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NMR SPECTRA OF CYCLIC NITRONES.

4.* SYNTHESIS AND ^{13}C NMR SPECTRA OF 4H-IMIDAZOLE N-OXIDES AND N,N-DIOXIDES

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4H-Imidazole 1,3-dioxides and 4H-imidazole 3-oxides were obtained by oxidation of 1-hydroxy-3-imidazoline 3-oxides and 1-hydroxy-3-imidazolines with lead and manganese dioxides or the stable nitroxyl radical, while 4H-imidazole 1-oxides were obtained by thermal decomposition of 1-acetoxy-3-imidazoline 3-oxides. Facile oxidation of the ethyl group in 5-ethyl-4H-imidazole 1,3-dioxide and the formation of 5-acetyl-4H-imidazole 1,3-dioxide and 5-acetyl-4H-imidazole 3-oxide were observed. It is shown that a strictly determined region of chemical shifts of the $C_{(2)}$, $C_{(5)}$, and $C_{(4)}$ atoms is characteristic for each group of 4H-imidazole N-oxides in the ^{13}C NMR spectra; this makes it possible to clearly establish the position of the N-oxide oxygen atom.

Continuing our study of the NMR spectra of cyclic nitrones [1-3] we have examined the spectral characteristics of conjugated heterocyclic nitrones – 4H-imidazole N-oxides and N,N-dioxides. The interest in these few compounds, which have received little study [4], is due to the peculiarity of their chemical properties such as their ability to undergo facile covalent hydration [5] and the recently observed property of being able to undergo conversion to heterocyclic nitroxyl radicals, the structure of which depends on the orientation of the N-oxide groups in the 4H-imidazole. The methods that we used to obtain 4H-imidazole N-oxides and N,N-dioxides lead to compounds with known positions and numbers of N-oxide groups. Using these compounds as a base we compared the possibilities of various spectral methods for the determination of the structures of these compounds, viz., the

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*See [1] for Communication 3.

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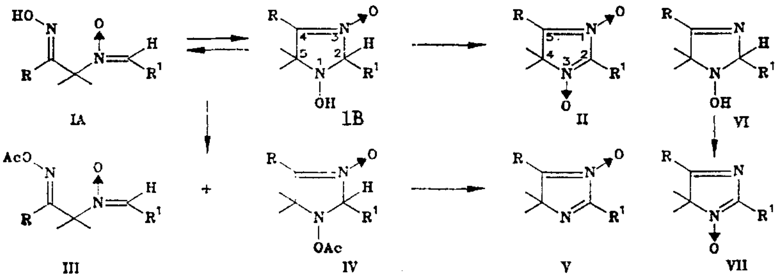
positions of the N-oxide groups. The need to solve problems of this sort may arise both in the analysis of 4H-imidazole N-oxides with unknown structures and in the analysis of other heterocyclic systems that have a similar conjugated C=N–C=N grouping with various orientations of the N-oxide groups.

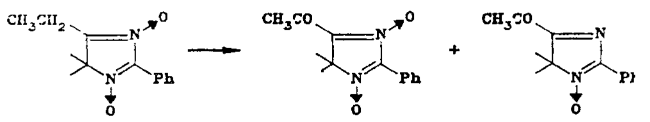


I—VII a—m,s $R=C_6H_5$, n R=2-furyl, o, p $R=5\text{-}CH_3\text{-}2\text{-furyl}$, q $R=C_2H_5$, r $R=CH_3CO$; a $R^1=H$, b $R^1=CH_3$, c,n,o,q,r $R^1=C_6H_5$, d $R^1=p\text{-}(CH_3)_2NC_6H_4$, e,p $R^1=m\text{-}NO_2C_6H_4$, f $R^1=o\text{-}HOC_6H_4$, g $R^1=$ 2-furyl h $R^1=$ 2-furyl, i $R^1=p\text{-}HO\text{—}C_6H_4$, j $R^1=p\text{-}CH_3OC_6H_4$, k $R^1=\alpha$-Py, ℓ $R^1=\beta$-Py, m $R^1=COOCH_3$, s $R^1=C_6H_5\text{—}CO$

The synthesis of new derivatives of 4H-imidazole N-oxides was carried out via the schemes proposed in [5, 7]. 4H-Imidazole 1,3-dioxides II and 4H-imidazole 3-oxides VII are formed for the most part in high yields in the oxidation of 1-hydroxy-3-imidazoline 3-oxides I [8] and 1-hydroxy-3-imidazolines VI [8] with lead or manganese dioxide in chloroform, acetone, or benzene. 4H-Imidazole 1-oxides V were obtained by acylation of 3-oxides I and subsequent thermal decomposition of 1-acetoxy-3-imidazoline 3-oxides IV. The spectral characteristics and results of elementary analysis are in agreement with the structures of the desired products (Tables 1 and 2).

The starting 3-oxides I used for the synthesis of II and VII exist in solutions in the form of a mixture of ring-chain tautomers IA ⇄ IB [8]. The position of the tautomeric equilibrium does not affect the yields of 1,3-dioxides II but may affect the direction of the acylation with acetic anhydride. Thus, the acylation of Ie, f leads to the formation of only IVe and IVf, while the acylation of Ig, h leads to mixtures of isomers IIIg, h and IVg, h, and the acylation of Ii-j leads to the formation of exclusively isomer IIIi. This imposes certain limitations on the possibility of the synthesis of 1-oxides V. The differences in the spectra of isomers III and IV are similar to the differences in the spectra of tautomers IR and IC.

While both 2- and 5-aryl- and hetaryl-substituted 1,3-dioxides II are stable compounds in most cases, 5-alkyl-4H-imidazole 1,3-dioxides are less stable; this is associated with the high lability of the protons of the alkylnitrone groups in these compounds. Thus, we were unable to isolate 5-methyl-4H-imidazole 1,3-dioxides in the free form, and 5-ethyl-4H-imidazole 1,3-dioxide IIq at room temperature in the solid state or in solution is converted completely in the course of 2 weeks to a mixture of compounds, from which 5-acetyl-4H-imidazole 1,3-dioxide (IIr) and 5-acetyl-4H-imidazole 3-oxide (VIIr) were isolated. A mixture of 4H-imidazole N-oxides IIr and VIIr in 10% and 25% yields, respectively, was obtained when a solution of IIq in chloroform was refluxed without access to air for 5 h. In the presence of excess MnO_2 as the oxidizing agent the oxidation of IIq or its precursor Iq in chloroform leads to the formation of the same products, but in 40% and 10% yields, respectively. The band of stretching vibrations of the C=O group in the IR spectrum of 1,3-dioxide IIr is located in the longer-wave region (by 30 cm^{-1}) as compared with the IR spectrum of 4H-imidazole VIIr – at 1660 and 1690 cm^{-1}, respectively (see [9]).

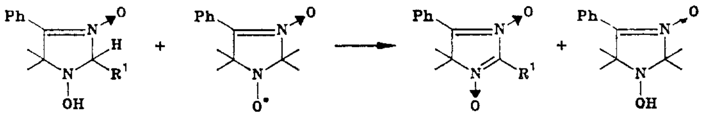


The signal of the carbonyl C atom in the ^{13}C NMR spectrum of 4H-imidazole 1,3-dioxide IIr is observed at stronger field (by 3.7 ppm) as compared with the corresponding signal in the spectrum of VIIr (Table 2); like the IR spectral data, this indicates conjugation of the C=O group in IIr with a nitrone group, whereas in VIIr it indicates conjugation with an imino group.

