2,2,4,5,5-Pentamethylimidazolidine-l-oxyl-3-borane (XXIII). A solution of XIV (0.23 g) in dry THF was stirred with NaBH₄ (0.2 g) for 1 h at ~20°C, evaporated, the resulting residue diluted with water, and extracted with CHCl₃. The extract was dried with MgSO₄, the solution evaporated, the residue washed with hexane, and compound XXIII filtered off.

Analogously from XV and XVI were obtained 2,2,5,5-tetramethyl-4-phenyl-(XXIV) and 4,5,5-trimethyl-2-spirocyclohexanimidazolidine-1-oxyl-3-borane (XXV). Compounds XXIII-XXV could also be obtained starting from borofluorides XX-XXII.

2,2,4,5,5-Pentamethyl-1-methoxy-3-imidazoline (XXVI). Compound XX (1 g) was added portionwise with stirring to a solution of methylmagnesium iodide (obtained from 0.52 g Mg and 2 ml of MeI in 30 ml of dry ether). After stirring for 2 h it was diluted with 20 ml water and the organic layer separated. The aqueous layer was extracted with ether. The ether extracts were dried (MgSO₄), evaporated, and XXVI [7] purified by silica gel chromatography using a mixture of ether and hexane (1:1). Yield: 0.35 g (46%).

Analogously from borofluorides XXI and XXII were obtained the methoxy derivative (XXVII) [7] with yield 35% and 4,5,5-trimethyl-l-methoxy-2-spirocyclohexan-3-imidazoline (XXVIII).

CONCLUSIONS

3-Imidazoline derivatives, when treated with NaBH₄ in the presence of BF_3 etherate, form adducts with borane, oxidation of which yields stable nitroxyl radicals. On treatment with methanol in the presence of base, the paramagnetic adducts are reduced to the corresponding imidazolidinoxyl derivatives.

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CONVERSION OF 3-IMIDAZOLINE-3-OXIDE NITROXYL RADICALS INTO NITRONYLNITROXYL RADICALS

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Continuing the studies of the effect of the pH of the medium on the EPR spectra of nitroxyl radicals (NR) containing acid-base functional groups at a distance of 2-3 σ -bonds from the radical center [1-4], we have examined the EPR spectra of NR (I) and (II), which contain OH groups in the 2-position of the heterocycle (formula, following page, below figure)

It is assumed that deprotonation of the OH group is accompanied by changes in the hfc constant a_N^{-1} and the g-factor, as for example, in the case of the radical (III) [5], as well as in radicals containing other groups [2-4]. At pH values ≥ 12 , however, the EPR spectra of aqueous solutions of radicals (I) and (II) undergo irreversible changes from a triplet to a more complex multiplet, similar to the spectra of nitronylnitroxyl radicals (NNR) (Figs. 1

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Fig. 2

Fig. 1. EPR spectra of (IV) at pH 12.2 (a) and 7.0 (b). Recording conditions for the EPR spectra: microwave power 5 MW, modulation amplitude 0.32 Oe, amplification $6.3 \cdot 10^4$, scanning rate of spectrum 50 Oe/200 sec, time constant 0.1 sec, sample temperature 23°C, concentration 10^{-5} mole/liter.

Fig. 2. EPR spectra of (V) at pH 12.2 (a) and 7.2 (b). Recording conditions as in Fig. 1.



and 2) [6, 7]. The EPR spectra of these solutions remain unchanged over periods of several days. The spectra have a quintet structure, with further splitting into four (Fig. 1) or three (Fig. 2) components. When similar experiments are carried out in D₂O, the additional hfs disappear as a result of deuterium exchange in the CH₃ groups of the radical (IV) and CH₂ in (V). A simulation of the EPR spectra was carried out, assuming splitting into two N nuclei $(a_N^{-1} \text{ and } a_N^{-3})$, with three or two equivalent H. This resulted in complete agreement between the calculated and experimental spectra (Table 1). In order to assign the nitrogen hfc constants, we synthesized radicals (I*) and (II*) containing the N¹⁵ isotope in the 3-position of the imidazole ring, from which were obtained radicals (IV*) and (V*). Comparison of the results of simulations of the EPR spectra of (IV) and (IV*), and of (V) and (V*), enabled unambiguous assignments of the hfc constants a_N^{-1} and a_N^{-3} (Table 1) to be made.

