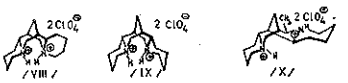
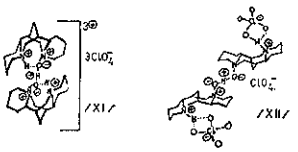
C. Diperchlorate salt of: sparteine (VIII)[3], alpha-isosparteine (IX)[3,7], 17-methylsparteine (X)[8]:



/VIII/ /IX/ /X/

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



/XI/ /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 . . . . . N N+ — H . . . . . O⁻ — N+
N+ — O⁻. . . H+ . . . O⁻ — N+ N+ — H . . . —$OClO_3$

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

N+ — O 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

W. Wysocka and J. Gawroński

Institute of Chemistry, A. Mickiewicz University, Poznań, Poland.

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).

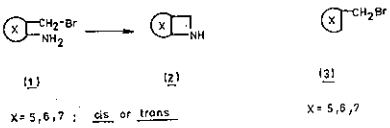
PO 56

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

Gy. Göndös, K. L. Láng and G. Bernáth

Institute of Organic Chemistry, József Attila University, Szeged, Hungary

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.

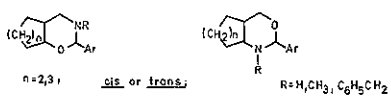
PO 57

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

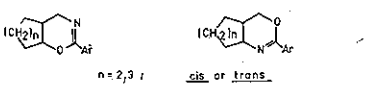
G. Bernáth, L. Gera, J. Kóbor*, A. Kálmán** and P. Sohár*

Institute of Organic Chemistry, József Attila University, Szeged, *Chair of Chemistry, Juhász Gyula Pedagogical Training College, Szeged, **Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, *Pharmaceutical Research Institute, Budapest

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-4H-1,3-oxazines and cis- and trans-4,5-tetramethylene- and pentamethylene-4,5-dihydro- and 2,3,4,5-tetrahydro-6H-1,3-oxazines were prepared.



n=2,3 ; cis or trans ; R=H, CH_3, $C_6H_5CH_2$



n=2,3 ; cis or trans