 36,7 CH ₉ N ₅ O ₂ 4,1 38,4 38,6 36,6 36,6 36,7 CH ₉ N ₅ O ₂ 4,1 38,4 36,6 36,6 36,7 CH ₉ N ₅ O ₂ 2,6 36,6 3,6 6,7,5	955, 975, 1	075,			(h211) 4,36 s (6H)	26,0	3,0	24,6	C ₅ H ₇ Cl ₃ N ₄	26,1	3,1	24,4	75
3138 9.97 7,36-7,64 m (5H) 57,8 4,2 38,0 $C_{H6}N_4$ 57,5 4,1 38,4 3156 9,48 8,00 m (4H) 44,2 2,6 36,7 $C_{H5}N_5O_2$ 44,0 2,6 36,5 3085 9,64 9,52 s (2H) 26,6 2,1 71,4 $C_{3}H_5N_5O_2$ 26,3 2,2 71,5 3171 8,66 - 17,4 1,5 81,1 $C_{2}H_5N_6O_2$ 26,3 2,2 71,5 3171 8,66 - 17,4 1,5 81,1 $C_{2}H_5N_6$ 17,4 1,4 81,2 3171 8,66 9,27 50,5 26,3 2,2 71,5 3120 9,27 5,05 (4H) 29,1 3,7 67,3 C ₄ H ₆ N_8 28,9 3,6 67,5	1020, 1083	, 1115,	3143	9,24	(H), 4,24 s.	34,2	5,6	32,5	C ₅ H ₁₀ N ₄ O ₃	34,5	5,7	32,2	58
3085 9,64 9,52 $(2H)$ $26,6$ $2,1$ $71,4$ $C_{3}H_{3}N_{7}$ $26,3$ $2,2$ $71,5$ 3171 $8,66$ $ 17,4$ $1,5$ $81,1$ $C_{2}H_{3}N_{8}$ $17,4$ $1,4$ $81,2$ 3120 $9,27$ $5,05_{5}$ $(4H)$ $29,1$ $3,7$ $67,3$ $C_{4}H_{6}N_{8}$ $28,9$ $3,6$ $67,5$	1018, 1084, 1084, 1078, 1	1126 1130	3138 3156		¤€	57,8 44,2	4,2 2,6	38,0 36,7	C ₇ H ₆ N ₄ C ₇ H ₅ N ₅ O ₂	57,5 44,0	4,1 2,6	38,4 36,6	82 83
3120 9,27 5,05 ₅ (4H) 29,1 3,7 67,3 C4H ₆ N ₈ 28,9 3,6 67,5	1033, 1072 983, 1017,	1025,	3085 3171		9,52 s (2H)	26,6 17,4	2,1	71,4 81,1	C ₃ H ₃ N ₇ C ₂ H ₂ N ₈	26,3 17,4	2,2	71,5 81,2	88
	1047, 1080 1025, 1100) , 1125	3120	9,27	1	29,1	3,7	67,3	C4H ₆ N ₈	28,9	3,6	67,5	60

*For compound Ib, nD²° 1.4595; for Ic, nD^{2°} 1.4605; for Id, nD^{2°} 1.4850; compound If was isolated in the hydrochloride; Ig is a nondistillable liquid that decomposes when heated above 140°.

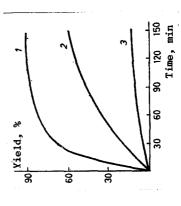
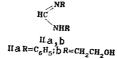
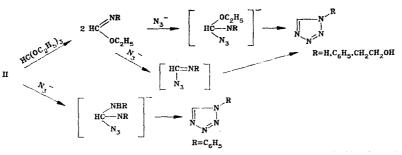


Fig. 1. Product yield in heterocyclization reaction as a function of temperature and basicity of original amine: 1) Ph-NH₂ at 90°; 2) Ph-NH₂ at 45°; 3) $p-NO_{z}$ -PhNH₂ at 45°.

both cases, the corresponding amidines IIa and IIb are formed as intermediates; these were recovered from the reaction medium in the form of the acetates.



