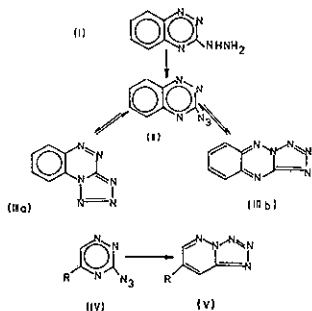


AN INTERESTING AZIDO-TETRAZOLO TRIPLE EQUILIBRIUM; STRUCTURE ELUCIDATION OF THE ANGULAR TETRAZOLO (5,1-c) BENZO-as-TRIAZINE

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It has been published¹ that the reaction of 3-hydrazino-benzo-as-triazine (I) with nitrous acid leads to the formation of 3-azido-benzo-as-triazine (II) which results, through an equilibrium, in the angularly fused tetrazolo (5,1-c) benzo-as-triazine (IIIa). Possible formation of the angular system (IIIa) instead of the other isomer (IIIb) was supported by theoretical consideration. Recently, W. Paudler et al.² criticized the angular structure of III. They found that 3-azido-as-triazine (IV) gives rise to the formation of tetrazolo(1,5-b)as-triazine (V). On the basis of this analogous system (V) they proposed the linearly fused structure (IIIb) instead of the angular (IIIa).



In order to prove the structure of the compound in question (III), ⁵N-containing IIIa and its dihydro derivative were synthesized and investigated by MS spectroscopy.

The azido-tetrazolo equilibrium of II and III was studied by ¹³CMR spectroscopy in detail. An interesting triple equilibrium of the azide (II) and the two tetrazoles (IIIa, IIIb) was observed. The results of the two spectroscopic methods unambiguously proved, however, major participation of the angular IIIa structure both in solution and in solid phase. Theoretical consideration points rather to formation of IIIa than IIIb.

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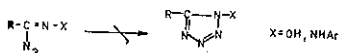
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CYCLIZATION OF STABLE AZIDOAOMETHINES TO TETRAZOLO DERIVATIVES

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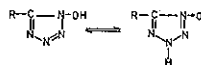
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It is known, that replacement of the halide from hydrozoyl halides¹ and hydroxamoyl halides² with azide ion yields the appropriate azides, which do not cyclize to the expected 1-hydroxytetrazoles:



As it was mentioned in the preliminary communication³, aromatic azidoximes can be cyclized by treatment with acyl halides. Recently I have established, that the first step of the reaction is the acylation of azidoxime, followed by protonation which causes cyclization to 1-O-acyloxytetrazole. O-Acyloxytetrazoles were next transformed into the appropriate hydroxy derivatives. The reaction was applied to preparation of aromatic, aliphatic and heterocyclic 5-substituted-1-hydroxytetrazoles.

For these compounds the existence in two tautomeric forms according to the following equilibrium is possible:



The results of spectral and chemical investigations supports the hydroxyimine structure concept.

The action of acyl halides on hydrozoyl azides is currently investigated.

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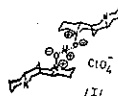
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INVESTIGATION ON THE HYDROGEN BONDING IN PROTONATED QUINOLIZIDINE DERIVATIVES

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The influence of intra- and/or intermolecular factors on stereochemistry of protonated molecules of parent diamines and their mono-N-oxides in the following compounds was studied:

A. Semiperchlorate salt of sparteine-epi-N(16)-oxide (I)¹:B. Monoperchlorate salts of: sparteine (II)², alpha-isosparteine (III)³, 2-methylsparteine (IV), 2-phenylsparteine (V), sparteine-N(16)-oxide (VI)⁴, 2-phenylsparteine-N(16)-oxide (VII)^{5,6}: