PO 52

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

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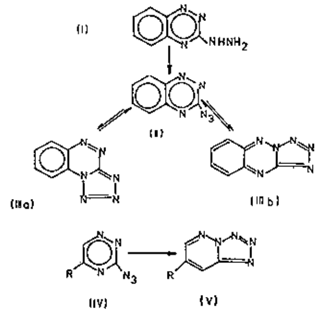
It has been published[1] that the reaction of 3-hydrazino-benzo-as-triazine (I) with nitrous acid leeds to the formation of 3-azidobenzo-as-triazine (II) which results, through an equilibrium, in the angularly fused tetrazolo (5,1-c) benzo-as-triazine (IIIa). Possible formation of the angular system (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), ^{15}N-containing IIIa and its dihydro derivative were synthesized and investigated by MS spectroscopy.

The azido-tetrazolo equilibrium of II and III was studied by ^{13}CMR 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 unambigously 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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PO 53

CYCLIZATION OF STABLE AZIDOAZOMETHINES TO TETRAZOLE DERIVATIVES

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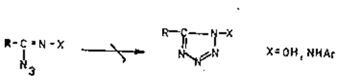
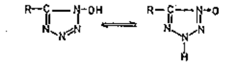
It is known, that replacement of the halide from hydrazonyl halides[1)] and hydroxamoyl halides[2)] with azide ion yields the appropriate azides, which do not cyclize to the expected 1-hydroxytetrazoles:



As it was mentioned in the preliminary communication[3)], 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 applyied to preparation of aromatic, aliphatic and heterocyclic 5-substituted-1-hydroxytetrazoles.

For these compounds the existance 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 hydrazonyl azides is currently investigated.

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PO 54

INVESTIGATION ON THE HYDROGEN BONDING IN PROTONATED QUINOLIZIDINE DERIVATIVES

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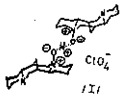
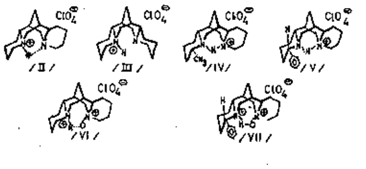
The influence of intra- and/or intermolecular factors on stereochemistry of protonated molecules of parent diamines and their mono-N-oxides in the following compounds was studied:

A. Semiperchlorate salt of sparteine-epi-N(16)-oxide (I)[1]:



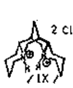
/I/

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]:



C. Diperchlorate salt of: sparteine (VIII)^{3}, alpha-isosparteine (IX)^{3,7}, 17-methylsparteine (X)^{8}:

/VIII/



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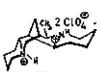
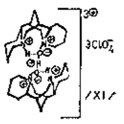


/X/

D. Sesquiperchlorate salts of: sparteine-N(16)-oxide (XI)^{9}, sparteine-epi-N(16)-oxide (XII)^{1,10}:



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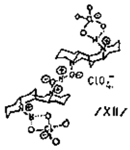

/XII/

On the basis of X-rays and complex spectroscopic data, the following problems are discussed:

— the length and the angles of the following hydrogen bonds:

$N^{+} — H \ldots\ldots N$ $\qquad$ $N^{+} — H \ldots\ldots O^{-} — N^{+}$

$N^{+} — O^{-} \ldots H^{+} \ldots O^{-} — N^{+}$ $\qquad$ $N^{+} — H \ldots — OClO_3$

— the influence of geometry of intramolecular hydrogen bond on torsion angles in the quinolizidine rings and on the length of bonds:

$$N^{+} — O \text{ and } N^{+} — C;$$

— the influence of methyl and phenyl substituents (in 2 and 17 positions) on the pKa values of investigated compounds and on the geometry of hydrogen bonds in these compounds.

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PO 55

TRANSANNULAR NITROGEN-CARBONYL INTERACTION STUDY IN SOME QUINOLIZIDONE-2 DERIVATIVES BY THE CIRCULAR DICHROISM METHOD

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CD data for 13-ketosparteines and related compounds provide direct evidence for the process of protonation, involving transannular interaction of the carbonyl and amine functions in the ring D-boat form. Transannular interaction is found to occur both in 11α and in (more rigid) 11β series. In the 11α series transannular interaction in ring D requires ring C to adopt a boat conformation.

The ring D-bridged forms are evidently stabilized in water and presumably in other protic solvents. In the absence of 2-oxo function the process of transannular interaction upon acidification is retarded due to the intramolecular hydrogen bonding between N(1) and N(16).

PO 56

THE AZETIDINE RING-CLOSURE REACTION OF **cis**- AND **trans**-2-(BROMOMETHYL)CYCLOALKYLAMINES

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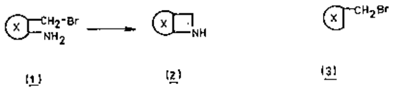
Azetidine ring-closure reaction of cis-and trans-2-(bromomethyl) cycloalkylamines (1), involving neighbouring group participation, was investigated by kinetic and preparative methods. Comparison was made with the solvolysis processes of the corresponding (bromomethyl)cycloalkanes (3) as reference compounds.



(1) (2) (3)

X= 5,6,7 ; cis or trans

X= 5,6,7

The first-order rate constants of the azetidine formation reactions as a function of the ring size follow the sequence cycloheptane ‹ cyclopentane ‹ cyclohexane for the **cis** isomers; and cycloheptane ‹ cyclohexane for the **trans** isomers. No azetidine formation could be induced from **trans**-2-(bromomethyl)cyclopentylamine. When the Δ^{++} values of the reactions are plotted as a function of ΔS^{++} — which the exception of **trans**-2-(bromomethyl)cyclohexylamine, where the main reaction is elimination — an isokinetic correlation is manifested.

The n.m.r. spectra of the azetidines and of the 2-(bromomethyl) cycloalkylamine hydrobromides, in which the protons of the bromomethyl group are not equivalent, are discussed.

PO 57

SYNTHESIS AND CONFORMATION OF STEREOISOMERIC **cis**- AND **trans**-TETRAMETHYLENE- AND PENTAMETHYLENE-DIHYDRO- AND TETRAHYDRO-1,3-OXAZINES

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Starting from **cis**- and **trans**-2-aminomethylcyclohexanol and **cis**-**trans**-2-hydroxymethylcyclohexylamine, as well as from the homologous cycloheptane derivatives, **cis**- and **trans**-5,6-tetramethylene- and pentamethylene-5,6-dihydro- and 2,3,5,6-tetrahydro-4**H**-1,3-oxazines and **cis**- and **trans**-4,5-tetramethylene- and pentamethylene-4,5-dihydro- and 2,3,4,5-tetrahydro-6**H**-1,3-oxazines were prepared.

n=2,3 ; cis or trans; R=H,CH$_3$, C$_6$H$_5$CH$_2$

n=2,3 ; cis or trans