Titration of solutions of radicals (IV) and (V) resulted in reversible changes in the EPR spectra over the pH range 8-11. The EPR spectra of (IV) and (V) at pH < 8 are shown in Figs. 1b and 2b. In the intermediate pH range 8-11, radicals (IV) and (V) showed superimposed EPR spectra (1a + 1b and 2a + 2b). When the acidity of the medium is increased to pH 0-1, the EPR signals of radicals (IV) and (V) disappear completely, but when the pH is again increased, they reappear with their original intensity, and the transformations of the EPR spectra in the pH range 8-11 described above take place in the reverse order. This cycle of changes may be carried out several times. It appears that, in acid solution, a reversible disproportionation reaction takes place, which is typical of NNR [8].

The changes in the EPR spectra when (I) and (II) are converted into (III) and (IV) are accompanied by the appearance of a crimson coloration. In the UV spectra of radicals (IV) and (V), bands appear at 300 (log $\varepsilon \approx 3.8$), 510 (log $\varepsilon \approx 1.6$), and 536 nm (log $\varepsilon \approx 1.8$) which are typical of NNR [6, 7]. It is noteworthy that these changes in the EPR and UV spectra occur only in the presence of atmospheric oxygen. When the experiments are carried out under argon, the triplet EPR spectrum disappears, but a multiplet spectrum (Figs. 1 and 2) is not seen. On contact with atmospheric oxygen, the crimson coloration is obtained together with the EPR spectra shown in Figs. 1a and 2a.



Com-	R	x	p	$H > pK_a + 1$	pH <pka-1,5< td=""></pka-1,5<>					
			a_{N}^{1}	$a_{ m N}^3$	a _H	a_{N}^{1}	$\begin{vmatrix} a_{\rm N}^3 \end{vmatrix}$	$a_{ m H}$	$a_{\rm N}({ m NH_2})$	
(IV) (IV *) (V) (V *) (XI) (XXV) (XXV) (XXVI)	$ \begin{array}{ c c } Me \\ Me \\ (CH_2)_4CHO \\ (CH_2)_4CHO \\ (CH_2)_4CONH_2 \\ Ph \\ Ph \end{array} $	OH OH OH NH ² OH NH ²	$\begin{array}{c} 8,67\\ 8,67\\ 8,73\\ 8,73\\ 8,73\\ 8,00\\ 8,50\\ 8,05\\ \end{array}$	8.28 11,65 8,22 11,57 8,00 8,00 8,05	$\begin{vmatrix} 3,13\\3,13\\1,93\\1,93\\1,90\end{vmatrix}$	8,0 8,06 8,00 7,60 7,93 7,60	8,0 11,34 8,00 11,34 7,60 7,93 7,60	3,13 3,13 1,93 1,93 1,90 a _H ((1,10 1,20 OMe)	
(VII) (X) (XXIV)	Me (CH ₂)4COOMe Ph	OMe OMe OMe	7,68 7,52 7,70 7,50 7,67 7,67		7,52 7,50 7,67		1,80 1,30		0,60 0,55	

These changes in the EPR and UV spectra are due to the oxidation of radicals (I) and (II) in the presence of the nucleophilic OH radical; thus forming NNR (IV) and (V), which contain a hydroxy-group which is sensitive to pH changes in the range 8-11. Chromatography (TLC) of the reaction mixture during the conversion of radical (I) to NNR (IV) shows the presence of 4H-imidazole-di-N-oxide (VI), which is apparently an intermediate in the reaction:



It is in fact found [9] that in aqueous alkali authentic (VI) has a crimson color and EPR and UV spectra similar to that of the radical (IV). It was not possible to isolate radicals (IV) and (V) in the pure state, apparently owing to the presence of a labile hydrogen atom in the hydroxy group. Treatment of (VI) with sodium methoxide in methanol gives the radical (VII), which was isolated in the pure state. This radical is also obtained by oxidizing (VI) with PbO₂ in methanol: (Formula, top, following page.) The structure of the radical (VII) was confirmed by high-resolution mass spectroscopy, and by its IR, UV, and EPR spectra. Radicals (VII) and (IV) have similar UV spectra. The IR spectrum of (VII) shows absorption at 2840 cm⁻¹ characteristic of stretching vibrations of the OCH₃ group. In the EPR spectrum of the radical (VII), unlike that of (IV), additional hfs is seen from the protons of the OCH₃ group (Table 1), which disappears when CD₃OD is used in the synthesis of (VII), i.e., on replacement



of OCH₃ by OCD₃. The EPR spectrum of (VII) remains unchanged over the pH range 1-13. This confirms the conclusion that the transformation of the EPR spectra of radicals (IV) and (V) over the pH range 8-11 is due to deprotonation of the OH group. At pH values ≤ 0 , reversible disproportionation takes place into diamagnetic products (cf. [8]), and at pH values >13 the EPR spectrum of the radical (VII) is gradually and irreversibly converted into the spectrum of the radical (IV), as a result of the replacement of the OCH₃ group by OH.

For these reasons, it may be assumed that all 5,5-disubstituted 3-imidazoline-3-oxides capable of oxidative conversion into 4H-imidazole-di-N-oxides are converted in the presence of a nucleophile, whatever the solvent, into nitronylnitroxyl radicals, by the general route:



In fact, the NNR (IV) and (VII) are readily obtained by oxidizing 1-hydroxy-2-acety1-2,5,5-trimethy1-4-pheny1-3-imidazoline-3-oxide (VIII) with PbO_2 in aqueous methanol, (VIII) being known to be readily converted into (VI) [10]. Oxidation of the spiro-compound (IX) [11] in methanol affords the NNR (X), which contains an ester grouping which appears in the IR spectrum as strong absorption at 1750 cm⁻¹.



Similar conversion of (IX) into the NNR takes place in the presence of another nucleophile: Oxidation of (IX) with PbO₂ in aqueous ammonia affords 4-amino-2-(4-carbamoylbutyl)-5,5-dimethyl-4-phenyl-2-imidazoline-3-oxide-1-oxide (XI). The IR spectrum of this radical contains absorption for amino- and amide groups, and two bands are present in the UV spectrum which are characteristic of NNR (see Experimental). The EPR spectra of radicals (X) and (XI) consist of a quintet of triplets, characteristic of these NNR (Table 1). The formation of an ester group in (X) and a carbamoyl group in (XI) indicates that in the oxidation of 1-hydroxy-2-acyl-3-imidazoline-3-oxides (VIII) and (IX), the nucleophile attacks the carbon atoms of both the nitrone and the leaving groups.

The conversion of 3-imidazoline-3-oxide NR into NNR also takes place in the presence of other functional groups in the 2-position of the imidazoline ring, for example oxime and hydrazone, but this conversion takes place much more slowly than in the 2-acyl compounds.

The conversion of 3-imidazoline-3-oxide NR into NNR also takes place readily when one of the groups in the 2-position of the heterocycle is hydrogen, since NR with α -hydrogen atoms are known to undergo facile conversion into nitrones by disproportionation [12]:



TABLE 2. Oxidation Potentials (E_p) for 1-Hydroxy-3-imidazoline 3-Oxides (XIII-XVII), and hfc constants (a_N and a_H) of the Corresponding Nitroxyl Radicals (XIX-XXIII)



1-Hydroxy-3-imidazoline-3-o				E _p , V	Com-	hfc constants CTB, Oe				
oxide						$a_{\mathbf{N}}^{1}$	$a_{\rm H}$	$a_{\rm N}^1$	$a_{\rm N}^3$	
com- pound	R1	R²	R3	R4		pound	pH	<9	pH>12 *	
(XIII) (XIV) (XV) (XVI) (XVI)	H H H Me H	Me H Ph Me H	Me Me Me H	Me Me Me H H	1,36 1,39 1,31 1,29 1,40	(XIX) (XX) (XXI) (XXII) (XXIII)	15 ,40 15,50 14,85 15,20 15,35	19,70 20,15 20,15 18,20 19,05	8,67 8,13 8,50	8,28 9,53 8,00

*At pH > 12, NR (XIX-XXI) are converted into the NNR.

1-Hydroxy-4-phenyl-3-imidazoline 3-oxides (XIII-XVII) (the values of substituents R1-R4 are given in Table 2), on oxidation with PbO₂ (or electrochemically) initially form radicals (XIX-XXIII), the EPR spectra of which, besides showing a triplet with a splitting constant for the ¹⁴N nucleus of the nitroxyl group (15-16 Oe), appear as hfc with the α -protons, the multiplicity corresponding to the number of α -protons, namely a doublet in the case of (XIX), (XXI), and (XXII), a triplet for (XX), and a quintet for (XXIII) (Table 2). In addition to the hfc at the N and H nuclei, Table 2 shows the oxidation potentials of (XIII-XVII) in water. Note that the electrochemical oxidation of the sterically hindered hydroxylamine (XII) (R^1 = $R^2 = R^3 = R^4 = CH_3$) is a two-electron process, the E_p value of 1.17 V being exactly the same as that for the one-electron reversible oxidation of the corresponding nitroxyl radical (XVIII) to the hydroxyammonium cation; in agreement with data for other sterically hindered hydroxylamines [13, 14]. The electrochemical oxidation of hydroxylamines (XIII-XVII), which have one or more α -hydrogen atoms, is irreversible, which according to the literature [13, 14] is due to rapid disproportionation reactions. Successive replacement of CH3 groups by hydrogen in hydroxylamines (XIII-XVII) results in an increase in the values of the oxidation potentials (Table 2), hydroxylamines with four α -hydrogens undergoing oxidation at 1.40 V relative to the sat. calomel electrode.

In the electrochemical oxidation of (VI) in water and methanol, irreversible oxidation peaks are seen at 1.26 and 1.28 V, respectively. Addition of sodium hydroxide solution to an aqueous solution of the dinitrone (VI) gives rise to the appearance of an oxidation peak at 1.11 V, and the addition of sodium methoxide to a methanol solution of (VI) results in a peak at 0.82 V, no peak for the oxidation of 4H-imidazole di-N-oxide being seen. Oxidation of authentic NMR (VII) in methanol also occurs in methanol at 0.82 V, and in water at 0.83 V. addition of sodium hydroxide to (VII) in aqueous solution results in the appearance of an oxidation peak at 1.11 V, no peak for the oxidation of the radical (VII) being present. This is in agreement with the results of a study of the hydrolysis of the methoxy group in (VII) from the EPR spectra (see above).

The electrochemical oxidation data suggest that 1-hydroxy- or 1-oxyl-3-imidazoline 3oxides are converted into NNR via the formation of 4H-imidazole di-N-oxide, which then undergoes conversion into the end-products via routes a and b: (Formula, following page, under figure.)

Route a takes place in weakly nucleophilic: media (water and methanol) with the intermediate formation b a cation-radical, followed by reaction with the nucleophile (NuH). Route b is more likely to be followed in strongly nucleophilic media (OH, OCH₃) by oxidation of the anion initially formed by the addition of Nu⁻. The results of electrochemical oxidation are in accordance with the UV spectral data, which are similar in heptane (λ 364 nm, log ϵ 4.12), methanol (λ 360 nm, log ϵ 4.11), and water (λ 354 nm, log ϵ 4.05); but in 0.1 N NaOH under argon this long-wavelength maximum is not seen, indicating the disappearance of the dinitrone group following addition of the nucleophile.







Fig. 4

Fig. 3. EPR spectrum of radical (XXV) at pH 12.0 (a), 9.3 (b), and 7.0 (c). For recording conditions, see Fig. 1.

Fig. 4. EPR spectrum of radical (XXVI) at pH 5.0 (a), 1.9 (b), and 0.5 (c). Recording conditions for EPR spectra: microwave power, 10 MW; modulation amplitude, 0.63 0e; amplification, $5 \cdot 10^3$ (a), $1.25 \cdot 10^4$ (b), and $5 \cdot 10^5$ (c); spectral scanning rate, 50 Oe/200 sec; time constant, 0.01 (a), 0.02 (b), and 0.1 sec (c). The decrease in signal intensity is due to disproportionation of the radical in acid solution. Sample temperature, 23° C; initial concentration, 10^{-5} mole/liter.



The stability of the NNR formed is largely dependent on the substituents in the 2-, 4-, and 5-positions of the 3-imidazoline 3-oxide, and on the type of nucleophile. The highest yield and most stable NNR (XXIV) are obtained by treatment of (XV) with PbO₂ in methanol. The radical (XXIV) is deep blue in color, which is typical of α -aryl NNR [6, 7]. As would be expected, no NNR are obtained when one or both of the substituents in the 5-position are hydrogen atoms.



Radicals (XXV) and (XXVI), which are formed by the oxidation of (XV) with PbO_2 , could not be isolated in the pure state, but they are fairly stable in solution (for several days),

and they were characterized by their EPR spectra (Table 1). The EPR spectra of these radicals are most simply interpreted by virtue of the occurrence of two hfc constants, a_N^{-1} and a_N^{-3} (Figs. 3 and 4). This enables the pK values of the 0H and NH₂ groups in these radicals to be measured with some accuracy. The values and signs of the changes in a_N on deprotonation of the OH groups ($\Delta a_N^{-1} = 0.57$ Oe, $\Delta a_N^{-3} = 0.07$ Oe) and NH₃⁺ ($\Delta a_N^{-1} = \Delta a_N^{-3} = 0.45$ Oe) are in agreement with the previously-observed [4] increase in a_N consequent upon the deprotonation of various functional groups in NR molecules. At pH 8-11, the radical (XXV) shows superimposition of the determination of the pK_a of radical (XXV), this enabled the previously-proposed [2] dependence of f on pH to be employed (Fig. 5a), reflecting the ratio of the neutral to the deprotonated form of the pH range 0.3-3 resulted in a progressive broadening of all the peaks of the quintet, followed by the appearance of an additional triplet structure (Fig. 4). These spectral changes may be regarded as being due to the occurrence of rapid proton exchange between the protonated and deprotonated forms of the neutral component of the spectrum shows three peaks with frequencies ω [15] (we here consider the central component of the quintet, which is virtually unchanged on protonation of the NH₂ group: $\Delta g \leq 0.15$ Oe).

$$\overline{\omega} (S_{\mathbf{z}}^{N} = 0, \pm 1) = (\omega_{0} + S_{\mathbf{z}}^{N} \delta_{0})(1 - f) + (\omega_{0} + S_{\mathbf{z}}^{N} \delta_{+}) f$$
⁽¹⁾

where ω_0 is the Zeeman frequency for peaks with $S_Z N = 0$; δ_0 is the hfc constant for the N atom of the NH₂ group; δ_+ is the hfc constant for the N atom of the NH₃⁺ group; and f is the proportion of the protonated form of the radical (0 < f < 1).

Simulation of the EPR for a given pH value gives the splitting between the components of the triplet $\Delta \omega = \omega(S_z = +1) - \omega(S_z = 0) = \omega(S_z = 0) - \omega(S_z = -1)$. According to expression (1), $f = (\Delta \omega - \delta_0)/(\delta_+ - \delta_0)$. The EPR spectra with f = 0 and 1 gave the hfc constants $\delta_0 = 0.2 \pm 0.1$ and $\delta_+ = 1.2 \pm 0.1$ Oe. The dependence of f on pH thus obtained for the radical (XXVI) gives a pK_a value of 1.75 \pm 0.1 (see Fig. 5b). The values found for the OH group in (XXV) and the NH₂ group in radical (XXVI) are some 6-7 units less than the values for aliphatic alcohols and amines [16]. It follows that the nitronylnitroxyl group is a powerful electron acceptor, resulting in an increase in the acidity of the OH group and a reduction in the basicity of the NH₂ group in the α -position to the radical center.

EXPERIMENTAL

EPR spectra were recorded on a Bruker ER-200D spectrometer in a flat cell. Aqueous solutions of the radicals (of concentrations 10^{-4} M or less) were titrated with NaOH or HCl solutions until the required pH values were obtained, these being measured with an OR-205/1 pH meter (Hungary) to an accuracy of ±0.05 pH unit.

Simulation of EPR Spectra. In order to determine the set of hfc constants, the frequencies and statistical weights of the Zeeman transitions were calculated. For each frequency, the peak was assumed to be of the Lorentz form and the same width. In calculating the function f for radicals (XXV) and (XXVI), simulation of the EPR spectra was carried out on the assumption that the peaks were of the same width in the protonated and deprotonated forms. The calculated EPR spectra were plotted on a graph plotter, and compared with the experimental plots. The accuracy of determination of the hfc constants was ± 0.05 Oe.

UV spectra were recorded on a Specord UV-VIS spectrophotometer, and IR spectra on a UR-10 spectrophotometer for 1-5% solutions in CCl₄ and CHCl₃, or in KBr disks (C ~ 0.25%). Mass spectra were obtained on an MS-902 with direct sample introduction (accelerating voltage 6 kV, ionizing voltage 70 eV, inlet temperature 60-100°C, depending on the volatility of the compound). Voltammetric plots were obtained using a modified LP-7e polarograph at a sweep rate of 0.4 V/min. The anode used was a stationary platinum needle electrode of area 8 mm², and the cathode a platinum wire of area 100 mm². The reference electrode was sat. aqueous calomel. In recording the plots, 10^{-4} - 10^{-3} M aqueous solutions of the compounds were used. The base electrolyte was an 0.1 M solution of tetraethylammonium perchlorate (twice recrystallized from a 3:1 mixture of water and acetonitrile). The accuracy of measurement of the oxidation potentials E_p was ±0.01 V.

 $\frac{2-(1-\text{Hydroxyethy1})-2,5,5-\text{trimethy1}-4-\text{pheny1}-3-\text{imidazoline }3-\text{Oxide }1-\text{Oxy1} \text{ (I).} \quad \text{To a solution of }1 \text{ g (3.8 mmole) of (VIII) in 10 ml of ethanol was added a solution of 0.2 g (5.3 mmole)}$

(1)



Fig. 5. Dependence of f on pH for the radical (XXV) (a) [1) calculated as $I^{\circ}/I^{\circ} + I^{-}$; 2) observed for the unadjusted EPR simulation spectrum] and for the radical (XXVI) (b). The f values observed for the EPR simulation spectrum agree with the expression (1) for the central quintet component.

of NaBH₄ in 5 ml of water, and the mixture kept for one hour. The ethanol was removed, and the residue treated with 10 ml of water, extracted with chloroform, the extract dried over MgSO₄, filtered, and the filtrate evaporated. The residue was dissolved in 20 ml of acetone, 3 g of PbO₂ added, and the mixture stirred for one hour. The solution was filtered, the filtrate evaporated, and the residue chromatographed on a column of silica gel (eluent chloroform). There were successively obtained one of the diastereoisomeric alcohols (I) (50%) and the 4-imidazole di-N-oxide (VI) (20%), formed from the second diastereoisomer of the alcohol (I), mp 138-140°C (from hexane-benzene) (cf. [9]). For (I). Found: C 63.9, H 7.5, N 10.7%.

Similarly, from (IX) there were obtained the two diastereoisomeric alcohols (IIa) (40%), mp 142-145°C (from ethanol) and (IIb) (50%), mp 155-160°C (from ethanol). For (IIa) and (IIb) respectively: Found: N 9.8 and 9.8%. $C_{16}H_{21}N_2O_3$. Calculated: N 9.7 and 9.7%.

