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MESOIONIC COMPOUNDS WITH A BRIDGED NITROGEN ATOM.

8.* INVESTIGATION OF THE STRUCTURES OF CONDENSED THIAZOLE DERIVATIVES BY PMR SPECTROSCOPY

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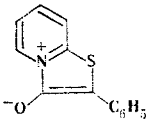
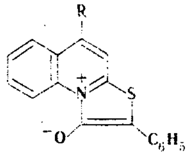
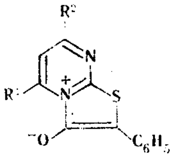
The structures of thiazolopyridinium, thiazoloquinolinium, and thiazolopyrimidinium oxides were studied by PMR spectroscopy with the aid of a lanthanide shift reagent [Eu(DPM)$_3$].

In a previous communication [1] we described the synthesis of a number of condensed thiazole derivatives that have mesoionic structures. In order to perform conformational analysis and confirm the structures we investigated the PMR spectra of I-VIII (Table 1).


I

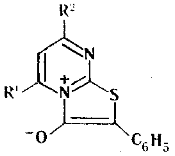

II, III

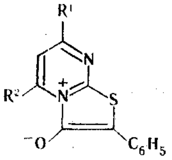

IV–VIII

II R=H; III R=CH$_3$; IV R^1=R^2=H; V R^1=H, R^2=CH$_3$; VI R^1=H, R^2=C$_6$H$_5$; VII R^1=R^2=CH$_3$; VIII R^1=CH$_3$, R^2=CF$_3$

A characteristic feature of these spectra is the appreciable paramagnetic shift of the signal of the aromatic proton or the CH$_3$ group in the vicinity of the oxygen atom. Thus in the spectrum of product I the signal of the proton in the 5 position is shifted almost 1 ppm to the weak-field side relative to the signals of the other aromatic protons. This fact can be explained not only by the effect of the electron-acceptor quaternary nitrogen atom but also by the unbonded coupling of this proton with the unshared electron pairs of the oxygen atom, which bears a negative charge (compare this with the analogous effects of the carbonyl oxygen atom [2]). This shift is manifested particularly clearly in the spectra of II and III, in which the proton in the 9 position is even closer to the oxygen atom. The chemical shift of the 9-H signal reaches 10.35 ppm in this case.

It follows from the method used to prepare them [1] that IV-VIII can have one of the alternative structures


A


B

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*See [1] for Communication 7.

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TABLE 1. Chemical Shifts (ppm) in the PMR Spectra of I-VIII (the lanthanide induced shifts are given in parentheses)

Compound	o-H ($2\text{-}C_6H_5$)	5-R[a]		6-H	7-R[b]		8-H
		H	CH_3		H	CH_3	
I	7,87 (7,3)	8,78 (9,5)	—	7,48 (1,4)	—[c]	—	7,65 (2,7)
II	7,90 (7,3)	10,35 (11,0)	—	—[c]	7,07 (1,6)	—	—[c]
III	7,80 (7,8)	10,35 (12,1)	—	—[c]	—	2,55 (0,8)	—[c]
IV	7,93 (10,4)	8,95 (12,5)	—	—[c]	8,52 (1,9)	—	—
V	7,88 (7,8)	8,80 (9,3)	—	—[c]	—	2,76 (0,8)	—
VI	8,10 (7,6)	8,93 (8,9)	—	—[c]	—[c]	—	—
VII	7,70 (7,6)	—	3,30 (9,1)	6,53 (2,3)	—	2,50 (1,1)	—
VIII	7,92 (12,4)	—	3,50 (13,8)	7,25 (2,4)	—	—	—

[a] The corresponding groups in the 9 position for II and III.
[b] The corresponding groups in the 5 position of II and III.
[c] The chemical and induced shifts were not determined because of the superimposition of other signals.

