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NMR SPECTRA OF CYCLIC NITRONES.

6.* TAUTOMERIC EQUILIBRIUM OF β-OXO-NITRONES – 3-IMIDAZOLINE 3-OXIDE DERIVATIVES

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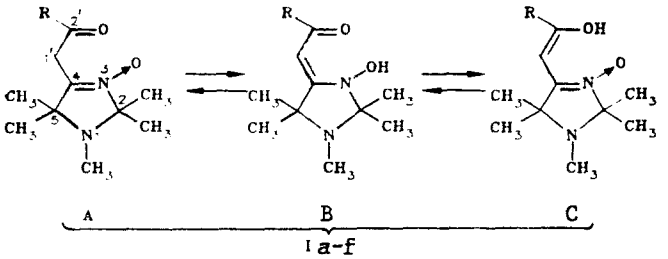
UDC 543.422.25:547.781.3.04:541.623

It is demonstrated by ^{13}C NMR spectroscopy that β-oxo nitrones (3-imidazoline-3-oxide derivatives) exist in the form of an equilibrium mixture of three tautomeric forms with preponderance of the enolo nitrone and enehydroxylamino ketone forms.

We have previously shown that cyclic β-oxo nitrones (pyrroline derivatives) exist in the form of a mixture of two tautomeric forms — oxo nitrone and enehydroxylamino ketone forms [2]. Enolo nitrone structures were assigned to the acyclic β-oxo nitrones (pyrroline 1-oxide derivatives) on the basis of an analysis of the UV spectra [3]. At the same time, the incorrectness of this assignment only on the basis of UV spectral data has been noted [4]. It was pointed out that acyclic β-oxo nitrones of the 3-imidazoline 3-oxide series exist in solutions in the enolized tautomeric form, but the question of the pathway of enolization has remained open [4].

We have investigated the tautomeric equilibrium of β-oxo nitrones Ia-f of the 3-imidazoline 3-oxide series using ^{13}C NMR spectroscopy.



I a-f

I a R=H; b R=CH_3; c R=C_6H_5; d R=$(CH_3)_3C$; e R=α-naphthyl; f R=CF_3

*For communication 5, see [1].

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TABLE 1. PMR Spectra of β-Oxo Nitrones Ia-f

Compound	δ, ppm ($CDCl_3$), s						Yield of form A, %
	N—CH_3	2-CH_3	5-CH_3	—CH=	—CH_2—	R	
Ia	2,12	1,22	1,01	4,41 d*	—	6,88 d*	0
Ib-B, Ib-C*	2,28	1,33	1,18	4,76	—	1,90	12
Ib-A**	2,32	1,31	1,15	—	3,43	2,13	
Ib-B, Ib-C	2,19	1,29	1,08	4,43	—	1,85	10
Ib-A	2,24	1,31		—	3,29	3,13	
Ic-B, Ic-C	2,23	1,38	1,19	5,25	—	7,3 (3H,m)	Traces
Ic-A	2,22	1,37	1,18	—	3,97	7,7 (2H, m)	
Id-B,** Id-C**	2,31	1,36	1,21	4,71	—	1,12	10
Id-A**	2,33	1,33	1,17	—	3,57	1,18	
Id-B, Id-C	2,12	1,20	1,01	4,51	—	0,95	13
Id-A	2,16	1,21	0,99	—	3,37	0,98	
Ie	2,30	1,52	1,25	5,09	—	7,7 m	0
If	2,27	1,38	1,19	5,11	—	—	0

*J = 6 Hz.
**In d_6-DMSO.