TABLE 1. Characteristics of II-V and VII

Compound	mp, °C	UV spectrum (alcohol), λ_{max}, nm (log ε)	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N (S)		C	H	N (S)	
IIa	155...156	360 (4,02), 275 (3·72), 250 (4,00)	65,0	6,0	13,6	$C_{11}H_{12}N_2O_2$	64,7	5,9	13,2	50
IIc	105...107	370 (3,88), 290 (4,36), 255 (3,96), 245 (3,98)	72,9	5,8	9,7	$C_{17}H_{16}N_2O_2$	72,8	5,8	10,0	80
IId	178...180	340 (4,13)	70,6	6,5	12,8	$C_{19}H_{21}N_3O_2$	70,6	6,6	13,0	30
IIe	156...157	375 (3,89), 300 (4,53)	62,6	4,4	13,1	$C_{17}H_{15}N_3O_4$	62,8	4,7	12,9	95
IIf	165...167	365 (4,01), 280 (4,35)	69,0	5,5	9,5	$C_{17}H_{16}N_2O_3$	68,9	5,4	9,5	30
IIg	130...133	345 (3,91), 250 (4,57)	66,3	5,3	10,4	$C_{15}H_{14}N_2O_3$	66,7	5,2	10,4	85
IIh	102...104	385 (3,88), 315 (4,49), 310 (4,50)	63,1	4,9	9,8 (10,8)	$C_{15}H_{14}N_2O_2S$	62,9	4,9	9,8 (11,2)	80
II*l*	125...127	372 (3,93), 296 (3,93)	68,7	5,4	15,1	$C_{16}H_{15}N_3O_2$	68,3	5,4	14,9	75
IIm	122...125	370 (3,82), 320 (3,86), 273 (4,19)	59,5	5,5	10,6	$C_{13}H_{14}N_2O_4$	59,5	5,4	10,7	20
IIn	144...146	394 (3,92), 299 (4,39), 243 (3,83)	66,2	5,2	10,4	$C_{15}H_{14}N_2O_3$	66,7	5,2	10,4	90
IIo	149...150	408 (4,13), 302 (4,51), 243 (3,91)	67,5	5,9	9,6	$C_{16}H_{16}N_2O_3$	67,6	5,7	9,9	90
IIp	204...205	410 (3,99), 300 (4,38), 243 (4,11)	58,0	4,5	12,6	$C_{16}H_{15}N_3O_5$	58,4	4,6	12,9	95
IIq	117...119	261 (4,48), 223 (4,12)	66,9	7,4	11,7	$C_{13}H_{16}N_2O_2$	67,2	6,9	12,1	50
IIr	102...104	365 (3,78), 283 (4,48)	63,8	6,0	11,4	$C_{13}H_{14}N_2O_3$	63,4	5,7	11,4	40
IIId	160...163	365 (4,59), 230 (4,09)	71,5	6,9	11,8	$C_{21}H_{25}N_3O_3$	71,8	7,2	12,0	30
IIIf	151...153	340 (4,06), 290 (3,78)	67,2	6,0	8,3	$C_{19}H_{20}N_2O_4$	67,0	5,9	8,2	80
IIIg	141...143	314 (4,45)	65,0	5,9	8,9	$C_{17}H_{18}N_2O_4$	65,0	5,8	8,9	60
IVd	159...161	270 (4,43)	71,9	7,1	11,7	$C_{21}H_{25}N_3O_3$	71,8	7,2	12,0	40
IVe	147...150	290 (4,20)	61,8	5,2	11,1	$C_{19}H_{19}N_3O_5$	61,8	5,2	11,4	5
IVf	130...134	290 (4,09)	67,5	6,3	8,3	$C_{19}H_{20}N_2O_4$	67,1	5,9	8,2	10
Vd	155...157	340 (4,39), 295 (4,36), 240 (4,21)	74,7	6,9	13,5	$C_{19}H_{21}N_3O$	74,2	6,9	13,7	70
Ve	181...184	345 (3,98), 250 (4,40)	66,5	4,9	13,6	$C_{17}H_{15}N_3O_3$	66,0	4,9	13,6	30
Vf	112...113	335 (4,24), 255 (4,09)	72,4	6,2	9,6	$C_{17}H_{16}N_2O_2$	72,9	5,8	10,0	5
VIIa	71...73	360 (4,58), 265 (4,13), 235 (4,43)	69,8	6,4	14,9	$C_{11}H_{12}N_2O$	70,2	6,4	14,9	70
VIIc	119...121	370 (3,93), 280 (4,49), 270 (4,50), 230 (4·17)	77,2	6,1	10,4	$C_{17}H_{16}N_2O$	77,3	6,1	10,6	80
VIId	148...150	410 (3,92), 340 (4,56), 260 (4,11)	74,2	7,0	13,6	$C_{19}H_{21}N_3O$	74,2	6,9	13,7	80
VIIe	206...209	370 (3,85), 270 (4,16)	65,5	4,9	13,7	$C_{17}H_{15}N_3O_3$	66,0	4,9	13,6	85
VIIf	139...141	340 (4,12), 275 (4,10)	73,1	6,0	10,0	$C_{17}H_{16}N_2O_2$	72,9	5,8	10,0	70
VIIg	150...152	390 (3,88), 295 (4,60)	70,5	5,4	11,0	$C_{15}H_{14}N_2O_2$	70,9	5,6	11,0	95
VIIi	261...264	390 (3,68), 300 (4,47), 243 (3,97)	72,7	5,7	9,7	$C_{17}H_{16}N_2O_2$	72,9	5,8	10,0	60
VIIj	140...143	385 (3,79), 300 (4,58), 242 (4,07)	73,5	6,6	9,4	$C_{18}H_{18}N_2O_2$	73,5	6,2	9,5	90
VIIk	171...173	375 (3,93), 269 (4,33)	72,7	5,8	16,0	$C_{16}H_{15}N_3O$	72,4	5,7	15,8	95
VIIq	94...96	330 (3,95), 247 (4,44)	72,5	7,9	13,1	$C_{13}H_{16}N_2O$	72,2	7,5	13,0	70
VIIr	116...117	400 (3,34), 276 (4,21), 222 (4,00)	67,9	6,1	11,6	$C_{13}H_{14}N_2O_2$	67,8	6,1	12,2	20

In contrast to 1,3-dioxide IIq, 5-ethyl-4H-imidazole 3-oxide (VIIq) is stable and can be stored at room temperature for a long time.


I a,m VIII IIa,m

It should be noted that, in contrast to most of the 1,3-dioxides II obtained, 2-unsubstituted IIa and 2-methoxycarbonyl-4H-imidazole 1,3-dioxide (IIm) are formed in very low yields (2 and 5%, respectively) under the described conditions for the oxidation with PbO_2 or MnO_2. The yields of these compounds increase substantially when the stable nitroxyl radical that has highly developed oxidizing properties such as 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline 3-oxide 1-oxyl (VIII) [10] is used as the mild oxidizing agent.

In comparing the IR spectra of II, V, and VII one observes a peculiarity that makes it possible to distinguish 1-oxides V from 1,3-dioxides II and 3-oxides VII. The IR spectra of V contain a band at 1650-1690 cm^{-1}, which is characteristic only for V and is absent in the IR spectra of II and VII. In most cases the analysis of the IR spectra of II, V, and VII in the region of the stretching vibrations of the multiple bonds (1500-1700 cm^{-1}) is rather complicated, since in this region there are a number of bands with different natures: $\nu_{C=N}$, $\nu_{C=N\rightarrow O}$, and $\nu_{C=C}$ of aryl and hetaryl groups. An attempt to use the IR spectra and Raman spectra in conjunction was previously made to solve this problem [11]; however, this investigation was carried out with a limited number of compounds and does not yet give distinct recommendations for unambiguous assignments.

The UV spectra of 4H-imidazole N-oxides II, V, and VII depend markedly on the nature of the R and R^1 substituents; this is primarily manifested in the position of the long-wave absorption maximum, which may vary over a rather wide range. Nevertheless, as in the case of the IR spectra, the UV spectra of V differ appreciably from the UV spectra of II and VII, which, in turn, are similar to one another in many cases. This is explained by the fact that II and VI have the same conjugation system with a terminal nitrone group, which also determines the position of the long-wave absorption maximum. However, the presence of an N-oxide group in the middle of this conjugation system in 1,3-dioxides II leads in some cases to a shift of the long-wave absorption maximum to the short-wave region (for example, compare IIg and VIIg in Table 1). Thus, a comparison of the UV spectra of 4H-imidazole N-oxides in the general case does not always make it possible to determine the position of the N-oxide oxygen atom.

The NMR spectra are more informative from the point of view of establishing the position of the N-oxide group. In the ^1H NMR spectra the principal differences are observed for the protons in the ortho position with respect to the nitrone or imino group and are due to the deshielding effect of the N-oxide group [12]: the signals of the ortho protons in α-arylnitrones are found at weaker field (by 0.3-0.4 ppm) than the signals of the ortho protons in α-arylimines. The signals of the ortho protons of the R^2 group in 4H-imidazole 1,3-dioxides II experience the greatest shift to weak field as a consequence of the simultaneous effect of two N-oxide groups.

In the ^{13}C NMR spectra a strictly defined region of chemical shifts for the signals of the C atoms of the imino and nitrone groups belongs to each type of 4H-imidazole N-oxide. In the case of 1,3-dioxides II both signals of the nitrone carbon atoms lie in the region that is usual for nitrones, viz., 126-150 ppm (Table 2) [2, 3]. As a consequence of the difference in the relaxation conditions for the $C_{(2)}$ and $C_{(5)}$ atoms their signals have different intensities: with the exception of IIa, the $C_{(2)}$ signal has a lower intensity; this, together with an analysis of the tendency of the effect of substituents on the chemical shifts (CS) was used in the assignment of the signals (Table 2). The degree of the effect of the R and R^1 substituents on the position of the signals of the nitrone $C_{(2)}$ and $C_{(5)}$ atoms is the same as in derivatives of 3-imidazoline 3-oxide [2, 3] and acyclic nitrones [13-15]. Thus, in the spectra of 2- and 5-furyl-2- (IIg, n, o) and thienyl-2- (IIh) derivatives one observes a decrease in the CS of the nitrone carbon atom that is characteristic for such conjugated α-hetarylnitrones [8, 15]. Intensification of the electron-acceptor character of the R or R^1 substituent leads to a shift to strong field of the signal of the

TABLE 2. ^{13}C NMR Spectra* of 1,3-Dioxides II, 1-Oxides V, and 3-Oxides VII of 4H-Imidazole

Compound	$C_{(2)}$	$C_{(5)}$	$C_{(4)}$	R¹ b				R² b				4,4-$(CH_3)_2$
				C_{ipso}	C_{ortho}	C_{meta}	C_{para}	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	
IIa	135,7	142,7	79,3	126,0	126,2	128,9	130,6					24,0
IIb	143,6	142,1	76,3	126,0	126,0	128,9	130,5	7,3				
IIc	139,7	142,4	76,5	126,2	126,3	128,9	130,5	121,9	127,7	128,7	131,1	24,3
IId	139,7	142,6	75,1	126,4	126,4	128,8	130,5	108,7	129,8	110,4	151,5	24,4
IIe	138,3	143,5	77,6	125,8	126,5	128,9	131,2	123,3	123,7 134,1	147,7, 128,9	125,6	25,2
IIf	145,4	146,2	76,0	125,6	126,9	129,0	131,8	109,2	159,4, 130,8	119,6 120,4	134,7	25,0
IIg	134,8	142,6	77,0	126,2	126,3	128,8	130,6	137,6	112,0	117,2	145,7	24,3
IIh	138,0	142,8	76,4	126,0	126,5	128,9	130,6	127,1	130,6	121,3	132,3	24,3
II*l*	138,9	143,0	77,5	126,2	126,6	129,0	131,0	119,1	149,2, 136,3	123,1	151,2	24,5
IIm	135,1	142,3	80,3	126,0	126,4	129,0	131,2	154,2	53,2[c]			24,4
IIn	139,6	135,7	75,0	143,0	112,7	115,1	145,7	122,0	127,8	128,4	131,2	23,3
IIo	139,5	135,7	74,8	141,7	116,7	109,4	155,5	122,1	127,8	128,4	131,2	23,4
IIp	137,3	135,4	75,4	141,2	116,8	108,9	155,3[d]	122,3	123,4 133,3 -	147,1 129,1	124,8	23,0
IIq	138,8	149,7	76,5	9,3	17,4[e]			122,3	128,0	128,4	131,2	21,9
IIr	142,0	126,9	77,2	187,1	31,5[f]			121,3	128,3	129,1	131,8	23,3
Vb	163,3	153,5	72,7	126,5	126,7	128,8	130,9	12,0				24,8
Vc	160,8	155,9	72,3	126,5	126,9	128,8	131,1	126,7	128,2	129,7	131,7	25,0
Vd	160,2	155,6	71,2	126,9	126,9	128,7	130,8	112,9	130,8	110,8	152,3	25,3
Ve	159,8	158,1	73,3	126,3	127,3	128,9	131,6	128,2	125,1, 135,6	148,0 129,3	126,3	25,3
V	155,9	159,6	76,7	125,9	127,0	128,9	131,6	133,8	129,6	129,4	135,7[g]	24,6
VIIa	137,9	176,3	78,8	130,3	126,8	129,2	131,6					23,2
VIIb	146,6	175,6	78,4	130,0	127,0	129,2	131,6	11,8				23,2
VIIc	144,0	175,0	81,4	130,1	126,9	129,1	131,8	126,8	127,2	128,5	130,4	23,7
VIId	144,5	175,0	79,9	130,3	127,1	129,1	131,6	114,8	128,5	111,1	151,2	23,7
VIIe	144,1	175,9	82,4	130,5	127,3	129,0	132,0	127,3	122,4 132,7	148,5 129,4	124,5	24,4
VIIf	150,1	181,2	80,8	129,3	128,0	129,3	131,1	114,0	159,1, 133,0	119,1 119,3	134,1	23,4
VIIg	139,1	175,8	79,9	130,1	127,2	129,2	131,9	142,3	112,4	114,0	144,6	23,6
VIIi	144,6	175,7	80,6	130,3	127,4	129,4	131,9	118,7	129,4	115,5	159,6	23,7
VIIj	144,2	175,1	80,9	129,8	127,2	128,9	131,7	119,9	128,7	112,2	160,4	23,5
VIIk	145,2	175,4	82,0	130,2	127,3	129,0	131,7	145,5	123,1	149,7 136,7	124,7	23,9
VIIq	144,3	185,5	81,9	9,4	21,7[e]			127,8	127,4	128,6	130,4	23,0
VIIr	145,8	169,7	82,2	190,8	24,3[f]			127,8	127,8	128,2	130,4	22,7