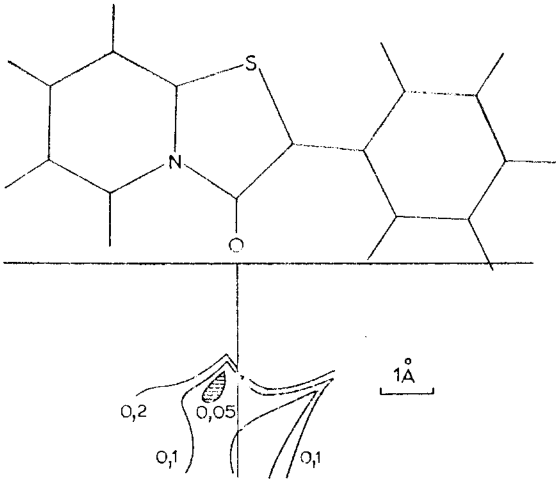

Fig. 1. Contour map of the agreement (R) between the calculated induced shifts and the experimentally found lanthanide induced shifts (LIS) for the adduct of VII with $Eu(DPM)_3$. The values of the R factor (mean square deviations) are presented beside the contour lines. The range of location of the lanthanide ion in the adduct (with a probability of 90%) is indicated by shading.

Some preliminary judgements relative to the structures of these compounds can be made on the basis of their PMR spectra. Thus in the spectrum of reaction product VII, which contains two methyl groups in the pyrimidine fragment of the molecules, the chemical shift of the signal of one of them is 3.30 ppm, while the shift of the other is only 2.50 ppm. This difference in the chemical shifts should be explained by unbonded coupling of the protons of one of them with the unshared electron pairs of the oxygen atom. Compound VIII contains only one CH_3 group, and its chemical shift is 3.50 ppm. This constitutes evidence that the methyl group is close to the oxygen atom; thus the VIII molecule probably has the A structure ($R^1 = CH_3$). At the same time, the chemical shift of the methyl group of V is 2.50 ppm, and the methyl group consequently occupies the R^2 position in structure A. It is not possible to draw an unambiguous conclusion regarding the structures of IV and VI on the basis of only the chemical shifts. To solve this problem and to confirm the assignments of the signals in the PMR spectra that we made above we measured the spectra of oxides I-VIII in the presence of of a lanthanide shift reagent (LSR), viz., europium(III) tris(dipavaloylmethanate) [$Eu(DPM)_3$].

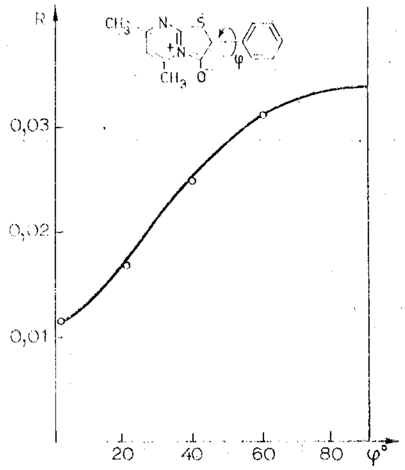

Fig. 2. Graph of the dependence of the R_{min} values for the adduct of VII with $Eu(DPM)_3$ on the angle of rotation (φ) of the phenyl residue in the 2 position relative to the plane of the pyrimidothiazole system.

The only effective center of coordination of the LSR with I-VIII is the oxygen atom. If IV-VIII have structure A, large lanthanide induced shifts (LIS) should therefore be expected for the signals of the protons of substituent R^1, and there should be large LIS for substituent R^2 in the case of isomeric structure B.