TABLE 2. Data from the ^{13}C NMR Spectra of β-Oxo Nitrones Ia-f

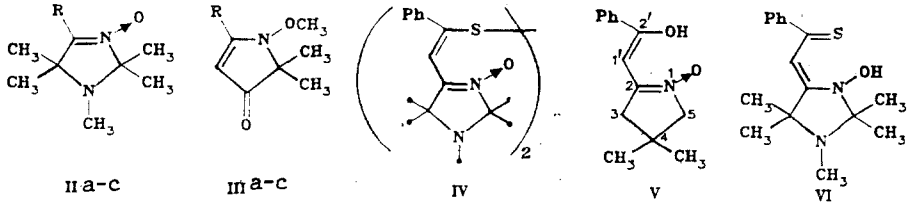
Compound	δ, ppm ($CDCl_3$)							
	N—CH_3	$C_{(2)}$	$C_{(4)}$	$C_{(5)}$	$C_{(1')}$	$C_{(2')}$	2,5-$(CH_3)_2$	R
Ia	26,41	86,75	151,98	62,83	86,12	163,91	23,60; 23,29	—
Ib B, C	26,65	86,36	152,30	63,19	84,04	176,21	23,58; 24,00	23,09
A	—	89,06	—	63,03	38,61	—	—	29,76
Ib-B,* Ib-C*	26,66	86,21	152,18	63,18	84,22	175,71	23,57; 23,87	22,97
Ib-A*	—	88,48	—	62,89	—	—	—	29,60
Ic	26,63	86,64	152,81	63,44	82,84	171,37	24,10; 23,64	126,21; 127,76 133,12; 136,88
Id B, C	26,20	88,14	152,65	63,13	79,69	185,53	23,62; 23,13	31,81; 27,69
A	—	88,70	141,75	62,86	37,90	207,15	23,16; 22,64	—
Id-B,* Id-C*	26,59	86,11	152,65	63,26	79,88	185,17	23,53; 23,93	31,93; 28,08
Id-A*	—	—	—	62,88	37,89	207,7	22,92; 25,92	—
Ie	26,74	86,88	153,01	63,49	87,78	175,02	24,11; 23,79	124,5 ... 136,93
If	26,39	87,75	154,89	63,91	83,23	162,45	23,79; 23,61	118,74

*The spectrum was recorded in d_6-DMSO.

One might have assumed that the tautomeric equilibrium of β-oxo nitrones of the 3-imidazoline 3-oxide series has intrachelate character and is fast on the NMR time scale. As a consequence of this, model compounds with fixed tautomeric forms are necessary to establish the position of the tautomeric equilibrium. However, the alkylation of Ic with methyl iodide [4] and dimethyl sulfate takes place only at the $C_{(1')}$ atom, and the O-acyl derivatives of these compounds are unstable. In this connection, as model compounds we selected nitrones IIa-c of the 3-imidazoline 3-oxide series with a substituent in the 4 position containing C=C or C=N bonds conjugated with the nitrone group and enehydroxylamino ketones IIIa-c of the pyrroline series. The chemical shift of the signal of the nitrone $C_{(4)}$ atom in the ^{13}C NMR spectra of IIa-c is found at 142-144 ppm [5]. The signal of the $C_{(4)}$ atom is also found at 142.7 ppm in the ^{13}C NMR spectrum of IV. On the basis of these data we assumed that the chemical shift (CS) of the $C_{(4)}$ atom in enolo nitrone tautomeric form C is located in the same region. The CS of the $C_{(4)}$ atom in the spectrum of enehydroxylamino ketone tautomeric form B is 175 ppm, which corresponds to the CS of the carbon atom of the enehydroxylamino group in IIIa-c. The CS of the signal of the carbon atom depends only slightly on substituent R [2].

An analysis of the PMR spectra of Ia-f in DMSO and $CDCl_3$ shows (Table 1) that β-oxo nitrones Ia, e, f exist in solution only in the enolized form, while ~10% of form A is present in the tautomeric equilibrium of Ib, d. The percentage of form A for Ic is less than 1%. In the ^{13}C NMR spectra of Ia-f (Table 2) in the region characteristic for sp^2-hybridized carbon atoms we observed three signals that can be assigned to tautomeric forms B and C — at 79.7-87.8 ppm due to the $C_{(1')}$ atom, at 152.0-154.9 ppm due to the $C_{(4)}$ atom, and at 162.5-185.5

ppm due to the $C_{(2')}$ atom. This form of spectrum can be explained by the existence of a fast intrachelate equilibrium between forms B and C, which follows from the position of the signal of the $C_{(4)}$ atom – intermediate between the enehydroxylamino and nitrone forms. The CS of the $C_{(4)}$ atom makes it possible to evaluate the contribution of the B form in the B ⇄ C equilibrium as ~30%. It should be noted that the B:C ratio remains virtually unchanged on passing from $CDCl_3$ to DMSO.



II a-c III a-c IV V VI

II a $R=C_6H_5$, b $CH=NC(CH_3)_3$, c CH=NOH; III a $R=CH_3$, b $R=CF_3$, c $R=C_6H_5$

The chemical shifts of the carbon atoms of the imidazoline ring are found in the same regions as for the previously described 3-imidazoline 3-oxide derivatives IIa-c with the exception of the $C_{(2)}$ atom, the signal of which is shifted 1.0-2.5 ppm to strong field, which is associated with a change in the hybridization of the $N_{(3)}$ atom in the B form.

The ^{13}C NMR spectrum of β-oxo nitrone V, to which enolo nitrone structure C was assigned in [3], is similar to the spectrum of Ic in the region of the signals of the sp^2-hybridized carbon atoms. On the basis of this it may be asserted that two enolized tautomeric forms B and C, with a certain degree of preponderance of the C form, are also realized in this case. A signal of methylene protons of tautomeric form A, the percentage of which in solution in $CDCl_3$ is 6%, is observed in the PMR spectrum of V.

In contrast to Ia-f, the sulfur-containing analog (β-thioxo nitrone VI) exists, according to PMR data, in solution in $CDCl_3$ and DMSO only in the enolized form. A signal of the $C_{(4)}$ atom in the ^{13}C NMR spectrum is observed at 179.15 ppm, which is close to the CS of the C atom in the enehydroxylamino form and may constitute evidence for the existence of VI in enehydroxylamino thiono form B. In conformity with this, the signal of the $C_{(2)}$ atom in the ^{13}C NMR spectrum is found at stronger field (by 1.4 ppm) than the signal of the $C_{(2)}$ atom in the spectrum of IV with an sp^2-hybridized $N_{(3)}$ atom.

EXPERIMENTAL

The IR spectra of KBr pellets (concentration 0.25%) were recorded with a UR-20 spectrometer. The UV spectra of solutions in ethanol were recorded with a Specord UV-vis spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded with a Bruker AC-200 spectrometer at 300 K under pulse conditions. For the measurements we used 10-15% solutions in $CDCl_3$ and d_6-DMSO. The CS were measured relative to the signal of the solvent (relative to the residual protons of the solvent in the case of PMR). Compounds Ia-f were synthesized by the methods in [4, 6], while V was synthesized by the method in [3].

The results of elementary analysis of the synthesized compounds for C, H, N, and S were in agreement with the calculated values.

3-Hydroxy-1,2,2,5,5-pentamethyl-4-thiophenacetylidenimidazolidine (VI, $C_{16}H_{22}N_2OS$). A solution of 1.7 g (10 mmoles) of 1,2,2,4,5,5-hexamethyl-3-imidazoline 3-oxide in 10 ml of absolute ether was added dropwise with stirring to a solution of phenyllithium prepared from 2.1 g (20 mmoles) of bromobenzene and 0.28 g (40 mmoles) of lithium in 30 ml of absolute ether. The reaction was carried out in an argon atmosphere at 20°C. Stirring was continued for 15 min, and a solution of 3 g (18 mmoles) of ethyl thiobenzoate in 5 ml of ether was added dropwise with stirring. The mixture was then stirred for 1 h, 20 ml of water was added, and the aqueous mixture was stirred for 5 min. The aqueous layer was separated, and the ether solution was extracted with 2% NaOH solution (two 20-ml portions). The combined aqueous solution was washed with ether (two 20-ml portions), neutralized to pH 7 with 5% HCl, and extracted with $CHCl_3$ (three 30-ml portions). The extract was dried with $MgSO_4$, and the solution was evaporated to give 0.9 g (31%) of VI with mp 116-117°C (ethyl acetate–hexane). UV spectrum (ethanol), λ_{max}, nm ($\log\varepsilon$): 288 (4.07), 378 (3.88). PMR spectrum ($CDCl_3$): 2.33 (3H, s, N–CH_3), 1.31 (6H, s), 1.49 [6H, s, 2,5-$(CH_3)_2$], 6.26 (1H, s, –CH=), 7.3 (3H, m), 7.7 (2H, m, C_6H_5), 12.19 ppm (1H, br.s, OH). ^{13}C NMR spectrum ($CDCl_3$): 23.91, 24.23 [2,5-$(CH_3)_2$]; 26.73 (N–CH_3); 64.81 ($C_{(5)}$); 87.23 ($C_{(2)}$); 105.62 (–CH=); 127.15, 127.56, 128.82 (C_6H_5); 159.26 (C=S); 179.15 ppm ($C_{(4)}$).

Bis[2-(1,2,2,5,5-pentamethyl-3-oxido-3-imidazolin-4-yl)-1-phenylethylene] Disulfide (IV, $C_{32}H_{42}N_4O_2S_2$). A solution of 0.29 g (1 mmole) of VI in 20 ml of dry ether was stirred for 2 h with 1 g of MnO_2, after which the excess oxidizing agent was removed by filtration, and the solution was evaporated. The residue was diluted with 5

ml of hexane, and the precipitated disulfide was removed by filtration and dried to give a product with mp 145-147°C (ethyl acetate). IR spectrum (KBr): 1660, 1640 cm^{-1} (C=C, C=N). UV spectrum (ethanol), λ_{max}, nm (log ε): 245 (4.27), 294 (4.1 sh). PMR spectrum ($CDCl_3$): 1.09 (6H, s), 1.26 [6H, s, 2,5-$(CH_3)_2$], 2.25 (3H, s, N—CH_3), 5.86 (1H, s, —CH=), 7.2 ppm (5H, m, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$): 23.95, 24.98 [2,5-$(CH_3)_2$]; 26.94 (N—CH_3); 62.97 ($C_{(5)}$); 89.83 ($C_{(2)}$); 113.73 (—CH=); 127.91, 128.32, 128.73, 139.34 (C_6H_5); 142.70 ($C_{(4)}$); 150.54 ppm (=C—). The yield was 0.2 g (70%). PMR spectrum ($CDCl_3$) of V: 1.05 [6H, s, $(CH_3)_2$], 2.41 (3H, br.s, forms B and C), 2.46 (3-CH_3—, form A), 3.56 (3H, br.s, forms B and C), 3.63 (5-CH_2—, form A), 4.05 (br.s, $COCH_2$—, form A), 5.20 (1H, br.s, —C=, forms B and C), 7.2 (3H, m), 7.7 ppm (2H, m, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$): 27.48 [4-$(CH_3)_2$] (B, C); 27.72 [4-$(CH_3)_2$] (A); 34.39 ($C_{(4)}$) (B, C); 36.89 ($C_{(4)}$) (A); 46.22 ($C_{(3)}$) (A); 47.48 ($C_{(3)}$) (B, C); 71.10 ($C_{(5)}$), (B, C); 74.43 ($C_{(5)}$), (A); 85.96 (—CH—), (B, C); 126.53, 128.0, 129.94, 133.52 (C_6H_5) (B, C); 129.12, 128.59 (C_6H_5) (A); 137.02 ($C_{(2)}$) (A); 151.64 ($C_{(2)}$) (B, C); 171.61 (=C—OH) (B, C); 194.06 ppm (C=O) (A).

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SYNTHESIS OF A DONOR-ACCEPTOR PHOTOSYNTHETIC SYSTEM CONTAINING COVALENTLY BOUND AMINE, PORPHYRIN, AND QUINONE

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The synthesis of a diquinone derivative of the amino-containing analog of hematoporphyrin IX, obtained by the sequential modification of the tetramethyl hematoporphyrin IX, was accomplished.

A key stage in photosynthesis is the separation of the charges in the reaction centers with the subsequent stabilization of this state by the transfer of an electron across a series of intermediate acceptors of the chlorine structure to the primary quinone acceptor [1]. Covalently bound porphyrin—quinone compounds containing the main components of the electron transport chain (the photosensitizer and the electron acceptor) serve as convenient synthetic models for the study of the processes associated with the absorption and transformation of solar energy in photosynthesis [2, 3] (see scheme on following page).

Investigations performed recently [4, 5] have shown the principle possibility of the utilization of the diquinone derivatives of deuteroporphyrin IX (Ia, b; IIa, b) for the simulation of the intermediate stage of the primary separation of the charges in photosynthesis — the stage of the transfer of the electron from the pheophytin to the quinone. The main idea of the experiment consisted of the preliminary photoreduction of the porphyrin fragment in the compounds (Ia, b) and (IIa, b) by an electron-donor solvent — triethylamine. The dark transfer of the electron to the quinone fragment was accomplished in the final stage. However, the products of the photoreaction — the anion radicals of the porphyrin and the quinone — could only be detected successfully at a low temperature

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