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[a] The spectra of IIe, f, Ve, and VIIe were recorded in $CHCl_3$. [b] The ortho, meta, and para positions are reckoned from the imidazoline ring on the substituent side. For the 2-furyl and 2-thienyl derivatives the C_{ipso}, C_{ortho}, C_{meta}, and C_{para} atoms correspond to the carbon atoms in the 2, 3, 4, and 5 positions of the heteroring. [c] Chemical shift (CS) of the methoxycarbonyl group $COOCH_3$. [d] CS of 5-CH_3 13.1 ppm, CS of CH_2CH_3. [f] CS of $COCH_3$. [g] CS of C=O 185.9 ppm.

nitrone carbon atom that is bonded directly to it; this is in agreement with the data in [3, 13, 14]. As a consequence of this, the signals of the $C_{(2)}$ atom in the 2-methoxycarbonyl derivative (IIm) and the $C_{(5)}$ atom of the 5-acetyl derivative (IIq) are found at strongest field (Table 2), while the signal of the $C_{(5)}$ atom of the 5-ethyl derivative (IIp) is found at weakest field. A characteristic (for aldonitriles) shift to strong field of the chemical shifts (CS) is also observed for the $C_{(2)}$ atom in the spectrum of IIa as compared with the 2-methyl and 2-aryl derivatives (see [3]). The formation of a hydrogen bond with the N-oxide oxygen atom leads to a shift to weak field of both signals of the nitrone $C_{(2)}$ and $C_{(5)}$ atoms of 3-5 ppm in the spectra of 5-(o-hydroxyphenyl)-4H-imidazole 1,3-dioxide in solution in both DMSO and $CHCl_3$. This corresponds to approximately half the $\Delta\delta$ value in the formation of a similar hydrogen bond in o-hydroxyphenylnitrones [16].

In the spectra of 4H-imidazole 3-oxides VII – compounds in which the N-oxide oxygen atom is found at the end of the conjugated system – the signals of the imine $C_{(5)}$ atom and the nitrone $C_{(2)}$ atom show up in the regions that are customary for these groups: ~175 and 145 ppm (Table 2, Fig. 1b). Let us note that, as compared with the position of the signals

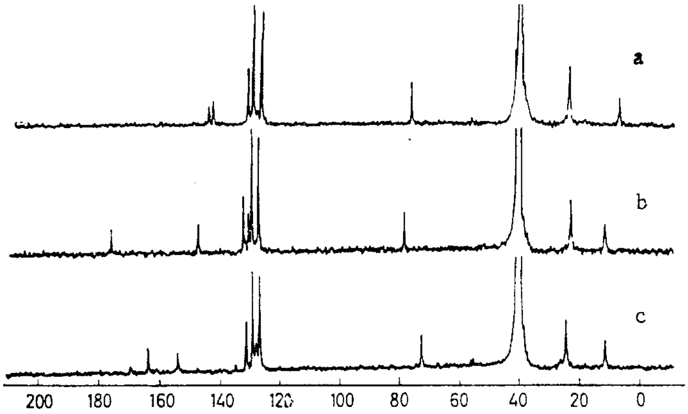

Fig. 1. ^{13}C NMR spectra (in DMSO): a) 1,3-dioxide IIb; b) 3-oxide VIIb; c) 1-oxide Vb.

of analogous but isolated imino or nitrone groups in the composition of 3-imidazolines or 3-imidazoline 3-oxides [2, 3], one observes an increase in the CS of 4-5 ppm in the CS of the corresponding signals. The effect of the nature of the substituents and the hydrogen bonds on the CS is similar to that described above. Thus, the formation of hydrogen bonds in VIIf leads to shifts to weak field of the signal of the $C_{(2)}$ atom of 7 ppm and of the $C_{(5)}$ atom of 6 ppm.