Significant paramagnetic shifts of the signals of all of the protons occur when the LSR is added to all of the investigated compounds (see Table 1). In the case of IV-VIII the signals of precisely that substituent which experiences unbonded coupling with the oxygen atom are shifted most strongly. This confirms that it occupies the R^1 position in structure A. The PMR spectra of I and VII make it possible to obtain the most reliable LIS parameters. We used the method in [3] to determine the geometrical structures of their adducts with the LSR. The contour map for agreement factor R, which makes it possible to determine the location of the europium atom in the adduct of VII with $Eu(DPM)_3$, is shown in Fig. 1. The bottom of the shaded region [the minimum of the agreement factor (R_{min})] here corresponds to the minimum of the mean square deviation between the calculated induced shifts (Δ^{calc}) and the experimentally found LIS (Δ^{exp}) of the magnetic nuclei of the substrate, in this case the aromatic o-H protons (the ortho protons of the phenyl ring in the 2 position), 6-H, and the 5-CH_3 and 7-CH_3 groups, i.e., the most probable position of the europium atom. The point with R_{min} lies near the extension of the C—O bond at a distance $r = 2.3$ Å from the oxygen atom. A similar structure of the adduct was also obtained for I ($r = 2.6$ Å). In the case of alternative structure B we were unable to detect a correlation between Δ^{calc} and Δ^{exp} for these two compounds. Thus coordination of the LSR with mesoionic heterocycles that contain a $C-O^-$ group takes place rather effectively, and the location of the europium atom is close to that in adducts of carbonyl compounds with the LSR (cf.[2, 4]).

All of the products obtained contain a phenyl substituent conjugated with a heterocyclic system. The LSR method makes it possible to determine the preferred location of the phenyl group relative to the plane of the heterocyclic ring (angle φ between them) [5]. The preferred conformation corresponds to the minimum of the function $\varphi = f(R_{min})$. The graph of this function for adducts of VII with various test φ angles is presented in Fig. 2. It is apparent that the best agreement between Δ^{calc} and Δ^{exp} occurs for a planar conformation of the molecule ($\varphi = 0$). A similar result was also obtained for the adduct of I with $Eu(DPM)_3$. An analysis of scale structural formulas of the compounds under consideration by the method in [6] showed that their structures should be close to planar.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ were measured with a ZKR-60 spectrometer (60 MHz) with tetramethylsilane as the internal standard. The method used to determine the LIS is presented in [7].

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MASS-SPECTROMETRIC STUDY OF THE CYCLIZATION OF DIAZO KETONES.

5.* CYCLIZATION OF PHTHALOYL DIPEPTIDE DERIVATIVES OF DIAZOMETHANE

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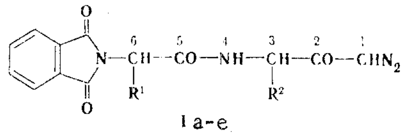
An analysis of the electron-impact mass spectra of phthaloyl dipeptide derivatives of diazomethane made it possible to conclude that a certain percentage of the $[M - N_2]^+$ ions have the 1,3-oxazin-5-one structure, while some of them undergo fragmentation without cyclization. The Wolff rearrangement does not occur. Alkyl substituents in the 4 position of the resulting heterocycle hinder cyclization. Under chemical-ionization conditions the $[MH - N_2]^+$ ions exist in similar forms. The cyclization process is hindered in this case by the introduction of a benzyl substituent in the chain.

We have previously shown [1-4] that some types of diazo ketones eliminate a molecule of nitrogen under the influence of electron impact (EI) and under chemical-ionization (CI) conditions, and the resulting fragment cyclizes to a certain extent without undergoing the Wolff rearrangement [5, 6]. This sort of cyclization process is similar to the chemical transformation of these diazo ketones in the condensed phase under the influence of acidic agents. In the present research in order to predict the possible cyclization reactions in solutions we studied the EI and CI mass spectra of a series of phthaloyl dipeptide derivatives of diazomethane (I), the chemical transformations of which have not been investigated.



I a-e

I a $R^1=R^2=H$; b $R^1=CH_3$, $R^2=H$; c $R^1=CH_2C_6H_5$, $R^2=H$; d $R^1=R^2=CH_3$; e $R^1=CH_3$, $R^2=CH_2C_6H_5$

As expected [1-4], peaks of molecular ions (M^+) of diazo ketones I are completely absent in the EI mass spectra; however, a peak of $[M - N_2]^+$ ions, the relative intensity of which is considerably higher in the mass spectra of Ia-c, in which $R^2 = H$, is observed in

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*See [1] for Communication 4.

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