The stereochemistry of the diastereoisomeric radicals (I) and (II) was not investigated, since all the reactions described led to the same results.

5,5-Dimethyl-2,4-diphenyl-4-methoxy-2-imidazoline 3-Oxide l-Oxide (XXIV). To a solution of 0.5 g of the imidazoline (XXI) in 50 ml of methanol was added 3 g of PbO₂, and the mixture stirred for 24 h at ~20°C. The solution was filtered, the solvent removed, and the residue chromatographed on a silica gel column (eluent chloroform), to give 0.42 g (85%) of (XXIV), mp 159-161°C (from ethanol), UV spectrum (ethanol, λ_{max} , nm (log ε): 238 (3.94), 268 (4.15), 350pl (3.94), 366 (4.08), 628 (2.95). Mass spectrum, m/z: M⁻¹ 311, 1449 (calculated 311.1395). Found: C 69.2, H 6.2, N 9.0%, C₁₈H₁,N₂O₃. Calculated C 69.4, H 6.1, N 9.0%.

Similarly, from (VIII), (VI), and (XIII) there were obtained 5-10% yields of 4-methoxy-2,5,5-trimethyl-4-phenyl-2-imidazoline 3-oxide 1-oxyl (VII); and from (IX) 60% of 4-methoxy-5,5-dimethyl-2-(4-methoxycarbonylbutyl)-2-imidazoline 3-oxide 1-oxide (X).

The radical (VII) was an oil, UV spectrum (ethanol, λ_{max} , nm (log ε): 218(3.54), 230(3. 69), 316(3.91), 541(3.02), 570(3.09). Mass spectrum, m/z: M⁺ 249, 1257 (calculated for C₁₃-H₁₇N₂O₃, 249.1239).

Radical (X), oil, UV spectrum (ethanol, λ_{max} , nm (log ε): 218(3.96), 230(3.64), 321(4.06), 551(3.16), 576(3.25). Found: C 62.2, H 7.2, N 7.8%. C₁₈H₂₅N₂O₅. Calculated: C 61.9, H 7.2, N 8.0%.

 $\frac{4-\text{Amino}-5,5-\text{dimethyl}-2-(4-\text{carbamoylbutyl})-4-\text{phenyl}-2-\text{imidazoline }3-\text{Oxide }1-\text{Oxyl (XI)}.}{\text{A suspension of 0.2 g of (IX) and 0.5 g of PbO₂ in 5 ml of aqueous ammonia was stirred for 24 h, then filtered, the solution extracted with chloroform, the extract dried over MgSO₄, filtered, and the chloroform removed. The residue was chromatographed on a silica gel column (eluent chloroform-ethanol (20:1)) to give 0.12 g (60%) of (XI) as a crimson oil. UV spectrum (ethanol, <math>\lambda_{\text{max}}$, nm (log ε): 241(3.30), 319(4.08), 527(3.15), 555(3.20). IR spectrum (chloroform, ν , cm⁻¹): 3530, 3490, 3420, 3350 (NH), 1680 and 1600 (amide (I) and amide (II). Mass spectrum, m/z: 287 [M - 32]⁺.

CONCLUSIONS

1. 1-Hydroxy- or 1-oxyl-3-imidazoline 3-oxides with acyl, hydroxyalkyl, or oxime groups, or a hydrogen atom, in the 2-position of the heterocycle undergo oxidation in the presence of nucleophiles with the intermediate formation of 4H-imidazole di-N-oxides, to give nitronylni-troxyl radicals.

2. A new series of stable nitronylnitroxyl radicals with a functional group in the 4-position have been obtained.

3. The electronic effects of the nitronylnitroxyl group have been determined from measurements of the pK_a values of the OH and NH_2 groups in 4-hydroxy- and 4-amino-5,5-dimethyl-4-phenyl-3-imidazoline 3-oxide 1-oxyl using EPR spectroscopy.

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