In the spectra of 1-oxides V, in which the N-oxide atom is located in the middle of the conjugated system, one observes mutual drawing together of the signals of the imine and nitrone carbon atoms (Fig. 1c). As compared with the corresponding 4H-imidazole 3-oxides VII, the signals of the imino groups in the spectra of V are shifted 15 ppm to strong field, while the signal of the carbon atoms of the nitrone groups are shifted 10-15 ppm to weak field. The assignment of the signals to the $C_{(2)}$ and $C_{(5)}$ atoms, the CS of which in a number of cases are extremely close to one another and may change places, is based on the previously ascertained principles of the electronic effect of substituents on the CS of the nitrone carbon atom [2, 3]. Intensification of the electron-acceptor character of the R^2 substituent attached to the $C_{(2)}$ atom should lead to a shift of the signal of the $C_{(5)}$ atom to weak field, and this is observed in the Va-e series, while such intensification should lead to a shift of the signal of the $C_{(5)}$ atom to weak field, and this is observed in the Va-e series, while such intensification should lead to a shift of the signal of the $C_{(2)}$ atom to strong field. On the basis of this the signal at 159.6 ppm in the spectrum of Ve, which has the most electron-acceptor C_6H_5CO substituent attached to the $C_{(2)}$ atom, was assigned to the nitrone $C_{(5)}$ atom, and in the examined V series the weakest-field CS of the $C_{(5)}$ atom and the strongest-field CS of the $C_{(2)}$ atom are observed for Ve, so that the reverse order of the positions of the signals of the imine and nitrone carbon atoms is observed for it (Table 2).

The positions of the signals of the $C_{(4)}$ atoms for each type of 4H-imidazole N-oxide is also quite characteristic and follows the principles previously observed for 3-imidazoline 3-oxide derivatives [2, 3]. According to the data in [2] the signal of the $C_{(4)}$ atom should experience a weak-field shift when an N-oxide group is introduced at the $N_{(3)}$ atom, and, vice versa, one should observe a strong-field shift when it is introduced at the $N_{(1)}$ atom. In conformity with this signals of the $C_{(4)}$ atom are observed for 1-oxides V at strongest field at 71-76 ppm. Upon addition of N-oxide to the $N_{(3)}$ atom, i.e., on passing to 1,3-dioxides II the signal of the $C_{(4)}$ atom is shifted to weaker field (75-80 ppm), whereas on passing to 3-oxides VII the $C_{(4)}$ atom experiences the greatest electron-acceptor effect of the adjacent groups, and its signal is observed at 80-83 ppm (Table 2, Fig. 1c). An increase in the acceptor properties of the substituent attached to the $C_{(2)}$ atom also leads to a weak-field shift of the $C_{(4)}$ atom.

The signals of the R^2 group are also quite sensitive to the presence of N-oxide oxygen atoms. Thus, the C_{ipso} signal in the spectra of 1,3-dioxides II is found at stronger field (by 5-6 ppm) than in the spectra of the analogous 4H-imidazole 1- and 3-oxides V and VII. The signals in the R^1 group of V and VII are very close to one another, and the degree of their difference from the corresponding signals in the spectra of 3-oxides VII is equal to the degree of difference in the corresponding signals in the spectra of 3-imidazoline 3-

oxides and 3-imidazolines [2, 3]: $\Delta\delta C_{ipso} \simeq -4$ ppm, $\Delta\delta C_{ortho} \simeq -0.6$ ppm, $\Delta\delta C_{meta} \simeq -0.3$ ppm, and $\Delta\delta C_{para} \simeq -1.0$ ppm.

Thus, an analysis of the ^{13}C NMR spectra at 120-190 ppm makes it possible to unambiguously determine the position of the N-oxide atom in 4H-imidazole N-oxides and also makes it possible to rely upon the use of this approach for other heterocyclic systems with a similar orientation of conjugated C=N and $C{=}N \rightarrow O$ groups.

EXPERIMENTAL

The synthesis of IIb, c, Vb, s, and VIIb was described in [5, 7, 17]. The UV spectra of solutions in ethanol were recorded with a Specord UV-vis spectrophotometer. The ^{1}H NMR spectra of 5-10% solutions were recorded with a Varian A56-60A spectrometer with hexamethyldisiloxane (HMDS) as the internal standard [0.04 ppm from tetramethylsilane (TMS)]. The ^{13}C NMR spectra were recorded with an HX-90 Bruker Physics spectrometer (22.63 MHz) under pulse conditions. The measurements were made in 10-15% solutions of the compounds in DMSO ($CHCl_3$, CCl_4); 10% d_6-DMSO ($CDCl_3$) was added to stabilize the deuterium nuclei resonance conditions. The chemical shifts were measured relative to the signal of the solvent (40.4, 77.2, or 96.0 ppm from TMS, respectively); the accuracy in the measurements was ±0.05 ppm. The assignment of the signals was made on the basis of a comparison of the intensities in the spectra with complete suppression of the spin–spin coupling of the ^{13}C and ^{1}H nuclei and in conformity with the data in [1-3, 13-16].

The characteristics of the synthesized compounds are presented in Tables 1 and 2.

