dine, with mp 147°C (mp 148°C [2]), and the corresponding base were isolated in the reaction of salts II-V with aniline.

The method described above can be used for the synthesis of pyridinium and imidazolium salts and salts of other heterocyclic cations with an imidoyl residue attached to the nitrogen atom.

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SIMPLE SYNTHESIS OF 1-AMINOTETRAZOLE

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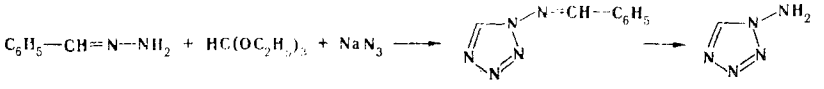
UDC 547.796.1.07

Tetrazoles are promising substances for a number of purposes [1]; however, many of them (even the simplest, including 1-aminotetrazole) are still difficult to obtain and have not been characterized very well.

The direct amination of tetrazole with hydroxylamine-O-sulfonic acid gives the product in low yield and is complicated by the formation of a mixture of two isomers, the separation of which is hazardous because of the increased dangerously explosive character of 2-aminotetrazole [2]. A multistep method of synthesis, according to which the corresponding imido ester is obtained from benzaldehyde hydrazone and an ortho ester at 140°C, and the product is cyclized with NaN_3 in the course of 24 h, is more convenient. However, the latter method is time consuming, and requires a threefold to fourfold excess of the ortho ester and sodium azide, and the overall yield of 1-aminotetrazole is 37% [3]. We have studied the possibility of the one-step realization of this reaction and have found that in acetic acid the reaction of benzaldehyde hydrazone, ethyl orthoformate, and sodium azide proceeds readily at 75-85°C and is complete in 2.5 h with the formation of 1-benzylideneaminotetrazole, the hydrolysis of which gives 1-aminotetrazole in 60-62% yield:



The method of synthesis can be used for the simple and rapid preparation of N-substituted 1-aminotetrazoles from the corresponding aryl(alkyl)hydrazines.

A 250-ml sample of acetic acid was added with stirring to a mixture of 60 g (0.5 mole) of benzaldehyde hydrazone, 39 g (0.6 mole) of NaN_3, and 150 ml (0.9 mole) of ethyl orthoformate, and the mixture was heated at 75-85°C for 2.5 h. It was then poured with stirring into 1.3 liters of water, and the precipitate was removed by filtration and washed with water. Water (250 ml) and 120 ml of concentrated hydrochloric acid were added to the reaction product, and the benzaldehyde was removed by steam distillation. The residue was neutralized and evaporated, and the residue was extracted with ethyl acetate. The extract was dried with $MgSO_4$, and the solvent was removed by distillation to give 26.2 g (62%) of 1-aminotetrazole in the form of a clear yellowish liquid (n_D^{20} 1.5140, d_4^{20} 1.363) that crystallized upon prolonged cooling to 0°C to give colorless acicular crystals with mp 8-10°C. IR spectrum (thin layer): 975, 1105, and 1190 (ring δ); 1623 (δ NH_2); 3155 (νCH); 3215 and 3340 cm^{-1} (νNH_2). PMR spectrum (DMSO): 7.05 (s, 2H, NH_2) and 9.16 ppm (s, 1H, CH). The benzaldehyde derivative had mp 92-93°C, in agreement with the literature value [3]. 1-Aminotetrazole explodes under pronounced friction and upon impact.

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SYNTHESIS OF ANTHRA[1,9-cd]-6-ISOXAZOLONES UNDER INTERPHASE-CATALYSIS CONDITIONS

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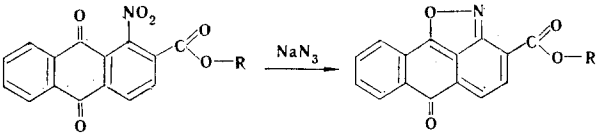
It has been shown [1] that 1-azidoanthraquinones (II) are formed in the reaction of 1-nitroanthraquinones (I) with alkali metal azides in polar aprotic solvents. Anthra[1,9-cd]-6-isoxazolones (III) were synthesized by thermal cyclization of these products in nonpolar solvents [2], whereas the thermolysis of azides II in aprotic solvents leads to reductive cleavage of the resulting isoxazolone [3] and does not make it possible to synthesize heterocycles III in one step.

We have found that anthra[1,9-cd]-5-isoxazolones IIIa,b are formed when 1-nitroanthraquinones Ia,b are refluxed for 5 h with NaN_3 (in a molar ratio of 1:3) in toluene in the presence of 18-crown-6 ether or dicyclo-18-crown-6 ether.



I a, b III a, b

I, III a R=*n*-C_3H_7; b R=*n*-C_4H_9

The structure of isoxazolones IIIa,b was proved by their independent synthesis from the known [1] 1-azido-2-alkoxycarbonylanthraquinones, and their compositions were proved by the results of elementary analysis. 3-n-Propoxycarbonylanthra[1,9-cd]-6-isoxazolone (IIIa), with mp 158-159°C (from chlorobenzene), was obtained in 65% yield. UV spectrum (dioxane), λ_{max} (log ε): 460 nm (4.0). 3-n-Butoxycarbonylanthra[1,9-cd]-6-isoxazolone (IIIb), with mp 167-168°C (from toluene), was obtained in 84% yield. UV spectrum (dioxane), λ_{max} (log ε): 460 nm (4.0).

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