The amidine IIa, specially prepared by a procedure given in [8], is subject to heterocyclization with sodium azide in acetic acid, forming l-phenyltetrazole. No success was achieved in performing such a reaction with compound IIb [6]: The amidine grouping in this case proved to be resistant to attack by the azide ion. Likewise, there is no reaction with the unsubstituted formamidine $HN=CH-NH_2$. In the presence of the ortho ester, however, both these reactions proceed readily, forming the corresponding tetrazoles. From these results, when we consider the literature data on the conversion of amidines to iminoesters [9], it follows that the reaction, even though it begins with the formation of the amidine, can then proceed along the following most probable paths, depending on the nature of the substituent R:



In the IR spectra of all of the tetrazoles Ia through In, along with the absorption bands of the substituents we find strong bands in the 980-1100 cm⁻¹ region that are characteristic for stretching and bending vibrations of the tetrazole ring. Also characteristic is a strong absorption band in the 3100-3150 cm⁻¹ region pertaining to stretching vibrations of the CH bond of the tetrazole ring, and, in the PMR spectra, a singlet of the 5-H proton in the 8.4-10.0 ppm region.

EXPERIMENTAL

The PMR spectra were obtained in a Jeol JNM-PS-100 spectrometer in CD₃Cl and DMSO-D6, internal standard HMDS. The IR spectra of the substances were taken in a thin layer (liquids) or in KBr tablets (solids) in UR-20 and Specord IR-75 spectrophotometers. The individuality of the compounds was also monitored by means of TLC on plates of the Silufol UV-254 type.

<u>Tetrazoles Ia through In.</u> To a suspension of 0.1 mole of the amine or its hydrochloride, sulfate, nitrate, or oxalate and 7.8 g (0.12 mole) of NaN₃ in 22 ml (0.15 mole) of ethyl orthoformate, 35-50 ml of glacial acetic acid was added while stirring, and the mixture was heated while stirring on a boiling water bath for a period of 2.5-3 h. Then the reaction mixture was cooled; if the free amines were used, 0.12 mole of concentrated HCl was added, and the mixture was filtered. The filtrate was evaporated under vacuum, and the residue was extracted with hot ethanol (If,g,i, 7 ,m), acetone (Ih,n), or ethyl acetate (Ie). The solvent was driven off, and the crude product was recyrstallized from ethanol (If, 7 ,n), 2-propanol (Ij,k,m), or ethyl acetate (Ie,h), or it was vacuum-distilled (Ia,b,c,d) or purified by adduct formation (Ig,k) [10]. In the synthesis of compounds Ig and Ik, after evaporating down the reaction mixture, a 3-5% HCl solution was added to the residue. The precipitate that formed was separated by filtration, washed with water, and dried.

<u>1-Phenyltetrazole (Ij).</u> To a mixture of 0.1 mole of the amidine IIa and 0.12 mole of NaNH₃, 50 ml of glacial acetic acid was added while stirring, and the mixture was then stirred for 2-2.5 h at 95-100°. The resulting mixture was cooled and filtered. The filtrate was evaporated under vacuum, and a 3% aqueous HCl solution was added to the residue. The precipitated cyrstals were filtered off, dried, and recrystallized from 2-propanol. Sometimes, after the aqueous HCl solution was added, the 1-phenyltetrazole separated out in the form of an oil, which crystallized in 3-4 h. Yield 52-55%.

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SYNTHESIS AND INVESTIGATION OF STYRYL DERIVATIVES OF 5,6-BENZO-2,2'-DIQUINOLYL

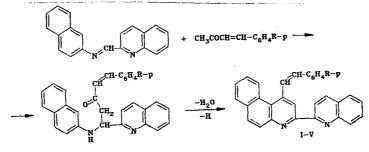
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A. L. Gershuns, * A. A. Verezubova L. M. Ptyagina, and Z. M. Nartova

By catalytic condensation of quinolidene- β -naphthylamine with benzalacetone and its derivatives, previously undescribed styryl-5,6-benzo-2,2'diquinolyls have been synthesized. Complexes of these compounds with univalent copper ions have been studied, the spectral characteristics of the reagents and complexes have been reported, and a hypothesis has been advanced on the relationship between the structure of the ligands and the intensity of coloration of the metal complexes.

We had reported previously [1-3] of the possibility of using derivatives of 5,6-benzo-2,2'-diquinolyl for the photometric determination of copper. With the aim of further study of the dependence of the complex-forming properties of the ligands on their structure, it was of interest to synthesize new derivatives of benzoquinoline containing substituents with a multiple bond.

By catalytic condensation of quinolidene- β -naphthylamine with benzalacetone and its derivatives, new compounds were obtained through the scheme



I R=H, II R=CI, III R=OCH₃, IV R=N(CH₃)₂, V R=NO₂

*Deceased.

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