General Method for Obtaining 4H-Imidazoles 1,3-Dioxides IIc-e, ℓ-q. A suspension of 3.5 mmoles of 3-imidazoline 3-oxide Ic-e, ℓ-q and 3 g of lead dioxide in 20 ml of $CHCl_3$ was stirred with a magnetic stirrer for 5 h [until the spot of the starting compound obtained via TLC on Silufol UV-254 plates in a chloroform–ethanol system (50:1) disappeared]. The oxidizing agent was removed by filtration, and the 4H-imidazole 1,3-dioxides were isolated by chromatography with columns packed with silica gel using chloroform as the eluent and recrystallized from ethyl acetate–hexane (1:3).

Compound IIq was obtained analogously by oxidizing PbO_2 in chloroform for 20 minutes, the oxide was filtered off and chloroform evaporated. The mass formed was treated with ether, the residue filtered off and was reprecipitated from ethylacetate with hexane.

Compounds IIf-h. These compounds were obtained similarly by oxidation of 3-imidazoline 3-oxides If-h with MnO_2. The oxidation of Iq with manganese dioxide in chloroform for 2 days gave 5-acetyl-4,4-dimethyl-4H-imidazole 1,3-dioxide (IIr) and 5-acetyl-4,4-dimethyl-4H-imidazole 3-oxide (VIIr), which were separated by column chromatography on silica gel using chloroform as the eluent (these compounds had identical R_f values in the indicated system). The ratio of IIr and VIIr was determined from the ^{1}H NMR spectrum of the mixture. Pure IIr and VIIr were isolated by column chromatography on silica gel using ether as the eluent and were recrystallized from ethyl acetate–hexane (1:3). Compounds IIr and VIIr were obtained in 10 and 25% yields by refluxing IIq in chloroform in a stream of argon for 5 h and subsequent separation of the mixture via the method described above.

Oxidation of 1-Hydroxy-5,5-dimethyl-4-phenyl-3-imidazoline 3-Oxide (Ia) with Nitroxyl Radical VIII. A mixture of 10 mmoles of Ia with 20 mmoles of VIII in 20 ml of chloroform was refluxed for 2 h, after which it was cooled to −5°C and allowed to stand for 10 h. The resulting precipitate was removed by filtration, and the solution was evaporated. The resulting mass was chromatographed with a column packed with silica gel using chloroform as the eluent. The 4,4-dimethyl-5-phenyl-4H-imidazole 1,3-dioxide (IIa) was recrystallized from ethyl acetate–hexane (1:1).

Oxidation of 1-Hydroxy-5,5-dimethyl-2-methoxycarbonyl-4-phenyl-3-imidazoline 3-Oxide (Im) with Nitroxyl Radical IX. A 20-mmole sample of 2,2,3,5,5-pentamethyl-4-phenyl-3-imidazolinium methylsulfate 1-oxide (IX) [10] was added to a solution of 10 mmoles of Im in 50 ml of ethanol, and the mixture was allowed to stand for 48 h. The alcohol was evaporated. The resulting mass was extracted with chloroform (two 40-ml portions), and the extract was dried with $CaCl_2$, filtered, and evaporated. The 4,4-dimethyl-2-methoxycarbonyl-5-phenyl-4H-imidazole 1,3-dioxide (IIm) was chromatographed as described in the preceding experiment.

General Method for Obtaining 4H-Imidazole 1-Oxides Vd-f. Compounds Id-g were acylated as described in [7], and the products were separated by column chromatography on silica gel with chloroform as the eluent. The ratio of the products was determined from the ^{1}H NMR spectra of the mixture. A 2.5-mmole sample of 1-acetoxy-3-imidazoline 3-oxide (IV) was placed in a round-bottomed flask and heated for 30 min to 180°C in the vacuum created by a water aspirator (15-20 mm). The resulting mass was cooled, and 1-oxides V were isolated by chromatography with columns packed with silica gel with chloroform as the eluent and subsequent recrystallization from ethyl acetate—hexane (1:1).

A mixture of III and IVg-f without separation can be used to obtain 4H-imidazole 1-oxides Vd-f.

General Method for Obtaining 4H-Imidazole 3-Oxides VIIa, c-g, i-k. A suspension of 3.5 mmoles of 1-hydroxy-3-imidazoline VI and 3 g of MnO_2 in 20 ml of $CHCl_3$ was stirred for 3 h, after which the oxidizing agent was removed by filtration, and the chloroform was evaporated. Compound VIIa was recrystallized from hexane, while VIIc-g, i-k were recrystallized from hexane—ethyl acetate (1:1).

Compound VIIa. This compound was similarly obtained by oxidation of 3-imidazoline VIq with lead dioxide.

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